Priority Existing Chemical Assessment Report No. 31

Australian Government
Department of Health and Ageing
NICNAS

Sodium Cyanide

FEBRUARY 2010

NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION AND ASSESSMENT SCHEME
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Assessing chemicals for your protection

ISBN 978-0-9807221-0-9

Preface

This assessment was carried out under the National Industrial Chemicals Notification and Assessment Scheme (NICNAS). This Scheme was established by the *Industrial Chemicals (Notification and Assessment) Act 1989* (Cwlth) (the Act), which came into operation on 17 July 1990.

The principal aim of NICNAS is to aid in the protection of people at work, the public and the environment from the harmful effects of industrial chemicals.

NICNAS assessments are carried out in conjunction with the Australian Government Department of the Environment, Water, Heritage and the Arts (DEWHA), which carries out the environmental assessments for NICNAS. This assessment is specifically focused only on the assessment of risks to the environment.

NICNAS has two major programs: the assessment of the health and environmental effects of new industrial chemicals prior to importation or manufacture; and the other focussing on the assessment of chemicals already in use in Australia in response to specific concerns about their health or environmental effects.

There is an established mechanism within NICNAS for prioritising and assessing the many thousands of existing chemicals in use in Australia. Chemicals selected for assessment are referred to as Priority Existing Chemicals.

This Priority Existing Chemical report has been prepared by the Director, NICNAS, in accordance with the Act. Under the Act manufacturers and importers of Priority Existing Chemicals are required to apply for assessment. Applicants for assessment are given a draft copy of the report and 28 days to advise the Director of any errors. Following the correction of any errors, the Director provides applicants and other interested parties with a copy of the draft assessment report for consideration. This is a period of public comment lasting for 28 days during which requests for variation of the report may be made. Where variations are requested the Director's decision concerning each request is made available to each respondent and to other interested parties (for a further period of 28 days). Notices in relation to public comment and decisions made appear in the *Commonwealth Chemical Gazette*. A person may apply (within 28 days) to the Administrative Appeals Tribunal (AAT) for review of decision(s) where the Director has refused to vary the draft report as requested.

In accordance with the Act, publication of this report revokes the declaration of this chemical as a priority existing chemical, therefore manufacturers and importers wishing to introduce this chemical in the future need not apply for assessment. However, manufacturers and importers need to be aware of their duty to provide any new information to NICNAS, as required under Section 64 of the Act.

For the purposes of Section 78(1) of the Act, copies of assessment reports for New and Existing Chemical assessments are freely available from the web (www.nicnas.gov.au). Summary Reports are published in the *Commonwealth Chemical Gazette* (http://www.nicnas.gov.au/Publications/Chemical_Gazette.asp).

Copies of this and other priority existing chemical reports are available on the NICNAS website. Hard copies are available from NICNAS from the following address:

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Other information about NICNAS (also available on request and on the NICNAS website) includes:

- NICNAS Service Charter;
- Information sheets on NICNAS Company Registration;
- Information sheets on the Priority Existing Chemical and New Chemical assessment programs;
- Safety information sheets on chemicals that have been assessed as Priority Existing Chemicals;
- Details for the *NICNAS Handbook for Notifiers*; and
- Details for the *Commonwealth Chemical Gazette*.

More information on NICNAS can be found at the NICNAS web site:

http://www.nicnas.gov.au

Other information on the management of workplace chemicals can be found at the web site of Safe Work Australia

http://www.safeworkaustralia.gov.au

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Overview

Sodium cyanide (CAS No 143-33-9; NaCN) was declared a priority existing chemical on 7 May 2002 in response to environmental concerns. Reasons for declaration included reports of mass bird poisonings (occurring prior to nomination of sodium cyanide for review in 1999) as a result of consumption of cyanide-contaminated water at tailings dams, the potential release of toxic and flammable hydrogen cyanide gas when sodium cyanide comes in contact with water, the high acute toxicity to aquatic life, birds and animals, and high chronic toxicity to aquatic life.

The purpose of this assessment is to test the validity and impact of the issues raised in the declaration and to identify the potential environmental exposure in Australia from the industrial use of sodium cyanide, to characterise the hazards associated with sodium cyanide, and to determine the risk of adverse effects to the environment. It should be noted that the scope of the review pertains to the use of sodium cyanide and not other cyanide salts. This assessment does not address the human health effects of sodium cyanide.

This assessment has drawn upon international assessments, information provided by applicants, and both published and unpublished data obtained from various sources. The current controls by industry have been assessed to identify whether these are adequate to protect the environment. Finally, this assessment has made recommendations for minimising any environmental risks associated with industrial uses of sodium cyanide in Australia. This overview summarises the major findings of the report.

Manufacture, transport and use

Australia is a major global manufacturer and exporter of sodium cyanide, with manufacturing facilities in Western Australia and Queensland. About 100 000 tonnes of sodium cyanide are manufactured each year, of which about 40%-60% is exported. There are several companies that also import sodium cyanide and/or reformulate small quantities. Imports have increased in 2008 as compared to 2004 onwards.

Sodium cyanide is a highly soluble, white deliquescent crystalline powder. For gold mining use in Australia, it is manufactured as solid briquettes, or provided in a liquid form containing approximately 30% NaCN. In water, the cyanide is present as cyanide ion (CN^-) or the dissolved gas hydrogen cyanide (HCN). The liquid product is made highly alkaline in order to minimise loss of HCN by volatilisation.

In Australia, sodium cyanide is mainly used in the mining industry to recover gold from ore. Approximately 40 000-60 000 tonnes per annum (tpa) is used for this purpose, with the amounts used in each state and territory related to the relative sizes of the gold mining industries. Bulk quantities of sodium cyanide in solid or liquid form (~30% solution) are transported by road and rail from the manufacturing sites to gold mines. Lesser amounts of sodium cyanide are used for ore flotation of base metals (e.g. copper, lead, zinc) and in the electroplating and metal (case) hardening industries. A small quantity of sodium cyanide is used for analytical laboratory testing purposes.

Cyanide (CN) is ubiquitous in the environment at generally low but variable concentrations due to natural (e.g. micro-organisms, plants, animals) and anthropogenic (e.g. industrial) sources. However, free cyanide (cyanide present in water as hydrogen cyanide or cyanide ion, rather than cyanide in inorganic compounds or complexes, or attached to sugars or other organic substances) is very reactive and does not occur commonly in nature. Free cyanide reacts with various metals and their compounds, hence its uses in industry and mining.

Gold cyanide complexes are soluble in water, and consequently cyanide enables low levels of gold to be extracted from ore and the gold is then recovered by further processes. The treatment of the ore with cyanide (known as gold ore beneficiation) may occur in two basic ways after the ore is extracted from the ground, referred to as tank leaching and heap leaching. With tank leaching (the main method used in Australia), the ore is milled and mixed with the cyanide solution in large tanks, and the used cyanide solution and exhausted ore are disposed of to tailings storage facilities. With heap leaching, the cyanide solution is applied to the tops of large heaps of crushed ore, the solution containing dissolved gold is collected at the bottom, and the solution recirculated after the gold is removed, or treated to destroy the cyanide residues before disposal. In both cases, the concentrations of sodium cyanide used to obtain the gold from the ore are typically 100-500 mg CN/L.

Environmental fate

The overall fate of sodium cyanide and its products in the environment is complex and depends on a wide range of site specific and operational factors. In solution, the amount of HCN present increases with decreasing pH and an important form of release at the pH range in the normal environment is volatilisation of gaseous HCN. In addition to volatilisation, reactions that can occur include complexation with various metals, adsorption, reaction with various forms of sulphur, oxidation, hydrolysis, and aerobic and anaerobic degradation reactions. Metallocyanide complexes may form insoluble precipitates, and if exposed to light, iron-cyanide complexes may undergo photolysis reactions releasing HCN. Products such as cyanate and thiocyanate may decompose further. Some forms of cyanide, such as weak metallocyanide complexes, may release bioavailable cyanide at the low pH in the stomachs of birds and mammals, and therefore potentially contribute to cyanide toxicity. Forms of cyanide available at the low pH in the stomachs of birds and mammals are commonly measured as Weak Acid Dissociable cyanide (WAD CN).

In tailings storage facilities (TSFs) and heap leach piles, cyanide may be lost by volatilisation of HCN, degraded by various abiotic and biotic processes, fixed within the site by precipitation and adsorption of metallocyanides, and may potentially migrate in seepage to underlying strata and groundwater. The extent to which seepage occurs varies widely between individual sites. The amount of cyanide going to TSFs or remaining in them may be reduced by recovering the cyanide-containing water for re-use in the process, or by using various chemical processes to convert cyanide to cyanate, or potentially to recover free cyanide from other forms of cyanide. As a result of process and tailings management and other site factors, WAD CN concentrations in surface waters at operational TSFs vary widely. Concentrations >50 mg WAD CN/L are usually the result of high concentrations of metallocyanide complexes. Concentrations may range from ~1-10 mg WAD CN/L where cyanide has been largely destroyed through natural degradation processes and/or deliberate measures, to >100 mg WAD CN/L without measures to limit the concentration in tailings effluent.

Most sodium cyanide-derived waste from non-mining uses is expected to be treated to destroy free cyanide before delivery to landfill, where dissipation, degradation and fixation processes are expected to occur. Cyanide-resistant micro-organisms capable of biodegrading cyanide have been identified in aerobic sewerage treatment systems and the small amounts of cyanide arising from industrial discharge into sewers are likely to be destroyed during secondary treatment.

Environmental exposure

Exposure of terrestrial and avian wildlife and aquatic organisms to anthropogenic sodium cyanide, or cyanide forms arising from it, could potentially occur at various stages in the life cycle of sodium cyanide; namely, from manufacture, to transport, use and ultimate release to the

environment. Terrestrial and avian wildlife may be exposed to cyanide residues in water at TSFs, and to cyanide solutions applied to or draining from heap leach facilities. Aquatic organisms may be exposed to cyanide in water released from these facilities into downstream areas. Measures which are used to limit exposure of wildlife to cyanide residues include restricting or preventing access by birds, bats and terrestrial animals to water containing toxic cyanide levels (e.g. netting, fences), ensuring such areas are not attractive to birds or bats (e.g. avoiding the formation of nesting or roosting sites in the vicinity), and/or using deterrents.

Groundwater near tailings storage and heap leach facilities may be contaminated by seepage. This varies widely between sites, and some seepage can be assumed despite careful design.

Exposure may arise if NaCN spills occur during transportation. Some spills of NaCN have occurred during road or rail transport in Australia, and in one incident wildlife were reported to have been affected. Environmental damage was minimised at other incidents where significant spills occurred, due to emergency response measures to contain and recover the spilt material and remove contaminated soil or water. However, some overseas incidents where significant release of NaCN occurred to water led to downstream environmental contamination and harm to aquatic organisms.

Unintended releases of material containing cyanide have also occurred overseas and in Australia due to incidents ranging from minor leaks causing no environmental harm to major structural failures leading to significant environmental harm due to physical effects and other toxic components, in addition to cyanide residues. These incidents indicate the need for appropriate monitoring and response measures for operations on an ongoing basis, as well as correct design and operation of TSFs and heap leach facilities.

Emission of hydrogen cyanide to air may occur as a consequence of the manufacture, transport and use of sodium cyanide. The major use of sodium cyanide is in the gold industry.

Environmental effects

In determining the effects of NaCN on the environment, data on sodium cyanide were supplemented with data from other cyanogenic compounds, because the free cyanide formed when sodium cyanide dissolves in water may also be present in aqueous environments from a number of other sources. These sources include dissociation or release from cyanogenic compounds (e.g. certain other metal cyanides and cyanide complexes, depending on their solubility, the pH and other conditions), and catabolism of cyanogenic glycosides in plant tissue.

These data showed that cyanide has very high acute (e.g. single dose) toxicity to aquatic and terrestrial animals and is also toxic to plants and certain micro-organisms. It also can produce chronic toxicity following long-term or repeat-dose exposure, such as adverse impacts on egg production and spawning in fish. Once in the bloodstream, cyanide rapidly forms a stable complex with enzymes involved in cellular respiration, resulting in cytotoxic hypoxia or cellular asphyxiation. The lack of available oxygen causes a shift from aerobic to anaerobic metabolism, leading to the accumulation of lactate in the blood. The combined effect of the hypoxia and lactate acidosis is depression of the central nervous system (CNS) that can result in respiratory arrest and death. A range of other enzymes and biological systems, other than the CNS, are also affected by cyanide.

In general, the effects of small non-lethal doses of cyanide tend to be reversible over time due to metabolic processes leading to cyanide degradation. There is a range of debilitating signs of sublethal cyanide poisoning (cyanosis), and fitness is likely to be impaired during the recovery phase. Greatest attention was paid in this report to the toxicity of cyanide to birds, as prior to

nomination of sodium cyanide for review in 1999, there had been reports of incidents in Australia where hundreds or thousands of birds have been killed within a relatively short period at a single gold ore processing site through exposure to cyanide residues in a TSF or associated facilties or heap leach site. A significant, well documented incident occurred at Northparkes Gold Mine in 1995, while other reports were anecdotal, with details lacking and with no formal source indicated.

There is now a body of evidence from various anecdotal and scientific observations and incident reports at mine sites that where significant mortalities are observed, WAD CN concentrations are > ~50 mg WAD CN/L, and that relatively few or no mortalities are observed at lower WAD CN concentrations. However, some caution is needed because field observations to determine the extent of sublethal effects are lacking. On the other hand, it should also be noted that there is a level of background mortality due to other causes, and from available information the contribution of cyanide toxicity to overall deaths at WAD CN levels below 50 mg WAD CN/L cannot be determined with certainty.

Laboratory studies have been conducted where birds were exposed to cyanide in drinking water, which is expected to be the most significant exposure route at mines. Drinking water studies based on standard test guidelines indicated avian LC50 values for bobwhite quail and mallard ducks of 374 mg CN/L and 180 mg CN/L, respectively. However, these studies were considered unreliable due to uncertain actual concentrations and exposure. The toxicity of cyanide in mine effluent and tap water with single or repeated exposure of mallard ducks has also been investigated, with LC50 values of 181-212 mg WAD CN/L and 136-158 mg WAD CN/L respectively. The results were interpreted as indicating an overall LC01 (1% mortality) of 50 mg/L for repeat exposure, which appears to be a further basis for selection of 50 mg WAD CN/L as a protective value. However, the original reports have not been seen, very limited information on the studies was available and the results are considered to be unreliable.

Other brief exposure (2-4 h) studies with mallards indicate a short exposure LC50 of ~115 mg WAD CN/L, which is consistent with field observations on acute mortality. An assessment factor of 10 could be applied to these, suggesting a concentration of ~12 mg WAD CN/L would be safe to protect mallards from any lethal effects with short term exposure. However, in extending these results to other species with different drinking behaviours and bodyweights, the relative size of a single dose would need to be considered (e.g. a dose of ~8-10 mL used for the ~1 kg mallards is relative to a total day's consumption of ~60 mL. Mallards would be expected to take six or more drinks per day, whereas a bird weighing ~50 g would consume around 10 mL water per day, and depending on the species, may only arrive to drink once or twice per day).

The most reliable data available for cyanide toxicity in birds were from acute oral toxicity tests with seven bird species. In this assessment, modelling based on these results has estimated a Predicted No Effect Concentration (PNEC) of ~1 mg/L, noting some limitations in the size and quality of the dataset. The use of acute toxicity data for assessment of toxicity from drinking water consumption requires interpolation of the results using estimated daily water consumption. As birds (and animals) may be able to detoxify cyanide if sufficient time elapses between the intake of sublethal doses, assumptions also need to be made regarding the proportion of daily water consumption that birds would ingest in each dose. In a worst case, it is necessary to consider ingestion of the entire day's consumption in a single dose. This is appropriate for species that arrive at water sources only once or twice per day, but is clearly conservative (or perhaps not even appropriate) for species such as waterbirds (e.g. mallards), which take several drinks over the day. Such differences in drinking behaviour between species make it difficult to extrapolate toxicity results from one species to another.

There are also studies of biochemical effects and effects on pigeon flight time from cyanide exposure, which indicate effects at relatively low doses. Expressed as the concentration given in a single dose of 10 mL (compared to an expected approximate daily water consumption of ~50-60 mL), significant biochemical effects occurred at concentrations as low as 20 mg free CN/L, and significant pigeon flight time effects at 50-80 mg free CN/L. The metabolism of the birds may recover from such doses, but while affected, birds may be more likely to succumb to predators or suffer reduced flying capacity. However, there is no conclusive evidence from observations or incident reports that these effects occur in the field, although in any case they would be very difficult to detect because they would occur at diffuse locations distant from the site where exposure occurred.

Observations also indicate that birds do not become averse to drinking cyanide-contaminated mine waste water. In fact, they may remain in a pond and take further drinks even after awakening from cyanide stupefaction. A bird that does not fly off may continue to take in further doses, leading to a cumulative toxicity effect. Depending on drinking behaviour (e.g. species differences) a bird may also take in a greater relative dose. However, it is also noted that birds are averse to drinking hypersaline water (salinity exceeding 50 000 mg/L TDS [Total Dissolved Solids]) and field studies show that in hypersaline situations, mortalities due to cyanide are not likely to occur even at WAD CN concentrations exceeding 50 mg/L.

Similarly, the most reliable toxicity data for mammals were acute oral toxicity studies, and modelling based on these results and drinking water consumption tables again estimated a Predicted No Effect Concentration (PNEC) of ~1 mg/L.

For aquatic assessment, a range of acute and chronic toxicity data are available with free cyanide, as considered in the development of the *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*. The cyanide trigger value for protection of 95% of aquatic organisms is 0.007 mg free CN/L at the boundary of freshwater mixing zones, or 0.004 mg free CN/L at the boundary of mixing zones if release is to coastal waters.

Risk characterisation and management

In order to characterise the health risk, the potential exposure level for wildlife is compared to the level of the substance where toxic effects are observed. Factors that affect wildlife exposure include the bioavailability of the substance to an organism. With regard to residues from gold mining operations, measurements of free cyanide in contaminated water are not an adequate indicator of the concentration of cyanide which is bioavailable to birds and mammals. This is because the amount of free cyanide originally present is increased after ingestion of the water due to release from various cyanide compounds and complexes under low gastric pH conditions. Consequently, in this assessment, the estimated environmental concentration endpoints for risk assessment to birds and mammals have been based on analyses of the WAD CN content of such waste.

Risks to the environment from the manufacture and storage of NaCN were considered to be acceptable if existing Commonwealth and state/territory legislation and voluntary measures are properly implemented and applied. However, it is recommended that the adequacy of existing measures for transport of NaCN be reconsidered in the light of the road transport incident which occurred in February 2007 in the Northern Territory.

This risk assessment has concentrated on uses in gold mining, where both the amount of sodium cyanide used and the likelihood of environmental exposure are greatest.

Terrestrial and aerial (birds and bats) wildlife may be exposed to residues of NaCN at gold mines. Initially, a risk quotient approach based on laboratory toxicity data was used to assess

the risk to wildlife at gold mine TSFs. While wildlife at these facilities may be exposed to material containing cyanide residues by various routes, consumption of drinking water is likely to be the major route of exposure. Assessments of risk to wildlife were therefore based on consumption of contaminated water containing a range of possible concentrations of WAD CN, together with the toxicity reference values determined for birds and mammals. On this basis, the risk assessment using a risk quotient approach based on laboratory toxicity data indicated a highly conservative WAD CN concentration in water of $\leq$ 1 mg/L (based on acute toxicity studies) in order to assure protection of sensitive avian species from acute mortality and from potentially harmful sublethal effects that might lead to delayed mortality. However, there are difficulties in relating risk assessment based on laboratory data with sodium cyanide to the risk in the field, particularly due to differences in the form of cyanide present in the field and in drinking behaviour of animals. This low level may not be justified based on other evidence and difficulties with extrapolating acute toxicity data from laboratory studies to the risk in the field, nor may it be practical with present technology. Field data generally indicate that incidents of mortality are very few at WAD CN concentrations < ~50 mg/L.

Recent studies indicate that higher WAD CN concentrations are likely to be safe in hypersaline situations because the very high salinity prevents animals consuming the cyanide-containing waters. There may be other site specific factors for which scientific argument can be presented, e.g. to allow a higher limit to apply in certain areas of a site such as in the vicinity of the tailings spigot where conditions ensure minimum access by birds.

Environmental exposure to cyanide residues is expected to be much lower when used in ore flotation at base metal operations, as the processes used are quite different to those used in gold mines. The level of bioavailable cyanide residues in waste streams transferred to TSFs is expected to be much lower in ore flotation, as the pH of the waste stream is low, and the composition of material in the TSFs is different to that in TSFs from gold mines using sodium cyanide. However, risk management for cyanide in TSFs at facilities using sodium cyanide should be consistent with those that at gold mines. Prevention of exposure to cyanide-containing solutions is essesstial at heap leach facilities, as concentrations cannot be reduced for efficacy reasons.

Risks to the aquatic environment, groundwater and vegetation were also examined and considered acceptable if existing Commonwealth and state/territory legislation and voluntary measures are properly implemented and applied. However, the importance to protect the environment by active monitoring and management of groundwater seepage is stressed.

Industrial uses of cyanide with metals occur at enclosed industrial sites, and under existing legislation and voluntary measures, any unconsumed cyanide is generally destroyed prior to disposal. Hence environmental risks from these uses are expected to be acceptable.

Releases of HCN to the atmosphere are unlikely to cause ecotoxicity, except possibly near the surface of tailings storage facilities (TSFs), where toxicity due to consumption of water containing cyanide is the greater concern. Flammability is also not considered to pose a significant environmental risk. Total releases of HCN from gold industry or other uses of sodium cyanide, while substantial, are considered unlikely to lead to significant increases in air concentration or to result in harmful global effects through action as a greenhouse gas or ozone depletor. Hence risks to the environment from gaseous hydrogen cyanide as a consequence of sodium cyanide use are considered acceptable.

The assessment findings indicate that for a number of steps in the supply chain (for manufacture, storage, release of cyanide during gold ore beneficiation use, base metal flotation and minor industrial uses), implementation and monitoring of compliance with existing Commonwealth and state/territory legislation and voluntary measures results in low risks to the

environment. However, based on the assessment of field data together with laboratory data, NICNAS recommends to better manage risks to the environment by improvements to existing measures, including compliance with best practice principles for transport of sodium cyanide, and a framework approach to minimise the risks to wildlife at TSFs and heap leach facilities where sodium cyanide is used.

While this review is about industrial uses of sodium cyanide, similar issues would be relevant for potassium cyanide and other simple cyanide salts. Thus, chemical users should take note of the recommendations for sodium cyanide when using these other salts.

Recommendations

This chapter provides recommendations arising from this Priority Existing Chemical assessment of sodium cyanide. Consideration has been given to where the manufacture, handling, storage, use or disposal of sodium cyanide gives rise, or may give rise, to a risk of adverse environmental effects. Recommendations are directed at regulatory and non-regulatory bodies and industrial users of sodium cyanide.

The recommendations address seven different issues, as follows:

1. Manufacture
2. Storage
3. Transport
4. Release of cyanide during gold ore beneficiation use, including:
    a. Prevention and management of environmental incidents arising from unplanned releases of material containing cyanide
    b. Protection of groundwater from contamination by cyanide in seepage from TSFs or heap leach facilities and associated dams
    c. Protection of aquatic organisms from planned releases of water from disposal facilities following sodium cyanide use for gold ore processing
5. Protection of wildlife during gold ore beneficiation use, including:
    a. Protection of wildlife at gold tank leach processing facilities
    b. Protection of wildlife at gold heap leach processing facilities
    c. Need for suitable monitoring and response programs to support wildlife protection measures
6. Base metal flotation uses
7. Minor industrial uses

Due to the complexity surrounding the assessment of sodium cyanide, each recommendation is accompanied by a separate preamble to briefly provide the rationale supporting the recommendation. For a full understanding of reasons, the main report should be consulted.

1. Manufacture

Existing Commonwealth and state/territory legislation and voluntary measures provide adequate controls and guidance for managing the design and operation of sodium cyanide manufacturing facilities to protect the environment from exposure to harmful levels of cyanides.

These measures include legislation relating to Major Hazard Facilities, waste management, and emissions management and monitoring, and the involvement of industry in various voluntary Codes of Practice, including the International Cyanide Management Code for the Manufacture, Transport, and Use of Cyanide in the Production of Gold (ICMC) and those under the international Responsible Care® program.

Recommendation 1:

Industry should continue to comply with existing Commonwealth and state/territory legislation and to implement voluntary measures to ensure an acceptable risk to the environment during the manufacture of sodium cyanide. State/territory governments should continue to monitor compliance.

2. Storage

There is potential for exposure of the environment to cyanide during the filling, transport and unloading of sodium cyanide containers, or through breaching of a storage container in an accident.

Existing Commonwealth and state/territory legislation and voluntary measures provide adequate controls and guidance for managing the storage of sodium cyanide in order to protect the environment from exposure to harmful levels of cyanide.

For storage and handling the existing guidance include the National Standard and Code of Practice for the Storage and Handling of Dangerous Goods (NOHSC, 2001a, 2001b), National Standard and Code of Practice for the Control of Major Hazard Facilities (NOHSC, 1996, 2002a), Australian Standards applying to storage and handling, complementary state/territory legislation to these, other related Commonwealth and state/territory legislation, and the involvement of industry in various voluntary Codes of Practice.

Recommendation 2:

Industry should continue to comply with existing Commonwealth and state/territory legislation and to implement voluntary measures to ensure an acceptable risk to the environment during storage of sodium cyanide. State/territory governments should continue to monitor compliance.

3. Transport

Sodium cyanide in either solid or liquid form may be transported by rail or road in bulk quantities, often long distances from the manufacturing sites to remote areas (for example, for use in gold beneficiation and in base metal flotation).

Existing Commonwealth and state/territory legislation and voluntary measures provide controls and guidance for managing transport of sodium cyanide in order to protect the environment from exposure to harmful levels of cyanide. For land transport within Australia, these measures include the Australian Code for the Transport of Dangerous Goods by Road and Rail (ADG Code) (NTC, 2007).

The International Cyanide Management Code for the Manufacture, Transport, and Use of Cyanide in the Production of Gold, and for manufacturers, the international Responsible Care® program also provide guidance.

Transport of sodium cyanide in solid form occurs in composite intermediate bulk containers (CIBCs) inside freight containers holding 20 CIBCs. Solid sodium cyanide manufactured at Gladstone in Queensland is also transported in larger (e.g. 20-22 tonne) specially designed solid-to-liquid (StoLs) isotainers.

Transport of sodium cyanide in liquid form is restricted to land transport in isotainers and occurs predominantly in Western Australia, but some transport in liquid form also occurs from the Gladstone site in Queensland.

It would be more difficult to contain, treat and recover releases in liquid form, but releases in the solid form would dissolve rapidly if rain or surface water were present, with potential for runoff to surrounding areas.

A truck accident in the Northern Territory in 2007 resulted in spillage of sodium cyanide, and while minimal environmental harm resulted, the incident suggests there may be improvements that could be made to current legislation and guidance in various jurisdictions. Key recommendations from a review of this incident were the adoption of the 7th Edition of the Australian Dangerous Goods Code (ADG7) and improvements to coordination across Government agencies, both for compliance monitoring arrangements and for emergency response procedures.

Recommendation 3:

Transport of sodium cyanide should be conducted according to the requirements specified in the Australian Code for the Transport of Dangerous Goods by Road and Rail (7th edition - ADG7) and the associated State/Territory legislation that gives it effect.

The Australian Dangerous Goods Code, and other relevant transport requirements, codes and guidance material, provide best practice provisions in order to reduce the likelihood of, or lesson the impacts of accidents leading to sodium cyanide release to the environment.

These provisions include the following:

- **Compliance with dangerous goods transport regulations for bulk container design, packaging, placarding and safety equipment;**
- **Selection of mode of transport;**
- **Where alternative routes are available, careful route selection to minimise travel through environmentally sensitive areas;**
- **Optimisation of load size to minimise overall risk, and compliance with local transport requirements such as Restricted Area Vehicle permits;**
- **Driver training covering vehicle handling, bulk transfer procedures and emergency response; and**
- **Access by transporters to appropriately trained and equipped emergency responders that can respond in a timely manner.**

Implementation and adequacy of these measures should be monitored by the relevant state and territory authorities. Industry should continue to comply with Commonwealth and state/territory legislation and to implement voluntary measures to ensure an acceptable risk to the environment during transport of sodium cyanide.

4. Release of cyanide during gold ore beneficiation use

Tank and heap leaching operations using the cyanidation process for gold beneficiation form the principal route of environmental exposure to sodium cyanide. This is the case in terms of both the extent of use and the nature of release to the environment, noting much of the cyanide used is not consumed or lost in the process, but is deposited with tailings into tailings storage facilities in the case of tank leach processes, or remains in the solutions flowing from heap leach piles or in immobile forms within those piles.

Replacement of sodium cyanide with other substances is not yet generally practicable. Recovery of cyanide for re-use on site is possible for some operations and would minimise release to the environment.

a. Prevention and management of environmental incidents arising from unplanned releases of material containing cyanide

International incidents have demonstrated the potentially serious consequences for the environment from structural failures, overtopping, or spillage or leakage from heap leach piles, TSFs and associated equipment and facilities.

Monitoring programs to check for operational problems are in place at mine sites and have been operating satisfactorily and allow suitable corrective and preventative action to be taken. Currently available regulatory and voluntary measures are considered sufficient to ensure that the design, construction and operation of ore beneficiation sites, TSFs and associated facilities are adequate to protect the environment from structural failures, with additional measures to capture and control overflows, seepage, spillages and leaks at the mill, TSF and other areas of the site where cyanide residues may be present.

Recommendation 4a

Industry should continue to comply with existing Commonwealth and state/territory legislation, and to implement voluntary measures to ensure acceptable risks to the environment from releases of cyanide containing material arising from the failure of structures containing cyanide residues or from dam overtopping, leaks and spills. State/territory governments should continue to monitor compliance.

b. Protection of groundwater from contamination by cyanide in seepage from TSFs or heap leach facilities and associated dams

Under the National Water Quality Management Strategy (ANZECC/ARMCANZ, 1995), operations are required to manage seepage from tailings storage and heap leach facilities to protect the beneficial uses of groundwater and prevent ecological damage from cyanide (and other constituents) in the event that groundwater reaches surface waters.

Monitoring of the groundwater enables seepage to be detected and appropriate action taken. Protection of groundwater is currently addressed through environmental impact assessment, the site design and work plan approval and monitoring process, and through inspection and reporting processes by state/territory agencies and is also addressed in the ICMC.

It is considered that existing regulatory processes are appropriate for groundwater protection to be planned and managed, based on site assessments and regular review and with regard to the existing quality of the groundwater.

Recommendation 4b

Industry should continue to comply with existing Commonwealth and state/territory legislation, and to implement voluntary measures to ensure acceptable risks to the environment from releases of cyanide due to seepage from TSFs and other structures holding water containing cyanide. State/territory governments should continue to monitor compliance.

c. Protection of aquatic organisms from planned releases of water from disposal facilities following sodium cyanide use for gold ore processing

Exposure to aquatic organisms is not a concern in the TSF or associated dams and ponds used for storage of decant, process or drainage water on the site, but may be a concern if downstream areas were to be contaminated, for example, where intended discharges of TSF or heap leach waters to surface waters need to occur in high rainfall areas.

Most states and territories review plans for facilities which may release cyanide to surface waters in the context of the *Australian and New Zealand Guidelines for Fresh and Marine Water Quality* (2000a) cyanide trigger value for protection of 95% of aquatic organisms, specifying appropriate compliance limits in water discharged from TSFs at suitable measuring points.

Existing Commonwealth and state/territory legislation and voluntary measures provide adequate controls and guidance for managing risks to the Australian environment arising from planned releases of water from disposal facilities following sodium cyanide use for gold ore processing.

Recommendation 4c

Industry should continue to comply with existing Commonwealth and state/territory legislation, and to implement voluntary measures to ensure acceptable risks to the environment from planned releases of water from disposal facilities following sodium cyanide use for gold ore processing. State/territory governments should continue to monitor compliance.

5. Protection of wildlife during gold ore beneficiation use

a. Protection of wildlife at gold tank leach processing facilities

At gold tank leach processing facilities, gold is removed from the ore using sodium cyanide in water, and the remaining material in solution is placed in tailings dams, which are often substantial structures.

Birds and other wildlife may drink the contaminated water in the tailings dams, particularly when alternative water sources are limited, and may also use the area for refuge.

Available information indicates birds do not avoid drinking cyanide-contaminated mine waste water. However, as birds are averse to drinking hypersaline water, cyanide intake may be reduced where the water is hypersaline.

The assessment has determined that risks to wildlife from operations using sodium cyanide in tank leach operations for extracting gold from ore are such that improved management to reduce risks from exposure is needed.

Detailed consideration of risk mitigation strategies to protect wildlife, particularly birds, from the harmful effects of cyanide at these facilities is essential. Two risk mitigation pathways have been considered in this assessment, one controlling concentrations of cyanide levels available in TSFs and the other controlling exposure, by reducing access to wildlife. These two risk mitigation pathways can also be used together to protect wildlife.

Concentration controls

In the Australian mining industry the majority of cyanide residue is released to TSFs, which is the main source of release to the environment. There are a large number of TSFs of various designs and with differing processing procedures and tailings stream management strategies operating in Australia,. These vary according to climate, topography, geographic location, operational requirements of the mine, processing water quality, ore composition and various other factors. Ore composition also varies at different minesites, and this affects the concentration of cyanide required by the process and the concentration of free CN or WAD CN resulting in the tailings stream. The amount of free CN or WAD CN in the tailings stream cyanide cannot be predicted reliably. Thus it would not be appropriate to establish a single benchmark for all mines, and active monitoring of CN levels is necessary for optimising the beneficiation process and to enable cyanide levels in the tailings stream to be managed.

There is now a body of evidence from various scientific observations, incident reports at mine sites and anecdotal information that significant mortalities are observed at concentrations > ~50 mg WAD CN/L, and that relatively few or no mortalities at lower WAD CN concentrations. However, some caution is needed with the latter because field observations to determine the extent of sublethal effects are lacking. On the other hand, it should also be noted that there is a level of background mortality due to other causes, and from available information the contribution of cyanide toxicity to overall deaths at WAD CN levels below 50 mg WAD CN/L cannot be determined with certainty.

While the above is generally the case, studies in hypersaline areas have demonstrated that wildlife mortalities due to cyanide do not occur, even where WAD CN concentrations significantly exceed 50 mg/L. Investigations have shown that this is because exposure of wildlife is minimised, as even species adapted to saline water (14 000 – 50 000 mg/L TDS) do not drink hypersaline water (> 50 000 mg/L TDS) and receive minimal exposure through diet or other sources. The chemistry of the tailings discharge in hypersaline situation was also shown to favour degradation of the WAD CN, provided pH and salinity were at appropriate levels and the Cu content within appropriate limits for the WAD CN content. There may also be other circumstances where a WAD CN limit could exceed 50 mg/L without adverse effects to wildlife; following a case-by-case site-specific analysis in consultation with the relevant state or territory regulator.

Concentration levels protective of birds are also considered protective of bats and terrestrial vertebrates such as macropods and reptiles. Where concentration controls are used, appropriate programs should be in place to monitor WAD CN concentrations at appropriate locations and intervals, and specification of control concentrations should address statistical considerations.

In situations where TSF waters may need to be released, it may be necessary to ensure WAD CN concentrations remain lower than they would otherwise need to be to protect terrestrial and avian wildlife, in order to reduce the risk to aquatic wildlife further downstream. Before ultimate release of effluent to aquatic areas, remaining cyanide concentrations would then need to fall to specified compliance limits at suitable measuring points (see Recommendation 4).

Exposure controls

An alternative approach to mitigating the risk to wildlife is to minimise exposure by restricting or preventing access by birds and bats to water containing toxic cyanide levels, ensuring such areas are not attractive to birds or bats, and/or using deterrents. The measures need to be considered on a site specific basis with knowledge of the species (Section 11.13).

Protective action needs to be balanced against the possibility that it may itself cause harm to wildlife, and needs to be practicable in the local situation, as separate issues to the costs involved.

In all cases, appropriate monitoring programs should be in place so the operator can react promptly to exposure events with active deterrent and corrective measures as necessary, and preferably, anticipate and prevent exposure events by avoiding the development of habitat attractive to wildlife in areas where waters containing potentially harmful concentrations of cyanide are released (see Recommendation 5c).

Recommendation 5a

Management of risks to avian and mammalian wildlife at tailings storage facilities requires improvement. Regulators and operators should adopt a framework strategy (see Table - Recommendation 5a) combining benchmark limits with other measures appropriate to the environmental risks at the individual site.

A framework for the management of risks to wildlife from sodium cyanide use in gold mining is presented in the Table below. Differences in geology, topography, water quality, climate, geographical location, local standards etc make it difficult to have a single benchmark across Australia. Accordingly, a flexible, framework approach is proposed incorporating the use of alternative measures to limit exposure together with a range of benchmark concentrations according to site factors. The following points form the basis of the proposed framework:

i. At concentrations $\geq$ 50mg WAD CN/L, deaths of a significant proportion of birds exposed may occur. At tank leach facilities where it is very difficult or impracticable to lower WAD CN below 50 mg WAD CN/L and the waters are not hypersaline, concentration control measures cannot be relied upon. In these exceptional situations, comprehensive measures must be taken to prevent exposure of wildlife to waters containing > 50 mg WAD CN/L, together with measures to minimise the attractiveness to wildlife of the habitat in and around the tailings storage facility.

ii. At tank leach facilities where WAD CN concentrations in waters accessible to wildlife and the waters are hypersaline, a 50 mg/L WAD CN limit is not required, as studies in hypersaline areas have demonstrated that hypersalinity is protective of wildlife. However, appropriate target levels for WAD CN, salinity, pH and Cu must be agreed for the specific site, and measures must also be taken to minimise the attractiveness to wildlife of the habitat in and around the tailings storage facility, with exclusion of access to specified areas.

iii. In general, except at hypersaline sites and exceptional other sites, process controls and cyanide destruction facilities should be in place to enable WAD CN to be maintained at an agreed level below 50 mg/L. Adoption of a level of 50 mg WAD CN/L as a general maximum target at non-hypersaline sites is consistent with that used by the ICMC, as field observations indicate that few wildlife mortalities are likely to occur at WAD CN concentrations below this level. Measures must also be taken to minimise

the attractiveness to wildlife of the habitat in and around the tailings storage facility, and may be required to exclude access to specified areas. A range of 10-50 mg WAD CN/L was selected because of the uncertainty as to which point and which species are susceptible to lethal and sub-lethal effects, and secondly to enable a statistical description of the concentration to be specified by regulatory authorities.

iv. There are also sites where WAD CN is reduced to around 10 mg/L or less for other reasons, e.g. where downstream release may occur. A high level of protection to avifauna and terrestrial wildlife exposed to waters at WAD CN concentrations < 10 mg/L is therefore likely from the concentration control achieved.

This framework could be enhanced in the light of further laboratory data, field evidence and experience. For example, the ICMC allows mines to present peer-reviewed scientific studies which show that WAD CN concentrations exceeding 50 mg/L may be acceptable for a specific site (with no adverse effects to wildlife) for reasons other than hypersalinity, and such arguments could be evaluated by state/territory agencies.

It is envisaged that the framework will operate through state/territory agencies working together with mines in planning wildlife protection measures through the initial Environmental Impact Statement, and site design and work plan approval processes, followed by ongoing interaction through monitoring, inspection and reporting processes with state/territory agencies. Facilities should aim to achieve maximum WAD CN concentrations below 50 mg/L in waters accessible to wildlife by the end of 2012 unless they can demonstrate to the satisfaction of state/territory agencies that local conditions warrant a higher target and that other factors or measures taken adequately prevent exposure of birds and animals to water containing higher concentrations of cyanide. Subject to agreement by state/territory agencies, this may be adequately demonstrated by certification by the International Cyanide Management Code.

While 50 mg WAD CN/L is proposed as the general overall maximum concentration target to minimise the risk of significant bird death incidents occurring, as concentrations may fluctuate widely, it is necessary to set appropriate statistical limits below this so that the maximum level is not exceeded. An example would be 30 mg WAD CN/L (90th percentile of time) and 50 mg WAD CN/L (not to be exceeded), cf. NSW DECC, but other standards may be selected. Situations such as areas where rare or threatened species are present may warrant a further level of protection. An example would be 20 mg WAD CN/L (90th percentile) and 30 mg WAD CN/L (maximum), cf. NSW DECC for a more sensitive site. Such levels may be established by an EIS. Lowering the concentration levels may also be required if monitoring shows that harmful impacts to birds are occurring despite the relevant target levels being met and other management steps having been taken, particularly if threatened species are present.

Data show that factors such as time of day affect concentrations at points distant from the outlet to the TSF, for example, because degradation caused by sunlight is reversible at night. For this reason, benchmark targets should apply to tailings effluent at the point of discharge to the TSF, supported as necessary for local requirements by testing at other points, such as supernatant water and decant ponds.

Research has shown the importance of copper in stabilising WAD CN, and copper soluble cyanide complexes in the WAD cyanide concentrations have caused some mine sites to discharge tailings solutions in excess of 50 mg/L. In some circumstances it may be appropriate to measure other components of tailings solutions such as copper, as recommended for hypersaline sites by Adams et al. (2008b).

Recommendation 5a: Framework for management of risks to wildlife from sodium cyanide use in gold mining

Proposed target WAD CN concentration at the discharge point to the tailings storage facilities (TSF)	Strategy	Comments	Notional implications for wildlife protection
Category 4 ≥50 mg WAD CN/L and the tailings stream is not hypersaline (see Category 3)	**Reliance on prevention or avoidance of wildlife exposure as the sole protection mechanism** • This category may be preferred where there are clear reasons why reducing WAD CN to <50 mg/L is not feasible, for example the nature of the ore or water source requires high CN input concentrations and it is difficult to lower CN to acceptable levels by destroying or recovering the cyanide, or this is a heap leaching operation.	• Where it is not feasible to lower WAD CN concentrations to acceptable levels, exclusion of wildlife by comprehensive measures is essential • Process controls/monitoring to site specific targets for CN (potentially also other components, as in Category 3) • Access must be excluded to all waters containing WAD CN > 50 mg/L, monitor nets etc to ensure they remain secure • Habitat control/monitoring is essential to minimise attractiveness (high standard) • Wildlife monitoring for visitation & mortalities – daily while >50 mg/L, 2-3 times/week if below • Response program available if impacts occur	At concentrations ≥50 mg WAD CN/L, deaths of a significant proportion of birds exposed may occur. Hence, at such concentrations strong measures to minimise exposure are required.
Category 3 ≥50 mg WAD CN/L and the tailings stream is hypersaline [≥ 50 000 mg/L Total Dissolved Solids (TDS)]	**Reliance on the hypersalinity of the water minimising ingestion of cyanide by wildlife, in combination with other wildlife exposure minimisation measures** • This category may be preferred where hypersalinity in water containing residues of cyanide makes it sufficiently unpalatable that birds do not drink sufficiently from it to obtain a toxic dose.	The following measures are recommended: • Process controls/monitoring to site specific targets for CN, salinity, pH & Cu • Habitat control/monitoring & covering open seepage trenches with gravel (specific recommendations for such sites) • Wildlife monitoring for visitation & mortalities – daily while >50 mg/L, 2-3 times/week if below • Rainfall observations, as rain water	Provided birds do not drink from contaminated water because hypersalinity makes it highly unpalatable, and do not become exposed by diet or other means, avoidance of exposure minimises the risk of mortality from cyanide consumption.

Proposed target WAD CN concentration at the discharge point to the tailings storage facilities (TSF)	Strategy	Comments	Notional implications for wildlife protection
		has possible implications for salinity levels • Response program available if impacts occur.	
Category 2 10-<50 mg WAD CN/L, according to the performance of other measures and other site specific factors	**Reliance on a combination of concentration control and wildlife exposure minimisation strategies to protect wildlife.** • This category may be preferred where WAD CN concentrations in water accessible to wildlife can be maintained consistently below 50 mg/L	• Process controls/monitoring to site specific targets for CN (potentially also other components, as in Category 3) • Actual level of CN & statistical description, & where to sample, must be agreed on a site specific basis. • Limitation/prevention of access to waters in specified areas • Habitat control/monitoring to minimise attractiveness • Wildlife monitoring for visitation & mortalities – 2-3 times/week while ≤50 mg/L, increased frequency if issues arise • Response program available if impacts occur	At concentrations of <50 mg WAD CN/L, available field data indicate that few acute mortalities are likely to occur. Insufficient field evidence is available regarding the likelihood of sublethal effects arising such as greater predator susceptibility and reduced flying ability (important for migratory birds). Mortality or sublethal effects could vary between species (e.g. with drinking and swimming behaviour as well as species sensitivity), and with behaviour affected by local conditions (e.g. whether or not alternative water sources are available). Greater risks of mortality would be expected as the concentration in this range increased and with decreasing effectiveness of alternative measures.
Category 1 <10 mg WAD CN/L	**Stronger concentration controls are in place for other reasons**. • e.g.because the effluent is already treated to protect downstream aquatic areas (i.e. where water is released). See Recommendation 4.	• Process controls/monitoring to site specific targets for CN • As a contingency precaution, it is still necessary to have steps in place to minimise wildlife visitation and for monitoring, e.g. in the event of detoxification malfunction.	At concentrations <10 mg WAD CN/L, no acute mortalities and minimal sublethal effects are expected.

Further comments:

1. At each level, particularly Categories 2 to 4, appropriate ongoing monitoring and response programs for both wildlife impacts and cyanide concentrations present are necessary, together with auditing/reporting mechanisms (see Recommendation 5c). This is to ensure that the stated concentration level is being achieved and that harmful impacts on wildlife are not occurring, and so that if wildlife are present they can be discouraged by active response measures. Where relevant, monitoring should also ensure that habitat attractive to wildlife does not develop and that exclusion structures such as netting and fences remain in good condition.
2. There is significant uncertainty as to the concentrations at which lethal and sublethal effects would occur for different bird species in the field.
3. The categories are not intended to indicate a progression in environmental safety: a similar level of environmental safety should be possible by an appropriate combination of exposure minimisation measures for the WAD CN concentration range, but within each category an increasing level of protection could be achieved by the combination of measures selected.
4. The concentration categories have been based on WAD CN concentrations at the point of discharge to the TSF, where they are likely to be maximal. This gives further protection to areas beyond that point (e.g. the decant pond), as WAD CN concentrations would be expected to fall over time and distance, as further reactions and loss of HCN occur. WAD CN concentrations in tailings dams are also more likely to fluctuate diurnally due to photolysis effects.
5. Attention needs to be given to the capacity of a facility to adequately monitor concentrations of cyanide, including the frequency of sampling, timeliness of analysis and reliability of the analysis. More demanding additional measures may then be appropriate to minimise potential exposure of wildlife at these sites.

An important aspect of a benchmark concentration-based system is the ability to adequately monitor the WAD CN concentration. The reliability, accuracy and consistency of analytical results need to be assured. Capabilities differ between large and small sites. For example, small facilities may not currently have any capacity to measure WAD CN on site. If WAD CN concentration is relied upon as the main prevention measure, the frequency of measuring, timeliness of obtaining results, and the accuracy of the results are important to avoid undetected problems arising. Such difficulties with monitoring concentration heighten the importance of monitoring for wildlife incidents as well.

b. Protection of wildlife at gold heap leach facilities

In gold heap leach facilities, free CN (rather than WAD CN) concentrations in solutions applied to heap leach piles may exceed 100 mg/L, and concentrations may remain high in pregnant (containing the gold complex) solution that has leached through the pile and subsequent process water ponds at heap leach facilities.

Birds (and possibly bats) may consume this solution as a consequence of ponding on the surface of the heap leach pile. There are also risks that birds may also drink from the pregnant solution and other ponds containing cyanide residues.

For efficacy reasons, steps to reduce WAD CN concentrations to safe levels are not appropriate for waters containing elevated concentrations of cyanide at heap leach facilities. Under these circumstances, steps must therefore be taken to prevent access by birds to toxic cyanide solutions.

Ponding on the surface of heap leach piles must be minimised in both area and duration by steps such as treatment of the ore to ensure satisfactory water infiltration (e.g. agglomeration) and by ensuring that the irrigation rate of process water to the heap does not exceed the infiltration rate. Access of birds and terrestrial animals to any such waters should be prevented by steps such as enclosing, netting or covering them with gravel, by filling drains with rubble or by using pipes instead of open drains.

Recommendation 5b

To manage risks to avian and mammalian wildlife at heap leach facilities using sodium cyanide for extracting gold from ore, the requirements pertaining to Category 4 in the above framework (Table - Recommendation 5a) should apply. In particular, operators should minimise ponding on heap leach piles and prevent access of birds and other wildlife to waters containing WAD CN concentrations >50 mg/L. Industry should also continue to comply with existing Commonwealth and state/territory legislation and to implement voluntary measures. State/territory governments should continue to monitor compliance.

c. Monitoring and response programs to support wildlife protection measures

Response programs, which involve monitoring, are needed to support the wildlife protection measures, in order to ensure that the measures are successful, and determine if modifications are needed. Three monitoring programs are required: monitoring of wildlife, monitoring of cyanide levels in TSFs and monitoring of habitats near TSFs, so they are not an attraction to birds.

An important outcome of recent research projects such as 'Risk Assessment of the Effects of Cyanide-Bearing Tailings Solutions on Wildlife', managed by the Australian Centre for Mineral Extension and Research (ACMER), and 'Cyanide Ecotoxicity at Hypersaline Gold Operations' funded by the Minerals and Energy Research Institute of Western Australia (MERIWA), and of previous research in the Northern Territory, has been the recognition of the importance of the habitat in and near TSFs for attracting birds, as well as influencing how long they remain in the area. Hence monitoring of habitat based on guidance that has emerged from this research is essential.

Wildlife monitoring techniques and timing need to be adequate to detect incidents promptly, to spot affected animals before they are scavenged or buried, and to ensure an extra level of protection is maintained for threatened species. Routine observations therefore need to be conducted and recorded in a consistent fashion so that increases or decreases in the presence of wildlife and in impacts are evident. Observers need to be trained in appropriate observation techniques to record the birds or type of animals affected on a routine basis.

This assessment has found that most regular observers at mine sites are not bird experts and therefore could not be relied upon to correctly identify to species level the multitude of birds that may arrive at a site over time. Consequently, to ensure that impacts occurring to threatened species are not overlooked, other mechanisms need to be in place, such as less frequent monitoring by skilled personnel to identify species present at the site and further evaluation to species level when mortalities occur, particularly if threatened species have been observed or may be anticipated at a site.

Suitable programs should be in place to monitor WAD CN concentrations in tailings discharge, with sampling conducted sufficiently frequently so that increases above target levels are avoided or detected promptly. This will enable corrective action to be taken and minimise the likelihood of harmful effects developing. Occasional monitoring at other points, such as in TSF supernatant, decant and return water ponds, seepage trenches etc, may also be needed, particularly where water in them is accessible to wildlife. Sample collection and storage and analysis techniques should be scrutinized to ensure they provide adequate consistency and accuracy. There are strong reasons for favouring the point of tailings discharge as the prime point where concentration limits should be applied, as this is where concentrations in tailings would be expected to be highest.

With monitoring of WAD CN levels in water, of impacts on wildlife and of changes in the habitat present, plans must be in place for appropriate responses to concentration exceedances or wildlife incidents that do occur, or for habitat correction to the extent possible. These should include short-term contingency plans to respond appropriately to exceedance problems, e.g. taking active measures to disrupt bird activity (‘bird frite’) while toxic concentrations are present, taking steps to reduce concentrations in the water, and temporary plant shutdown to prevent further build up of cyanide levels. Action to avoid an ongoing or recurring event should be pursued as necessary.

Monitoring for various purposes is included in the ICMC and monitoring is already addressed in existing procedures by mines and requirements by regulators. However, it is considered that at many sites improvements in the standards of monitoring conducted and in the associated response and reporting plans may be necessary.

Monitoring and reporting programs should be agreed between the state/territory regulator and the mine operator. An agreed reporting schedule is necessary to enable regular evaluation by the regulator of the adequacy of ongoing cyanide management procedures at the site, as well as early awareness of events which are considered significant due to their scale and/or the species affected. There should be a clear and unambiguous agreement as to what sort of information is required, how often it should be provided, and when an event ranks as 'significant'.

There are various voluntary industry strategies and programs in place to manage the risks to the environment from sodium cyanide. These strategies/programs should be managed with a view to continuous improvement.

Recommendation 5c

To ensure that risk mitigation measures are effective, industry, in agreement with the relevant state/territory government agencies, must ensure that suitable habitat, wildlife and cyanide concentration monitoring and response programs are in place and operating satisfactorily at sites using sodium cyanide for extracting gold from ore.

Industry should use the monitoring data obtained to report to the relevant government agencies, according to an agreed process to allow significant incidents to be brought to the attention of the agencies promptly so that government agencies can confirm the adequacy of ongoing cyanide management procedures at each site.

6. Base metal flotation uses

Sodium cyanide is used as a depressor in the flotation of base metals, and cyanide residues may therefore be deposited with the tailings stream into tailings storage facilities. The quantities of sodium cyanide used for this purpose at any given site are typically much less than those used for extracting gold from ore.

Cyanide concentrations arising in tailings storage facilities are supposedly very low, and the free cyanide is largely destroyed in the process, but there were no measured data available to confirm this for Australian ore processing facilities.

Delivery to a TSF of cyanide as free cyanide or various other forms of WAD CN would present similar risks to the environment to those from use in the gold industry. For this reason it is appropriate that similar action to that recommended for the gold industry be taken to protect the environment.

Recommendation 6

Current risk management procedures for the use and disposal of sodium cyanide when used as a depressor in base metal flotation are acceptable. Industry together with state/territory governments should ensure that cyanide management of tailings storage facilities at these sites provide a consistent level of protection to those applying to gold operations. Where WAD CN concentrations in tailings discharge exceed 10 mg/L, the same framework approach (Table – Recommendation 5a) and monitoring requirements applying to gold mines should be used.

7. Minor industrial uses

There is little potential for environmental exposure to arise from non-mining uses of sodium cyanide, including electroplating, surface treatment of iron and steel (metal hardening), metal cleaning and laboratories. In these relatively minor use situations, used cyanide solutions or solids are generally contained and treated on or off site prior to disposal to the sewer or controlled landfill, and/or only small quantities are used on each occasion. Furthermore, the use of sodium cyanide in these industries has already declined due to the availability of viable alternatives, particularly in the electroplating industry.

Existing Commonwealth and state/territory legislation and voluntary measures provide adequate controls and guidance for managing risks to the Australian environment arising from the use of sodium cyanide in the electroplating and metal hardening industries, for metal cleaning, and in laboratories.

These measures include the National Standard for the Storage and Handling of Workplace Dangerous Goods, provision of information in MSDSs, and state/territory environment protection and waste management legislation.

Recommendation 7

Industry should continue to comply with existing Commonwealth and state/territory legislation and implement voluntary measures to ensure that risks to the environment during the use and disposal of sodium cyanide when used in non-mining situations are acceptable. State/territory governments should continue to monitor compliance.

Secondary Notification

Under Section 65 of the *Industrial Chemicals (Notification and Assessment) Act, 1989* (Commonwealth), a secondary notification of sodium cyanide may be required where a manufacturer or introducer of the chemical becomes aware of circumstances that may warrant a reassessment of its environmental hazards and risks. Specific circumstances include:

- the method of manufacture of sodium cyanide in Australia has changed, or is likely to change, in a way that may result in an increased risk of adverse environmental effects;
- the method of use of sodium cyanide in the mining industry in Australia has changed, or is likely to change, in a way that may result in an increased risk of adverse environmental effects; and
- additional information has become available to the manufacturers, importers and applicants of the assessment of sodium cyanide as to the adverse environmental effects of the chemical, including wildlife mortality incidents at WAD CN concentrations below 50 mg/L.

The Director must be notified within 28 days of the manufacturer/importer becoming aware of any of the above or other circumstances prescribed under Section 65 of the Act.

Acronyms and Abbreviations

ACGIH	American Conference of Government Industrial Hygienists
ACMER	Australian Centre for Mineral Extension and Research (formerly Australian Centre for Mining Environmental Research
ACT	Australian Capital Territory
ADG Code	Australian Dangerous Goods Code (NTC, 2007)
AF	assessment factor
AMIRA	Australian Mineral Industries Research Association Limited
ANZECC	Australian and New Zealand Environment and Conservation Council
ANZMEC	Australian and New Zealand Minerals and Energy Council
APHA	American Public Health Association
ARMCANZ	Agricultural and Resource Management Council of Australia and New Zealand
ASTM	ASTM International (originally known as the American Society for Testing and Materials)
ATP	adenosine triphosphate
ATSDR	Agency for Toxic Substances and Disease Registry (USA)
BMTF	Baia Mare Task Force (Romania)
$Ca(CN)_2$	calcium cyanide
CAS	Chemical Abstracts Service
CCREM	Canadian Council of Resource and Environment Ministers
CME	Chamber of Minerals and Energy of Western Australia
CMSA	Chamber of Mines of South Africa
CN	cyanide
CNS	central nervous system
CO_2	carbon dioxide
CSIRO	Commonwealth Scientific and Industrial Research Organisation (Australia)
CuCN	copper cyanide
Cwlth	Commonwealth
DEWHA	The Department of the Environment, Water, Heritage and the Arts (previously the Department of the Environment and Water Resources, prior to that the Department of the Environment and Heritage and prior to that, Environment Australia)

DHA	United Nations Department of Humanitarian Affairs
DIN	Deutsches Institut für Normung e.V. (Germany)
DITR	Australian Government Department of Industry, Tourism and Resources
DITRDLG	Australian Government Department of Infrastructure, Transport, Regional Development and Local Government
DRET	Australian Government Department of Resources, Energy and Tourism
ORS	Office of Road Safety (Australia)
EC50	The concentration of a test substance which results in an effect on 50% of the test species.
EINECS	European Inventory of Existing Chemical Substances
EIS	Environmental Impact Statement
FAO	Food and Agriculture Organisation of the United Nations
HCN	hydrogen cyanide
HSDB	Hazardous Substances Data Base
ICAO	International Civil Aviation Organisation
ICMC	International Cyanide Management Code for the Manufacture, Transport and Use of Cyanide in the Production of Gold
ICME	International Council on Minerals and the Environment
ICMI	International Cyanide Management Institute
ICMM	International Council on Mining and Metals
ICOLD	International Commission on Large Dams
IIED	International Institute for Environment and Development
IMO	International Maritime Organisation
ISO	International Organisation for Standardisation
KCN	potassium cyanide
LC50	Lethal Concentration 50 (concentration necessary to kill 50% of the organisms being tested, e.g. mg/L in water to aquatic organisms, or ppm diet or drinking water to birds or mammals)
LD50	Lethal Dose 50 (median dose of a toxicant that will kill 50% of the test animals within a designated period after a single dose is administered)
LOEC	lowest-observed-effect concentration
MAC	Mining Association of Canada
MCA	Minerals Council of Australia
MCMPR	Ministerial Council on Mineral and Petroleum Resources
MERIWA	Minerals and Energy Research Institute of Western Australia

ML	megalitres (million litres)
Mm^3	million cubic meters
MOH	Ministry of Health, Singapore
Mt	megatonnes (million metric tonnes)
NaCN	sodium cyanide
NEPM	National Environment Protection Measures
NEPC	National Environment Protection Council, Australia
NHMRC	National Health and Medical Research Council, Australia
NICNAS	National Industrial Chemicals Notification and Assessment Scheme, Australia
NIOSH	National Institute for Occupational Health and Safety, Australia
NMDA	*N*-methyl-D-aspartate
NOEC	no-observed-effect concentration i.e. the test concentration at which no effect is observed
NOEL	no-observed-effect level
NOHSC	National Occupational Health and Safety Commission (now Safe Work Australia)
NSC	National Safety Council, Australia
NSW	New South Wales
NT	Northern Territory
NT DBIRD	Northern Territory Department of Business, Industry and Resource. Development
OASCC	Office of the Australian Safety and Compensation Council (now Safe Work Australia)
OECD	Organisation for Economic Cooperation and Development
OPPT	Office of Pollution Prevention and Toxics (USA)
OSS	Office of the Supervising Scientist, NT, Australia
PACIA	Plastics and Chemicals Industries Association
PAWA	Northern Territory Power and Water Authority
PEC	predicted environmental concentration
ppm	parts per million
QDME	Department of Mines and Energy, Queensland Government
QEPA	Queensland Environmental Protection Agency
Qld	Queensland

RCR	respiratory control ratios
RQ	risk quotient
SA	South Australia
SDS	Safety Data Sheet
SWA	Safe Work Australia (formerly OASCC or NOHSC)
Tas	Tasmania
TDS	Total Dissolved Solids
tpa	tonnes per annum
TRV	toxicity reference value
TSF	tailings storage facility
TV	trigger value
UNEP	United Nations Environment Programme
US ACHPPM	United States Army Center for Health Promotion and Preventative Medicine
US EPA	United States Environmental Protection Agency
Vic	Victoria
WA	Western Australia
WA DoIR	Western Australian Department of Industry and Resources
WAD	weak acid dissociable (complexes of cyanide).
WHO	World Health Organization
WWTP	wastewater treatment plant

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1. Introduction

1.1 Declaration

Sodium cyanide (CAS No 143-33-9) was declared a priority existing chemical under the *Industrial Chemicals (Notification and Assessment) Act 1989* (Commonwealth) (the Act) by the Minister for Health and Ageing by notice in the *Commonwealth Chemical Gazette* of 7 May 2002. The grounds for declaring sodium cyanide a priority existing chemical were:

- widespread use would provide a number of ways for the chemical to enter the environment;
- reported avian poisonings in Australia as a result of consumption of cyanide-contaminated environmental media (e.g. surface water) at tailings dams;
- production of highly toxic and flammable gas when in contact with water;
- high acute toxicity to aquatic life and to birds and animals; and
- high chronic toxicity to aquatic life.

1.2 Objectives of the assessment

This is a full environmental risk assessment, covering all industrial uses of sodium cyanide in Australia. The objectives of this assessment are to:

- identify the potential for environmental exposure in Australia;
- identify the environmental hazards of sodium cyanide and determine the risk of adverse effects to the environment;
- investigate the risks of sodium cyanide in Australia making use of any international assessments;
- assess current controls for sodium cyanide and identify whether these are adequate; and
- make recommendations on control measures for the management of environmental risks, where appropriate.

This assessment does not address public health or occupational health and safety concerns of sodium cyanide.

1.3 Sources of information

In accordance with the Act, manufacturers and importers of sodium cyanide were required to apply for assessment and supply relevant data. Applications and responses were received from 27 manufacturers, importers, formulators, some end users of sodium cyanide, some government regulatory agencies and a community group. Relevant agencies in each state/territory were consulted to provide information regarding aspects of the assessment. Public meetings were

held in 2004 in Sydney, Brisbane and Perth to discuss the preliminary findings of the assessment.

The applicants listed in Section 1.5 provided some information. Further information was obtained from some users of sodium cyanide who were not applicants, as referenced in the report. A comprehensive literature search was undertaken to obtain information on the environmental hazards of sodium cyanide. Consistent with the objectives, this report presents a review and critical evaluation of relevant information relating to the potential environmental hazards and risks from sodium cyanide. Key studies were obtained and reviewed during this assessment. Due to the availability of a peer-reviewed international assessment report (Agency for Toxic Substances and Disease Registry; ATDSR, 1997), peer reviewed databases (e.g. Hazardous Substances Data Base), and consolidated reports (e.g. ANZECC/ARMCANZ, 2000a), not all references in these key studies were evaluated. However, many relevant studies published prior to and since the cited reviews were obtained and assessed on an individual basis.

The import of sodium cyanide into Australia was monitored through information provided by the Australian Customs Service.

References in the report that have not been sighted are marked with an asterisk. The information provided for these studies reflects the level of information reported in the secondary source.

Data supplied by manufacturers/importers

The following data were originally received from manufacturers/importers and where necessary updated figures have been obtained:

- quantities of sodium cyanide imported and/or manufactured (as 'pure' cyanide or in products/mixtures);
- quantities of sodium cyanide that are formulated into products/mixtures and the concentrations of sodium cyanide in these products/mixtures;
- uses or potential uses of sodium cyanide and products containing the chemical;
- methods used or proposed to be used in handling, storing, manufacturing and disposing of sodium cyanide;
- some information on environmental exposure and methods of analysis;
- risk management initiatives (e.g. environmental management systems);
- safety information (e.g. safety data sheets (SDSs), emergency procedures, container labelling);
- end-users of sodium cyanide; and
- some unpublished reports and data on environmental fate, toxicity and risk associated with sodium cyanide

1.4 Peer review

During all stages of preparation, this report has been subject to internal review by the Department of the Environment, Water, Heritage and the Arts (DEWHA) and NICNAS. Sections discussing environmental exposure and fate, metabolism in animals, and environmental hazard and risk characterisation were reviewed by Dr Jenny Stauber, Senior Principal Research Scientist (Centre for Environmental Contaminants Research, CSIRO Energy Technology, Sydney, NSW), and Mr Paul Howe, Ecotoxicologist (Centre for Ecology and Hydrology, Monks Wood, Cambridgeshire, United Kingdom). Sections discussing chemical composition and identity and environmental fate were reviewed by Mr William Staunton, Principal Gold Metallurgist (Extractive Metallurgy, School of Chemical and Mathematical Sciences, The Parker Centre, Murdoch University, WA). The draft report has also been reviewed by state and territory environment protection agencies.

1.5 Applicants

Following the declaration of sodium cyanide as a Priority Existing Chemical, 27 companies or organisations applied for assessment of this chemical.

In accordance with the *Industrial Chemicals (Notification and Assessment) Act 1989*, applicants were provided with a draft copy of the report for comments during the corrections/variation phase of the assessment. The applicants were as follows:

AngloGold Ashanti Australia Ltd 44 St Georges Terrace Perth WA 6805	**DuPont (Australia) Limited** Locked Bag 2067 North Ryde BC NSW 1670
Amtrade International Pty Ltd PO Box 6421 St. Kilda Road Central VIC 8008	**Evonik Degussa Australia Pty Ltd** P.O Box 996 Dandenong, Vic 3175
Australian Gold Reagents Pty Ltd (AGR) Kwinana Beach Road Kwinana Beach 6167, WA	**Gold Fields Australia Pty Ltd** Level 5 50 Collin Street West Perth, WA 6005
Barrick Gold Australia Level 10, 2 Mill Street Perth, WA 6000	**Kwinana Progress Association** 67 Westbrook St, Calista,WA 6167
Biolab (Aust) Pty Ltd PO Box 9092 Scoresby VIC 3179	**Lomb Scientific (Aust) Pty Ltd** PO Box 2223 Taren Point NSW 2229
Chamber of Minerals and Energy of Western Australia Inc Locked Bag N984 Perth WA 6844	**Merck Pty Ltd** 207 Colchester Road Kilsyth VIC 3137

Minerals Council of Australia PO Box 4497 Kingston, ACT 2604	**Quantum Chemicals Pty Ltd** PO Box 4107 Dandenong South BC VIC 3164
Mitsui & Co (Australia) Ltd Level 46, Gateway, 1 Macquarie Place, Sydney 2000	**Redox Chemicals Pty Ltd** Locked Bag 150 Minto NSW 2566
Newmont Australia Pacific GPO Box 1652 Perth, WA 6904	**Sigma-Aldrich Pty Ltd** PO Box 970 Castle Hill NSW 1765
NSW Department of Environment and Climate Change PO Box A290 Sydney South, NSW 1232	**Sigma Chemicals Pty Ltd** PO Box 567 Balcatta WA 6021
Nuplex Industries (Aust) Pty Limited Locked Bag 6, Botany NSW 1455	**Tennant Limited** Level 2, 40 Yeo Street, Neutral Bay NSW 2089
Orica Australia Pty Ltd GPO Box 4311 Melbourne Vic 3001	**Tradechem Pty Ltd** PO Box 1394 Ashfield NSW 1800
P & M Kepert 38 Bedwell Crescent Booragoon WA 6154	**What a Breeze** 82 James St Dunoon NSW 2480
Peacebus.com Studio 4 Lot 11 Kenwood Road, Wederburn NSW 2560	

2. Background

2.1 International perspective

Sodium cyanide (NaCN) is a significant nitrogen-based commodity chemical, used worldwide for a range of industrial manufacturing and processing purposes. It is generally manufactured from the gas hydrogen cyanide (HCN) and may be used as a chemical intermediate for industrial purposes where there is no local supply of HCN (Suresh and Kishi, 2003a), or to generate HCN for fumigation purposes (IPCS, 2004), as well as directly for various purposes.

While chemical uses predominate in Japan and Europe, the major application for NaCN in Australia, North and South America, South Africa and China is use as a lixiviant (leaching solution) in the beneficiation and processing of gold and silver ore (Suresh and Kishi, 2003b). The cyanidation reaction that this involves was first discovered by Scheele in Europe in 1783. It was developed into a practicable mining process in the 1880s, and sodium cyanide is now the most generally used lixiviant for extracting gold from ore. Sodium cyanide is also used in other mining and metal industries, as a depressor agent in base metal flotation, for electroplating copper and other metals to metal surfaces, for surface hardening of iron and steel, and as a metal cleaning agent. There are various purposes for which sodium cyanide has evidently been used in the past, but where other alternatives are now preferred, e.g. photography (ATSDR, 2006).

According to World Health Organization (WHO) data cited by various sources (Buffington, 2002; Morna and Clarke, 2002; MCA, 2005), global production of hydrogen cyanide is ~1.4 million tonnes annually. Of this, ~20% is used to produce sodium cyanide (i.e. ~280 000 tonnes HCN, or ~500 000 tonnes NaCN – a figure consistent with more recent estimates by Suresh and Kishi, 2003ab), of which 90% (~450 000 tonnes NaCN) is used in the mining industry, primarily for gold and silver mining. According to Mudder and Botz (2000), ~13% of HCN production (i.e. ~330 000 tonnes NaCN) is converted into sodium cyanide for use in beneficiation of gold and silver ores (i.e. ~66% of NaCN production). At the turn of the 21st century, there were about 875 gold and silver operations throughout the world, of which about 460 utilised cyanide (Mudder and Botz, 2000).

Internationally, there have been various environmental incidents involving sodium cyanide or cyanide compounds derived from sodium cyanide (breakdown products) including spill incidents, transportation accidents, and tailings dam overflows and failures (e.g. Baia Mare, Romania, 2000). These have led to international focus on the uses of sodium cyanide and the environmental protection measures employed at facilities manufacturing and using sodium cyanide, their emissions and waste management practices.

Internationally, regulatory approaches to the management of cyanide in gold mining vary among jurisdictions depending on local conditions, the level of public concern and past incidents. A range of environment protection guidelines have been published covering most aspects of cyanide management in mining such as handling, transportation, storage, use, tailings storage facilities (TSF) design and construction, water and wastewater management, TSF and tailings

management, reporting, occupational safety and emergency response. Of note is the recent and comprehensive International Cyanide Management Code for the gold mining industry prepared by the International Cyanide Management Institute (ICMI, 2006) in consultation with the United Nations Environmental Program (UNEP), the then International Council on Metals and the Environment (ICME – now the International Council on Mining and Metals (ICMM)), the Gold Institute, the International Finance Corporation (IFC) and the Worldwide Fund for Nature (WWF). Chemical industry initiatives, such as the Responsible Care® program provide a comprehensive risk management framework for sodium cyanide management (refer Section 11.11).

2.1.1 International assessments

Internationally, sodium cyanide toxicity has been assessed by the Agency for Toxic Substances and Disease Registry within the United States Department of Health and Human Services (ATSDR, 2006). The International Programme for Chemical Safety (IPCS) of the World Health Organisation (WHO) has recently published a Concise International Chemical Assessment Document (CICAD) on human health aspects of hydrogen cyanide and cyanides (IPCS, 2004).

2.2 Australian perspective

Australia is a significant producer, user and exporter of sodium cyanide, with annual production ~100 000 tonnes. Of this ~40%-60% is exported, leaving ~50000 tonnes manufactured and used in Australia. A much smaller amount of sodium cyanide is imported (< 1000 tonnes in most years).

There is one manufacturing facility in Western Australia (WA) and one (formerly two) in Queensland (Qld). Production at these facilities uses relatively modern technology, with production facilities having been established in the last seventeen years. Both liquid and solid forms of sodium cyanide are produced in Australia, with exports in solid form.

Sodium cyanide is primarily used in Australia by the gold mining industry, where it is used in the cyanidation process to extract gold from ore. About 98% of Australia's gold production is dependent on the use of sodium cyanide for gold ore beneficiation. This process enables relatively high recovery of gold (and other precious metals) from ore. A lesser amount of sodium cyanide is used in Australia for ore flotation and in the electroplating, metal cleaning and metal hardening industries.

In recent years, there have been a few environmental incidents in Australia involving sodium cyanide arising from inappropriate or inadequate planning, design, storage, handling, transportation, use, and waste management. These and overseas incidents have raised community concerns. The major industries, including chemical and mining, and environment protection agencies have responded with reviews of procedures and development of new guidance, codes of practice, procedures and regulations to minimise safety and environmental risks.

Although there have been restrictions on the manufacture, handling, transport, storage and use of sodium cyanide in Australia, this report represents the first comprehensive environmental risk assessment by a national agency.

3. Chemical Identity and Composition

3.1 Chemical identity

3.1.1 Chemical name

Sodium cyanide

3.1.2 Registry numbers

Sodium cyanide is listed on the Australian Inventory of Chemical Substances (AICS). Chemicals on AICS can be imported or manufactured in Australia without prior notification and assessment by NICNAS.

CAS (Chemical Abstracts Service) Registry Number	143-33-9
EINECS *	205-599-4

* EINECS: European Inventory of Existing Commercial Substances

3.1.3 Other names

Cyanide of sodium	Cyanobrik ® (DuPont)
Cyanogran ® (DuPont)	Cyanodol ®
Sodium cyanide (ACGIH).	Cymag
Hydrocyanic acid (sodium salt)	Prussiate of soda
CyPlus ® (De Gussa)	

3.1.4 Molecular formula and structure

Formula: NaCN or CNNa

Structure: $Na^{+}C{\equiv}N^{-}$

3.2 Physical and chemical properties

3.2.1 Physical state

Sodium cyanide is a white deliquescent crystalline powder (Weast, 1988). Crystals of the dihydrate $NaCN.2H_2O$ form when saturated solutions of sodium cyanide cool at temperatures below 35°C (DuPont, 1996). It is odourless when dry (Budavari, 1996), but may have an odour of bitter almonds and/or ammonia in moist air (NOHSC, 1993; NSC, 2002). In water solutions (30% commercial product), sodium cyanide is a clear, colourless to red brown liquid with an odour of ammonia (CSBP, 2003a).

3.2.2 Physical properties

Physical properties of sodium cyanide are presented in Table 3.1.

Table 3.1 . Physical properties of sodium cyanide (NaCN)

Property	Value	Reference
Molecular weight	49.01	ATSDR (2006)
Melting point	563.7°C	ATSDR (2006)
Boiling point	1496°C	ATSDR (2006)
Specific gravity, solid	1.595 at 20°C 1.6 at 25°C	Gerhartz (1985) DuPont (1996)
Specific gravity, liquid	1.16 to 1.19 at 25°C (~30% solution in water - commercial product)	CSBP (2003a)
Apparent bulk density (solid products)	0.75-0.96 kg/m^3	DuPont (1996), CSBP (2003b)
Vapour pressure (mm Hg)	0.76 at 800°C 1 at 817°C 10 at 983°C 89.8 at 1200°C 314 at 1360°C	Clayton and Clayton (1994), DuPont (1996), ATSDR (2006)
Heat of vaporisation	3041 J/g	Kirk-Othmer (1991)
Henry's Law constant (K_H)	No data for NaCN; For HCN (pertinent to NaCN in solution): $5.1x10^{-2}$ atm-m^3/mol at 25°C and saturation pressure $1.32x10^{-2}$ atm-m^3/mol at 25°C and infinite dilution, increasing with ionic strength and temperature	ATSDR (2006) ATSDR (2006) Lye (2002), Staunton (pers. comm. 2005)
Partition co-efficient (Log P_{ow})	0.44	ATSDR (2006)
Sorption co-efficient (Log K_{oc})	No data	ATSDR (2006)

Flash point	No data for NaCN; For HCN: -17.8°C (closed cup)	ATSDR (2006)
Autoignition temperature	No data for NaCN; For HCN: 538°C	ATSDR (2006)
Solubility in water	Freely soluble in water: 480 g/L at 10°C 580 g/L at 20°C HCN is miscible with water	ATSDR (2006) IPCS (2003)
Solubility in other solvents	Slightly soluble in ethanol and formamide, 1.235 g/100 g in 100% ethanol at 25°C Dissolves in methanol 60.5 g/L (saturated solution at 15°C) Dissolves in liquid ammonia 37 g/L NH_3 at –33°C	ATSDR (1997), Gerhartz (1985) DuPont (1996) DuPont (1996)
Flammability limits	Cyanide salts are not combustible, but HCN, which may be produced by solid cyanides on contact with heat or water, is a flammable gas. Dry chemical fire extinguishers or sand are therefore stipulated for fire control and carbon dioxide must not be used (see Section 6.3.1).	NOHSC (1993)
Explosive limits	Cyanide salts are not explosive under normal conditions, but may explode if melted with nitrite or chlorate at about 232°C. Cyanide reacts violently with magnesium, nitrites, nitrates, and nitric acid. HCN gas is potentially explosive when concentrated. There is also a risk of explosion when water comes into contact with molten cyanide.	NOHSC (1993) NSC (2002)
Odour threshold	NaCN is odourless when dry, emits slight odour of HCN in damp air, HCN odour threshold is 0.8-4.4 ppm v/v in air, 0.17 mg/L in water.	ATSDR (2006)

3.2.3 Chemical properties

Cyanide referred to in this report includes all cyanide compounds determined to have the cyanide ion (CN^-), by the methods described in APHA (1998). In CN, the carbon is triple bonded to the nitrogen (Mills, 2001). The cyanide compounds in which cyanide can be obtained as CN^- are classified as simple and complex cyanides (APHA, 1998; Table 3.2).

Table 3.2 Selected common metal-cyanide complexes and compounds

Term and Degree of Complexity	Examples of Species or Compound
Free cyanide	CN^-, HCN
Simple Compounds	
a) Readily soluble compounds	KCN (solid), $NaCN.2H_2O$ (solid), $Ca(CN)_2$ (solid)
b) Relatively insoluble compounds	CuCN (solid), $Zn(CN)_2$ (solid), $Ni(CN)_2$ (solid)
Weak complexes	$Cd(CN)_4^{2-}$, $Zn(CN)_4^{2-}$
Moderately strong complexes	$Ni(CN)_4^{2-}$, $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, $Cu(CN)_4^{3-}$, $Ag(CN)_2^-$
Strong complexes	$Fe(CN)_6^{4-}$, $Fe(CN)_6^{3-}$, $Au(CN)_2^-$, $Co(CN)_6^{4-}$
Other cyanide-related species	
Thiocyanate, cyanate	SCN^-, OCN^-
Cyanogen	$(CN)_2$

Principal source: Scott and Ingles (1987).

Sodium cyanide is one of a number of simple cyanide compounds or salts. Simple cyanides are represented by the formula $A(CN)_x$, where A is an alkali metal (sodium, potassium, with ammonium behaving similarly) or other metal, and x the valence of A, is the number of CN groups (APHA, 1998).

Complex cyanides have a variety of formulae, but the alkali-metallic cyanides normally can be represented by $A_yM(CN)_x$, where A represents the alkali metal y times, M is a metal (ferrous and ferric iron, cadmium, copper, nickel, silver, zinc and others), and x the number of CN groups. X is the valence of A taken y times plus that of the metal.

HCN molecules will polymerise to form extremely inert HCN polymer if solutions are made without alkali addition. In dilute solutions, HCN polymer will generate colours ranging from pale yellow to dark reddish brown. In stronger alkaline solutions, a dark brown precipitate resembling iron rust can form. High pH solutions (e.g. pH 12) will limit the potential for HCN formation and consequently the potential for HCN polymerisation (DuPont, 1996).

HCN is a weak acid with an ionisation constant (pKa) of 9.31 - 9.35 at 20°C (Section 6.3.1) and 8.99 at 35°C (Izatt et al., 1962).

3.2.4 Conversion factors

Table 3.3. Conversion factors

Hydrogen Cyanide (HCN)	Conversion
In Air:	
HCN mg/m^3 to ppm in air at 20°C	1 mg/m^3 = 0.890 ppm (v/v)*
HCN mg/m^3 to ppm in air at 25°C	1 mg/m^3 = 0.90 ppm (v/v)**

* ATSDR (2006); ** based on equation: C_{ppm} = 1 mg/m^3 x 24.45/gram molecular weight of 27.03, where 24.45 is the molar volume of air in litres at normal temperature and pressure (25°C and 760 torr).

3.3 Methods of analysis

3.3.1 Analysis of cyanide compounds

Methods of sample preservation, handling and analysis of environmental media containing cyanide compounds have been described by Zheng et al. (2003), Schulz (2002), USEPA (1999), APHA (1998), Noller (1997), Smith and Mudder (1993) and Noller and Schulz (1997, 1995). The cyanide content of a sample of environmental media (water, slurry, soil, sediment etc) can be composed of many different cyanide compounds and there are several methods available for their extraction and analysis. In general, most analytical methods contain an analogue separation procedure whereby the cyanide content to be measured is obtained as a gas (i.e. HCN; Kjeldsen, 1999). The content and composition of cyanide present varies with when and where samples are taken and with subsequent treatment and handling, the appropriate preservation methods vary with the type of analysis to be performed, and the type/s and accuracy of analysis needed vary with the purpose for which the information is required. Hence decisions regarding where and how to sample, how to prepare the sample and what and how to analyse are all important to the subsequent interpretation of the data and addressing the purpose for which the samples are taken (Schulz, 2005)

Cyanide analyses have historically been identified in one of three commonly used categories: free cyanide, weak acid-dissociable (WAD) complexes of cyanide and total cyanide.

- Free cyanide is the sum of cyanide present as molecular HCN and ionic CN^- (Schulz, 2002). Free cyanide is included in WAD complexes of cyanide and total Cyanide.
- WAD cyanide consists of a range of compounds that can be liberated as HCN by addition of a given acid (Kjeldsen, 1999). In general, WAD cyanide analysis includes all free cyanide and most of the weak cyanide complexes of copper, nickel, silver, zinc and cadmium (Schulz, 2002). The quantity of WAD cyanide dissociated during analysis depends upon the acid used, the pH, and the duration of the acid extraction process (Kjeldsen, 1999).
- Total cyanide generally includes all free cyanide, all dissociable cyanide complexes and all strong metal cyanide complexes including ferrocyanide ($Fe(CN)^{64-}$), ferricyanide ($Fe(CN)^{63-}$), and depending on the method used, portions of hexacyanocobaltate ($Co(CN)^{63-}$) (Schulz, 2002). It also includes

cyanide complexes of gold, platinum and other noble metals, though the latter would not be expected to still be present in gold mining tailings. The related or derived compounds of cyanate (OCN) and thiocyanate (SCN) are excluded from the definition of total cyanide (Schulz, 2002), as are certain nitriles (organic molecules containing a $^{-}$CN group, such as acetonitrile, CH3CN) (Kjeldsen, 1999).

Analyses of free, WAD and total cyanides do not include the CN-containing forms cyanate (OCN^-), thiocyanate (SCN^-), cyanogen ($(CN)_2$) or cyanogen chloride (CNCl), which are potential chlorination/oxidation products of different cyanide forms. Each of these requires specific analytical determination. As noted above, SCN^- may cause interference to some total cyanide determination methods and the result then needs to be corrected accordingly. Strong complexes of cyanide (e.g. cobalt) may not be determined through total cyanide analysis.

However, with the advancement of analytical methods, categorisation is defined not only by the specific chemical speciation in each group, but by the technical definition based on the type of analysis performed. This is particularly relevant for WAD forms of cyanide due to the various analytical methods available and the variations in the analytes included in each analysis. However, overestimation of free cyanide may occur with some methods, and inclusion of thiocyanate with some total cyanide methods may lead to an overestimate in total cyanide.

Appendix 1 provides a list of analytical methods and description for commonly analysed cyanide compounds in various environmental media. As indicated in Appendix 1, there are several methods available for cyanide extraction and determination of cyanide concentration. Each method is subject to positive and negative interferences, and these are typically described in the method protocol. Improper choice of sampling technique, sample preservation and analysis method may produce significantly erroneous analytical results. To minimise errors, the choice of method used should be aligned to particular sample requirements, and multiple analyses using several methods may be undertaken to minimise analytical uncertainties. Furthermore, the specific method of analysis, pH and type of extractant used should be reported along with the analytical results.

WAD CN is widely used in an attempt to measure 'biologically available' cyanide because it includes free cyanide and various forms of cyanide which may release free cyanide once consumed by an animal, but not forms of cyanide that are unlikely to release free cyanide to an animal. Therefore WAD CN is considered the most appropriate general measure on which to base environmental monitoring for cyanide toxicity, and the term is referred to extensively in this report and its recommendations. Some further discussion of the adequacy of WAD CN as an indicator of biological availability is provided below.

Methods for WAD CN analysis include distillation methods APHA 4500 CN-I and ASTM Method D and the Picric Acid Method (colorimetric; Smith and Mudder, 1993).

Kjeldsen (1999) indicates that there are at least two extraction methods available for analysis of WAD cyanide compounds based on different pH. The choice of method used will depend on the objective of the analyses, suggesting that the

lower pH be used when attempting to simulate gastro-intestinal bioavailability. The methods include:

- extraction in acetate buffer for 60-90 minutes with a pH of 4.5 to 5.0 (e.g. pH conditions that may be experienced in nature during decomposition of organic matter); and
- extraction in sulphuric acid for 60 minutes with an approximate pH 1 (e.g. pH conditions that may be experienced in the digestive systems of some animals).

Henny et al. (1994) suggest that total reliance on conventional WAD cyanide analysis may not account for all of the cyanide potentially available to wildlife ingesting cyanide solutions. Only cyanide that dissociates at pH ≥4.5 is represented by the conventional WAD cyanide analysis. Some common metal-cyanide complexes dissociate below pH 4.0, as likely occurs when exposed to gastric juices of some aquatic birds (pH 1.0-2.0; Duke, 1986) and some raptorial species (as low as pH 1.3; Duke et al., 1975) and other animals (Kjeldsen, 1999). Henny et al. (1994) indicated that the effects might be counteracted by a potentially slower rate and degree of dissociation of the metal-cyanide complexes and by the alkalinity of the ingested solution. Henny et al. (1994) indicated that the presence of cyanide in weakly complexed forms in waters, as often found in association with ore processing wastes, may potentially have the effect of increasing the dose required to promote the onset of acute lethal effects due to the slower rate of dissolution and gastrointestinal absorption, but may lengthen the duration of sublethal effects. Thus, delayed or prolonged sublethal effects may be evident when WAD cyanide concentrations, measured using conventional analytical methods, would suggest otherwise.

The various methods for analysing WAD cyanide compounds all attempt to measure 'biologically available' cyanide, and each measures nearly the same species of cyanide. The cyanide amenable to chlorination (CATC) method has been largely replaced by the WAD cyanide method, which is essentially the same, but more rapidly performed. CATC is reportedly highly susceptible to poor accuracy and precision due to interferences (Smith and Mudder, 1993). USEPA Method OIA-1677 was recently developed to analyse 'available cyanide' in water and wastewater by flow injection, ligand exchange and amperometric titration. It is considered a more robust and accurate method for determining available cyanide (USEPA, 1999; Milosavljevic et al., 1995). Method OIA-1677 may be undertaken under field conditions using a Perstop 3202 CN analyser with results available 1-2 hours after sampling (Evans et al., 2003), which is advantageous for field-based operations. Evan et al. (2003) indicate that Method OIA-1677 (modified) is superior to APHA Method 4500 CN-I when using a Perstop analyser due to lower interferences (sulphides, metals) and more precise and accurate results.

The traditional WAD CN method (4500 CN-I) uses a weak acid distillation method to release cyanide from the defined metal complexes for subsequent distillation and analysis. With Method OIA-1677, using a Perstop analyser, a proprietary ligand exchange reagent is used to chemically bind WAD metals thus releasing free cyanide for flow injection analysis. Evans et al. (2003) indicate that Method 4500 CN-I (WAD CN) has the potential to underestimate WAD CN concentrations, particularly when high metals concentrations are present, due to

the inability (periodically and randomly) of the weak acid to break down some of the metal cyanide bonds in order to free the cyanide for analysis, a problem that was not evident with the proprietary reagent.

USEPA (1999) indicate that method OIA-1677 is less subject to interference by sulphide, relative to CATC methods. However, Evans et al. (2003) indicate that there are several minor but critical amendments that should be made to Method OIA-1677 when using a Perstop analyser in order to minimise interferences from sulphides and high metals concentrations. These amendments include always assuming there are sulphides in the sample and pretreating accordingly, even when screening test results show otherwise, substitution of lead acetate for lead carbonate to precipitate sulphide, and use of a limited amount (i.e. 1%) of lead acetate, otherwise the ligand reacted only with the lead acetate and not the metals from metal cyanide complexes.

Zheng et al. (2003) evaluated seven alternative methods for the analysis of cyanide species or groups of species in reagent water and five different contaminated water matrices, including five species-specific methods (weak acid dissociable (WAD) cyanide, free cyanide by micro diffusion, Available Cyanide, automated WAD cyanide by thin film distillation, metal cyanides by ion chromatography), and two automated techniques for total cyanide (total cyanide by thin film distillation and total cyanide by low-power UV digestion). All seven methods evaluated achieved low, ppb-level, detection limits and exhibited satisfactory accuracy and precision for most contaminated waters tested. Analysis of low concentrations of cyanide species in raw wastewater was problematic for Available Cyanide and Ion Chromatography Methods, which experienced significant interference problems and/or low recoveries. Sulphide interference in the Available Cyanide method when using sewage treatment plant clarifier effluent may be corrected using the amended method described above (Evans et al., 2003). There was recovery of significant diffusible cyanide in the Micro diffusion tests with nickel-cyanide-spiked samples, reflecting dissociation of this weak metal-cyanide complex during the test and demonstrating that the test can recover some WAD cyanide in addition to free cyanide. The automated Total Cyanide methods, which involved UV digestion, achieved low detection limits for most waters tested, but exhibited low recoveries for some waters tested. The conventional WAD cyanide method, along with its automated version (WAD-TFD), performed well, yielding acceptable cyanide recoveries in all water matrices tested and excellent accuracy for the performance evaluation samples. The Available Cyanide method was also satisfactory when interferences are accounted for. The CATC method was problematic for measurement of weak acid dissociable cyanide in contaminated waters.

3.3.2 Atmospheric monitoring

Sampling of hydrogen cyanide gas can be either continuous, using electronic detection equipment, or semi-batch, using air pumps and sampling tubes. The former gives a faster response and allows more time for action in emergency situations (Environment Australia, 1998). Several types of portable and stationary air HCN sampling devices are available. According to IPCS (2004), detection limits for the different methods for hydrogen cyanide in air samples range from 0.8 to 400 mg/m^3.

3.3.3 Biological monitoring

The rapid metabolic processes that degrade cyanide to thiocyanate complicate biological monitoring for cyanide (Ramey et al., 1994). Monitoring for cyanide may involve measuring cyanide (HCN) in whole blood or selected target organs (Troup and Ballantyne, 1987; Lundquist et al., 1985; Logan, 1996; Calafat and Stanfill, 2002) or monitoring analytes that indicate exposure to cyanide (e.g. urinary thiocyanate, rhodanese enzyme; Schulz, 1984); however, these indicator analytes may be non-specific (Sittig, 1985). Thiocyanate and 2-aminothiazoline-4-carboxylic acid may also be measured in urine (Lundquist et al., 1995).

4. Manufacture, Importation and Use

4.1 Sodium cyanide in Australia

Sodium cyanide is introduced into Australia through importation and manufacture. Sodium cyanide has been manufactured in Australia since the late 1980s. There were three dedicated sodium cyanide manufacturing facilities in Australia, one located in WA (the Australian Gold Reagents Pty Ltd [AGR] plant at CSBP's chemical and fertiliser complex at Kwinana) and two in Qld (the Orica Chemicals and Ticor Chemical Company plants at Yarwun, near Gladstone), but the Ticor plant closed in 2004. Total Australian production has continued to be approximately 100 000 tonnes per annum since 2000 despite this plant closing, with increased plant capacity added at both sites. This is a significant proportion of world sodium cyanide production, which is of the order of 500 000 tonnes per annum.

4.2 Manufacture, formulation and transport

4.2.1 Manufacture

Worldwide, almost all sodium cyanide is manufactured by reacting hydrogen cyanide (HCN) with sodium hydroxide (NaOH), a process sometimes referred to as the neutralisation-wet process (i.e. $HCN + NaOH \rightarrow NaCN + H_2O$). The HCN may be obtained from purpose-built HCN plants or may also be sourced as a by-product of an acrylonitrile manufacturing process (Mills, 2001). In general, the most popular processes for manufacturing HCN include the Shawinigan Process ($3NH_3 + C_3H_8 \rightarrow 3HCN + 7H_2$), the Andrussaw Process ($CH_4 + NH_3 + 1.5O_2 \rightarrow HCN + 3H_2O$), and the BMA Process ($CH_4 + NH_3 \rightarrow HCN + 3H_2$). Sodium cyanide is also sometimes prepared by melting sodium chloride with calcium cyanamide or by heating sodium amide salt with carbon (IPCS, 2004).

Australian sodium cyanide manufacturing facilities use the Andrussaw process, reacting methane and ammonia to produce hydrogen cyanide gas (HCN), and then absorbing the cyanide into a solution of sodium hydroxide. The result is an aqueous solution of sodium cyanide (NaCN). Sodium hydroxide is introduced into the process as a 50% w/w solution, at a rate that maintains the system pH at or above 12.5. A high pH maximises the absorption of cyanide into solution, and stabilises the product while in storage, limiting HCN evolution. A liquid product containing approximately 30% w/w sodium cyanide is marketed from this, or the solution is further treated to arrive at a solid form of sodium cyanide. The solid sodium cyanide process involves evaporating a significant proportion of the water from the cyanide solution to yield a slurry. The slurry is then centrifuged, and the crystals put through a series of drying stages, before being compressed to form the final product, such as briquettes (J. Fozdar, CSBP Chemicals, pers. comm. 2005).

4.2.2 Formulation and transport of products

Solid form

Sodium cyanide is manufactured as solid briquettes, tablets ('cyanoids') or granules/flakes containing approximately 96%-99% NaCN (refer Table 4.1), or in a

liquid form containing approximately 30% NaCN. The majority of sodium cyanide manufactured in Australia is sold in the solid form, including all exports of the substance.

Table 4.1. Typical constituents of formulated solid sodium cyanide

Constituent	Approximate Concentration (% by weight)
Sodium cyanide (NaCN)	> 97 *
Sodium carbonate (Na_2CO_3)	< 2.5
Sodium formate (HCOONa)	< 0.5
Sodium hydroxide (NaOH)	< 0.5
Water (H_2O)	Remainder

* Granules and tablets of other commercial products may be reformulated to a lesser concentration (e.g. 62% by weight). Source: This example is from the MSDS for the CSBP solid briquette product (CSBP, 2006a).

Solid sodium cyanide may be formed into uniform briquettes, with dimensions and weight varying between manufacturers. In Australia, briquettes are typically pillow shaped, weigh ~20-30 g each and have approximate dimensions of 40 x 35 x 20 mm to 47 x 37 x 20 mm. Alternatively, solid sodium cyanide may be provided commercially as granules or flakes. These are irregularly shaped particles typically sized to generate a minimum of dust (e.g. granules with 80% passing a 9.5 mm screen and 3% passing a 0.3 mm screen). All solid sodium cyanide currently manufactured in Australia is produced in briquette form, whereas imports may be in the granular form.

Within Australia, sodium cyanide is transported mainly by road and rail. The two current manufacturers supply solid forms of sodium cyanide in bulk quantities packaged either in:

- solid and flexible Composite Intermediate Bulk Containers (CIBCs) of various types and capacities (e.g. bag/bag, bag/box generally of 800 to 1100 kg). CIBCs are generally transported on pallets and inside freight containers, which typically hold 20 CIBCs, i.e. ~20 tonnes solid NaCN (Fozdar, pers. comm.. 2005);
- larger (e.g. 20-22 tonne) specially-designed containers, including solid-to-liquid (StoLs) isotainers (International Standards Organization (ISO) containers).

StoL isotainers are tanks which are typically purpose-built for rail or road transportation. Solid cyanide is added to the containers at the manufacturing facility and transported to the customer's site in this form. Upon delivery, the cyanide is dissolved in the isotainer by addition of water at the mine site and the liquid drained into on-site storage tanks. This reduces the requirement for manual handling of solid as well as minimising possibilities of spillage during transfer and handling at the minesite storage facility (Environment Australia, 1998).

Neither factory in Australia has facilities for filling smaller containers, hence all product sold in smaller quantities (~50 kg to <1 kg) is imported. Much of this is sold in the containers in which it is imported, but several companies in Australia reformulate solid sodium cyanide into smaller, more manageable quantities for specialist uses.

Liquid form

Liquid sodium cyanide is supplied for use in reasonable proximity (< ~1000 km) to production plants, with transport by road and rail in specially designed isotainers. The isotainers used in Western Australia are filled with 20.6 tonnes of solution, which translates to ~17.5 kL, containing ~6.25 tonnes of NaCN in the loaded solution (Fozdar, pers. comm. 2005). Those in Queensland are similar, holding ~18 000 L, equivalent to 6 tonnes NaCN (J. Cowan, Orica Australia Pty Ltd, pers. comm. 2005).

Approximately half of the NaCN produced in Western Australia is sold in the liquid form, but the majority of product from the Queensland factory is sold in the solid form. The liquid form is preferred by some mines because of handling advantages over solid NaCN at the mine site (i.e. when supplied in CIBCs) and/or where supply already dissolved in water is an advantage because of local water quality problems. However, transport in liquid form becomes uneconomical over larger distances. Table 4.2 describes the typical constituents of liquid sodium cyanide.

Table 4.2. Typical constituents of liquid sodium cyanide

Constituent	Approximate Concentration (%)
Sodium cyanide (NaCN)	28.0-31.5 *
Sodium carbonate (Na_2CO_3)	< 4.0
Sodium formate (HCOONa)	< 1.0
Sodium hydroxide (NaOH)	0.4
Ammonia solution as NH_3	< 0.3
Water (H_2O)	Remainder

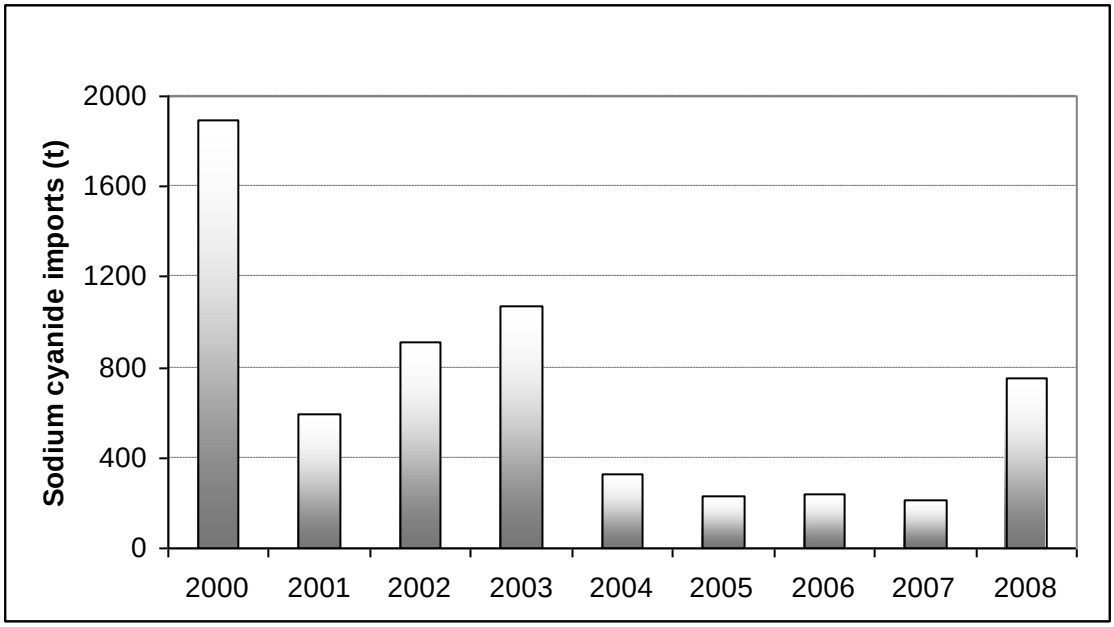
* 30% solution. Approximately 300 g/kg. Source: This example is from the MSDS for the CSBP product (CSBP, 2006b). The presence of NaOH in the solution maintains a high pH (~13 in the neat solution) in order to minimize the concentration of HCN above the solution (see Section 6.3.2).

4.3 Imports and exports

Imports of sodium cyanide over the period 2000 to 2008 have fluctuated widely (from ~1900 tonnes in 2000 to ~210 tonnes in 2007 - Figure 4.1), but except for 2000 have remained below ~1% of Australian production. More detailed data from importers for the years 2000-2002 indicate that higher imports in 2000-2002 were associated with use in gold mining, and it is likely that relatively high imports in 2003 and 2008 were also for use in mining.

Sodium cyanide has been imported in solid forms in various quantities and containers ranging from 205 L steel drums or 1 tonne bag/box configurations on pallets, to 50 kg drums (18 per pallet), to smaller containers (e.g. 500 gram). It is likely that except when used for gold mining, most of the imported cyanide is in drums or other small packages. Small quantities (e.g. <10 kg/annum) are imported by airfreight as a component (e.g. <7% w/w) of electroplating solution. Imports of sodium cyanide have clearly not been affected by the closure of the Ticor plant.

Figure 4.1. Sodium cyanide imports into Australia (Source: Australian Customs Service and importer data)



Sodium cyanide has been exported from Australia to countries including Canada, Chile, Ecuador, Fiji, Ghana, India, Indonesia, Jamaica, Namibia, New Zealand, Papua New Guinea, Peru, Russia, South Africa, Tanzania and Zimbabwe. Estimates of export quantities are limited; however, in recent years exports have been ~40-60% or more of production, leaving approximately 40 000-60 000 tonnes per annum for domestic use.

4.4 Uses of sodium cyanide in Australia

4.4.1 Overall range of uses

Sodium cyanide is used in specific industrial applications and is probably best known for its major application in Australia in the gold mining industry (Environment Australia, 1998). Most of Australia's gold production (~98%) is reliant on sodium cyanide (Chemlink, 1997) and the majority of sodium cyanide manufactured in Australia and not exported is used in the gold mining industry, with a relatively minor amount used for other purposes at a scale which can use bulk quantities, such as ore flotation. Imports are generally used for other purposes, e.g. because the smaller package sizes are more appropriate, but imports have supplied gold mining uses in the past and may do so in some circumstances at present. Relatively small quantities of $Ca(CN)_2$ and KCN are also used by the gold mining industry in some locations (Mills, 2001). However, during cyanidation the counter-cation has no effect on the leaching process and the lower cost NaCN is widely used in preference to KCN, which is unlikely to have been used for this purpose in Australia.

According to the information obtained during this assessment, the main industrial uses of sodium cyanide in Australia include:

- Gold and silver ore recovery/beneficiation (e.g. cyanidation) and mineral processing (i.e. smelting and refining) of gold and silver (Sections 4.4.2 and 5.2.3);

- Ore flotation during smelting of metals (e.g. silver, nickel, copper, lead, zinc), where cyanide acts as a depressor to assist the separation of minerals (Section 5.2.4);
- Electroplating, where alkaline cyanide baths are used to deposit decorative and/or functional metal coatings onto a variety of objects (Section 5.2.5);
- Metal cleaning (Section 5.2.5);
- Case hardening of steel and similar processes: various surface hardening processes may use NaCN in molten salt baths, including carburising and carbonitriding (case hardening), nitrocarburising, and commercial processes based on these techniques, such as the Tufftride® salt bath nitrocarburising processes (Section 5.2.5);
- Analytical testing at laboratories (e.g. geological/metallurgical laboratories - (Section 5.2.6).

Other forms of cyanide may also be used in ore flotation and for the above industrial purposes. Currently, sodium cyanide is not registered by the Australian Pesticides and Veterinary Medicines Authority (APVMA) for any agricultural or veterinary purpose in Australia. However, sodium and potassium cyanide have been used in Australia in the past in baits as a means to census/control foxes and for vertebrate pest control due to its rapid lethality (Environment Australia, 1998; Marks et al., 2002; Bubela et al., 1998; Marks and Gigliotti, 1996; Algar and Kinnear, 1990; Connolly, 1988; Busana et al., 1998; Warburton and Drew, 1994; Connolly and Simmons, 1984; Savarie and Sterner, 1979; Bischoff, 1975), and approvals have been granted to allow limited research to be conducted. Various Australian state and territory laws established penalties for the unlawful use of cyanide for vertebrate pest control (e.g. Rural Lands Protection Act 1985, Qld (however, this is not specifically identified in the new Act - Pests and stock route management Act 2002); Agricultural and Veterinary Chemicals {Control of Use} {Agricultural Spraying} Order 1996, Tasmania).

An illegal use of sodium cyanide is cyanide fishing, which occurs particularly in South-east Asia. Liquefied sodium cyanide is used as an asphyxiant for the collection of live aquarium specimens and for killing fish for human consumption (Jones and Stevens, 1997). No documented evidence of cyanide fishing in Australian waters was found during this assessment, and no evidence for cyanide fishing has been recorded in northeastern Australian waters (M. Bishop, Great Barrier Reef Marine Park Authority, pers. comm. 2004).

4.4.2 Gold ore beneficiation and processing

In general, gold operations consist of three major steps: extraction, beneficiation, and processing. Extraction in this context is analogous to mining and is defined as removing gold ore material from a geological deposit. It does not involve the use of cyanide. In-situ leaching (underground cyanidation without ore extraction) has been used internationally, but not in Australia. Beneficiation is the separation of the gold from unwanted material in the ore, for which cyanidation is one of the techniques available. Processing in this context refers to recovery of the gold subsequent to beneficiation, and processing operations may also involve the use of cyanide using activated carbon.

Cyanidation and other techniques of beneficiation

Four main techniques that have been used in the beneficiation of gold ore are:

- cyanidation (the most commonly used process today - the original MacArthur-Forrest Process was patented in 1887);
- flotation (chiefly used on ore that is finely disseminated and contains small quantities of gold in association with base metals – USEPA, 1994);
- amalgamation with mercury (was used from the late 19th to the middle of the 20th century in Australia and is still used by artisanal or small scale miners in some countries, but is inferior to cyanidation for large scale mining and presents major environmental and health issues – Dhindsa et al., 2003; USEPA, 1994); and
- gravity concentration (placer/nugget mining).

In Australia, cyanidation is the major technique in current use, but flotation and gravity concentration are used in some situations, e.g. where base metals are also being mined. Only cyanidation involves the use of cyanide. Cyanide is not used in gold flotation, but gold-containing material separated by flotation may subsequently be treated by cyanidation, and cyanide may be used for the separation of other minerals by flotation, e.g. zinc and iron sulphides from lead and copper sulphides and arsenic from nickel ores (Section 5.2.4).

Various alternative lixiviants to cyanide have been used or investigated, as have microbiological beneficiation methods for removing gold from ore (e.g. Yestech, 2002). However, there are considerable technical difficulties to be overcome before even the most promising alternative lixiviant (thiosulphate) can become practicable, and significant changes to other processes, such as gold recovery from solution, may be needed (Ritchie et al., 2001; Nicol and O'Malley, 2001). Some alternatives are only suitable for certain types of ore, e.g. acid thiourea, which is unsuitable for use in soils with soluble iron and clays, as typical of Australia (Chemlink Consultants, 1997). The various alternatives also have their own significant environmental and health hazards. In several cases, alternative lixiviants are required in greater concentrations than cyanide, possibly making the resulting hazard greater despite lower absolute toxicity, in some cases potentially mobilising other metals at the pHs used, and some may leave long-lasting residues (McNulty, 2001; Young, 2001; Gos and Rubo, 2002; Environment Australia, 1998). Further investigation of the use of thiosulphate is continuing under a project at the Parker Centre in WA (AMIRA P420C Gold Processing technology)[1].

Cyanidation is the process of using cyanide solutions to dissolve gold. In this process, ore is exposed to cyanide solution, and the gold dissolves by forming the cyanoaurite ion. The gold cyanidation process may be represented by Elsner's equation:

$$4Au + 8CN^- + O_2 + 2H_2O \Leftrightarrow 4Au(CN)_2^- + 4OH^-$$

or alternatively (which of these equations is correct is not absolutely agreed) by Bodländer's equation (AMIRA, 1991a, Habashi, 1998; Heath and Rumball, 1998):

$$2Au + 4CN^- + O_2 + 2H_2O \Leftrightarrow 2Au(CN)_2^- + H_2O_2 + 2OH^-$$

[1] Project Website, accessed May 2007, http://parkercentre.com.au/research/Gold_Market_research.html)

As shown by these equations, the process requires oxygen. The reaction is generally considered most effective at a pH of 9.5-11, with the optimum being pH ~10.5 to maximise the proportion of free cyanide present as CN^- present, without reaching more basic conditions which tend to slow the process (USEPA, 1994). However, practices may vary according to mineral content of ores. For example, it is common in many Western Australian mines in the Eastern Goldfields to use a pH of ~9.0-9.2 due to the large amount of magnesium (Mg) present in these ores or hypersaline groundwater: buffering effects mean that elevating the pH above this would consume large amounts of lime to form $Mg(OH)_2$ before the pH could rise further (W. Staunton, Parker Centre/Division of Science and Engineering, Murdoch University, pers. comm. 2005).

In practice, a large excess of cyanide is used and the amount which needs to be added per tonne of ore varies widely. Adams et al. (2008a) state: 'Cyanide dosing strategies will necessarily change over time as different parts of the ore body, containing different sulphide and gangue mineralogy, are mined. Ores containing high soluble copper generally require higher cyanide dosages to ensure that sufficient free cyanide is available in solution for efficient leaching to occur. Ores that are high in silver often also need higher cyanide dosing to account for the slower leaching silver minerals. … The nature of metallurgical process plants is … such that these dynamic systems are constantly varying, and this will influence the cyanide and other species and levels that are presented to tailings.'

Using data obtained from company reports for gold mines in various countries over the period 1991-2006, Mudd (2007) related cyanide consumption (kg CN/kg gold produced – presumably actually referring to NaCN) to gold grade (g Au/t ore), in a paper discussing sustainability issues in gold mining. Overall average cyanide consumption from the data obtained was 141 kg CN/kg gold. However, for high grade mines (> 6 g Au/t ore) cyanide consumption was commonly < 100 kg CN/kg gold, while for lower grade mines (< 2 g Au/t ore) the consumption of cyanide tended to increase as the grade declined, reaching as high as ~1000 kg CN/kg gold. Mudd (2007) fitted a power regression which showed a general trend of increasing cyanide consumption as gold grade of the ore decreased ($y = 332.03x^{-0.8725}$, $r^2 = 0.5468$, >50 data points). However, some caution is needed in interpreting this relationship, as inspection of the plotted data shows that the amount of cyanide used is clearly affected by factors other than the gold grade. At low grades: cyanide consumption at ~1 g Au/t ranged widely, from <50 kg CN/kg Au to ~1000 kg/kg Au; and cyanide consumption at a few individual sites at ~3-5 g Au/t ranged well above other sites, from ~400 kg CN/kg gold up to almost 1250 kg CN/kg gold. Mudd (2007) argued that as there is a declining trend in ore grades in the countries he reviewed (Brazil, South Africa, Canada and the United States – average grades in Australia in 2003 = ~2 g/t), average cyanide consumption per kg gold is likely to increase gradually in the medium term. Mudd (2007) also discussed the similar implications of ore grades for energy and water consumption and greenhouse gas production. He noted that many companies now publish sustainability reports which give details of water and energy use, but few also include cyanide consumption. He suggested that 'to improve transparency in the gold mining sector and demonstrate continuing evolution in sustainability performance, there is a strong case for reporting of cyanide.'

Recovery processes used with cyanidation

There are two main types of processing technique which are currently used to recover gold when cyanidation is used for ore beneficiation:

- cyanidation-zinc precipitation (or zinc cementation, the Merrill-Crowe process), where the gold is precipitated with zinc dust – this older technique has been replaced by carbon adsorption in many cases, but is better suited to gold ore containing large amounts of silver; and
- cyanidation-carbon adsorption, where the gold is adsorbed onto activated carbon – this is the most commonly used method.

There are many variants of these processes, and sometimes adsorption on activated carbon may be used in series after zinc precipitation (Smith and Mudder, 1993; USEPA, 1994).

With cyanidation-zinc precipitation, zinc displaces gold in the sodium cyanoaurite and precipitates the gold. Steps involved in this include leaching, clarification (filtering), deaeration (oxygen inhibits gold recovery) and precipitation, followed by recovery by smelting the gold-containing material after filtering and sometimes other treatment. The barren solution that remains can be chemically treated (neutralised) or regenerated and returned to the leach circuit. Zinc precipitation wastes include filter cake material and spent leaching solution that is not returned to the leaching process. These may contain cyanide residues as well as zinc and lime and are typically disposed of with tailings (USEPA, 1994).

Cyanidation-carbon adsorption involves four steps: leaching, loading, elution, and recovery. The activated carbon can be regenerated and re-used numerous times by acid washing and reactivation in a kiln. Small amounts of cyanide residues are present on the carbon after the elution process, but this is likely to be released and converted to ammonia (NH_3) under the conditions in the reactivation kiln (Staunton et al., 2003). Up to 10% of the carbon may be lost during each cycle through abrasion to suboptimal size, ashing, or incidental loss. Waste carbon fines and acid wash may contain some residual base metals and cyanide. Most operations capture suboptimal size carbon particles for recovery of additional gold via incineration or concentrated cyanide leaching. The acid wash solution is treated and recirculated or disposed of in the general tailings stream (USEPA, 1994).

Ion exchange resin (Resin-in-Pulp) is a new processing technology which could be a future alternative to carbon adsorption. Other very uncommon techniques used to separate and recover gold after cyanidation include solvent extraction and direct electrowinning (USEPA, 1994).

Cyanidation –carbon adsorption operations

In general, there are two basic types of cyanidation-carbon adsorption operations, tank (mill) leaching and heap leaching (Logsdon et al., 1999; USEPA, 1994). These are described further below.

Tank leaching

Figure 4.2 presents a simplified and generalised flow diagram of gold ore beneficiation and processing technologies used with tank and heap leaching in Australia (adapted from DEWHA, 2006). As indicated in Figure 4.2 for tank leaching sodium cyanide is added during the cyanidation process to the process ore slurry to promote the dissolution and complexing of the gold to cyanide. The pH of the slurry is typically raised using lime to minimise cyanide losses due to volatilisation as HCN. Typical concentrations of cyanide used with tank leaching are 100-500 mg CN/L.

Tank leaching with activated carbon may include one of two distinct types of operations, Carbon-in-Pulp (CIP) or Carbon-in-Leach (CIL). In CIP operations, the ore pulp is leached in an initial set of tanks with carbon loading occurring in a second set of tanks. In CIL operations, leaching and carbon loading of the gold occurs simultaneously in the same set of tanks. Most gold mining operations in Australia currently use tank leaching with CIP or CIL.

Sodium cyanide is also added during the carbon loading (e.g. CIP or CIL) process. CIP involves the removal of complex gold ions from solution by adsorption onto activated carbon. The slurry that has undergone cyanidation is passed through a cascade of agitation tanks. As the slurry moves down the cascade, gold is adsorbed onto granular activated carbon, which is then retrieved and processed. The main difference between CIP and CIL is that in the CIL process the cyanidation and adsorption processes are not staged separately, so that gold dissolution and recovery from the slurry proceed simultaneously in each CIL tank.

Sodium cyanide is also added during the elution process, which involves the washing of gold-loaded charcoal in hot water, caustic soda and cyanide solution to remove the gold from the washing liquor. The resulting liquor is known as pregnant solution. Gold is recovered from the pregnant solution by electrowinning (electrodeposition on a steel wool or copper cathode) and subsequent smelting, or by zinc precipitation (as described above) (USEPA, 1994).

The residues from tank leach operations are deposited into tailings storage facilities (TSFs), as discussed in Section 5.2.3. The potential fate of cyanide in TSFs is described in Section 6.6.

Heap leaching

The heap leach process is an alternative cyanidation process for relatively low-grade gold bearing ores (also shown in Figure 4.2). Heap leaching is also used to extract copper from ore using sulphuric acid. Heap leaching has been used in relatively few gold mining operations in Australia, and then often as a secondary treatment (e.g. re-treating old tailings piles), whereas it has been extensively used in the USA. Reasons for low use in Australia include the following (Staunton, pers. comm. 2005):

- recovers a lower proportion of the gold present and there is a prolonged delay (several weeks or months) before gold production starts;
- Australian producers build tank leach plants relatively cheaply;
- Australian ores are typically high in clay, making agglomeration treatment necessary to achieve satisfactory permeability;
- in many cases the more amenable surface ores have been mined already and subsurface ores are more refractory.

In general, the gold-bearing ore (crushed ore, run-of-mine rock or occasionally mill tailings) is placed onto lined 'leach pads' (e.g. ~plastic geomembranes, asphalt or clay, and composite liners using these materials) on the ground to prevent loss of the precious metal-bearing solution and to protect groundwater. Steps taken to assist drainage at the base of the pad may include constructing it with a slope (1%-6% or more), placing a permeable crushed rock drainage system onto it (i.e. an 'overliner'), and installing a drainage pipe network. Ore heaps of 50-230 m final height and 150-

200 hectares have been constructed or are being developed internationally using this process (Thiel and Smith, 2003).

Four types of leach pads are identified (Thiel and Smith, 2003):

- conventional (flat) pads: constructed on relatively flat land, either graded smooth or with terrain contouring. Ore is stacked in thin (5-15 m) lifts;
- dump leach pads: similar to conventional but constructed on undulating terrain. Ore is stacked in thicker lifts (~50 m);
- valley fills: constructed in valleys with a buttress dam at the bottom of the valley or a levelling fill within the valley; and
- on/off (dynamic) pads: constructed on flat ground using a robust liner and overliner system, thin lifts (4-10 m thick) are loaded and leached, with the leached (spent) ore ('ripios') removed for disposal and the pad recharged with fresh ore. Usually loading is automated using conveyors and stackers.

A sodium cyanide solution is applied using drip, spray or pond irrigation on the top of the heap, typically at ~250-500 mg CN/L (USEPA, 1994). Concentrations used for heap leaching at Nevada gold mines sites evaluated by Henny et al. (1994) ranged from 13-265 mg CN/L.

Lime is usually added to the cyanide solution to curtail the loss of cyanide through volatilisation of HCN. As the reaction is oxygen dependent, the solution is oxygenated prior to or during spraying. The solution slowly infiltrates through the ore heap, dissolving the gold into solution. The leaching process may continue for several weeks or months. The dissolved gold in solution collects in surface drains and sumps at the edges of the heap and is pumped to a lined holding pond or tank (pregnant pond) and from there onto gold recovery (Figure 4.2).

After the gold is extracted the remaining solution is moved into another lined pond, which is commonly called the barren pond. The cyanide concentration in this pond may then be increased so that the solution is again suitable for use in the leaching process, and the solution is used again on the ore heap. Gold is recovered from the pregnant solution generated from heap leaching using adsorption in a series of columns containing activated carbon (Carbon-in-Column), or by zinc precipitation (USEPA, 1994a; USGS, 1999).

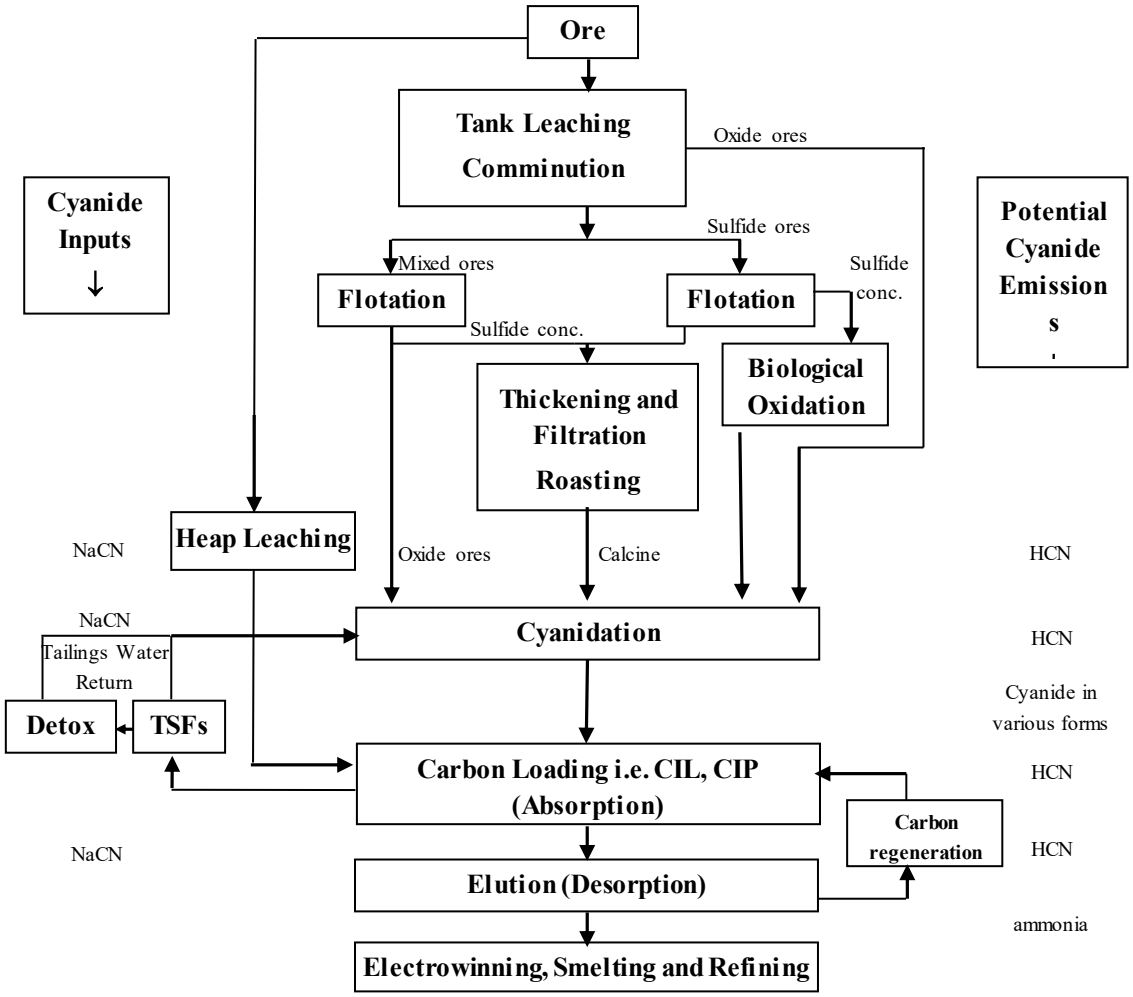
After the leaching cycle for soluble gold residues has been completed, the spent ore and remaining cyanide solution become wastes. During the decommissioning process, the heap is typically rinsed with mine water or mill waste water to leach the heap of remaining soluble cyanide residues. This may continue for some time until testing shows acceptably low levels of cyanide, and after other reclamation steps the heap may then be left in place. Alternatively (e.g. where there are impermeable sections of ore or the leach pad area is to be reclaimed), the heap may be dismantled and the ore treated in batches (USEPA, 1994c).

To enhance percolation of the lixiviant through the heap, a process called 'agglomeration' may be used to aggregate small particles together and prevent fine particles blocking pores. This typically involves crushed ore being mixed with portland cement and/or lime, wetting the ore evenly with cyanide solution before the heap is built, and mechanically tumbling the ore mixture so fine particles adhere to the larger particles. This improves the efficiency of extracting gold from the heaped ore and may

increase the rate of flow of cyanide solution through the heap by a large factor (e.g. 6000 fold), decreasing the overall leaching time needed (USEPA, 1994). It is also a means of reducing the duration and extent of surface ponding of cyanide solution on the heap. However, there are additional costs involved and potential problems if the treated material should de-agglomerate.

The potential fate of cyanide in heap leach operations is described in Section 6.7.

Figure 4.2. General gold ore processing: cyanide inputs and potential emissions (adapted from DEWHA, 2006)

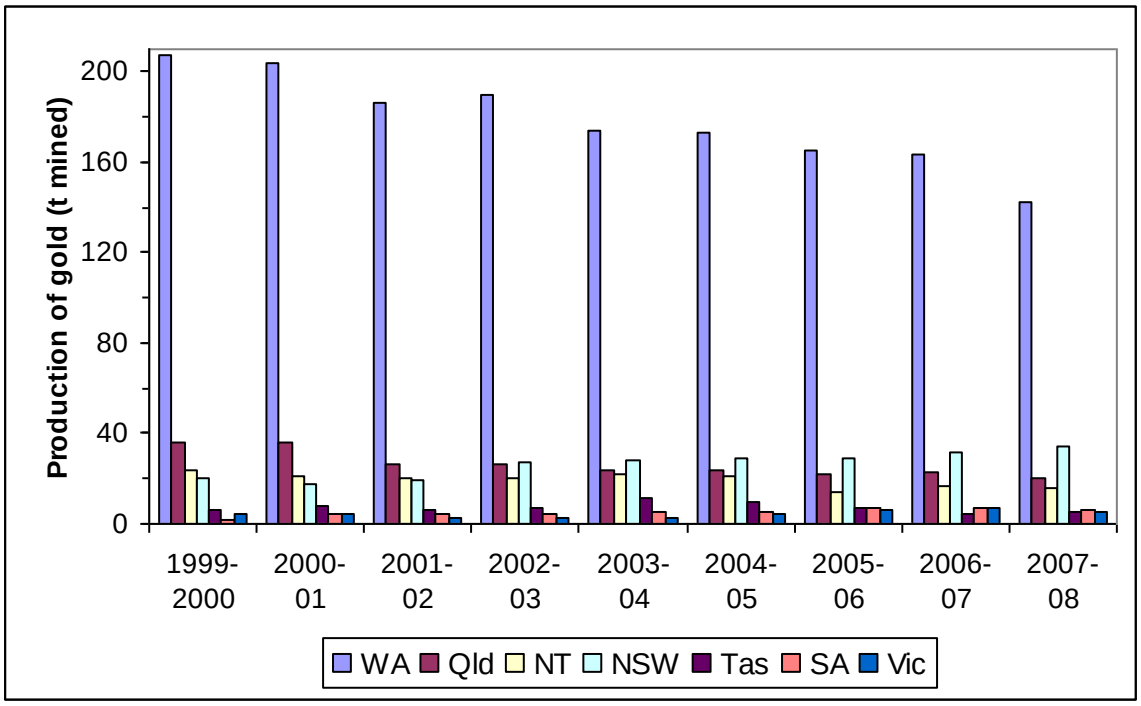


Scale and distribution of the Australian gold mining industry

Gold production

Most of the gold produced in Australia in recent years has been obtained using sodium cyanide beneficiation. Data for the amount of gold mined therefore give a broad indication of the likely relative amount of sodium cyanide used, except for the few mines in that period where gold beneficiation occurred without the use of cyanide, and noting that the amount of cyanide which needs to be added per g of gold or per tonne of ore varies widely (see above). These data (Figure 4.3) follow a broadly similar pattern to data for the numbers of gold mines and gold operations discussed below.

Figure 4.3. Gold production in Australian states and territories during the years



1999 to 2008 (Source: ABARE, 2002-2009)

Number of gold mine operations and tailings dams

Estimates of the number of gold mines operating in Australia are not completely accurate and are subject to variation due to mine closures and openings. However, available data in 2005 (former GeoScience Australia website; K. Porritt and M. Huleatt, Minerals Resources and Advice, Geoscience Australia, pers. comm.. 2005) indicated a total of approximately 122 mines operating in Australia had gold as their most significant commodity (some of these also produced other minerals, such as silver or copper, or in a very few instances zinc, lead or molybdenum). The great majority of these mines were in Western Australia (95 in WA, 8 in Queensland, 7 in NSW, 6 in the Northern Territory, 3 in Victoria, 2 in Tasmania and 1 in South Australia). There were an additional 17 mines where gold was considered a secondary or very minor commodity (e.g. where copper is the principal commodity). The number of operating mines in WA has fallen significantly since then: Geoscience Australia (2009) indicates that in early 2009 there were 97 mines with gold as the most important commodity (69 in WA, 9 in Queensland, 6 in NSW, 6 in the Northern Territory, 4 in Victoria, 2 in Tasmania and 1 in South Australia). There were a further 12 mines where gold was a secondary commodity (4 in WA, 7 in Queensland and 1 in NSW), and 10 mines where it was only a minor commodity.

These data refer to individual open pits or underground mines, whereas a gold processing facility may treat ore from more than one pit successively or concurrently, or may re-treat existing tailings heaps. A few gold processing facilities do not use cyanide to produce gold, e.g. because they only use gravimetric or flotation processes to separate gold or produce a gold-rich concentrate. Mines where gold is a secondary commodity may or may not use the cyanide process – e.g. cyanide was used for the initial, oxide ore phase at Northparkes, but not in the second stage.

Thus the number of sites using sodium cyanide for ore beneficiation is significantly less than the number of mines indicated above. Estimations from GeoScience Australia (Huleatt, pers. comm. 2005) are that in the March Quarter of 2005, there were 51 primary gold processing facilities, and gold was produced as a by-product from another 12 operations.

Mines producing other metals, such as zinc, lead and nickel, may use NaCN in their flotation circuit, but in relatively minor quantities compared to gold processing facility use.

Depending on its size and age, a gold processing facility may have multiple active or decommissioned tailings storage facilities (TSFs) associated with it, typically 1 to 3. The Western Australia Department of Industry & Resources estimates that there are approximately 370 TSFs in the state (i.e. for all minerals, not just gold), of which ~200 are active, with 15 new proposals current at the time (2004). The Northern Territory Department of Business, Industry and Regional Development estimates that there are 50-150 tailings dams in the Northern Territory. Estimates of the number of TSFs which are active or recently active in other states total at least ~75. However, based on the estimated number of gold mining operations above, there would be ~50-150 TSFs receiving cyanidation wastes at present in Australia.

5. Sources of Environmental Exposure

This chapter describes the sources of cyanide in the environment from the manufacture and use of sodium cyanide. Exposure to cyanide also occurs from natural sources and industrial uses of hydrogen cyanide.

5.1 Environmental release of cyanides generally

Cyanide is ubiquitous in nature, present mostly at low concentrations. Higher concentrations may occur in the environment due to anthropogenic sources.

5.1.1 Natural sources of cyanide

General comments

Cyanides can occur naturally at low concentrations in ground and surface waters (Environment Australia, 1998), and the concentration of naturally occurring free cyanide in water supply systems is usually less than 0.01 mg/L (NHMRC, 2004). Low concentrations of cyanides may occur in tap waters, either derived from the source waters or from the distribution system (CalEPA, 1997); however, this is probably a rare occurrence. Natural sources of cyanide include degradation products from some micro-organisms and plants that synthesise cyanogenic glycoside compounds. There is a cyanide group in the molecule of vitamin B_{12} (cyanocobalamine), which is required at trace levels by many animals, including humans, in their diet. Cyanide-containing chemicals (all forms) are produced by many organisms (bacteria, fungi, algae, invertebrates and higher plants) as part of their normal metabolism (NSC, 2002; Irwin et al., 1997; Ciba Foundation, 1988; Vennesland et al., 1981; Ferris, 1970).

Cyanogenic glycosides in plants

Cyanogenic glycosides are cyanide containing organic compounds that occur in at least 2000 species of plants (WHO, 1992; Knight and Walter, 2004). Examples of species containing cyanogenic glycosides include sorghums (Johnson grass *Sorghum halepense*, Sudan grass *Sorghum almum*), millet (*Panicum millaceum*; Poaceae), flax (*Linum usitatissimum*; Linaceae), elderberry (*Sambucus canadensis*; Caprifoliaceae), pits of *Prunus* spp. (plums, cherries, cherry laurel, pears, apricot, apple, peach, almond; Rosaceae) (CCWHC, 1999), sweet potatoes (*Ipomoea batatas*), corn (*Zea mays*), linseed (*Linum* sp.) (Irwin et al., 1997), spotted emu bush (*Eremophila maculata*), birdsfoot trefoil (*Lotus australis*), *Lomatia silaifolia*, milkweed (*Asclepias curassavica*; Asciepiadaceae), manna gum (*Eucalyptus vimilalis*; Myrtaceae) (McKenzie, 1997), *Eucalyptus cladocalyx* (Gleadow and Woodrow, 2000), cassava (*Manihot esculentum*; Euphorbiaceae), bamboo shoots (*Bambusa vulgaris*; Bambusaceae), lima beans (*Phaseolus lunatus*; Fabaceae) (Conn, 1979a-b), roses (Rosaceae) (MOH, 2000), and grasses such as button grass (*Dactyloctenium radulans*; Poaceae; Ballenger and Allan, 2001) and purple plume grass (*Triraphis molis*; Poaceae; Ballenger and Allan, 2002). Cyanogenic species also occur in other plants in the Leguminosae and in the Compositae and other plant families (Knowles, 1988).

There are approximately 25 different types of cyanogenic glycosides known including amygdalin, dhurrin, linamarin, lotaustralin, prunasin and taxiphyllin (WHO, 1992). Another naturally occurring group of organic cyanides (nitriles) is the highly toxic pseudocyanogenic glycosides, especially cycasin (Cycadaceae), and these have been implicated in a variety of tropical diseases of the nervous system, and partial or total blindness. Other nitriles found in plants include the lathyrogenic compounds, glucosinolates, and the cyanopyridine alkaloids (Irwin et al., 1997).

Cyanogenic glycosides are stored in plant cell vacuoles (Rothman, 1999). Consumption and masceration of plant parts by herbivores/omnivores leads to the release of the enzyme β-glucosidase, which hydrolyses the cyanogenic glycosides to sugar and aglycone and subsequently to hydrogen cyanide (HCN), particularly in alkaline rumen conditions of ruminant herbivores. The HCN is subsequently detoxified in animals by metabolic processes (refer Chapter 8) or potentially excreted as a gas; however, adverse effects may occur if the capacity for detoxification is exhausted. In such instances, livestock losses may occur due to sublethal cyanide poisoning (cyanosis) (DPI, 2003). The release of HCN from endogenous cyanide-containing compounds in plants has been suggested as an effective herbivore deterrent (Gleadow and Woodrow, 1999). In addition to consumption and masceration, other damage to plants (e.g. wilting, drought, bruising, trampling, intense heat, frost, etc) may also result in contact between cyanogenic compounds and hydrolytic enzymes (Tsai, 2001; Rothman, 1999).

Invertebrates

Various invertebrate species, including some centipedes, millipedes, beetles, moths and butterflies produce and secrete cyanogenic glycosides for defensive purposes in repelling predators (Duffey, 1981; Nahrstedt, 1988). The cyanogenic system comprising cyanogenic glycosides, cyanohydrins, betaglucosidases, and nitrile lyases occurs in several species of arthropods, including the tiger beetle (*Megacephala virginica*), leaf beetle (*Paropsis atomaria*), zygaenid moths, and certain butterflies (e.g. *Heliconius sara*) (Nahrstedt, 1988; Engler, 2000). In *Zygaena trifolii*, cyanide compounds seem to function as protection against predators (Nahrstedt, 1988). Defensive secretions of cyanide have also been reported in polydesmid millipedes, and these organisms seem to be more tolerant than other species when exposed to HCN (Towill et al., 1978). In a millipede (*Apheloria* sp.), cyanide is generated in a two-compartment organ by hydrolysis of mandelonitrile; cyanide generation occurs outside the gland when the components of the two compartments are mixed during ejection (Towill et al., 1978).

Micro-organisms

Many bacteria produce cyanogenic compounds (e.g. *Chromobacterium violaceum* and many strains of *Pseudomonas aeruginosa* and *P. fluorescens*; Knowles, 1988). Further details are provided in Section 9.6.

Bushfires

Bushfires can be a source of cyanide release into the atmosphere, especially on a local scale (CalEPA, 1997), and HCN can be detected in atmospheric plumes from large scale fires (wild fires or deliberately set for agricultural regeneration, clearing etc). HCN is mainly released upon the incomplete combustion of biomass, during low temperature smouldering (Barber et al., 2003). During bushfires, most cyanide compounds produced are emitted to the atmosphere, and a relatively small fraction

resides in ash and may be leached by rain, potentially leading to cyanide in surface runoff waters (Barber et al., 2003). Biomass burning is considered to be the dominant source of HCN in the atmosphere (Section 6.3.3).

Other sources

In addition to producing nitrogen oxides (NO_x), it has been suggested that lightning may also produce HCN in the atmosphere, but this is considered to be a negligible source in the earth today (Chameides and Walker, 1981; Cicerone and Zellner, 1983). This has been discussed as a possibility more recently by Lary (2004) but appears not to have been supported. Another possible source in the atmosphere is reaction of the gas acetonitrile (CH_3CN – derived from various natural and anthropogenic sources) with hydroxyl radicals (Kleinböhl et al, 2006).

Cicerone and Zellner (1983) also noted that thermodynamic equilibrium calculations indicate volcanoes can emit HCN, but that this source was difficult to quantify and is probably relatively small.

5.1.2 Anthropogenic sources of cyanide

Cyanide releases to the environment may originate from a range of anthropogenic sources additional to the use of sodium cyanide for the mining and industrial purposes described in this review. Such sources include processes using other forms of cyanide, most notably HCN. HCN may be used as a fumigant, but more importantly is used as a precursor for the production of a wide range of products including plastics and synthetic fibres, herbicides, photographic development chemicals, anti-caking agents (i.e. sodium and potassium ferrocyanide), animal feed proteins (e.g. methionine) and explosive compounds (e.g. mercury and silver fulminate).

HCN is released upon the incomplete combustion of several materials, including wool, silk, polyacrylonitrile, nylon, polyurethane, and paper (CalEPA, 1997) and coal (Wójtowicz et al., 1995). The amounts of cyanide released depend on the conditions of combustion (Pauluhn, 1992). Detonation of TNT also releases HCN, at a rate of 13 kg/tonne (Environment Australia, 1999f).

Cyanide is found in association with spent pot linings (SPL) that are derived from aluminium smelting. Typically, SPL wastes have historically been sent to landfill for disposal under license; however, treatment procedures have been developed to detoxify the cyanide present in these wastes to minimise environmental releases. Residues resulting from previously used practices are also found at coal gasification/gasworks sites (Kunze and Isenbeck-Schröter, 2000; Hathaway, 2000; Meehan, 2000; Kjeldsen, 1999; Kaminski, 2003).

Coal contains about 0.5% to 1.5% by weight of nitrogen bound into the organic structure of the coal. When coal is heated, much of the nitrogen is released during the devolatilisation stage as HCN, other cyano species, and as ammonia (NH_3). These species are rapidly converted into NO_x or N_2, and thus are generally not emitted directly from coal combustors associated with power plants. Emissions may occur at metal manufacturing facilities in association with coke oven facilities, where cyanide may be generated under sub-optimal conditions.

In the United States, of the total cyanide released to air (then estimated at 20 000 tpa), which accounts for about 60% of the environmental load of total cyanide, about 90% is due to the fuel combustion emissions from vehicles (Hagelstein and Mudder, 1997a).

The second largest source of release of cyanide to air in the US is from facilities that manufacture organic chemicals (i.e. methylmethacrylate and acrylonitrile) and HCN (USEPA, 1981). Releases of cyanide to land in the United States are mainly through landfill disposal and the use of cyanide-containing road salts. Releases of cyanide to waters in the United States are derived mainly from anthropogenic sources, with most originating from discharges from wastewater treatment plants (WWTPs). Electroplating and heat treatment facilities account for the majority of influent into WWTPs. Non-point sources of cyanide are derived from agricultural and road run-off, due to the use of ferrocyanide-containing anti-caking ingredients in road salts (not used in Australia).

Data for anthropogenic cyanide release in Australia is discussed in the following section.

5.1.3 National emissions of cyanide (National Pollutant Inventory)

General comments

The National Pollutant Inventory (NPI) is a database administered by the Department of the Environment, Water, Heritage and the Arts, to provide information on the types and amounts of certain substances being emitted into the Australian environment (DEWHA, 2009a; EPHC, 2007b). The NPI data for environmental emissions of 'inorganic cyanides' (including all forms encompassed under the definition of total cyanide – Section 3.3.1) for the period 2007-08 have been summarised in the following sections.

For the purpose of reporting to the NPI, 'emission' means emission of a substance to the environment whether in pure form or contained in other matter, and whether in solid, liquid or gaseous form. Individual facilities are required to report emissions of NaCN (listed by the NPI as a 'Category 1' substance) when their use totals ≥ 10 tonnes of the substance per year. 'Emissions' do not necessarily reflect the extent to which different uses occur– there are limitations in the data due to factors such as the scale for reporting individual sites, and different processes may result in widely different proportions of reportable emissions (e.g. total emissions recorded for the gold industry are of the order of 1500 tonnes, compared to ~50,000 tonnes used).

'Emissions' data does not included deposit of a substance to landfill; or discharge of a substance to a sewer or a tailings dam; or removal of a substance from a facility for destruction, treatment, recycling, reprocessing, recovery or purification. These activities are classed as transfers and in the past have not reported under the NPI. Procedures for reporting transfers of NPI substances in waste to their final destination have now been developed and data for transfers are currently being collected and will be published alongside the 2008-09 emissions data.

It should also be noted that the NPI data do not distinguish between inorganic cyanide emissions derived from sodium cyanide and those emissions derived from other cyanide compounds (e.g. HCN, KCN). There is insufficient information available to evaluate the relative contribution that sodium cyanide-derived cyanide contributes to the total amount of environmental releases of cyanide relative to all other natural and anthropogenic sources of cyanide compounds. However, information is available on the quantity of sodium cyanide manufactured and used in Australia (Section 4). In addition, knowledge of the cyanide product used by various industries provides an indication of the parent compound used and thus the origin of the cyanide compounds released into the environment by that industry (Section 4.4). For example, the

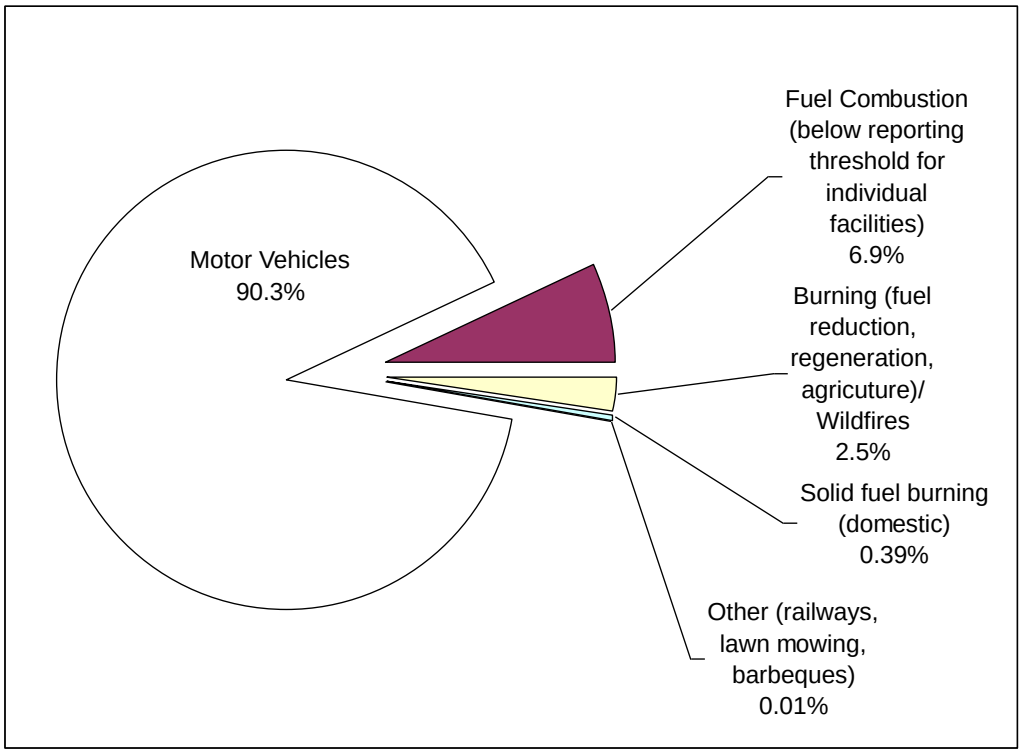
Australian gold mining industry is a major user of sodium cyanide for ore beneficiation and cyanide emissions from this industry are largely derived from this use, while electroplating industries use heavy metal cyanides in addition to sodium cyanide or potassium cyanide (Sections 4.4.2 and 5.2.5).

Release from diffuse sources

In addition to reporting emissions from industrial point sources, the NPI reports estimated releases from diffuse sources. For total inorganic cyanide, the estimated total annual emission of inorganic cyanides from diffuse sources in 2007-2008 was 610 tonnes, primarily from motor vehicles, and all considered to go to air (Figure 5.1). These sources involve releases of cyanide through processes such as combustion, rather than the use of cyanide salts such as sodium cyanide.

The estimated release from these sources is approximately 45% of that estimated from industrial point sources in Australia. However, this and the relative contribution from different NPI diffuse emission categories appear to contrast markedly with estimates of HCN emission to the atmosphere on a worldwide scale, where biomass burning is considered the major source and HCN has been proposed as a sensitive tracer of biomass burning on a large scale for observations from space (Rinsland et al, 2001, 2005; Li et al, 2003; Singh et al, 2003).

Figure 5.1. Contribution of major diffuse sources of emissions of inorganic cyanide to air in Australia reported by the National Pollutant Inventory (2007-2008).



Release from industrial point sources

The 2007-08 year was the tenth year of NPI reporting and there have been significant fluctuations in the data for total inorganic cyanide between years as experience with reporting and categorising emissions has developed, rather than due to changes in the quantity used. The total inorganic cyanide release recorded on the NPI from industrial point sources was 464 tonnes in 1998-99 and has fluctuated between 1298 and 5167 tonnes in subsequent reporting years. Through the NPI program, DEWHA instigated a survey and review of cyanide emissions from gold mining facilities. This found very low confidence in the accuracy of the emission values reported from these facilities (Staunton et al., 2003). This report prompted a review of the emission estimation techniques used in calculating emissions by facilities and a revised NPI emission estimation technique manual for gold ore processing was released in December 2006 (DEWHA, 2006).

The NPI indicates that reporting facilities (i.e. major Australian industrial facilities) estimated that they emitted a total of 1426 tonnes of inorganic cyanides into the environment in 2007-08 (DEWHA, 2009a). These emissions correspond to approximately 1%-2% of the total quantity of sodium cyanide manufactured in and imported into Australia each year (Sections 4.2 and 4.3).

Emissions from TSFs to the atmosphere and land, including groundwater, are included in the overall figure. Some cyanide is also consumed during processes for which it is used or destroyed before release. However, it is clear that a major reason for the large difference between emissions and use is that much of the sodium cyanide used in Australia is transferred to tailings storage facilities at mine sites, where much of the material transferred is stored indefinitely as stable cyanide products or as cyanide breakdown products, or broken down and emitted as simple substances such as ammonia and carbon dioxide, rather than as cyanide.

As agreed in a variation to the NPI NEPM (June 2007), facilities will be required to report transfers of NPI substances in waste to final destination – including tailings storage facility, sewerage system, underground injection or for destruction. The reporting of transfer of NPI substances to a destination for re-use, recycling, reprocessing and other similar practices is to be voluntary. The current NPI Guide, which assists facilities in estimating their emissions, has been amended to include information on calculating transfers. In addition, a transfers booklet has also been published (DEWHA, 2009b).

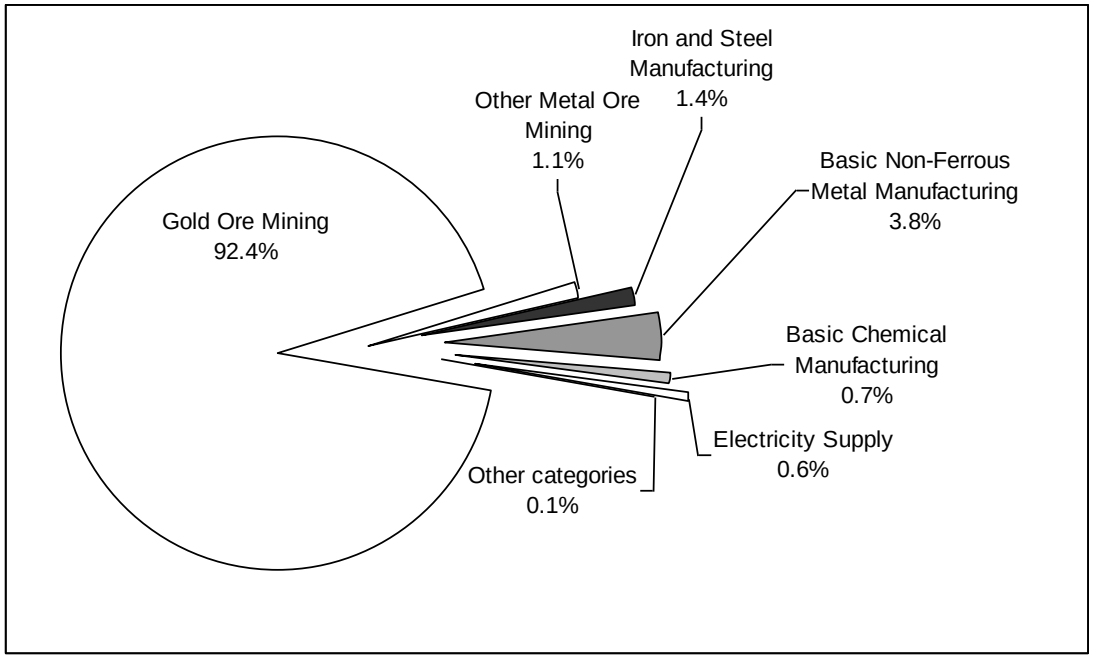
The following sections provide an analysis of the relative percentages of emissions in 2007-08 by location and industry type. Taking into account the data quality limitations mentioned above, the estimates provided below should be interpreted as indicative.

Point source releases by industry type

The percentage contribution from metal ore mining industries, primarily gold mining, to total inorganic cyanide emissions has remained at a similarly high level over the years NPI has reported, i.e. ~91% to 98% over 1998-99 to 2007-2008. The contribution reported from gold mining alone has been slightly more variable (75%-97%) and some other categories have fluctuated more widely relative to their size. According to the database, in 2007-08, metal ore mining emissions contributed about 93.5% of the total inorganic cyanide emissions Australia-wide, predominantly due to use by the gold ore mining industry (Figure 5.2).

According to the NPI, the majority (88.4%) of inorganic cyanide releases from reporting facilities in 2007-08 were to the atmosphere, principally as HCN, with 11.2% to land and only 0.4% to water.

Figure 5.2. Contribution of industry types to inorganic cyanide emissions reported by the National Pollutant Inventory for 2007-2008.



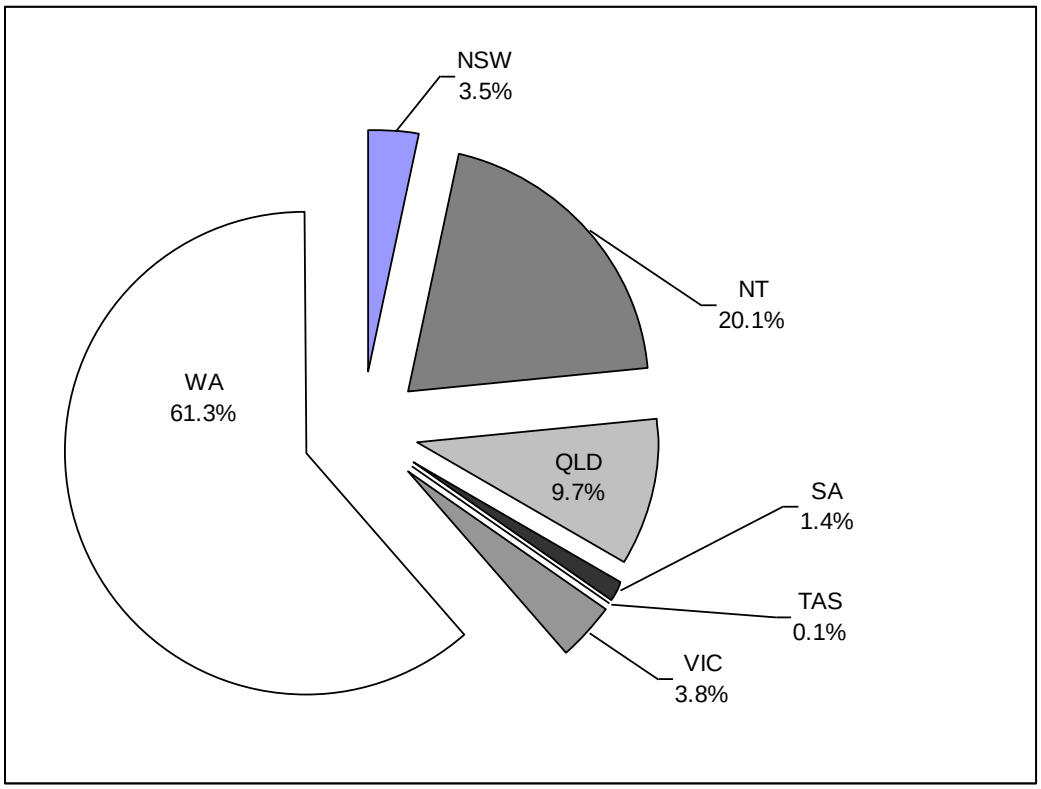
Differences in releases from point sources between states/territories

According to the NPI (DEWHA, 2009a, the majority (~61%) of point source environmental releases of inorganic cyanides in Australia from NPI Reporting Facilities in the reporting period 2007-08 occurred in Western Australia, followed in descending order by the Northern Territory, Queensland, Victoria, New South Wales , South Australia and Tasmania (Figure 5.3).

The great majority of emissions reported for industrial facilities in 2007-2008 were from gold ore mining, as in previous years. However, the point source release data for states/territories on the NPI do not fully reflect the relative importance of gold mining between states/territories (see Section 4.4.2 under Scale and distribution of the Australian gold mining industry). One factor possibly contributing to this is that some gold is obtained without the use of cyanide, and as noted in Section 4.4.2 the amount of cyanide which needs to be added per g of gold or per tonne of ore varies widely. According to the NPI data for 2007-08, in individual states/territories the contribution of gold mining to total CN industrial emissions exceeded 89% in WA, Qld, Vic, Tas and the NT, but other point sources were more important in NSW and SA. In NSW, iron and steel manufacture, electricity supply and gold ore mining accounted for respectively 40.1%, 16.1% and 41.9% of inorganic cyanide release, and in SA basic inorganic chemical manufacturing and gold ore mining accounted for respectively 18.9% and 76.3% of inorganic cyanide release. As with the total estimates of CN release, there have been significant fluctuations between years in these underlying data. Such differences may reflect inconsistencies and errors in accumulating the NPI data, as well as actual differences.

The following sections provide a more detailed analysis of the types of emissions of cyanide compounds from the major contributing industry sources in Australia.

Figure 5.3. State and territory contributions to total inorganic cyanide emissions (all industrial facilities) from the National Pollutant Inventory (2007-2008).



5.2 Release from sodium cyanide manufacture and industrial use

5.2.1 General comments

As indicated above, cyanide derived from the parent compound, sodium cyanide, is only one of a number of anthropogenic sources of cyanide released to the environment. This section describes potential emissions of cyanide to the environment that are derived solely from the use of sodium cyanide in industry. Unintentional incidents involving cyanide are discussed in Section 5.4.

5.2.2 Sodium cyanide manufacturing facilities

Sodium cyanide manufacturing facilities generate solid, gaseous and liquid wastes. According to the NPI (DEWHA, 2009a), environmental emissions from the two sodium cyanide manufacturing facilities operating during 2007-08 (including any releases from other operations at the same site) constituted 128 kg for the Orica Yarwun site (116 kg to air and 12 kg to water for the entire site) and 5922 kg for the CSBP (AGR) Kwinana site (5921 kg to air and 1 kg to water for the entire site). However, rather than indicating real differences in release of cyanide due to manufacture of NaCN, the differences in the data between the two sites may reflect release of cyanide as a consequence of the production of other substances at the same site, or could simply be due to differences in the way release of cyanide has been

estimated and reported to the NPI. In any case, the total discharge of inorganic cyanide at these two sites is a small percentage of their total production output (i.e. ~100 000 or more tonnes NaCN/annum) and of the total emission from industrial facilities reported to the NPI (Figure 5.2 – included under 'Basic chemical manufacturing'). Each of these manufacturing facilities had implemented cyanide recovery and wastewater re-use strategies and cyanide detoxification procedures in order to minimise emissions, is involved in Responsible Care® programs and has implemented a range of safety and environmental management programs (refer Section 11.11).

Solid wastes are mostly non-hazardous or are treated and certified as such prior to landfill disposal under license.

Gaseous emissions derive passively from storage tank vents and during the filling of transportation tanks (e.g. isotainers) and associated venting or from stacks associated with manufacturing plants. Stack emissions are monitored and undertaken in accordance with environment protection licences. No non-compliances have been identified, and data from one manufacturing facility indicated non-detection of HCN for every stack monitoring event.

Wastewaters containing free cyanide may be generated, particularly originating from the drying process during the manufacture of solid sodium cyanide. Plant wastewaters are mostly reclaimed back into the sodium cyanide manufacturing process. Alternatively, wastewaters are treated prior to on-site storage, testing, and batch-based discharge from the plant under state/territory environment protection license or trade waste licence. In one instance, both the sodium cyanide manufacturing plant and the manufacturing facility's on-site wastewater treatment plant operated under separate discharge licenses. Methods for treating free cyanide in wastewaters vary and may include automated dosing with peroxide and copper sulphate to convert cyanide to cyanate, or acidification resulting in the generation of HCN that is subsequently treated with sodium hydroxide to produce sodium cyanide that is reclaimed back into the manufacturing process. Alternatively, the acidified effluent is dosed with sodium hypochlorite to convert the cyanide into cyanate. Wastewaters discharged from the manufacturing plant may also be subjected to further treatment at on-site wastewater treatment plants, effluent ponds and dilution with other site wastewaters and through the use of effluent diffusers. Treated effluent is either discharged off-site to sewer for treatment and ocean outfall or directly to deep ocean outfall. The Licence concentration limit set by state agencies for discharge of solutions containing free cyanide from manufacturing plants is 1 mg CN/L. Wastewater monitoring data provided by manufacturers indicate that free cyanide concentrations in discharges to sewer/outfall are typically much lower than 1 mg/L (mostly <0.1 mg CN/L or <20 grams per day).

Cyanate, ammonia and nitrate are frequently detected analytes in sodium cyanide manufacturing plant wastewaters. Cyanate concentrations in wastewaters have been recorded up to 65 mg/L at two manufacturing facilities, but concentrations are mostly ~10 mg/L and total cyanate load was estimated at ~3000 kg/annum from the three facilities. Ammonia (NH_3-N) and nitrate (NO_3-N) are frequently detected analytes in manufacturing facility wastewaters, with average discharge concentrations of ~20 mg/L (7000 kg/annum) and ~1 mg/L (200 kg/annum), respectively. These average and loading estimates are based on a random selection of 1 month of monitoring data from 2002 from one facility, and variations will occur within and among facilities.

5.2.3 Cyanide use in gold beneficiation and recovery

Tailings storage facilities are the principal repository and potential source of cyanide release to the environment (Section 4.4.2).

Atmospheric emissions may potentially arise from the ore processing mill at solids/liquids mixing locations and from ore milling facilities (e.g. oxide leach tanks). Estimated losses through volatilisation as HCN from within the mill processing area of gold operations are about 1% of that used (Heath et al., 1998; Staunton et al., 2003). Similarly, air emissions of HCN during the elution and electrowinning processes are <1% of the cyanide being added to the total process operation. Electrowinning and carbon regeneration processes may result in the conversion of cyanide to ammonia. Figure 4.2 shows where cyanide-related emissions may occur.

Tailings storage facilities

With tank leach operations, the finely ground rock materials produced by milling and remaining after the gold (or other economic minerals) have been removed are termed 'tailings'. This material is suspended in the used process water, together with other substances added or generated during the beneficiation and processing stages. It is typically discharged to mine-site tailings storage facilities (TSFs), which may be of various types (below). The tailings stream bears cyanide, metallocyanide complexes, cyanates, thiocyanates and other chemical species dissolved from the ore (Smith and Mudder, 1993). The fate of cyanide in TSFs and with heap leach operations is described in Sections 6.6 and 6.7, respectively.

Tailings are predominantly discharged to tailings storage facilities (TSFs). The term TSF is defined as an area used to confine tailings and it refers to the overall facility. It may include one or more tailings (or water) dams or other tailings impoundments (MCMPR/MCA, 2003). Types of tailings impoundments used to confine tailings include tailings dams, mined-out voids, valleys in overburden stripping or underground mined areas (WRC, 2000c). A tailings dam is defined as the actual artificial embankment used to retain tailings (MCMPR/MCA, 2003). The ultimate purpose of a tailings impoundment is to contain tailings, often with a secondary purpose of interim storage of water for reclamation in the mine or ore processing mill (MCMPR/MCA, 2003; WRC, 2000c).

There are important considerations in site selection for a tailings dam and in choosing a suitable storage facility design and construction technique for the site, including meteorology, topography, geotechnical and geochemical factors, groundwater, seismology, and tailings properties (EPA, 1995b; MPD, 2004; Williams and Jones, 2005; DITR, 2007). The structural stability of the dam is important because of the possible release of large volumes of water and semi-fluid tailings, should failure occur. Appropriate design and management plans for the TSF are also important to minimise, monitor and if necessary control seepage into groundwater and to control any surface water generated (e.g. seepage into drains, rainfall run-off and accidental spills). Groundwater monitoring is highly important even after site selection, design and management plans have been thoroughly considered, as there are limitations in the modelling and other techniques used in the site selection and design phases. As well, any TSF that is very large will have the potential for water that is contaminated to seep into the groundwater. Monitoring of the groundwater gives a good basis for ongoing management of the facility.

As will be discussed later (Section 11.13), appropriate TSF design and management strategies may also be important to minimise potential impacts on wildlife. Appropriate measures also need to be considered to protect and restore the environment when the facility is no longer required (e.g. containment/encapsulation, drainage systems, and ongoing monitoring and control of surface and groundwater). There are various state/territory control measures and legislative requirements for TSF design, operation and subsequent maintenance to ensure adequate safety of the structure, prevent and/or manage groundwater contamination and minimise other potential impacts. Guidance on dam design and operation is available from various sources (Section 11.6.3). Cyanide is not the only contaminant present and TSFs may contain various heavy metals that may be mobilised, and acid drainage may be generated from the oxidation of sulphides (USEPA, 1994c).

MPD (2004) notes that as tailings material must be securely stored for an indefinite period and present no hazard to public health and safety or the environment, the closure of a TSF and rehabilitation works must be inherently stable, resistant to degradation and consistent with the surrounding landscape. Planning and preparation for ultimate restoration start early, including setting aside of topsoil and other material for covering the closed TSF (Section 10.4).

MPD (2004) indicates that potential environmental impacts of decommissioned TSFs include groundwater contamination, acid drainage and erosion of material by water and wind. The threat of catastrophic failure is usually reduced due to the de-watered nature of the deposit, but under some circumstances remains an important consideration. The operator should design a post-closure monitoring program including revegetation performance, flood mitigation and drainage control, seepage, erosion control, control of pests, plants and animals, groundwater quality, and should demonstrate that completion criteria have been met and the site is safe and stable. Even the best designed facilities will require maintenance or care, and proponents and operators of a TSF should make provision for the long term costs associated with the TSF and its maintenance.

Information received on a number of gold mines in Australia shows that most have paddock type TSFs, typically rectangular structures with 1, 2 or 3 cells. Tailings is discharged into these facilities from spigots usually located at several points along one or more edges, with a central point or area at one end where the decant water is collected. A number of mills also use in-pit tailings facilities, placing tailings into mined-out pits, with suitable precautions to prevent seepage near the surface and manage drainage. At least one facility uses an alternative to the paddock system, with thickened tailings discharged from one or more points towards the centre of an approximately circular structure (Central Tailings Discharge - CTD) to produce an essentially conical formation, the decant water being collected into a dam at the lowest point on the edge of the shallowly sloped cone. These systems have various advantages and disadvantages in the way they need to be managed and in their performance. TSFs can be quite large, e.g. with each paddock cell ~50 ha, and one example with a three-cell paddock facility occupying 284 ha, and with heights up to ~10-50 m.

In general, mills seek to recover as much water as possible from the tailings before and/or after deposition to the TSF, to minimise the amount of water and toxic solutes which need to be disposed of, to maximise the use of residual free cyanide, and to maximise water use efficiency. Temporary pools of supernatant form before the water drains through or off the surface of the TSF. Typically, water drains from the freshly applied slurry and supernatant areas to a collection point, where it flows or is pumped

into a decant pond. Drainage and surface seepage from elsewhere in the site or from run-off or overflow from the TSF are directed into the decant pond and/or other temporary storage ponds and if necessary pumped back to the TSF or into the decant or process water ponds. Water from the decant pond is pumped back to the mill for re-use in the process.

Conventional (unthickened) slurry from gold tailings typically contains <45% solids (Williams and Jones, 2005). Partially removing water prior to discharge produces a thickened discharge (~60% solids) which still flows as a slurry, but behaves differently when deposited in the TSF (e.g. forming a natural beach slope suitable for the CTD system – DMEWA, 1999). This helps limit the amount of free water available to pond on the surface of the TSF, hence reducing its area, depth and the time taken for it to drain away. Water extraction can be carried further to form a paste, which is then deposited by a technique known as dry stacking, with loss of water from the TSF by evaporation and little or no generation of decant water (DMEWA, 1999; Norman and Raforth, 1998). Water extraction can be carried further to produce a filter cake (>75% solids - Williams and Jones, 2005).

Concentrations of cyanide and related substances in TSF tailings

There are a large number of TSFs operating in Australia, all different, and the prediction of a particular tailings cyanide concentration to describe all tailings is not possible. However, a range of concentrations present in Australian mine tailings may be determined. Reported WAD CN concentrations in TSFs in Australia range from 10 to >380 mg WAD CN/L (Staunton, 1991b-d; ERA Environmental Services, 1995; Donato, 1999; Donato et al., 2008; Adams et al., 2008a,b,c; Griffiths et al., 2009; OSS, 1995). Unpublished data provided by the industry indicate that in exceptional cases, discharge of tailings containing as much as ~600 mg WAD CN/L has been occurring. The imposition of regulatory discharge limits is established in some states for cyanide in tailings on a site by site basis (Section 11.6), and some mining operations establish self-regulating programs for tailings (e.g. ≤50 mg WAD CN/L, or ≤30 mg WAD CN/L).

Concentrations of cyanate and thiocyanate have been investigated by Staunton (1991b-d) at three gold mine TSFs operating in the early 1990s (Table 5.1). As indicated in Table 5.1, analyte concentrations in tailings, TSF pore waters from shallow cores (0-2 m) and decant and reclaim waters varied widely within and between operations. Measured cyanate and thiocyanate tailings concentrations ranged up to 320 and 610 mg/L, respectively. Free and WAD CN concentrations in tailings ranged up to 210 and 340 mg/L, respectively. However, generally cyanide addition is more carefully controlled in recent years, so these numbers may be larger than average numbers at the present time (Staunton, pers. comm. 2005).

Tailings constituents may vary temporally within the one operation. For example, monthly cyanide (free, WAD, total) monitoring data collected from the discharge point from a tank mill process leading to a TSF were available for this assessment from a gold mill in Western Australia. The samples were collected between 1995-2002. In summary, the data (73 samples) indicated free CN contributed between 3%-100% of the WAD CN concentration and WAD CN contributed between 34%-100% of the total CN concentration. Average tailings concentrations were 71 mg/L (range 2.9-190, SD±31) for free CN, 94 mg/L (32-220, SD±30) for WAD CN and 122 mg/L (42-230, SD±31) for total CN. In 2002, free, WAD and total CN concentrations averaged 58 (5.1-100), 84 (35-120) and 151 (87-180) mg/L, respectively. However, data for free

CN concentration should be considered with care, as there may be significant uncertainty in accuracy due to changes in the form of cyanide present after sampling and methodology difficulties (R. Schulz, Environmental Chemist, Consultant and Auditor, pers. comm. 2006).

Table 5.1. Tailings, TSF pore water (0-2.0 m), decant and reclaim water concentrations (mg/L) of cyanate, thiocyanate and cyanide forms (after Staunton, 1991 b-d)

Mine/Material	Free CN	WAD CN	Total CN	Cyanate	Thiocyanate
Tailings pulp	29-76	320-340	510-700	51-320	540-610
Tailings disch. Pt.	120-210	130-230	130-250	7.5-110	5.4-9.3
Tailings disch. Pt.	65-72	78-87	83-97	44-48	13-16
Tailings (fresh)	120	130	130	110	9.3
Surface 1 day	9.5	6.5	37	180	21
Surface 1 week	50	---	170	---	75
TSF (pore water) cores (0-1.0 m)	<0.2-39	1.8-58	11-120	94-110	8.9-19
TSF (pore water) cores (0-1.6 m)	0.32-290	<0.3-630	0.32-1300	<30-2100	28-2100
TSF (pore water) cores (0-2.0 m)	0.8-38	1.6-34	8.4-580	24-150	<15-160
Decant solution	110	90	110	---	55
Reclaim dam	18	8.5	19	200	22
Return water	27	35	43	63	12

Unpublished data provided by the industry for a range of sites showed they could be grouped as follows on the basis of measured WAD CN levels:

- Sites using processes such as the Inco process (Section 0) to 'kill' cyanide to very low levels before release of the tailings, resulting in WAD CN concentrations in the tailings and in dams typically <1 mg/L.
- Sites which generally or always meet a 50 mg/L WAD CN limit for the protection of wildlife and livestock other than aquatic organisms, as may be required by state/territory agencies and as recommended under the International Cyanide Management Code (ICMC - Sections 11.10.3, 11.12.4). This may be achieved through monitoring of the process and tailings streams and steps such as adjusting the concentrations used in the process, dilution, or if necessary, treatment with detoxifying agents (e.g. metabisulphite, ferric sulphate or Caro's acid). In some cases lower levels (e.g. 30 mg/L) were targeted to meet limits set by state/territory agencies (e.g. NSW – Section 11.10.2) or company policy, and these were achieved in decant water, if not also in tailings discharge.
- Sites which frequently exceed the 50 mg/L WAD CN limit, usually having WAD CN in the 50-100 mg/L range and at times higher. These may be situations where detoxifying agents are not used and/or where ore and water characteristics make it more difficult, to achieve a 50 mg/L target (e.g. where the process is carried out at pH ~9.2 rather than 10.5 – Section 4.4.2, and/or where significant copper concentrations are present [Environment Australia, 1998]).

- One particular site, where mean WAD CN at the tailings spigot and in the decant pond was well above 100 mg/L, due to high cyanide concentrations required for the type of ore treated. Rather than seeking to lower WAD CN to safer levels, the approach taken at this site has been to adopt other measures, including netting of the decant pond.
- Sites where NaCN is not used - where gold-rich concentrate is produced for processing elsewhere and no cyanide is present in tailings.

As far as could be determined during preparation of this report, there are no mills in Australia routinely using lixiviants other than sodium cyanide on any significant scale.

The Western Australian Department of Industry and Resources (WA DoIR) indicated that in the past companies have usually discharged at 50-100 mg/L WAD CN, which reflected a balance between having sufficient CN in solution to extract the gold from the ore without discharging excessive CN to the TSF (this may have altered where the ICMC has been adopted). With current standards required by state/territory regulators and progress in adoption of the ICMC, it appears that an increasing number of mines are seeking to limit the concentration of WAD CN in discharge with a view to meeting limits of 50 mg/L WAD CN or lower, except for mine sites which are hypersaline (see Section 10.2.3).

It is important to be aware of where samples for analysis are taken, as data generally show a clear decline in WAD CN concentration away from the discharge point. The ICMC 50 mg/L limit does not apply to open-topped process tanks and vessels such as CIL tanks, but at the spigot discharge point or other areas where wildlife may seek access to tailings solutions. There may be exceptions for specific sites where scientific argument can be presented to argue for a higher limit to apply at certain points without adverse effects to wildlife, e.g. in the vicinity of the spigot discharge point (see Section 10.2.3).

5.2.4 Flotation use in base metal ore processing

Flotation is a process for separating fine particles in suspension in water on the basis of differences in their physico-chemical surface properties. Its use for base metal ore processing involves bubbling a continuous stream of air up through water containing the suspended mineral particles and chemical adjuvants (frothers and various other substances, such as xanthates as a promoter for sulphide flotation). Hydrophobic (water repellent) minerals attach to the bubbles and are carried to the surface, where they form a stable froth, leaving more hydrophilic particles that do not attach in the water. The froth and minerals contained in it can then be removed from the top of the flotation cell, achieving the desired separation (Lehne, 2003). Flotation is the process for separating fine particles in suspension in water on the basis of differences in their physico-chemical surface properties. Its use for base metal ore processing involves bubbling a continuous steam of gas (usually air) through the water containing the suspended mineral particles. Although some minerals naturally possess desirable surface properties, the success of any flotation separation depends on the range of chemical reagents added to the system to control the surface behaviour of the minerals in the ore (Furesteneau 2007a). There are six broad types of reagents, three of which are discussed in further detail. Frothers are added to control bubble size and stability. Collectors, of which xanthates are the most commonly used for base metal flotation, are surface-active organic reagents that impart hydrophobicity to minerals when they adsorb at the mineral surface (making the surface of mineral particles repel water).

Depressants are reagents that prevent are reagents that prevent collector adsorption or prevent attachment to unwanted mineral surfaces (ibid). Hydrophobic (water repellent) minerals attach to the bubbles and are carried to the surface, where they form a stable froth, leaving the more hydrophilic particles that do not attach in the water. The froth and minerals contained in it can then be removed from the top of the flotation cell, achieving the desired separation (Lehne, 2003).

Sodium cyanide (or other cyanide salts, such as calcium cyanide) is used in sulphide mineral flotation circuits as a depressor for sulphide minerals, selectively suppressing them from floating in the froth when they would otherwise do so (Environment Australia, 1999a-d; Dr D. Muir, Parker Centre/CSIRO Minerals, pers. comm. 2005). For example, cyanide is used to suppress pyrite, pyrrhotite and marcasite (iron sulphide minerals) in the presence of other base metal sulphides (e.g. copper, zinc and lead), and arsenopyrite and enargite (arsenic-containing minerals) in the flotation of nickel minerals. In the case of iron sulphides, the cyanide acts by forming a passivating layer of ferrocyanide or ferricyanide on the iron sulphide surface, which inhibits xanthates adsorption in the subsequent flotation. Depression occurs at approximately neutral pH values of 6.5-7.0 (Furesteneau 2007b). Sodium cyanide is most commonly used but it is possible for other base metal complex cyanides (such as zinc and copper) to be used instead. Sodium cyanide may react with copper and zinc minerals first and then iron minerals.

Emission estimation technique manuals for the National Pollutant Inventory (Environment Australia, 1999a-d) indicate that the scale of use of inorganic cyanides (i.e. not necessarily NaCN only) at most facilities within the nickel concentrating, smelting and refining industry is unlikely to trigger the reporting threshold (i.e. 10 tonnes/annum), whereas reporting of cyanide emissions to the NPI will be triggered at most zinc, copper and lead concentrating, smelting and refining facilities (note that cyanide may instead be used for gold and potentially silver extraction from the ore, particularly where copper ores are processed). Emissions from these industries may potentially occur from chemical storage and mixing areas due to spills and leaks at process areas and from TSFs following process solution disposal.

Typical dosages for base metal flotation are 50-250 g/tonne added to the mill, and the amount added is normally consumed in the process (Muir, pers. comm. 2005). Hence dosing levels may be at similar levels to those used for gold cyanidation (of the order of 100-500 g/tonne of ore), but with cyanidation a large excess of cyanide is used, leaving a high percentage of unconsumed free cyanide. There may also be significant differences in the fate of the cyanide added between cyanidation and various flotation processes because the pH conditions and other characteristics of the processing streams differ significantly from those used for cyanidation (e.g. the waste stream may be acidified in steps subsequent to the use of cyanide as a suppressor).

Rates indicated by Von Michaelis (1984) for flotation use at Canadian base metal mines (zinc, zinc/copper, lead/zinc/copper, copper/molybdenum/others) were 0-25 g/tonne (0-0.05 lb/ton) in most cases, and 50 g/tonne (0.1 lb/ton) in one case. The author noted that cyanide used in selective flotation processes is carefully controlled by metering in weak solutions to selectively react with the surface of a small portion of the ore. Hence probable concentrations of complex cyanides in tailings were estimated to be 0-25 mg/L (ppm), or 35 mg/L at the zinc/copper mine with the highest addition rate (presumably this refers to total CN, as forms not included in WAD CN may be present, such as ferrocyanide). As some cyanides are oxidised to thiocyanates and cyanates in the flotation circuit, these estimates were considered likely to be high.

Higher concentrations of free cyanide remained in the tailings stream at a zinc-lead mine in South Africa, where free CN concentrations at the lead tailings thickener and concentrate thickener were, respectively, 53 mg/L and 60 mg/L (note that the recovered water was recirculated back to the ball mill and flotation plant). These concentrations were stated to be much higher than the amount required for depression of sphalerite (zinc blend, i.e. zinc iron sulphide), but there were difficulties at this site due to copper in the ore causing activation of the sphalerite (Coetzer et al., 2003; Seke, 2005).

Data for five lead-zinc mines in the USA showed the 'raw waste load' of cyanide was 0.013-0.109 g/tonne of ore milled, with the range of cyanide concentration (presumably free CN) in wastewater being 0.01-0.03 mg/L (USEPA, 1994b). USEPA (1994b) noted that another mine and associated mill had consistently exceeded the discharge limitations for cyanide, total soluble solids and heavy metals (the relevant concentrations were not stated). Discharge from the tailings pond at this site (which received all mine and mill waste waters and discharges from process area drains) had been shown to be toxic to aquatic life, but there is too little evidence to ascertain whether this was due to cyanide.

Thus material disposed of to the TSF evidently usually includes little or no residual free cyanide and consists of heavy metal cyanides and cyanide complexes such as ferrocyanide, though in some situations a significant proportion of free cyanide may be present. No actual Australian data were found for free, WAD or total cyanides in used process solution or in TSFs at such sites. Worst case concentrations of total CN would correspond to the input rate (i.e. ~0-250 mg/L), but these are likely to be somewhat reduced by degradation to forms such as cyanate and thiocyanate. The formation of HCN and volatilisation is also likely to be a more prevalent pathway for dissipation of CN from TSFs than that of gold processing TSFs. This is due to the pH at which depression of sulphide minerals occurs being lower than that for gold beneficiation. Although the subsequent flotation process may occur in a wide range of pH conditions (2-12), sulphidic mine wastes tend to become acidic with the oxidation of sulphide minerals primarily from pyrite and pyrrhotite forming sulphuric acid (Trefry et al. 2008).

The use of sodium cyanide in flotation in base metal ore processing presents similar issues to those presented by the use of sodium cyanide in gold mining, but in Australia the total amount of cyanide used for flotation is significantly less and other salts of cyanide may be used instead of NaCN. The information available suggests that the quantity of cyanide used at individual sites is relatively low compared to gold mine use and that concentrations of free or WAD cyanide in the tailings stream are also low compared to those commonly occurring at gold mining facilities.

5.2.5 Electroplating, metal cleaning and metal surface treatment

Electroplating and other metal cleaning or treatment processes that use cyanide may potentially generate air emissions and cyanide-containing wastewaters and sludges that require specialist treatment and disposal methods. No submissions were received from the electroplating, metal cleaning or heat treatment industries during this review, but information on the use of sodium cyanide in these industries in Australia has been obtained from the relevant industry associations and industry experts.

Electroplating

Alkaline cyanide baths are used to deposit decorative and/or functional metal coatings onto a variety of objects (D. Woodward and P. McIlverna, Australasian Institute of Metal Finishing (AIMF), pers. comm. 2005; World Bank Group, 1998). For this purpose, NaCN (relatively high purity compared to gold mining use) is obtained in solid form and is added together with alkali and the metal cyanide (e.g. copper or zinc cyanide) to form the electroplating solution. NaCN is added to achieve dissolution of the metal cyanide. KCN rather than NaCN is used for gold and silver plating and for some copper plating, where the better performance of KCN justifies its extra cost. The main electroplating use for NaCN is now copper plating, with some use for brass plating. NaCN was commonly used for zinc electroplating, but in the past decade non-cyanide alternatives have increasingly taken over for zinc plating. Cadmium plating is now used very little because of its associated toxicity problems.

Release of HCN from the electroplating solution during use is discouraged by the alkaline pH of the solution. Used electroplating solution is treated immediately with processes such as hypochlorite or chlorine to destroy residual cyanide. The pH is then lowered to precipitate metal hydroxide complexes and after flocculation the waste is filtered to separate the solid and liquid waste. Safety requirements for humans dictate various measures to avoid acidic solutions coming into contact with cyanide solutions prior to cyanide destruction, to avoid generation of HCN gas (NOHSC, 1989; World Bank Group, 1998). The solid waste is sent to landfill and/or recycled, and the liquid waste recirculated as far as possible or released to the sewer, under trade waste agreements with sewerage system utilities, landfill operators and licenses authorised by state and territory environment protection agencies.

Metal cleaning

A solution of NaCN together with NaOH is considered a very effective agent for metal cleaning, particularly for purposes such as cleaning electrodes and as an activator of surfaces such as nickel preparatory to electroplating (P. McIlverna, Australasian Institute of Metal Finishing (AIMF), pers. comm..). There have been changes to reduce the amount of NaCN present (originally approximately 50:50 proportions with NaOH and concentrations of ~80-100 g/L, more recently with the NaCN concentration reduced to ~15-20 g/L). The use of NaCN solutions for metal cleaning has to a large degree been supplanted by other products, due to both the costs of destruction for the used solutions and because of environmental and health awareness. However, there is still some use of NaCN for this purpose. As with electroplating and metal surface treatment uses of cyanide, waste solution requires treatment to destroy the cyanide and neutralise the alkali before disposal.

Iron and steel surface treatment

Various heat treatment processes (carburising and carbonitriding [case hardening], nitrocarburising, and commercial processes based on these techniques, such as the Tufftride® salt bath nitrocarburising processes) use molten salt baths containing NaCN and an alkaline earth salt (e.g. barium chloride) for the surface hardening of iron and steel (CHTA, 1996; Bull and Page, 2000). Depending on the type of process and end result required, this may occur at 'low' (560-720°C - nitrocarburising) or 'high' temperatures (800-940°C – carburising and carbonitriding), under various atmospheres, and with or without quenching or other steps in the overall process.

There are alternative carburising, carbonitriding and nitriding treatments that do not use molten salt baths and cyanide.

These methods obtain their surface hardening effects through the diffusion of carbon and/or nitrogen into the surface of the metal to depths up to several millimetres. In the molten salt bath carburising process, cyanide is consumed through oxidation to cyanate, which dissociates at the steel surface to form CO and results in impregnation of the metal by C and N (Bull and Page, 2000):

$4NaCNO \Rightarrow 2NaCN + Na_2CO_3 + CO + 2N_{Fe}$

$2CO \Rightarrow CO_2 + C_{Fe}$

There are both liquid and solid wastes from these processes. Solid residue from the baths is re-used and topped up, but ultimately needs to be disposed of due to the accumulation of sodium cyanate and residues from other components. Liquid wastes are generated from quenching of the treated metal and from washing out of vessels etc. Waste from these processes is generally collected by professional disposal companies, treated as necessary and disposed of or recycled under licenses authorised by state and territory environment protection agencies (J. Rea, Contract Heat Treaters' Association of Australia (CHTAA), pers. comm.. 2005). The likely reason for collection rather than on-site destruction is the generally smaller scale of heat-treating operations compared to electroplating facilities (H. DiSouza, Orica Chemnet, pers. comm., 2005).

5.2.6 Other uses

Relatively small volumes of NaCN, generally in small containers, are used for various purposes in laboratories. Advice to users of NaCN and other cyanides in laboratory situations emphasises various precautions because of the risk of HCN generation or potentially violent reactions, including avoiding contact with incompatible chemicals and using under a fume hood. Recommendations for dealing with spills, cleaning and disposal are based on steps such as washing with sodium hypochlorite solution, making solutions alkaline and adding excess ferrous sulphate solution to complex the cyanide into ferricyanide, or oxidising waste to the cyanate by adding potassium permanganate. Thus, according to laboratory protocols, cyanide residues in laboratory waste and spills should be treated prior to disposal. Disposal recommendations for the treated waste include discharge to the sewer (in ample water, for small quantities of waste and with any necessary permission from local Authorities), or by sealing in a container for storage then removal by a licensed waste contractor.

5.3 Release via sewerage plant effluent

As noted earlier (Section 5.1.2), electroplating and heat treatment facilities account for the majority of influent containing residues from sodium cyanide into WWTPs in the USA. Uses of various other forms of cyanide (i.e. inorganic salts and complexes other than sodium cyanide) may also lead to some release of cyanide to the sewer and may be more significant contributors than sodium cyanide uses, given the requirements for destruction and/or disposal of residues from the use of sodium cyanide for purposes such as electroplating (Section 5.2.5).

Data from Sydney Water (2005) where cyanide concentrations in sewerage discharge effluent were measured over a number of years are available for 17 locations around the Sydney Metropolitan area, including 15 discharge points to rivers and streams, and 2 ocean discharge points. Changes in the form of cyanide present and/or removal presumably occurred during sewerage treatment. All the discharges occurred after tertiary sewerage treatment, with the exception of one of the inland discharges and the Warriewood ocean discharge (both secondary treatment).

A number of exceedences of the 10 times detection limit threshold (i.e. 10 X 1 µg CN/L) for total inorganic cyanide were detected in 2001-02, but these were attributed to inter-laboratory problems with the analytical method then in use (Independent Pricing and Regulatory Tribunal, 2003). Due to this unreliability, NSW Water Corporation reverted from a micro-distillation method to standard APHA (1998) methods (APHA 20th ed. 4500 CN- – C & N) for total CN in water and wastewater.

In both 2002-03 and 2003-04, median total CN concentrations for all the measured discharge points were <5 µg total CN/L, with median values at river/stream discharge sites generally ≤1 µg total CN/L (4 sites had median values of 1.5-5 µg total CN/L in 2002-03). At inland sites, individual maximum values recorded in those two years were generally <5 µg total CN/L, though they sometimes reached 5-10 µg total CN/L. Peak concentrations at Cronulla and Warriewood were 20 µg total CN/L and 108 µg total CN/L, respectively, in 2002-2003, and <5 µg total CN/L and 19 µg total CN/L in 2003-2004.

These data indicate that controls on use for various forms of cyanide together with removal in the sewerage treatment process (Section 6.9) are adequately limiting total cyanide concentrations in water at the point of release, where further dilution can be expected to ensure concentrations in receiving waters are below ANZECC Guideline trigger values of 7 µg CN/L for inland waters and 4 µg CN/L for marine waters (Sections 9.8.2).

5.4 Release as a result of unintentional incidents

This section discusses incidents involving unintentional potential or actual environmental releases of sodium cyanide and products which have occurred. The information reviewed was obtained from applicants, published literature sources and internet sources. Incidents such as those described are often poorly reported and evaluated, details are often not available, and such information as is available may or may not be accurate or complete. However, the data listed for recent decades in Australia and overseas confirm the need for appropriate design and management to minimise the likelihood of such releases occurring and for appropriate response plans to recover or detoxify released material and restore affected areas to minimise harm to the environment if such release does occur.

5.4.1 Manufacturing facilities

No incidents involving uncontrolled environmental releases of sodium cyanide or cyanide wastes have been reported at Australian sodium cyanide manufacturing facilities.

5.4.2 Transportation

There are potentially serious consequences of accidents occurring during the transport of sodium cyanide, as evident in the following reports. Information of the causes of such accidents and the adequacy of measures taken to clean up spills and minimise environmental harm after an accident has occurred is useful to guide the future management of risks associated with cyanide transport.

Cyanide transportation incidents which have been reported by Mudder and Botz (2001), newspapers or various websites are summarised in Table 5.2 (claimed human impacts have not been presented). No reports of incidents occurring during storage or handling prior to delivery to minesites were encountered, with the exception of the incident listed for New Zealand in 2004, which was very minor from an environmental perspective.

Several transport incidents which have occurred in Australia are listed in Table 5.2. The number of incidents is small compared to the large number of journeys in that period over long distances by road and rail. Significant release of NaCN only occurred in three of the incidents listed: a truck accident in the NT in 2007, release of NaCN in solution in an incident in the Tanami Desert in 2002, and a train derailment near Condobolin in 1992. Only in the Tanami Desert incident were wildlife or aquatic life reported to have been affected by the release to the environment, due to prompt emergency response measures on the other occasions to contain and recover the spilt material and remove contaminated soil or water. In the 2007 truck accident and 1992 train derailment the NaCN was packed in CIBCs in a shipping container and release occurred after upheaval of the containers in high energy incidents. In the Tanami Desert incident liquid was released from a StoL container en route. Further details of the Northern Territory truck accident and Tanami Desert incident are given below.

Also listed are various transport incidents which have occurred overseas, some of which have involved significant release of NaCN, downstream environmental contamination and harm to aquatic organisms. Details for one of the major overseas incidents (in Kyrgyzstan) are also discussed further below.

Northern Territory truck accident

On 7 February 2007, two shipping containers of a three-container load of solid NaCN (pellets) tipped over in a road traffic accident, spilling their contents onto the side of the road and into a pond in a non-flowing watercourse (sources: various news reports; NRETA, 2007; NT Government, 2007; NT PFES, 2007). The NaCN was loaded in 1 tonne CIBCs in shipping containers each holding 20 CIBCs, which were carried on a road train with 3 trailers. NaCN was in direct contact with the ground and an amount had also gone into the watercourse. The product was en route from the Orica manufacturing plant in Gladstone to a Northern Territory mine, and the manufacturer was promptly involved to assist local agencies with the emergency response.

An earthen bund was placed on the upstream side of the spill to prevent water flowing into the spill as a result of rain, and sandbagging and earthen bunds were used to prevent any spread of liquid from the containment area. This minimised the risk of further environmental contamination over the period of 9 days before the recovery and clean-up operation was completed and the highway was re-opened to traffic. The contents of the 3 containers were fully salvaged without loss of product except for approximately half the contents of one container. Small amounts of sodium hydroxide

solution were added to minimise HCN fuming from the pond during the recovery by keeping the water pH alkaline.

The area was constantly monitored during the recovery period to prevent access by animals or humans. Equipment was washed down to decontaminate it before being taken away from the scene. Contaminated water (120 000 L) and soil (1000 m^3) were collected and disposed of at operating and closed mine sites. After testing had been conducted to confirm that the area had been decontaminated, it was indicated that the area would be remediated to restore it to a condition similar to its original condition. An investigation conducted by NT Worksafe concluded that the transport, packaging, placarding (signage) and licensing of both the transport and driver complied with the legislation at the time of the accident (NT DEET, 2007).

In response to this incident, the NT Government initiated a review of regulatory regimes governing the transport of dangerous goods in the Northern Territory (NT Government, 2007). Specific objectives were to identify 'weaknesses in the regulatory regimes which may increase the risks associated with the transport of dangerous goods in the NT, and strategies which would help address any identified weaknesses and thereby reduce the risks.' The scope of the review included various categories of dangerous goods, the nature of transport activity, classes of dangerous goods transported, quantity transported and transport modes used, considering both road and rail transport. Consideration of the regulatory regime encompassed elements of Federal, NT and other State legislation ranging from current and proposed Acts, Regulations and Codes, to compliance monitoring, enforcement, accident response, and training. Thus the review extended well beyond environmental safety issues with the transport of sodium cyanide.

The review report is not yet a public document, but NT WorkSafe advise that the key recommendations from that review were being actioned, including the adoption of the 7th Edition of the Australian Dangerous Goods Code (ADG7) and improvements to coordination across Government agencies, both for compliance monitoring arrangements and for emergency response procedures. All jurisdictions, including the NT, have either legislated already for the adoption of ADG7 or aim to legislate by the end of 2009. By 1 January 2010 all transport of dangerous goods across state borders, and within most states, will be required to fully comply with ADG7. NT WorkSafe also indicate that the principal transporters of sodium cyanide in Australia no longer use triple road-trains for the transport of solid sodium cyanide in containers. The mode of road transport used currently is either double road-trains with end-loading containers or road-trains with tank containers on drop decks. Tank containers are transported as triples. They note that both of these configurations would be considered lower risk than the configuration used at the time of the 2007 accident.

Tanami Desert incident

Cyanide poisoning resulting in mortality to wildlife (birds, kangaroos, dingo) followed a leakage incident during road transportation of liquefied sodium cyanide in the Northern Territory in February 2002 (DEET, 2002). An estimated 3000-6000 L of water containing free CN was discharged along the Tanami Highway, forming a pool confined to the spoon drain alongside the highway from which the animals drank. Tests found that the concentration of cyanide in the puddle contained 863 mg/L of cyanide, but sampling and analytical details were not available to confirm these results or the concentration variability.

It was suspected that this occurred from a delivery truck returning from The Granites site to Alice Springs, and that due to a hose, pump or procedural failure, the cyanide in the isotainer had not been completely removed during the StoL (solid to liquid) process at the mine. The incident caused a number of fauna deaths (reports vary, but the most detailed seen indicated ~800 Zebra Finches, 30 pigeons/doves, 2 Black Kites, 10 Singing Honeyeaters, 10 Fairy Martins, 1 Spotted Nightjar, 15 Budgerigars and 1 dingo died). However, there was no apparent effect on local vegetation.

An extensive clean-up & remediation operation was conducted by the mine's emergency response team. Initial detoxification was undertaken by spreading calcium hypochlorite, and the water and top 0.5 m of soil were removed and sent back to the gold mine for disposal onto the tailings storage facility, with further hypochlorite neutralisation.

The reporting and investigation of the cyanide incident was delayed due to the lack of clear procedures and strategies to deal with a major release of dangerous goods in the Northern Territory. Recommendations arising from the incident investigation were directed towards product inventory management at the mine, improvements to the StoL emptying process, locking of input and outlet valves on isotainers, driver training in dangerous good management and better government departmental co-ordination of chemical spill incidents.

Barskoon River incident in Kyrgyzstan

In 1998, approximately 1700-1800 kg NaCN was lost into the pristine Barskoon River in Kyrgyzstan as a result of a truck accident while en route to a nearby gold mine. Several domestic animals and some river trout were stated to have died as a result. There were serious impacts on the local community (local concerns reaching such an extent that the area was evacuated ~2 weeks after the incident occurred, well after the cyanide in the river had dissipated to safe levels), as discussed by Hynes et al. (1998) and Cleven and van Bruggen (2000).

On the day of the incident, efforts were made to assist decomposition of the spilt cyanide using an unidentified substance, thought to be either hydrochloric acid or sodium hypochlorite. It is not clear whether or not these measures had any beneficial effects. Worst case calculations indicated that the spilt NaCN would all have dissolved within at most 17 minutes of the spill and that the contamination front would have taken at least 7-8 h to reach the lake 14 km downstream. While initial CN concentrations in the river water must have been very high, degradation, loss as HCN, movement downstream and dilution meant that there were no long-lasting effects in the river and concentrations in the lake remained below potentially harmful levels.

Recommendations from Cleven and van Bruggen (2000) included guidance on safe concentrations of free cyanide for human, animal and plant life in soil (1 mg/kg), surface water (0.1 mg/L), and improved information and risk communication regarding cyanide.

Table 5.2. Environmental incidents that have occurred with cyanide during transport

Year	Location	Reported nature and scale of incident	Claimed environmental effects
Australia			
2007	Stuart Hwy 130 km North of Tennant Creek, NT[a]	In an accident involving a road train carrying 3 X 20 tonne containers of solid NaCN, two containers tipped over, spilling NaCN pellets onto the side of the road and into a non-flowing watercourse. Precautions were taken to prevent rain water flowing into the spill or spreading of the contaminated water from the containment area. Much of the spilt product was salvaged, and contaminated water and soil were collected and disposed of at mine sites.	The clean-up took 9 days, during which the area was constantly monitored to prevent animal access. The area will be remediated to restore it to similar to its original condition.
2007	Euabalong West, NSW[b]	A goods train derailed on 14 January was carrying 2 X 22 tonne StoL containers of NaCN, but the wagon bearing these was not derailed.	No release of NaCN occurred.
2005	Cracow Mine, Qld[c]	A 21 tonne container of liquid NaCN fell from a truck turning into the mine and leaked through a pressure valve. About 50-60 L of the liquid escaped from the container and was collected in drums.	
2002	Tanami Desert, NT[d]	Up to 6000 L of liquid containing CN spilled beside the road in the Tanami Desert.	Approximately 800 birds and a dingo were killed.
1999	NSW Southern Highlands[e]	Nine wagons of a Brisbane to Adelaide freight train carrying bulk quantities of NaCN among other dangerous goods were derailed, but no NaCN was part of the derailed freight.	No release of NaCN occurred.
1996	WA	A road haul tanker left the road and rolled over while transporting sodium cyanide solution. None of the solution was released.	No release occurred.

Year	Location	Reported nature and scale of incident	Claimed environmental effects
1992	Condobolin, NSW	A collision between a freight train carrying 120 tonnes solid sodium cyanide in 1 tonne containers within steel shipping containers and a semi-trailer at a railway level crossing resulted in derailment of 3 locomotives and 10 wagons and spillage of ~40 tonnes sodium cyanide.	The spilt material was recovered, with no rain occurring during the recovery period.
Overseas			
2004	New Zealand/Lower Hutt	Two 180 L drums of cyanide solution were damaged inside a freight depot, possibly by a forklift.	Presumably no significant release occurred to the external environment.
2003	Taiwan	A leak of liquid cyanide occurred from an overturned truck, flowing into a nearby sewer.	Harmful ecological effects were feared once the contaminated effluent flowed into the sea through Taichung Harbour.
2001	China/Henan Province[g]	11 tonnes of liquid NaCN leaked into the Luohe River in Henan province after a traffic accident.	Livestock animals were poisoned. Another report indicated that the river was temporarily sealed off and dosed with 500 tonnes of hypochlorite and that a large fish kill occurred.
2000	China/Shaanxi Province[h]	A truck accident spilled 5.2 tonnes of liquid sodium cyanide into the Tieyupu River, a small tributary of the Han River. The river was dammed up- and downstream of the accident site and treated with bleaching powder to destroy the cyanide.	Authorities reported that damage had been contained to within 14 km of the spill site. The contaminated area suffered severe damage to biological life.
2000	Papua New Guinea/Tolukuma[i]	Transportation accident releasing 100-150 kg of NaCN into waterways, when a 1 tonne bale of NaCN pellets being airlifted to a mine was dropped from a helicopter into rugged terrain (the balance was recovered).	Unknown

Year	Location	Reported nature and scale of incident	Claimed environmental effects
1998	Kyrgyzstan/Barskoon (Central Asia)[(j)]	A truck laden with a container holding 20 X 1 tonne packages of solid NaCN crashed at a bridge and fell into the Barskoon River while en route to a nearby gold mine. Two packages burst open and released 1700-1800 kg NaCN directly into the river water, which was described as a pristine, small stream from which irrigation water was drawn and which flowed into Lake Issyk-Kul, a major tourist destination.	Several domestic animals and some river trout were stated to have died.
1984	Papua New Guinea/ Torres Strait[(k)]	In June 1984, a barge carrying 2600 x 100 kg drums of sodium cyanide in 15 containers sank off the mouth of the Fly River while on route from Port Moresby to the Ok Tedi Gold Mine. One of the containers ruptured releasing approximately 100 drums, which were recovered; however, the other containers were not located or recovered.	Unknown.

General sources: Mudder and Botz (2001), http://www.mpi.org.au/campaigns/cyanide/cyanide_spills and various other non-government organisation websites.

Further sources for specific incidents:

(a) NRETA (2007), NT Government (2007) and various news reports;
(b) Britt (2007) and A. Lidbetter, Independent Transport Safety and Reliability Regulator NSW, pers. comm.. 2007;
(c) Rockhampton Morning Bulletin, 31 October 2005;
(d) DEET (2002);
(e) NSW Fire Brigades (2000);
(f) DoIR (2004);
(g) BBC News; http://www.mineralresourcesforum.org/initiatives/cyanide/steering5/index.htm
(h) BBC News; http://english.people.com.cn/english/200010/13/eng20001013_52537.html;
(i) ABC PM transcript, 23 March 2000, http://www.abc.net.au/pm/stories/s113011.htm
(j) Hynes et al. (1998); Cleven and van Bruggen (2000);
(k) Kelleher (1991); Australian Newspaper, 11 December 2000; Strait Times, 12 December 2000).

5.4.3 Use and disposal at gold or other mineral processing facilities

International reports

Table 5.3 lists brief details of environmental incidents involving cyanide that have occurred at mining operations around the world in recent decades (claimed human impacts have not been presented). Detailed, authenticated reports of incidents are often not readily obtainable, hence the table has been compiled from lists recorded by ICOLD/UNEP (2001), Mudder and Botz (2001), augmented by various other sources, including the press and internet websites. Many of the overseas incidents listed were major environmental incidents involving the release of several thousand cubic metres or more of tailings slurry or solution, with resultant impacts on humans or ecological systems, in particular aquatic life. Some relatively minor incidents have been listed for

Australia. NICNAS has not investigated the regulatory control measures that were in place in the various overseas jurisdictions at the time of these overseas incidents.

The dam failure incident involving the greatest release of cyanide-containing waste was at a gold mine in Guyana in 1995, which released an estimated 3.2 - 4 million cubic metres of waste. The greatest release listed for cyanide-containing waste from dam overtopping was 39 000 cubic metres in the US in 1991. Pipe failures have resulted in estimated environmental releases of up to 700 000 tonnes of cyanide-containing waste, in an incident in the Philippines in 1999 (ICOLD/UNEP, 2001; Mudder and Botz, 2001).

In particular, information on ecotoxicity effects is often minimal and/or unreliable, presumably because it is difficult to judge the extent of damage caused by the specific incident in a quantitative fashion, and because where effects are not independently assessed they may be either understated or exaggerated (e.g. note the discrepancy in reports for the 1995 incident in Guyana or that at Tarkwa [Ghana]) in 2001.) Details of incidents are generally lacking or differ between reports, and a confounding factor may be confusion between different incidents.

It should also be recognised that cyanide contamination may be just one of many harmful factors arising from accidental releases to the environment from ore processing sites and tailings storage facilities. Ecological damage can be expected from sudden large releases due to physical impacts, destroying and covering or washing away vegetation and streams and killing or injuring terrestrial and aquatic wildlife in the path of the release. Ecotoxicity effects may be caused in aquatic areas reached by slurry and liquid releases, through turbidity as well as various toxic components, including cyanide. Depending on the form and concentration of cyanide present, serious effects may be anticipated through acute toxicity to fish and other organisms as a contaminated front moves downstream, and these effects may be exacerbated and prolonged by the presence of other, more persistent toxins, such as heavy metals. Measures taken to destroy cyanide also have potential to have other harmful effects.

Thus some care is needed in interpreting the damage reported for various incidents in Table 5.3, but it appears clear that there have been incidents of sudden or ongoing releases of material containing cyanide to streams and other aquatic areas where cyanide has contributed to serious harmful effects on fish and other aquatic organisms, and sometimes also to animals drinking the affected water.

Romania/Baia Mare Mine incident

One of the most serious incidents, for which the cause and impacts have been described in detail in BMTF (2000); Lucas (2001) and ICOLD/UNEP (2001), is the dam failure at Baia Mare in Romania. This incident involved an Australian company. Water from heavy rain and melting ice and snow caused a breach 20 to 25 m wide in a dam encircling a tailings pond, resulting in a spill of about 100 000 m^3 of mud and wastewater effluent containing ~120 tonnes of CN to flow through different tributaries (minor tributaries into the Sasar, then Lapus and Somes Rivers) into the Tisza River and then into the Danube River, finally reaching the Black Sea. After several hours, the continuing discharge was treated with sodium hypochlorite to destroy the cyanide. Both this and an incident the same year at Baia Borsa, Romania not involving CN resulted from inappropriate design and construction of tailings waste storage facilities for the climatic (water balance) regime, and permitting and operational faults.

A 30-40 km long contaminated wave destroyed the flora and fauna along and in the central Tisza River. Acute environmental effects occurred along long stretches of the river system, down to its confluence with the Danube. Phyto- and zooplankton levels were at zero when the CN plume passed, and fish were killed in the plume or immediately afterward. Hungarian authorities estimated >1000 tonnes of fish were killed, with dead fish reported as far as the Yugoslavian part of the Tisza, but no major fish kills reported in the Danube. Due to unaffected water flowing from upstream, plankton and aquatic organisms recovered within a few days, but long term impacts were a possibility due to heavy metal contamination also resulting from the spill.

Table 5.3. Environmental incidents involving cyanide at gold ore processing facilities or heap leach operations

Year	Location	Reported nature and scale of incident	Claimed environmental effects
Australia			
2005	NT[a]	500 L of treated CN released when a cyanide tank ruptured during a clean-up operation at a disused gold mine in the NT.	The spill was contained within the bunded area and the free CN content was very low due to the treatment with H_2O_2 which was underway.
2001	Timbarra Mine, NSW	Overtopping of a storm pond at a heap leach gold mine dam resulted in discharge of water into the headwaters of the Clarence River and the Timbarra Wetland, but the mine had recently ceased full operations and free CN levels in the dam water were very low.	
1995	Tasmania	Dam failure at a gold mine near Mathinna, releasing 40 000 m^3 of material containing CN.	Polluted streams; fish kill.
1995	Tasmania	Dam overtopping at a gold mine near Launceston released 5000 m^3 of material containing CN.	
Overseas			
2006	China[b]	A dam burst triggered landslides and sent waters containing cyanide residues into the Huashui River. Coffer dams were erected in the original course of the river and the water treated with bleaching powder and lime. Upstream water was diverted through a 660 m long channel.	The polluted stretch of river extended at least 5 km.
2006	Ghana/Dumasi	Cyanide spill from a tailings dam	Fish, crabs and lobsters were

Year	Location	Reported nature and scale of incident	Claimed environmental effects
	[c]	into the Ajoo Stream/Aprepre River when a joint on the main tailings return pipe ruptured.	killed and the stream polluted.
2006	Czech Republic/Kolin [d]	A large leak of cyanide from a riverside chemical plant spilled into the Elbe (Labe) River in central Bohemia. The Czech Environment Ministry, Environmental Inspection learned of the spill when local fishermen began reporting thousands of dead fish in the river.	An 80 km stretch of river was contaminated and >9 tonnes of fish killed. A large decrease in concentrations to ~30 µg/L was expected downstream at the confluence of the Elbe and Vltava Rivers, hence no impact was expected by the time the polluted water reached Germany (10 µg/L was described as the permissible limit).
2005	Romania/Baia Borsa[e]	Some 300 m^3 of effluent containing cyanide was accidentally discharged into a drainage ditch at the Borsa mine. There have been other contamination events from mines in this region (Maramures County) since the Baia Mare incident discussed below, but these have largely been from base metal mines and did not lead to cyanide release.[g]	Discharge from the spill releasing cyanide then flowed into the Viseu River, a tributary of the Tisza, killing fish in a limited area.
2005	Philippines/Rapu-Rapu	Untreated wastewater with high cyanide content was discharged into creeks that emptied into the Albay Gulf due to a defective valve and heavy rains.	Fish kills alleged.
2005	Ghana/Wassa	Cyanide spill into the Kubekro River.	
2005	Laos/Phu Bia Mine[f]	Cyanide release (quantity unspecified) occurred when heavy rains coincided with the start of heap leach operations at the mine, thought due to a failure in the containment area for the agglomerator and cyanide addition facility used to prepare the ore for heaping, rather than the core heap and solution collection components of the operation.	Fish were killed in the Nam Ou River.

Year	Location	Reported nature and scale of incident	Claimed environmental effects
2004	Ghana/Dumasi (c)	Cyanide spill from a tailings dam into the Ajoo Stream/Aprepre River, evidently due to inadequate facilities to recover seepage at the time discharge of effluent into the new facility started.	Reports of hundreds of dead fish, crabs, shrimp and birds along the river banks and floating on the river.
2004	Papua New Guinea/Misima Mine	Cyanide discharge from a mine during decommissioning polluted ocean waters.	Reports of dead fish floating in the ocean.
2003	Nicaragua	Cyanide spill entered the Bambana River.	
2003	Western Honduras	Large (unspecified) cyanide spill at a mine contaminated the Lara River.	At least 18 000 dead fish were reported.
2002	USA/Nevada	40 000 gallon spill of 140 mg/L CN solution from a ruptured pipe at a heap leach site overflowed containment structures.	
2002	USA/Nevada	24 000 gallons of CN solution spilled at a mining facility, with 10 000 gallons entering a creek.	
2001	Ghana/Tarkwa (g)	A cyanide spill incident occurred as a result of a broken joint on a pipeline carrying cyanide solution to the leach pads. Subsequent investigations revealed constructional failures of bunds to contain the solution within the leach pad area. This has since been reconstructed and areas outside the bounds sloped to the emergency containment pond, to prevent future occurrence of cyanide solution excursion out of the operational area. Aquatic life is back to normal in the Sumang stream.	The solution eventually entered the Sumang stream affecting aquatic life. Emergency response procedures put in place contained the situation as cyanide levels fell below 0.2 mg/L shortly after the incident was detected. This included the application of detoxification chemicals such as sodium hypochlorite and hydrogen peroxide and the supply of alternative source of water to the affected communities. Another report indicated hundreds of dead fish, crabs and birds were seen littering the banks of the Asuman River. Another indicated that

Year	Location	Reported nature and scale of incident	Claimed environmental effects
			the spill was reported shortly after the break occurred; a small nearby lake was impacted and, a 3rd party inspection found there were 54 dead fish.
2000	Romania/Baia Mare[(h)]	A dam failure at this mine permitted a spill of about 100 000 m^3 mud and wastewater effluent containing 120 tonnes of CN to flow via various tributaries into the Tizsa River and then via the Danube River into the Black Sea.	Acute environmental effects occurred along long stretches of the river system, down to the confluence of the Tisza river with the Danube. Hungarian authorities estimated >1000 tonnes of fish were killed.
1999	Philippines/Surigao del Norte	Pipe failure at a gold mine, released 700 000 tonnes of cyanide contaminated tailings.	
1998	USA/S Dakota	Pipe failure at a gold mine, released 6-7 tonnes of tailings containing CN into a creek.	Resulted in a substantial fish kill.
1997	USA/Nevada	Failure of a leach pad structure released ~1 ML of material containing CN into two local creeks.	
1995	Guyana/Omai	Dam failure at a gold mine from internal dam erosion, released ~3.2 to 4 Mm^3 of slurry containing CN, entering the Essequibo River via the Omai River.	Cyanide contamination caused a minor fish kill in Omai river, with pollution of the much larger Essequibo river negligible; Another report indicated 80 km of the Essequibo River was declared an environmental disaster zone.
1992 and before	USA/Colorado	There were cumulative losses of CN and heavy metals from leaks into the underdrain system beneath a heap leach pad, and from direct leaks from a transfer pipe into a fork of the Alamosa River.	All aquatic life killed along a 27 km stretch of the Alamosa River.
1991	USA	Dam overtopping at a gold mine, released 39 000 m^3 of material containing CN.	

Year	Location	Reported nature and scale of incident	Claimed environmental effects
1990	USA/S Carolina[(i)]	Rains caused an earthen dam to collapse and release more than 38 ML of cyanide solution	11 000 fish claimed to have been killed along an 80 km stretch of the Lynches River.
1986	Philippines	A typhoon washed away a portion of a tailings dam at the seafront, followed by another collapse the next year.	Both incidents released effluent with high levels of cyanide resulting in fish kills.

General sources: ICOLD/UNEP (2001), Mudder and Botz (2001), USEPA (2004), http://www.mpi.org.au/campaigns/cyanide/cyanide_spills and various other non-government websites:

Further sources for specific incidents: Links to news items or other sources on the above websites, plus

(a) ABC Northern Territory Summer News, 2 February 2005; Northern Territory Department of Business, Industry and Resource Development (NTDBIRD) pers. comm.. 2005;
(b) http://english.sina.com/china/1/2006/0506/74868.html, BBC News and The Standard newspaper reports;
(c) http://www.ens-newswire.com/ens/jul2006/2006-07-25-05.asp;
(d) Czech Radio 7/Radio Prague reports;
(e) http://www.terradaily.com/2005/051127184923.y2mne94w.html, http://www.greentransylvania.ro/home.php?lang=en&kozep=1&id=8&m=1, http://news.bbc.co.uk/2/hi/world/europe/678407.stm;
(f) Pan Australian (2005);
(g) http://www.epa.gov.gh/2001ar.pdf;
(h) BMTF (2000); Lucas (2001);
(i) USEPA (1992b).

Further US data

USEPA (1997) summarised mining and mineral processing damage cases in a variety of mineral commodity sectors and states in the USA during 1990-1996 and discussed their causes and effects and the corrective or other action taken in each case. These included spills and leaks at gold beneficiation/heap leach operations using cyanide (most were relatively small scale and none have been included in Table 5.3).

Most releases involving cyanide occurred through spills resulting from equipment failure or damage, failure of containment tanks or storage units, or through failure of transport devices such as pipelines, with contributing factors including operator error and freezing weather. Most such releases were in the range 100-25 000 L per event, but there were a few much larger individual spillage events (~200 000-500 000 L). Other releases were caused by unusually heavy rains and high stormwater volumes, poor infiltration into a heap leach pile, and by seepage and groundwater movement.

In most cases, these spills and leaks resulted in surface soil contamination and were not reported to have caused harm to fish or other wildlife, whereas there were a few cases from other mining/mineral processing sites industries where biotic impacts such as fish kills occurred due to causes not associated with cyanide.

Further Australian data

A survey of all Australian state and territory mining and/or environment protection agencies (except ACT) was conducted during this assessment. Agencies were asked to provide information on cyanide-related incidents reported in the previous 3 years.

Incidents occurring during use at ore processing sites

In Western Australia in the 10 year period 1994-2003, there were ~75 incidents involving cyanide reported to the Department of Industry and Resources (WA DoIR, 2004). Most (~75%) were occupational incidents occurring at the gold ore processing (mill) area during unloading, handling, tank mixing, process operations, cleaning and maintenance or result from equipment failure (e.g. tank or pipe failure). Although many incidents involved release of cyanide solutions or vapours, these were typically only of occupational concern. Of the 75 incidents reported, ~19 (~25%) involved release or potential environmental release of cyanide solutions. Seven of the 14 incidents where environmental release did occur were at gold mill sites and included spills, leaks or tank overflows of process solutions (e.g. 20 tonne of 500 ppm), detoxified tailings or tailings slurry (e.g. 20 m^3). Releases were typically contained on hard stands or in bunded areas; however, in some instances released quantities exceeded bund capacity. Five of the 14 incidents involved the rupture of tailings pipelines and subsequent environmental release of tailings (up to 90 tonnes), typically in the vicinity of TSFs.

The Queensland Department of Natural Resources, Mines and Energy (DNRME, 2000) reported a gold ore processing incident involving a 200 m^3 CIP leach tank failure which resulted in discharge of its contents and those of interconnected tanks to their discharge level (another 200 m^3) into a bunded enclosure. Bunding could not contain the spillage, resulting in about 50 m^3 of cyanide-containing (70 ppm free CN) tailings breaching the enclosure. Tailings entered an adjacent bunded elution column area where HCl acid washes occur. While most of the spillage flowed into the tailings dam, additional earth bunding was constructed to contain the spill, which was neutralised with calcium hypochlorite. The incident was caused by chemical corrosion that had weakened the tank base, allowing tailings, under a significant hydraulic head, to be forced out through the concrete pedestal. Slurry agitation with an air spear may have accelerated the erosion. Inadequacy of the bunded enclosure meant that the discharge could not be contained. The situation was made worse by beaching of the solids around the ruptured tank and within the enclosure. The landform around the plant was such that not all discharge automatically went to the tailings dam. Inadequate capacity of the bund was not identified during plant design and construction. It is possible that no consideration was made for the 'footprint' of the leach tanks in the bunded area or for the interconnection of tanks allowing contents to gravitate freely from one tank to the other. The DNRME (2000) provided recommendations to minimise the risk of future incidents occurring.

Some further data were also available from individual mines, showing brief records of incidents that had occurred in the previous 3 years, usually involving tailings or solution leaks and spills. With a few exceptions, the reported incidents were generally minor in extent and/or were in areas designed to contain such spills (e.g. bunded areas and drains on site). In many cases, the risk was more to worker safety and wildlife were not actually or potentially affected. In most cases, the environment outside the facility was not exposed and the spill was collected and returned to storage or the process stream, or disposed of in the TSF. The incident reports provided indicate the

nature of procedures in place for documenting incidents, identifying their cause, and where appropriate, taking action to reduce the likelihood of their recurring.

Tailings storage facilities (TSFs)

WA DoIR indicated no incidents involving dam wall failures over the period 1994-2003. In one incident, seepage of 50 kL of tailings solution occurred through a dam wall, but the leak was contained. Alleged groundwater contamination issues arising from a TSF in Western Australia were raised in a report to the Western Australian Minister for State Development, the Honourable Clive Brown which resulted in further investigations and action (Cooke, 2004).

NT DBIRD indicated that there have been 2 TSF wall breakages in the history of mining in the NT, both years ago to old-fashioned, poorly constructed dams (they did not state whether CN release resulted or had any consequences). NT DBIRD also mentioned that more recently, an instance of groundwater contamination occurred in a confined aquifer when a pit was being used as a temporary TSF during a period when the operator was having trouble settling tailings out of process water. Levels of total CN were 9 mg/L, but WAD CN was only ~0.2 mg/L. The leak occurred through fractured ground and had limited movement.

The then Tasmanian Department of Primary Industries and Environment (Tas DPIWE) referred to two incidents of migration of CN in groundwater and surface water in recent years. A former gold tailings re-treatment project in the North East of the state had the contents of its TSF seep to groundwater, and through the dam wall to a downstream river, due to inadequately detoxified CN and poor dam construction standards. A recent report from one gold mine indicated that monitoring had shown some movement of cyanide species and metals beyond the confines of the dam, but confined within the mining lease. However, the site's two artificial wetland areas appeared to be reducing the concentrations of both thiocyanate and WAD CN as well as a range of other metals as surface water moves through them.

Breach of tailings cyanide discharge limits

In NSW, limits on the cyanide discharged into TSFs are stipulated under conditions of the operating licence. NSW Department of Environment and Climate Change (DECC) reported that a gold mine exceeded such a limit on a few occasions. More recently another exceedance was noted to be due to use of an inappropriate laboratory analytical method. Quality control procedures have apparently improved since this time.

Inappropriate disposal of sodium cyanide

In December 1995, 10 abandoned crates (900 kg) of NaCN were identified by NSW DECC during an inspection of a disused mine in NSW.

The Environment Protection Authority, Victoria (EPAV), reported an illegal disposal of a 50 L drum of NaCN dumped amongst roadside rubbish at Dandenong, Victoria, in May 2000. EPAV indicated that the cyanide had been stolen from a factory.

5.5 Summary of sources of environmental exposure

HCN, metal-cyanide complexes and other substances potentially formed as a consequence of sodium cyanide use may also arise from other sources in the environment, both natural and anthropogenic.

Organic substances containing cyanide are produced naturally by various organisms, including some micro-organisms, plants, algae, fungi and invertebrates. These substances include forms such as cyanogenic glycosides, where free cyanide may be released upon consumption by an animal, potentially causing poisoning if the amounts present exceed the detoxicification capacity of the animal. Burning vegetation can form HCN under some combustion conditions, and biomass burning is considered to be the major source of HCN in the atmosphere.

Cyanide may also be released to the environment from a wide range of activities by humans additional to those using sodium cyanide. As well as industrial uses of HCN and various cyanide salts, these anthropogenic sources include some sources where cyanides are not used directly, such as incomplete combustion of coal, oil and waste materials. Release from fuel consumption in vehicles is considered a major source of release of cyanide to air.

Releases of cyanide associated with sodium cyanide in Australia could potentially occur during its manufacture, storage and transport, during use, and during disposal of residues remaining after use. The major use in Australia is in the mining industry for the beneficiation of ores containing gold and other precious metals. Other uses include ore flotation with base metal mining, uses in metal industries for electroplating, cleaning, and for case hardening and similar processes for steel, and minor uses such as in analytical laboratories.

Gaseous HCN is used to produce sodium cyanide and may subsequently be emitted to the atmosphere from HCN in solution or from certain other reactions. Thus some release of HCN to the atmosphere may occur during the manufacture of sodium cyanide, storage, loading and unloading operations, transport, industrial and mining uses, and from residues remaining after use, such as in tailings storage facilities, heap leach piles, landfills, or sewage effluent. This is generally minimised by the highly alkaline conditions pertaining in manufacture, storage and transport of NaCN in liquid form, and in process streams.

Stack emissions of HCN at manufacturing facilities are monitored to ensure they comply with environmental protection licences, which place strict limits on release. Wastewaters containing free cyanide may be generated during the manufacturing process, and cyanide residues in these are recovered and used, or are treated to destroy free cyanide prior to disposal under environmental protection licence conditions (the discharge concentration limit is 1 mg CN/L, but monitoring shows discharges to sewer/outfall are typically much lower). After material containing cyanide is deposited in tailings storage facilities (TSFs) HCN emission to the atmosphere is expected as a significant means of dissipation.

After use, various substances originating from sodium cyanide may remain in aqueous or solid media, including process wastes from industrial treatments, or tailings and heap leach piles from the treatment of metal ores. As explained in the following chapter, cyanide may be present as free cyanide (HCN/CN^- in solution) or various metal compounds and complexes. Cyanide may also have been altered by processes to destroy cyanide and by natural degradation processes to form cyanate, thiocyanate and other nitrogenous products (e.g. ammonia, nitrite, nitrate). Weak acid digestible cyanide (WAD CN) measurements are used as a measure of forms of cyanide available at the pH of the stomachs of wildlife such as birds.

Gold beneficiation is the primary source of environmental exposure to CN. In mining situations where sodium cyanide is used in tank leach facilities, cyanide residues from

process streams are recirculated and/or disposed of in the tailings stream, with or without steps to reduce the amount of remaining free cyanide. As the majority of use in Australia is in tank leach facilities for gold beneficiation, tailings storage facilities are the principal repository and potential source of release to the environment for cyanide residues.

Concentrations of sodium cyanide used in tank leach facilities are typically in the range 100-500 mg CN/L, affected by factors such as the ore and dilution water characteristics. During the leaching process this is contained within large tanks. It is then released to the TSF, in some cases after treatments to recover the cyanide solution for re-use and to reduce loss to the TSF, or to destroy residual cyanide. Concentrations of WAD CN released into TSFs may therefore range widely, from as low as 1 mg WAD CN/L to well above 100 mg WAD CN/L (as high as ~600 mg WAD CN/L) at exceptional sites or under exceptional conditions.

The most exposed use situation is heap leach mining, where NaCN solution - at concentrations again typically ranging from 100-500 mg CN/L - is applied directly to the exposed ore heap. The solution containing gold is then collected at the bottom. However, these situations are engineered to enable control of the flow and storage of NaCN-containing water. Residues remaining after use in ore flotation are also disposed of to tailings storage facilities.

With mining use, cyanide or cyanide degradation products may potentially be emitted through seepage to groundwater or overflow/run-off, or in some situations through planned discharge. Tailings storage facilities (TSFs) and heap leach pads may be substantial structures holding large volumes of material containing heavy metals and other chemical species in addition to cyanide residues. Hence it is important that they have adequate capacity and are structurally sound, and are designed and operated correctly so that any releases to the aquatic or terrestrial environments are managed appropriately. To protect surface and groundwater from release of water containing cyanide residues, surface drains and bores are installed to intercept run-off and leaks and to monitor and if necessary intercept seepage in groundwater. Techniques to destroy cyanide to acceptably low levels are used where outflows are released to downstream aquatic areas.

In industrial situations with metals such as electroplating and case hardening, solid and liquid residues are treated to destroy free cyanide not consumed during the process, before release of the treated residues to landfill or the sewer. Laboratory protocols also indicate that cyanide residues in waste should be destroyed before disposal.

The hazards of cyanide in these use situations are well known and there is an extensive management regime established in Australia to manage them. However, unintentional incidents have occurred resulting in potential situations or actual releases (spills, leaks) of sodium cyanide during storage and transport. Some spills have occurred during road or rail transport in Australia, but only in one incident were wildlife or aquatic life reported to have been affected. Environmental damage was minimised at other incidents where significant spills occurred, due to emergency response measures to contain and recover the spilt material and remove contaminated soil or water. However, some overseas incidents where significant release of NaCN occurred to water led to downstream environmental contamination and harm to aquatic organisms. NICNAS has not investigated the regulatory control measures that were in place in the various overseas jurisdictions at the time of these overseas incidents.

Unintended releases of material containing cyanide have also occurred overseas and in Australia due to incidents such as leaks from pipelines containing slurry, overflows and leaks from TSFs and heap leach operations, and major structural failures. Such release varies widely in scale, from minor leaks that are soon corrected and cause no environmental harm, to major releases that have led to substantial environmental effects due to physical effects and other toxic components, in addition to cyanide residues. These incidents indicate the need for appropriate monitoring and response measures for operations on an ongoing basis, as well as correct design and operation of TSFs and heap leach facilities.

6. Environmental Fate

This chapter describes the fate in the environment of sodium cyanide and other forms of cyanide or breakdown products arising from it, including consideration of its fate with particular uses.

References in the report that have not been sighted are marked with an asterisk (*).

6.1 Overview of fate of sodium cyanide

The overall fate of sodium cyanide and its products in the environment is complex and depends on a range of factors such as its concentration, chemical speciation, form manufactured (solid, liquid), co-associated chemicals, pH, redox potential, temperature, and exposure to sunlight in the environment into which the cyanide is released.

The release of sodium cyanide in the relatively stable solid forms manufactured in Australia (e.g. briquettes) to dry land (e.g. through a spill event) is unlikely to result in migration in the short term from the point of release. However, when manufactured and supplied in the liquid form (~30% NaCN), or if the solid form comes into contact with water after an accidental release (e.g. released into a waterbody, rainfall, fire fighting water, and if left, absorption of water by deliquescence), dissociated sodium cyanide as free cyanide is likely and the potential for cyanide to migrate and to undergo further reactions with other chemicals, substances and biota is greatly enhanced.

The most commonly occurring forms of cyanide in soils following release of sodium cyanide include HCN, simple cyanides (e.g. inorganic salts), and iron-complexed cyanides (e.g. ferrocyanide and ferricyanide, also called hexacyanoferrate(II) and (III)). The iron-cyanide complexes occur in two oxidation states, with ferricyanide reduced to ferrocyanide only under reducing conditions (Kjeldsen, 1999). Nitriles, organic material with an R-CN composition, where R refers to the organic radical, and thiocyanates (-SCN), may also be present (Kjeldsen, 1999). The following section provides a summary of the general environmental fate of cyanide for the main environmental compartments into which it is released.

6.2 General degradation pathways

Cyanide in the environment may follow one or more degradation pathways (Smith and Struhsacker, 1988; Smith and Mudder, 1993) including:

Volatilisation	Free cyanide volatilisation to the atmosphere (i.e. as HCN gas) increases, particularly as pH decreases and the proportion of HCN increases: $CN^- + H_2O \Leftrightarrow HCN\uparrow + OH^-$
Complexation	Cyanide can potentially form complexes with ~28 elements including Cd, Co, Cu, Au, Fe, Hg, Ni, Ag, Zn (~72 metal complexes) (Ford Smith, 1964). e.g. $Cu^+ + 3CN^- \Rightarrow Cu(CN)_3^{2-}$

Adsorption	Adsorption of free and complexed cyanide forms onto solid phases.
Precipitation	Cyanide complexes forming solid metallocyanide precipitates.
Formation of thiocyanate	Reaction of cyanide with various forms of sulphur (e.g. polysulphides and thiosulphate): $S_x^{2-} + CN^- \Leftrightarrow [S_{(x-1)}]^{2-} + SCN^-$ and $S_2O_3^{3-} + CN^- \Leftrightarrow SO_3^{2-} + SCN^-$
Oxidation	Oxidation to various reaction products, such as cyanate and/or cyanogens, ammonia and water: $2HCN + O_2 \Leftrightarrow 2HOCN$ (hydrogen cyanate); $2CN^- + O_2 + catalyst \Leftrightarrow 2OCN^-$ (cyanate ion); $2Cu^{2+} + 2CN^- \Rightarrow 2Cu + (CN)_2$ (cyanogen) $HCN + 0.5O_2 + H_2O \Leftrightarrow CO_2 + NH_3$ $(CN)_2 + 2OH^- \Rightarrow OCN^- + CN^- + H_2O$ Formation of cyanate occurs when cyanide is in the presence of strong oxidisers (e.g. ozone, hydrogen peroxide, hypochlorite).
Photolysis	Photolysis of stable iron complex forms (e.g. ferrocyanides) to free cyanide: $Fe(CN)_6^{3-} + uv \Leftrightarrow Fe(CN)_5^{2-} + CN^-$, and $Fe(CN)_6^{4-} + uv \Leftrightarrow Fe(CN)_5^{3-} + CN^-$ With continuing UV exposure, similar reactions can continue through successive steps to release all the contained iron and cyanide, e.g. $Fe(CN)_6^{4-}$ ultimately forming $Fe^{2+} + 6CN^-$ Photodecomposition reactions in the presence of sunlight: $HCN + uv \Rightarrow H^+ + CN^-$ $HCN + uv + catalyst \Rightarrow + OCN^-$
Hydrolysis	As solution pH falls, the proportion of cyanide present as HCN increases. HCN may be volatilised from the water surface, or may be hydrolysed to formate, either as formic acid or ammonium formate: $HCN + 2H_2O \Rightarrow NH_4COOH$ (ammonium formate), or $HCN + 2H_2O \Rightarrow NH_3 + HCOOH$ (formic acid) Hydrolysis of cyanate: $HOCN + H_3O^+ \Leftrightarrow NH_4^+ + CO_2$ $OCN^- + NH_4^+ \Rightarrow (NH_2)_2CO$
Biodegradation	Aerobic: $CN^- + HCO_3^- + NH_3 \Rightarrow NO_2^- + NO_3^-$ $2HCN + O_2 + enzyme \Leftrightarrow 2HOCN$ Anaerobic: $CN^- + H_2S_{(aq)} \Leftrightarrow HCNS + H^+$ $HCN + HS^- \Leftrightarrow HCNS + H^+$

A more detailed discussion of each of these follows.

6.3 Environmental transport and distribution

6.3.1 Free cyanide

Alkaline solutions (e.g. pH >9.2) of sodium cyanide contain a high proportion of the free cyanide as the cyanide ion CN^-. Free cyanide is very reactive and does not occur commonly in nature (USEPA, 1980). In aqueous solutions of simple alkali cyanides, the CN group is present as the cyanide ion (CN^-) and molecular hydrogen cyanide (HCN), which may dissociate to form the cyanide ion depending on pH according to the reaction:

$H^+ + CN^- \Leftrightarrow HCN_{(g)}$

'Free cyanide' in water is generally considered as the sum of cyanide present as both HCN and CN^- (USEPA, 1980; Staunton et al., 2003). In most natural waters (e.g. pH 6 to 8), HCN predominates (APHA, 1998; Brix et al., 2000).

At any particular pH and temperature, the system is in equilibrium and the relative amounts of each can be determined from the following equation (interpreted from Smith and Mudder, 1993 and USEPA, 1985):

$K_a = [H^+].[CN^-] / [HCN] = \sim 4.5x10^{-10}$ to $6.0x10^{-10}$, pKa = 9.31-9.35 (at 20°C).

At a pH corresponding to the pKa value (i.e. pH ~9.3 at 20°C), the concentration of HCN and CN^- in solution are equal. Using a pKa value of 9.33, at 20°C the calculated concentrations of CN^- and HCN at other pHs are approximately as follows:

- at pH 10.5: 94% CN- and 6% as HCN;
- at pH 9: 32% CN- and 68% HCN;
- at pH 8: 5% CN- and 95% HCN; and
- at pH 7: 0.5% CN- and 99.5% HCN.

The pKa value decreases with increasing temperature, e.g. pKa = 9.63 at 10°C, 9.09 at 30°C and 8.72 at 45°C (calculated from an equation in USEPA, 1985). Under typical environmental conditions of pH <8 and water temperature <25°C, >94% of free cyanide exists as HCN. In the processing plant, temperatures may be elevated by residual heat in the slurry due to the milling process. At pH 9, HCN contributes ~55% of the free cyanide at 30°C and ~34% at 45°C. At pH 10.5, HCN contributes ~4% of the free cyanide at 30°C and ~0.5% at 45°C.

A reaction related to the release of HCN by decreasing pH is that with carbon dioxide (CO_2) in the presence of water:

$CN^- + CO_2 + H_2O \Rightarrow HCN + HCO^{3-}$

It is noted that because of the toxicity and flammability hazards presented by HCN gas, carbon dioxide is not used for control of fires involving sodium cyanide.

6.3.2 Volatilisation of HCN

HCN has a vapour pressure of 100 kPa (750 mm Hg) at 26°C and is regarded as highly volatile (Chatwin et al., 1987). The Henry's Law Constant (K_H = 0.132 L atm/mol at ~25°C – Lye, 2002; W. Staunton, pers. comm. 2005) indicates HCN also has high

volatility from water. HCN is lighter than air, with a relative vapour density = 0.94, compared to air = 1 (CDC, 2005).

Volatilisation can be a significant removal process for free cyanide from aqueous solutions and soils to air (Smith and Mudder, 1993). Volatilisation was considered a major loss mechanism for HCN from surface soils of pH <9.2 (Hagelstein and Mudder, 1997a).

The volatilisation rate of HCN from aqueous solutions (i.e. $HCN_{(aq)} \Leftrightarrow HCN_{(g)}$), with pH standardised, increases with increasing temperature (as does the Henry's Law Constant) and solution agitation (Lye, 2002; Staunton, pers. comm. 2005). There are also indirect influences which change the amount of HCN which volatilises with increasing ionic strength (lowering the pKa value), but effects of ionic strength are only significant for the hypersaline operations in WA (Staunton, pers. comm. 2005). Laboratory testwork reported in Adams et al, (2008abc) indicated that 90% HCN occurs at about pH 8.0 for fresh water solutions and 8.5 for solutions of total dissolved solids (TDS) of ~200,000 mg/L. Solution depth may also be an important factor affecting HCN volatilisation from surface waters (Chatwin et al., 1987).

The main factors affecting emission of HCN from soil include soil pH and availability of continuous vapour pathways (e.g. pores, cracks; Smith and Mudder (1993)).

Volatilising HCN gas in soils has five possible fates (listed below). Of these, the latter two are considered least significant (Chatwin et al., 1987):

- volatilisation of HCN to the surface and then the atmosphere;
- biodegradation and metabolism by micro-organisms;
- reactions with soil constituents in the subsurface, particularly at low soil moisture content;
- dissolution in soil moisture, particularly if the solution pH is high; and
- entrapment in cavities in the subsurface soil.

Volatilisation from groundwater is unlikely to be a significant transformation process.

HCN is lighter than air and rises from surfaces where it is released. Hence volatilised HCN is not expected to accumulate when released to the external environment, and its flammability is not an environmental concern.

6.3.3 Atmospheric fate of HCN

In air, inorganic forms of cyanide are found mainly as HCN gas and a smaller amount as fine dust particles (ATSDR, 2006). Cicerone and Zellner (1983) reviewed the atmospheric fate of HCN, and more recent observations by various means of HCN concentrations in the atmosphere have added to this knowledge (Li et al, 2000; Singh et al, 2003; Rinsland et al, 1996, 2001, 2005; Kleinböhl et al, 2006; Pumphrey et al, 2006). HCN is slightly lighter than air (Section 6.3.2) and therefore tends to rise from the immediate point of release, becoming mixed in the air as it does so. Atmospheric modelling indicates that HCN is well-mixed in the troposphere, but decreases in concentration in the stratosphere with increasing altitude.

In the troposphere, HCN may degrade via reactions with hydroxyl and oxygen radicals, with that involving hydroxyl radicals ($OH^{\bullet}$) thought to be the principal one, ultimately producing nitric oxide in a series of rapidly occurring reactions:

$HCN + OH^{\bullet} \Rightarrow \Rightarrow NO + CHO$

In the stratosphere, a UV photolysis reaction may also occur, followed by oxidation of the $CN^{\bullet}$ radical which is produced:

$HCN + uv \Rightarrow H^{\bullet} + CN^{\bullet}$

$CN^{\bullet} + O_2 \Rightarrow NCO^{-}$ and $NCO^{-} \Rightarrow N + CO$

Photolysis of HCN in the troposphere and lower stratosphere is negligible, and precipitation of cyanide in rainfall is a negligible sink for atmospheric HCN. HCN is a strongly bound molecule and Cicerone and Zellner (1983) estimated its atmospheric lifetime (the time taken for the concentration to fall to approximately 37% (1/*e*) of its initial concentration) based on reaction with hydroxyl radicals to be approximately 2.5 years (range 1 to 5 years).

However, Li et al. (2000) argued that the observed seasonal variations in atmospheric HCN concentrations imply an atmospheric lifetime of only a few months for HCN, i.e. much shorter than is commonly assumed if oxidation by $OH^{\bullet}$ is the main sink (i.e. as discussed above). They proposed that uptake by dry deposition to the ocean provides the missing sink and examined this using a global 3-D model simulation, with ocean uptake as the main sink and biomass burning as the main source. From this, they estimated an HCN atmospheric lifetime of 2-4 months on their standard assumptions, or 4.4 months with some different assumptions. Singh et al. (2003) and Li et al. (2003) incorporated measured data from in situ aircraft observations of HCN in the troposphere (rather than simply data from remote sensing of the total column of HCN in the atmosphere). Using different modelling approaches, they arrived at a tropospheric lifetime for HCN of 5-5.3 months.

HCN taken up by ocean waters is expected to be degraded by biological processes, and this uptake limits the amount of NO generation that would have been anticipated if the principal method by which HCN dissipated from the atmosphere were via reaction with $OH^{\bullet}$. Typical measured concentrations (mixing ratios) of HCN in the troposphere are ~180-250 parts per trillion by volume (pptv) in various studies.

Based on figures from Cicerone and Zellner (1983) and an estimate of the world's usage of NaCN for gold mining in the early-mid 1990's, De Vries (1996) argued that gold mining sources contributed only a minor proportion of annual HCN infiltration to the atmosphere and was an insignificant contributor to nitrogen oxide formation in the atmosphere. Total HCN release to the atmosphere from various biogenic and anthropogenic sources has more recently been estimated to be of the order of 1 million tonnes (1×10^{12} g) per annum globally in terms of the contained nitrogen (Li et al., 2003). To update the argument of de Vries (1996), if it is assumed that use of NaCN for gold mining is ~330 000 tonnes per annum and that at worst ~30%-50% of this quantity is ultimately released to the atmosphere as HCN (Sections 6.6.3 and 6.6.4), this equates to ~28 000-47 000 tonnes per annum N as HCN, or ~3-5% of estimated total HCN release. This is at most a relatively minor contribution to overall HCN release, comparable in scale to estimated global release via car exhaust (as listed by Li et al., 2003).

Small amounts of metal cyanides may be present as particulate matter in air, from which it is removed by both wet and dry deposition (HSDB, 1991). The average half-life and lifetime for particles in the troposphere are estimated to be about 3.5 to 10 days and 5 to 15 days, respectively.

6.3.4 Complexation

In solutions of simple metal cyanides, the CN group may also react with metals to form complex metal-cyanide anions of varying stability (ANZECC/ARMCANZ, 2000a; APHA, 1998).

Cyanide complexes, of which there are many combinations (Lye, 2002; Smith and Mudder, 1993; Table 3.2), are traditionally classified according to their stabilities as weak (cyanocomplexes of Ag, Cd, Cr, Cu, Hg, Mn, Ni, Zn) or strong (cyanocomplexes of Au, Co, Fe, Mo, W, Re, Pt-group) (Flynn and Haslem, 1995). Many simple metal cyanides are sparingly soluble in water (weak; e.g. CuCN, AgCN, $Zn(CN)_2$); however, a variety of soluble complex metal cyanides may be formed in the presence of alkali cyanides (APHA, 1998).

Some iron-cyanide complexes are not completely stable between aqueous and solid phases (Ghosh et al., 1999). Only Prussian Blue ($Fe_4(Fe(CN)_6)_3$) and Turnbull's Blue ($Fe_3(Fe(CN)_6)_2$) are stable in a wide range of pH and redox conditions. Other less complex iron cyanides, such as ferrocyanide ($Fe(CN)_6^{4-}$) and ferricyanide ($Fe(CN)_6^{3-}$), may be present in solution, with the ability to speciate to free cyanide depending on the pH and redox potential of the water. Ferro- and ferri-cyanides also act as non-adsorptive solutes in sandy gravelly aquifers (Ghosh et al., 1999).

6.3.5 Adsorption and mobility in soil

Distribution co-efficients (K_d) for soil and sediment adsorption by cyanide (sodium cyanide at pH 10.5) range from 5.04 to 14.5, indicating that the CN^- ion can bind to these media (USEPA, 2006c). However, due to its high water solubility, HCN is only weakly bound or partitioned to sediments, soils and organic matter, and its mobility in waters is potentially high (Callahan et al., 1979). In addition to low pH, cyanide mobility is relatively low in soils with a high concentration of free iron oxides, positively charged particles and clays such as kaolin, chlorite, gibbsite (Callahan et al., 1979). Alesii and Fuller (1976) indicated that soils with a high anion-exchange capacity, soils with high concentrations of manganese and hydrous oxides of iron, are more likely to attenuate cyanide. Mobility of cyanide is greater in soils with high pH, high concentration of free calcium carbonate (high negative charge) and low clay content (Callahan et al., 1979). Adsorption of HCN by soils containing strongly cation-exchanging materials (e.g. montmorillonitic clays) is fairly weak and is decreased by the presence of water (Alesii and Fuller, 1976; Callahan et al., 1979).

Chatwin et al. (1987) investigated the attenuation of cyanide in several soil types using soil column tests, revealing that soils can have significant cyanide attenuation abilities. Chatwin et al. (1987) identified two major physicochemical mechanisms that attenuate cyanide in soils including:

- volatilisation; and
- reaction or adsorption to alumina (bauxite or kaolinite) and organic matter, and to a lesser extent, plagioclase, potassium feldspar, ilmenite and hematite.

Cyanide adsorbed weakly to ferric forms of iron in the soils tested by Chatwin et al. (1987). Increasing the pH resulted in the solubilisation of this cyanide. Volatilisation was significant due to the moderately alkaline to acidic nature of the soils they tested.

Soil attenuation capacity for free cyanide is not limitless, as indicated by the Australian Minerals Industry Research Association (Staunton, 1991c-d). AMIRA (1991c) found, using trickle-flow column tests with soil from one mine site, that good initial attenuation of cyanide was exhibited, but that this fell rapidly as more cyanide solution passed through. In the results shown in Table 6.1, ~50% of the initially applied cyanide was converted to other forms, notably cyanate (OCN). However, attenuation soon fell to ~15%, with little evidence of continuing reactions with soil constituents (Table 6.1). In contrast, the soil continued to show good pH buffering capacity, with the soil pH remaining at a value intermediate between that of the applied solution (pH 10) and that in the original soil (pH ~5.5). The authors suggested that cyanate formation was due to organic carbon in the soil.

Table 6.1. Composition of leachate and % attenuation of applied cyanide in soil columns in laboratory tests (from Staunton, 1991c).

No. Pore Volumes	pH	WAD CN** (mg/L)	$Cu(CN)_3^{2-}$ (mg/L)	$Fe(CN)_6^{4-}$ (mg/L)	OCN*** (mg/L)	% CN attenuation
0.7	6.6	13	6.6	0.64	13	50
2.9	6.0	22	1.0	0.20	3	15
4.9	7.6	22	0.48	<0.14	<1	15
8.0	5.9	20	<0.06	<0.14	<1	23
11.0	7.2	21	0.37	<0.14	4	15

* Initial leachant concentration 26 mg/L with pH 10.0. Initial soil pH 5.6. ** Total CN concentration was in each case = WAD CN concentration. *** SCN concentration in each case <0.5 mg/L.

The persistence of cyanide in the groundwater environment is influenced by groundwater chemistry, aquifer composition and groundwater microbiology (Meehan, 2000). Free cyanide concentrations may decrease through chelating with transition metals (complexation; Smith and Mudder, 1993), which may result in precipitation from solution (Theis and West, 1986). Stable, insoluble ferro- and ferricyanide complexes may form, which precipitate in a range of pH and redox conditions. Based on its relative abundance in soils, Smith and Mudder (1993) indicated that the majority of cyanide metal complexation reactions in soils would involve iron.

Although dissolution of iron-cyanide complexes in soils can result in the release of free cyanide, these compounds are quite stable in soil, with long half-lives. Under acidic (pH 4) and reduced conditions the half-life of iron complexes may be in the order of 1 year; however, under conditions which would be considered normal for near surface soils (pH >6, aerobic conditions) the half-life is in the order of 100-1000 years (Kjeldsen, 1999).

Kjeldsen (1999) reported that free cyanide concentration in groundwater at Dutch gas works sites contaminated with iron-cyanide complexes constituted less than 1% of the total cyanide content, and spent bog iron leachate tests revealed no detectable free cyanide (Theis et al., 1994).

The sparingly soluble metal cyanides (e.g. copper, nickel, zinc) may adsorb onto particulates and partition to the sediment compartment (Hagelstein and Mudder, 1997a).

6.3.6 Cyanide complex precipitation

Ferrocyanide and ferricyanide ions form insoluble iron-cyanide precipitates with Fe, Cu, Ni, Mn, Pb, Zn, Cd, Sn, Cd, and Ag (Weast, 1969), through the pH range 2 to 11 (Hendrickson and Daignault, 1973). Examples include the iron complexes Prussian blue and Turnbull's Blue (Section 6.3.4). Iron complexes may react with thiocyanate to form stable complexes if sulphur is present in the soil (Smith and Mudder, 1993).

6.4 Abiotic degradation

6.4.1 Hydrolysis

As pH falls, HCN may hydrolyse to form formic acid (HCOOH) and ammonium formate (NH_4COOH; Smith and Mudder, 1993). Rates for cyanide hydrolysis of 2%-4% per month have been estimated, which is relatively slow compared with other cyanide degradation processes (Smith and Mudder, 1993).

6.4.2 Photolysis

The iron-cyanide complex compounds are generally very stable in the dark and elevated levels of HCN in solution are attained only in aged iron-cyanide complex solutions of high concentration (APHA, 1998). However, these complexes are subject to extensive and rapid photolysis, mobilising HCN on exposure to direct sunlight (APHA, 1998; ANZECC/ARMCANZ, 2000a; Kjeldsen, 1999). The rate of photodecomposition depends on exposure to ultraviolet radiation, and therefore is slow in deep, turbid or shaded waters (APHA, 1998) and negligible in subsurface soils or groundwater. Decomposition is typically complete and continues until ferric or ferrous ions and cyanide ions are released.

Meeussen et al. (1992) reported the results of a flask study where the cyanide present was initially in the form of iron complexes. Exposure to diffuse day sunlight produced a transformation to free cyanide at a decomposition rate of 8% per hour. Faster degradation rates than this were reported for groundwater contaminated with iron complexes exposed to artificial UV-light (Marsman and Appelman, 1995).

Free cyanide may be photolysed to cyanate (OCN^-), but this requires the presence of a catalyst (e.g. titanium dioxide, cadmium sulphide, zinc oxide; Frank and Bard, 1977). Cyanide may be converted to cyanate in the soil on the surface of organic and inorganic materials (Chatwin, 1988), and potentially in solutions.

The photochemical dissociation of $Fe(CN)^{x-}_6$ is known to proceed by an aquation mechanism forming the aquopentacyanocomplex, as follows for ferrocyanide (Kuhn and Young, 2005):

$$Fe(CN)_6^{4-} + 2H_2O + uv \Leftrightarrow Fe(CN)_5 \cdot H_2O^{3-} + HCN + OH^-$$

In alkaline solutions, the hydroxopentacyano complex can form subsequently by the reaction:

$$Fe(CN)_5H_2O^{3-} + OH^- \Leftrightarrow Fe(CN)_5 \cdot (OH)^{4-} + H_2O$$

The first reaction can proceed in reverse when illumination is stopped; although during prolonged exposure the reverse reaction is incomplete (Johnson et al., 2002).

Photodegradation rates for strong metallocyanide complexes vary according to sunlight intensity, light absorption within the water column, cyanocomplex concentration (assuming the reaction is first order), the quantum yield for the particular complex, temperature and any catalytic effects (Broderius and Smith, 1980; Kuhn and Young, 2005). $Fe(CN)_6^{x-}$ catalysts include mercury, silver and gold. Johnson et al. (2002) reported dissociation rate half-lives for $Fe(CN)_6^{x-}$ (or time to release 50% of contained CN^-) of 0.05 to 5 hours at 28°C and 0.3 to 2.7 hours in natural waters or deionised waters at 20°C.

6.4.3 Formation of cyanates and other products

In the presence of strong oxidisers (e.g. ozone, hydrogen peroxide, hypochlorite), cyanide in solution may oxidise to hydrogen cyanate (HOCN) and the cyanate ion (OCN^-). Although unlikely to be significant in the natural environment, this can occur during ore processing, such as where operations add strong oxidisers to degrade free cyanide to cyanate (e.g. alkaline chlorination), or during cyanide spill remediation works where detoxification chemicals are applied.

Alkaline chlorination may also form chloramine (NH_2Cl) or similar chlorinated compounds (Moran and Brackett, 1998).

Cyanogen gas ($(CN)_2$) may form under acidic conditions in the presence of an oxidant such as an oxidised copper mineral. The formation of cyanogen is unlikely where mining solutions remain alkaline; however, conditions conducive to acid formation (e.g. acid rock drainage) in the presence of cyanide solutions may potentially result in cyanogen formation (Moran and Brackett, 1998).

6.4.4 Thiocyanate formation

Cyanide may react with sulphur (e.g. thiosulphate, sulphide ions) to form thiocyanate as follows:

$S_x^{2-} + CN^- \Leftrightarrow [S_{(x-1)}]^{2-} + SCN^-$ and $S_2O_3^{3-} + CN^- \Leftrightarrow SO_3^{2-} + SCN^-$

Thiocyanate may decompose to carbon dioxide, ammonium and sulphate (Kjeldsen, 1999). Reaction of CN^- with sulphur may be slow; however, as the water flow rates in most soils (and bedrock) are also slow, if amenable sulphur is present, a significant proportion of the cyanide in solution can be converted to thiocyanate (Chatwin et al., 1987).

6.5 Biotic degradation

Cyanide can be produced, degraded or utilised by micro-organisms in both aerobic and anaerobic conditions (Watanabe et al., 1998). Cyanide is also a metabolic inhibitor for some micro-organisms (Chapatwala et al., 1995).

Biodegradation of cyanide in natural waters is dependent on such factors as cyanide concentrations, pH, temperature, availability of nutrients, and acclimatisation of micro-organisms (Hagelstein and Mudder, 1997a). During degradation, cyanide can be a source of nitrogen and carbon (Kao et al., 2002; Kjeldsen, 1999; Raybuck, 1992).

6.5.1 Aerobic conditions

In aerobic conditions, cyanide can be converted to formate and then to carbon dioxide by formate dehydrogenase (Knowles, 1976). Conversion is either direct (by nitrilase) or indirect (via formamide by cyanide hydratase and formamidase) to produce formate. Under these conditions, cyanide may break down to ammonia and carbon dioxide (Kjeldsen, 1999). Enzymic reactions can be summarised as substitution/addition reactions, hydrolysis, oxidation, and reduction (Watanabe et al., 1998). Various micro-organisms can apparently also convert cyanide into cyanate and then CO_2. Reported biodegradation pathways for cyanide complexes are listed in Table 6.2.

6.5.2 Anaerobic conditions

Under anaerobic conditions, biodegradation of cyanide is slower (Smith and Mudder, 1993). In anaerobic methanogenic conditions, HCN may be degraded to ammonia/ammonium and formate (HCOO), with the formate rapidly transformed to bicarbonate (Table 6.2; Nagle et al., 1995). Ammonia may be denitrified to nitrogen gas (N_2; Hagelstein and Mudder, 1997a; Ferguson, 1988). Thiocyanate may be metabolised by micro-organisms to carbonyl sulphide and ammonia (Katayama et al., 1992) and to cyanate, which may be biodegraded further to carbon dioxide and ammonia (Stratford et al., 1994b).

6.6 Fate of cyanide in tailings storage facilities

6.6.1 Tailings constituents

During the gold/metal leaching process within the mill, NaCN is added to the ore and under the alkaline conditions used, the free cyanide produced when it initially dissolves is predominantly present as CN^- (a greater proportion of HCN is present where suboptimal pH is used due to local ore or water conditions – see Sections 4.4.2 and 6.3). However, the reactive nature of this mixture leads to the formation of other compounds and products of the parent cyanide compound in the ore slurry (Moran and Brackett, 1998; Smith and Mudder, 1993; Lye, 2002).

With reference to the mining industry, tailings contain the fine-grained waste material remaining after the economically recoverable metals and minerals have been extracted from the ore (Section 4.4.2). The physical and chemical properties of tailings vary with the nature of the material being processed and the process itself, which may also vary over time (MCMPR/MCA, 2003).

In general, cyanide compounds and products in tailings may potentially include:

- free cyanide;
- a range of metal-cyanide complexes (simple to strong complexes);
- thiocyanate (following reaction with sulphur species)
- cyanate;
- nitrogenous compounds (e.g. ammonia, nitrite and nitrate);
- cyanogen and cyanogen chloride;
- formic acid/formate, ammonium formate;
- carbon dioxide and other simple compounds of carbon.

Table 6.2. Microbial cyanide degradation pathways (adapted from Meehan, 2000)

Condition	Microbe	Reaction	Reference
Aerobic			
HCN	*Pseudomonas fluorescens*	$NADH + H^+ + HCN + O_2 \Rightarrow HOCN + H_2O + NAD^+$ $HOCN + H_2O \Rightarrow CO_2 + NH_3$	Raybuck (1992)
	Stemphylium loti	$HCN + H_2O \Rightarrow HOCNH_2$	Knowles (1988)
	Alcaligenes xylosoxidans subsp. *denitrificans*	None stated in literature	Ingvorsen et al. (1991)
	Unidentified species	General conversion of cyanide to ammonia and nitrates	Towill et al. (1998)
	Klebsiella oxytoca	Mineralisation of cyanide to ammonia and methane, and nitrification to nitrite and nitrate.	Kao et al. (2002)
NaCN	*Pseudomonas putida*	None stated in literature	Chapatwala et al. (1995)
KCN	*Pseudomonas stutzeri* AK61	None stated in literature	Watanabe et al. (1998)
KCN	*Bacillus pumilus* C1	None stated in literature	Skowrinski and Strobel (1969); Meyers et al. (1993)
Organic cyanides	*Pseudomonas aeruginosa*	None stated in literature	Nawaz et al. (1991)
Anaerobic			
HCN	Non-specific mixed cultures	$HCN + 2H_2O \Leftrightarrow HCOO^- + NH_4^+$. Methanogenic.	Fallon (1992); Nagle et al. (1995)

A range of other compounds may also occur in tailings that are unrelated to cyanide. These may originate, for example, from the ore, from chemicals added during gold ore processing, or from abiotic and biotic reactions and products.

6.6.2 Processes for detoxifying or recovering cyanide in tailings

There are various processes available to detoxify cyanide (Botz, 2001; Young, 2001; Young and Jordan, 1995; USEPA, 1994c), some of them used within Australia to treat tailings, such as the following:

- The Inco SO_2/Air cyanide destruction process uses a mixture of SO_2 (as sodium bisulphite) and O_2 in the presence of soluble copper catalyst to oxidise WAD cyanide to cyanate, with dissolved metals reacting to form hydroxides. For example, this process is adopted at one particular mine in Australia which employs a carbon-in-leach (CIL) process. The cyanide concentration in the effluent solution is reportedly <1 mg WAD CN/L. This originates from a cyanide inflow concentration of ≤430 mg WAD CN/L (average 280 mg WAD CN/L). Nitrogenous compounds (e.g. ammonia/ammonium) are also formed subsequently, with some volatilising to air after tailings are discharged to TSFs.

- Sodium metabisulphite may also be used to detoxify cyanide, but without going to the low levels referred to above (e.g. 20 mg/L WAD CN).

- Hydrogen peroxide (H_2O_2) or Caro's acid (peroxymonosulphuric acid, H_2SO_5, formed from sulphuric acid + H_2O_2) are alternative processes sometimes used to detoxify cyanide in tailings by oxidising it to cyanate. Hydrogen peroxide was used to reduce WAD CN levels from ~350 mg/L to below 50 mg/L in an incident that occurred at Northparkes Gold Mine (Section 9.9; Environment Australia, 1998).

- Iron-cyanide precipitation: Ferrous sulphate is stockpiled at strategic points as a means of detoxifying cyanide spills during transport or use, including incidents such as leaks or spills of tailings. Free, WAD and total cyanides will all react with ferrous sulphate to yield ferrocyanide, Prussian blue and various other metal-iron complexes. Ferric sulphate is used in some situations to make arsenic insoluble in tailings, and it may also help detoxify cyanide.

- Biological treatment processes: these can be used to greatly increase the rate at which transformation of cyanide to ammonia and nitrates occurs compared to natural processes in a TSF, e.g. with the assistance of specially selected cyanide-degrading bacteria, conditions to favour bacterial growth (such as rotating biological contactors), and addition of phosphoric acid as a nutrient (Akcil and Mudder, 2003; USEPA, 1994c; Smith and Mudder, 1991).

- An older process is alkaline chlorination, which Young and Jordan (1995) described as being used ever since cyanide leaching of gold was developed commercially and having been the most commonly applied technique of cyanide destruction, though it appears that few gold mining operations currently use this technology (USEPA, 1994c). In this process, cyanide in solution is oxidized to cyanate using chlorine or hypochlorite in solution, with the pH maintained in the alkaline range by addition of lime. Precipitated metals are removed in a clarifier before the wastewater is discharged. Limitations of this process include that it does not remove iron cyanides, and chloramines and free chlorine/chloride remaining in solution may be toxic to fish (USEPA, 1994c; Young and Jordan, 1995).

There have also been processes developed commercially for regeneration of free cyanide from the tailings water so it can be re-used (Botz, 2001; Fleming, 2001; Barter et al., 2001; AMMTEC, 2005). These include:

- the acidification-volatilisation-neutralisation (AVN) and Cyanisorb® processes. The pH is lowered to < ~8 with sulphuric acid, where free cyanide and some WAD cyanide compounds are converted to HCN gas. This is air-stripped from solution and reacted with NaOH solution to regenerate NaCN.

- the SART process (Sulphidisation, Acidification, Recycling and Thickening). Soluble sulphide salts (e.g. sodium hydrosulphide) are added to the waste cyanide solution, followed by acidification, which results in the dissociation of metal cyanide complexes (e.g. Cu, Zn) and the formation of HCN. Insoluble metal sulphides are precipitated and can be recovered for subsequent processing (e.g. copper smelting). HCN can then be reacted with sodium hydroxide to regenerate sodium cyanide. This process is particularly suited to copper rich gold concentrates.

However, there are technical limitations and problems, and financial considerations that have so far limited the use of these techniques to a few sites worldwide. The Cyanisorb® process was developed in New Zealand in 1989 and used at the Golden Cross gold and silver mine in New Zealand. The SART process has been used at least at the pilot plant scale in Australia, including at the Telfer gold mine in WA, and has been operated in full scale plants overseas (Environment Australia, 1998).

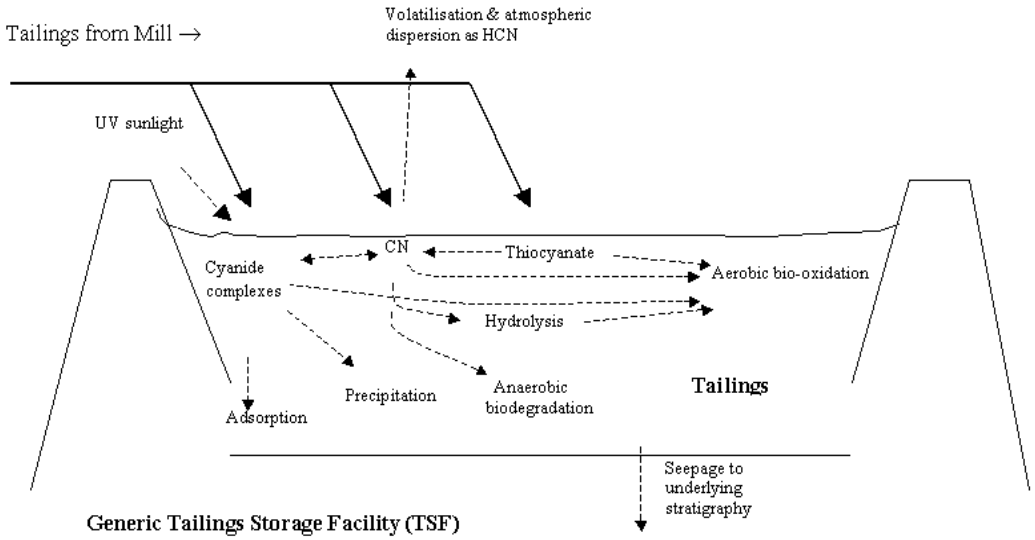
Eisler et al. (1999) commented that water hyacinth (*Eichornia cressipes*) has been proposed as the basis of a cyanide removal technology, as this water plant can survive for at least 72 h in a nutrient solution containing as much as 300 mg CN/L and can accumulate up to 6.7 g CN/kg DW plant material (citing *Low and Lee, 1981). However, Eisler et al. (1999) note that how to dispose of this plant material is then an issue, which may be one reason that large scale use of water hyacinths for this purpose has not yet been implemented.

6.6.3 Transformation in TSFs and migration

As indicated in Figure 6.1, the fate of cyanide compounds in TSFs is complex and a range of reactions may occur resulting in degradation and transformation, and atmospheric emissions occurring (e.g. Staunton, 1991c-d, Smith and Mudder, 1993; Ellis, 1997; Lye, 2002).

The kinetics of cyanide reactions are site-specific, being influenced by the general chemistry and geochemistry, including variations in pH, redox potential (Eh), salinity, temperature, density of solids, type of minerals, the individual metal cyanide complexes and their concentration, and the presence of any free cyanide (Environment Australia, 1999a-d). Ellis (1997) concluded from cyanide fate modelling that the main factors affecting natural degradation of cyanide in TSFs were pH, temperature, TSF size, presence of metal cations and the effect of discharging slurry over a sloping entry section (beach). Botz et al. (1995) considered that the main cyanide degradation mechanisms occurring in TSFs are the dissociation of metal cyanide complexes and volatilisation of cyanide as HCN, and the principal factors affecting degradation are pH, temperature, photolysis and volatilisation. It is likely that techniques used to minimise the amount of water delivered to a TSF would reduce the proportion of cyanide that is volatilised as HCN, as would free cyanide destruction processes (Staunton, pers. comm. 2005).

Figure 6.1. General fate of cyanide in tailings storage facilities (Smith and Mudder, 1993)



According to Smith and Mudder (1993), the main processes affecting cyanide in tailings in TSFs in the short term may be described on the basis of operational areas as follows:

- tailings pumping system: oxidation, precipitation, resolubilisation reactions;
- discharge onto TSF impoundment (e.g. spigots): oxidation, precipitation;
- TSF beach and pool: dilution, concentration, oxidation;
- oxidised tailings zone: precipitation, co-precipitation reactions or solution by acidification due to its secondary oxidation;
- drains/penstock/decant ponds: oxidation and precipitation; and
- water reclaim facility (if any): dilution, concentration processes and precipitation.

In general, while a proportion of cyanide will remain within a TSF for an extended period of time before eventually degrading or stabilising (Smith and Mudder, 1993; Staunton, 1991c-d), volatilisation of HCN will also account for a proportion of the cyanide added to a TSF (Ellis, 1997; Smith and Mudder, 1993; Simovic and Snodgrass, 1985; Staunton et al., 2003). In addition, depending on factors such as discharge volume and concentration, climate and structural integrity, there is an inherent potential for migration of contaminants in seepage of process water to underlying stratigraphy at some TSFs (DEWHA, 2006; Environment Australia 1999a-d; WRC, 2000b).

Often mining operations have water or cyanide reagent recovery systems in order to reclaim cyanide solutions from tailings, via a lined decant pond, for re-use in the gold ore beneficiation process.

6.6.4 Fate modelling and monitoring data

Trends in WAD CN over time and within a TSF

The Northern Territory Bird Usage of Tailings Storage Facilities Coordinating Group study (Donato, 1999) consistently reported lower WAD CN concentrations in TSF surface waters than at the points of discharge to the TSFs. Mudder and Goldstone (1989) monitored the fate of cyanide compounds in tailings decant for 4 weeks and in tailings pore waters for 12 weeks, finding that WAD CN concentrations declined by up to 95% during the period of the tests whereas the total cyanide concentration remained stable. Several studies, including AMIRA Projects P277 (1989-1991) and P497/497A (1997-2000) provide information on the fate of cyanide in TSFs. The development of a model to predict the deportment of cyanide in and around tailings structures was commenced by AMIRA during P497A and the work continued in AMIRA project P420B. Cyanide species deportment modelling was also evaluated in the Minerals and Energy Research Institute of Western Australia (MERIWA) project M398 discussed below (Adams et al., 2008b). However, Staunton et al. (2003) indicate that the application of mass-balance modelling to determine the fate of cyanide in TSFs is not appropriate due to substantial error inherent in the method and thus the potential for erroneous emissions and loss estimates.

Detailed data are available for WA gold mine operations participating in the studies reported by Adams et al. (2008a,b,c), namely Granny Smith Gold Mine, Kanowna Belle Gold Mine, and St Ives Gold Mine (the latter has both mill and heap leach operations). Granny Smith is a saline site (14 000-50 000 mg/L TDS in process waters) and the other two sites hypersaline (>50 000 mg/L TDS). Cyanide sampling conducted during the project showed that the three TSFs experience daily fluctuations in WAD cyanide discharge concentrations within the range of 35 to 170 mg/L. Limited evaluations were also conducted at a second saline site. In all cases there was a significant drop in WAD cyanide from spigot to supernatant, but evaluations in Phase II of the project showed hypersaline sites generally showed significantly greater cyanide degradation in the flume (turbulent slurry flow over the beach zone) than the saline sites. This was expected by the investigators, as it has been shown that the solubility of hydrogen cyanide is lowered with increasing salinity, and in addition, the pH values of hypersaline solutions are lower which also favours loss of cyanide by evaporation (Section 6.3.2 and below).

Volatilisation

The rate of HCN release (i.e. volatilisation) from cyanide solutions in TSFs is largely governed by the pH of the solution. The lower the pH, the greater the rate of HCN formation and evolution to air. The loss of cyanide can be managed through regulation of pH in process streams (CMEWA, 2002). Mill tailings ideally have a pH ≥10 (Smith and Mudder, 1993), but a significant proportion of Australian operations are at a pH of ~9.0-9.2 (Section 4.4.2). In either case, conditions in TSFs are generally less alkaline and create an environment conducive to HCN formation and volatilisation, whereas volatilisation losses during the process are low (Section 4.4.2).

AMIRA project 497A found that volatilisation of HCN is the main cyanide loss process from TSFs (Dilworth, 2000). Staunton et al. (2003) discussed the relevance of results reported by Schmidt et al. (1981), for an evaluation of cyanide loss in a barren solution bleed pond with no solid tails present. In that study, natural degradation mechanisms reduced the cyanide concentration by 99.9% over a four month period,

with volatilisation of free cyanide as HCN evidently the most important mechanism and oxidation to cyanate accounting for ~11% of the total cyanide loss. They noted that this test situation differs from that occurring in typical gold mining TSFs operating in Australia, where solution and solids are deposited together in the TSF. The solid and liquid phases partly separate, with some of the solution rising to the surface to form a tailings or decant pond, while the remainder of the solution is trapped below, within the consolidated solids (see Figure 6.1). The cyanide in the decant pond is available for volatilisation as HCN, and up to 90% of this cyanide may be lost as HCN. However, the solution trapped within the consolidated solids is not available for volatilisation and as discussed above, converts to more stable metal cyanides. Thus they concluded that the percentage of the cyanide entering a TSF which is evolved as HCN would be significantly less than 90%, but may possibly be as high as 30% or more.

Staunton (1991c) monitored degradation of free cyanide in a TSF, indicating that volatilisation of HCN is more significant immediately following discharge of tailings; however, over time and in conjunction with burial by overlying tailings, volatilisation becomes less significant. More stable, metal cyanide complexes are more apparent. Due to their stability, these complexes may persist within the TSF environment for an extended period of time (i.e. years; Kjeldsen, 1999).

Copper cyanides form the stable $Cu(CN)_3^{2-}$ species in tailings solutions that can significantly contribute to WAD cyanide, limiting volatilisation of HCN (Adams et al., 2008b,c). Synthetic copper cyanide degradation tests at different salinities conducted under the MERIWA project exemplified the stabilizing effect of copper on WAD cyanide, with cyanide degradation halting after about 24 h in all cases, with WADCN:Cu ratios remaining at ~0.8 from 24 h through to 120 h, consistent with the stable $Cu(CN)_3^{2-}$ remaining in solution for lengthy periods, confirming previous results.

Migration in seepage from TSFs

It is not possible to generalise regarding the potential for migration of cyanide and products from TSFs in seepage to groundwater, except that it may potentially occur, particularly below unlined TSFs, TSFs with poorly designed and constructed liners or where liner integrity is violated. The potential for, and rate of, seepage to underlying strata from TSFs is highly variable and varies site-specifically. Reviews by DEWHA (DEWHA, 2006; Environment Australia, 1999a-d) suggest that seepage rates of 0 to 10% have been quoted in the mining industry. Seepage is the rate of movement of process water to underlying stratigraphy relative to the inflow rate of process water. However, Staunton et al. (2003) indicated that a seepage rate of 10%, together with the assumption that the seepage will have a CN concentration equal to that of the TSF return water, will generally result in overestimation of cyanide migration as both figures are at the high end of the range.

Evaluation and modelling of seepage in AMIRA Project 497A found that cyanide may be incorporated into buried tailings after tailings settlement, as the stable iron-cyanide complex, ferrocyanide, which is chemically stable and of lower toxicity. The research was undertaken on five different types of TSFs and suggests that the process may be widespread. Instability of iron-cyanide complexes may occur in the presence of sunlight (photolysis), resulting in the formation of free cyanide. This would probably volatilise at the surface to air and concentrations are unlikely to be high. Dissolution of metallocyanide complexes may also occur in the presence of acid rock drainage (Dilworth, 2000).

Kjeldsen (1999) indicated that iron cyanide complexation may potentially account for a large proportion of the cyanide present, and that the stability and low solubility of these complexes under low pH (e.g pH ≤6) conditions has the potential to inhibit migration in seepage. However, strong alkaline conditions may increase cyanide dissolution and the relative potential for migration in seepage.

Table 5.1 summarises the result of TSF pore water samples from sediment cores (0-2 m) collected from three TSF operating in the early 1990s (Staunton, 1991b-d). Cyanate and thiocyanate tailings concentrations ranged up to 320 and 610 mg/L, respectively, and up to 2100 mg/L in TSF pore waters (0-1.6 m depth). Free and WAD CN concentrations ranged up to 290 and 630 mg/L, respectively. No samples from greater depths were available.

Staunton (pers. comm. 2005) commented on results of studies of the concentration of cyanide residues in a decommissioned site, at depths up to 6.5 m. Concentrations of WAD and total CN in a water extract from the entrained liquor (pore waters) tended to decrease with increasing depth, from a maximum of ~4-5 mg/L and ~32-38 mg/L, respectively, at 0.5-1 m, to a minimum at 2.5-3 m of ~1 mg/L and ~7 mg/L, respectively. They then increased to ~6 mg/L and ~27 mg/L, respectively, before again declining. In a separate study of an 'old' tailings facility, WAD and total CN concentrations in a water extract from the entrained liquor tended to fluctuate around 1 mg/L and 3-9 mg/L, respectively at 0.5-10.5 m, except for a marked peak of ~3 mg/L for WAD CN and 22 mg/L for total CN at 6.5 m. This presumably reflected different concentrations over time in the material deposited, as well as changes over time.

Staunton et al. (2003) indicate that seepage is highly variable and may range by ±5% of the cyanide added to a TSF. Smith et al. (1984) recorded total cyanide in seepage at a decommissioned TSF (20 years old) at various depths in the underlying stratigraphy (11 to 47 m) at concentrations up to 2.9 mg/L, but at the deeper locations (e.g. >30 m), concentrations were ≤1 mg/L. Staunton (1991c) reported on a study of groundwater quality down gradient from a TSF in Queensland, finding no evidence of migration of cyanide in seepage to groundwater. Groundwater monitoring data from a TSF in WA indicated relatively consistent concentration ranges for total, WAD and free cyanide over the 6 year monitoring period of 0.01–3.6, 0.01-0.66, 0.01-0.29 mg/L, with the majority of the cyanide associated with strong complexes (e.g. iron-cyanide complexes).

Groundwater monitoring in the vicinity of TSFs is a regulatory requirement of state and territory agencies in Australia. Consistent with ANZECC/ARMCANZ Guidelines (Section 11.6.2), the goal in most cases is to protect the groundwater as a future resource and hence to ensure that its potential uses are not affected by contamination of water from TSFs and other potential CN sources on the site, rather than necessarily stipulating that no contamination of groundwater with cyanide should occur at all, as is the case in some jurisdictions. Thus, it is considered that there is less need to protect hypersaline water that has no value for stock or irrigation use than water which is higher in quality and may be used for purposes other than mining and industry. There is a common (though evidently not general) licence limit for WAD CN in groundwater of 0.5 mg/L. Where this is exceeded in hypersaline areas, rather than requiring reinstallation or adaptation of the TSFs to minimise seepage, recovery bores are installed to intercept the water and return it for use in the process stream.

It should be recognised that there are also other important potential groundwater impacts to the environment from TSFs apart from cyanide. Tailings waters may

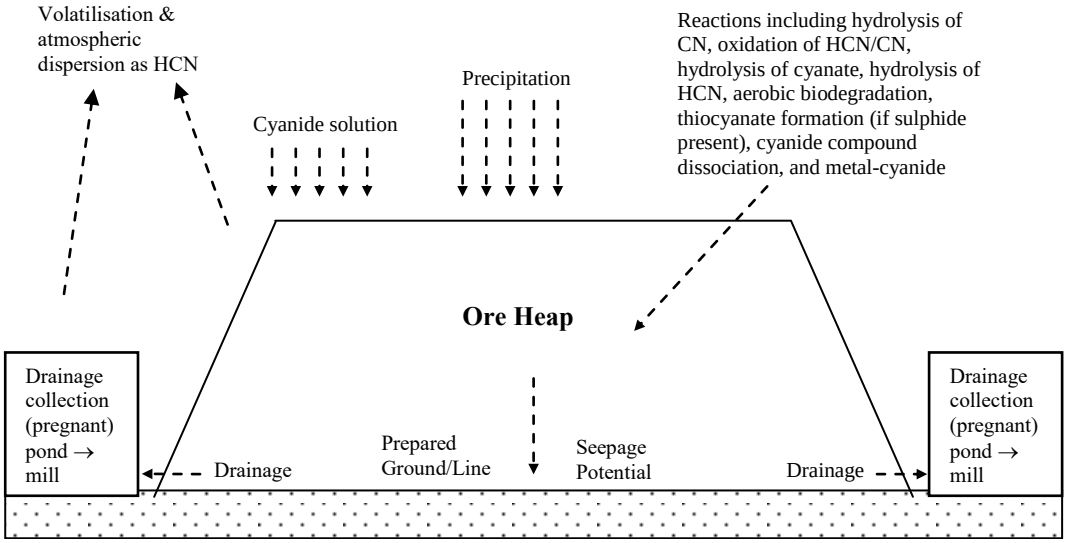
contain many other components of potential concern, which depending on local conditions, may affect pH, raise salinity and may contaminate the water with heavy metals and other potentially toxic elements such as arsenic and selenium. Changes in the original depth of the groundwater may also have effects on water quality, additional to quality effects from the TSF waters themselves, and shallow watertables (or groundwater mounds) are themselves a problem. Tolerances for salinity and pH impacts also vary with the quality of the original groundwater (on the principal of protecting future use as a resource). Groundwater is often a source for the process water used at gold processing sites, and at WA gold processing facilities in the Kalgoorlie/Laverton area it is often saline or hypersaline (e.g. >50 000 mg/L) and is only considered useful for mining.

6.7 Fate of cyanide in heap leach ore heaps

6.7.1 Changes in concentration and composition

The reactions of cyanide in a heap leach process initially involve reactions of free cyanide, but will later also involve secondary cyanide compounds (refer Figure 6.2; Smith and Struhsacker, 1988). Loss of free cyanide may occur in the ore heap, the drainage channels or drainage collection ponds due to a range of factors such as volatilisation, iron complexation and precipitation processes within the heap.

Figure 6.2. Prevailing geochemical conditions and typical cyanide reactions in the heap leach environment (Smith and Struhsacker, 1988; Hallock 1990)



Concentrations of cyanide compounds in porewaters and drainage vary temporally and site-specifically, and concentrations will be much higher during the operation phase than in the post-operational phase (Staunton, 1991d). Ore heaps may take some time to fully leach. Modelling technology is being developed and applied to predict the seepage lifetime of ore heaps (Mining Life-Cycle Center, 2003).

The extent of puddling observed on 24 active heaps at Nevada gold mines evaluated by Henny et al. (1994) was severe in at least one heap at 9 of the mines and slight at another 8. The degree of puddling seemed to be influenced by the amount of clay in the ore, the quality of distribution system maintenance, the application rate of the

cyanide solution, the degree to which compaction due to trucks and heavy machinery had occurred, and the duration of time that solution had been applied to the heap. Measured WAD CN concentrations in puddles at the top of the heaps ranged from 2 to 1120 mg/L. In some cases this was elevated above the stated concentration of NaCN used (e.g. WAD CN of 612 mg/L where NaCN was used at 265 mg CN/L), and in the case of the 1120 mg/L figure the application rate information was not available.

Smith and Mudder (1993) reported concentrations of WAD cyanide in drainage channels of ~130 mg/L. ERA Environmental Services (1995) reported WAD cyanide concentrations in a pregnant liquor pond of 200 mg/L, and ~30 mg/L in a drainage channel.

Johnson et al. (2002) investigated the drainage from a disused ore heap from the former Standard Hill gold mine, California, which had previously been subjected to cyanide solution application. Drainage effluent samples were collected from three locations including a drainage hole at the toe of the heap, an open receiving channel downstream of the heap, and from a holding pond into which the drainage discharged. The results are presented in Table 6.3.

Table 6.3. Cyanide products (mg/L) in drainage from an inactive ore heap

Analyte	Drain hole	Open channel	Holding pond	Trend
WAD CN	0.185	0.16-0.44	0.01-0.02	↓
Total CN	4.04	2.28-2.37	0.84	↓
$Fe(CN)_6^{x-}$	2.4	1.4-2.8	<0.2	↓
Nitrate	2400	2600-2700	2660-4100	↑
Nitrite	22	14-15	9-12	↓
Ammonia	2.5	0.7-0.8	0.1-0.2	↓
Thiocyanate	<0.2	<0.2	<0.2	---
Cyanate	<0.1	0.2	0.7	↑
pH	7.56	8.42	8.55-9.20	↑

Source: Johnson et al. (2002).

The most abundant cyanide species in the drainage waters sampled by Johnson et al. (2002) were the strong metallocyanide complexes (96% or 4040 µg/L), predominantly of iron and cobalt, with a smaller fraction (4% or 180-190 µg/L) of WAD cyanide in the effluent. Lower (80% less) cyanide concentrations were detected in the pond surface water samples than sampled earlier in the drainage path, apparently due to the greater potential for losses from photolysis of metallocyanide complexes and HCN volatilisation or oxidation, changing pH conditions and biodegradation. Cyanate concentrations were marginally higher in the pond waters. WAD cyanide species contributed a smaller fraction (1%) to the total cyanide content of pond waters, with strong metallocomplexes predominating (Johnson et al., 2002). The open channel effluent displayed regular diurnal changes in cyanide speciation. In the channel effluent, WAD cyanide varied from 0.7 mg/L (day) to 0.2 mg/L (night), whereas $Fe(CN)_6^{x-}$ (ferrocyanide + ferricyanide) showed the reverse effect (0.8 mg/L day and 1.9 mg/L night). However, there was also a net loss of free cyanide associated with this diurnal fluctuation, probably due to volatilisation. Iron and manganese concentrations

in solution were higher at night, but silver, gold, copper and vanadium concentrations were higher during the day. Nitrite concentration was highest during the day and ammonia highest during the night. These diurnal changes were not the result of processes occurring in the heap, but were apparently due to photolysis of the strong metallocyanide complexes to WAD cyanide (mainly as free cyanide at measured rates in this instance of 0.09-9 mg CN/L/hour) when exposed to sunlight in the open channel and subsequent reactions of by-products.

Staunton et al. (2003) indicated no reasonable estimates of relative cyanide volatilisation or migration in seepage from heap leach operations are available.

6.7.2 Migration in seepage from heap leach operations

As for TSFs, it is not possible to generalise regarding the potential for migration of cyanide and products from ore heaps in seepage to groundwater, except that it may potentially occur, particularly below unlined heaps, heaps with poorly designed and constructed liners or where liner integrity is violated.

White and Markwiese (1994) reported a 375 m long plume of cyanide-contaminated groundwater underlying a disused heap leach residue pile in New Mexico, with groundwater total cyanide concentrations up to 0.7 mg/L.

Staunton et al. (2003) indicated that the potential cyanide concentration in seepage is likely to be significantly lower than the concentration in solution added to the ore pile, and the presence of standard engineering controls (e.g. liner, under-drainage) would greatly reduce this potential.

A review of current international practices by Thiel and Smith (2003) indicates that seepage from leach pad operations can be avoided by construction of a liner (usually geomembrane). Typically, Australian heap leach operations construct geomembrane liners on ore heap pads to avoid risk of groundwater contamination. Thiel and Smith (2003) identify geomembrane puncture due to rocks or geomembrane susceptibility to chemical corrosion as key concerns at heap leach operations; however, chemical corrosion is unlikely with cyanide solutions. A range of guidance and regulatory requirements are established to manage the risk of groundwater contamination at mine sites within a risk-based approach (refer Section 11.6.2).

6.8 Fate of cyanide in landfills

Limited information on the fate of cyanide in landfills was located during this assessment. Cyanide residues are expected to undergo processes similar to those in soils and groundwater (volatilisation, complexation, biodegradation, adsorption, precipitation). Although disposed of to landfill, simple and complexed forms of cyanide rarely create environmental concern, with a low proportion (0.3%) of National Priorities List (NPL) mining-related sites in the United States listing cyanide as a chemical of potential concern. A relatively minor quantity of sodium cyanide is likely to be sent to landfill for disposal in Australia compared to other industrial and domestic sources of cyanides, with most sodium cyanide-derived waste being treated at the original site or by the waste contractor to destroy free cyanide before delivery. Regulatory controls are established throughout Australia for disposal of cyanide wastes to landfill (refer Section 11.8.4).

6.9 Fate of cyanide in sewerage systems

In a survey of 40 municipal sewage treatment plants (STPs) in the United States, the removal efficiency of cyanide was generally high (up to 98% with influent concentration up to 7 mg/L; Lue-Hing, et al., 1992). Cyanide is relatively biodegradable by aerobic (Knowles and Bunch, 1986; Haghighi-Podeh and Siyahati-Ardakani, 2000) and anaerobic (Fallon, 1992) metabolic pathways, and it may be removed from wastewater using an activated sludge (biological) secondary treatment process at influent concentrations up to 100 mg/L (Richards and Shieh, 1989). Haghighi-Podeh and Siyahati-Ardakani (2000) investigated the effect of cyanide on aerobic treatment systems in batch and continuous flow experiments. Cyanide-resistant micro-organisms capable of biodegrading cyanide identified in the culture included *Oscillatoria*, *Philodina*, *Carchesium*, *Pseudomonas* and *Bacillus* bacteria. The small amounts of cyanide from industrial discharge into sewers are likely to be destroyed during secondary treatment and are not concentrated into sludge (Lordi et al., 1980; Haghighi-Podeh and Siyahati-Ardakani, 2000). Data for effluent from Sydney Metropolitan Area sewerage plants (Section 5.3) also show only low levels of cyanide, but corresponding data for raw influent to determine the extent to which this is due to destruction during sewerage treatment are not available.

6.10 Summary of environmental fate

Solid NaCN is stable if completely dry, but tends to absorb moisture from the air (i.e. is hygroscopic) and can then release hydrogen cyanide (HCN) by various reactions, as may occur in solution. Once dissolved in water, NaCN is present as sodium ions (Na^+) and 'free cyanide'. Free cyanide is the sum of cyanide present as molecular hydrogen cyanide (HCN) and ionic CN^-. The amount present as HCN decreases with increasing pH, such that the proportion of HCN to CN^- is equal (pKa) at a pH of approximately 9.3 at 20ºC.

HCN is a highly volatile gas and is lighter than air, and also has high volatility from water despite being completely soluble (miscible) with water. The volatilisation rate is minimised if the solution is maintained at a high pH, as in NaCN manufactured in liquid form (~30% solution, pH ~13). However, under typical environmental conditions of pH<8 and temperature <25ºC, >94% of the cyanide is present as HCN. Thus volatilisation of HCN can be a significant removal process for free cyanide from aqueous solutions and soil to air.

Volatilising HCN in soil may reach the soil surface and pass into the atmosphere, or may be biodegraded and metabolised by micro-organisms, react with soil constituents in the subsurface, dissolve in soil moisture, or be entrapped in subsurface cavities. Volatilisation of HCN from groundwater is unlikely to be a significant transformation process. In the atmosphere, the lifetime of HCN is estimated to be a few months. Biomass burning is considered to be the main source, with release from the use of NaCN only a minor source. HCN may degrade via reactions with hydroxyl and oxygen radicals, but ocean uptake is considered to be the main sink for atmospheric HCN.

Cyanide is a highly reactive substance and once released into the environment may follow various degradation and reaction pathways. In addition to volatilisation, these include complexation with various metals, adsorption of free and complexed forms, formation of thiocyanate by reaction with various forms of sulphur, oxidation to cyanate and other products, hydrolysis of HCN to formate, and aerobic and anaerobic degradation reactions to form products such as cyanate, ammonia/ammonium and

nitrites/nitrates. Metallocyanide complexes may form insoluble precipitates, and if exposed to light, iron-cyanide complexes may undergo photolysis reactions releasing HCN. Products such as thiocyanate, cyanate and formate are much less toxic than cyanide and continue to degrade, ultimately into oxides of carbon and nitrogen and simple forms of sulphur.

The fate of cyanide compounds in TSFs is complex and a range of reactions may occur, influenced by the general chemistry and geochemistry at the site. These result in various degradation and transformation processes, as well as atmospheric emissions. Cyanide compounds and products present and formed in tailings may potentially include free cyanide, a range of metallocyanide complexes (simple to strong complexes), thiocyanate, cyanate, nitrogenous compounds (e.g. ammonia, nitrite and nitrate), cyanogen and cyanogen chloride, formic acid/formate/ammonium formate, carbon dioxide and other simple compounds of carbon. Similar types of reactions may occur in heap leach piles.

There are various chemical processes available to detoxify cyanide in tailings, some of which are in regular use in Australia. These generally act to convert cyanide to cyanate. Conversion of cyanide to iron-cyanide complexes by adding ferrous sulphate is the main method used to initially deal with spills of NaCN. Water containing free cyanide is often recycled back to the tank leach process, commonly by draining from a TSF into a decant pond, or also by extracting water before discharge of the tailings, depositing them as a thickened slurry or paste. There have also been chemical processes developed to regenerate free cyanide from the tailings water so it can be re-used, but with limited commercial success in Australia.

Ultimately, cyanide may be lost from TSFs and heap leach piles by volatilisation of HCN, may degrade by various abiotic and biotic processes, may be fixed within the site by precipitation and adsorption of metallocyanides, and may migrate in seepage to underlying strata and groundwater. The extent to which seepage occurs varies widely between individual sites.

In landfills, cyanide residues are expected to undergo processes similar to those in soils and groundwater (volatilisation, complexation, biodegradation, adsorption, precipitation). Most sodium cyanide-derived waste from non-mining uses is expected to be treated to destroy free cyanide before delivery to landfill. Cyanide-resistant micro-organisms capable of biodegrading cyanide have been identified in aerobic sewerage treatment systems, and the small amounts of cyanide arising from industrial discharge into sewers are likely to be destroyed during secondary treatment.

Thus the overall fate of sodium cyanide (NaCN) and its products in the environment is complex and depends on factors such as concentration, chemical speciation, form released (solid, liquid), co-associated chemicals, pH, redox potential, temperature, and exposure to sunlight in the environment into which the cyanide is released.

7. Environmental Exposure Assessment

This chapter provides an analysis of exposure of the environment to sodium cyanide arising from its various uses, including particularly exposure of wildlife and aquatic organisms to cyanide as a result of its major use in gold mining.

References in the report that have not been sighted are marked with an asterisk(*).

7.1 Exposure at manufacturing facilities

Sodium cyanide manufacturing facilities in Australia provide limited habitat for wildlife, being located in industrialised areas. These facilities must meet strict operational requirements managed by the Qld and WA Environmental Protection Agencies and/or local councils, including licence limits on emissions of HCN, NH_3 and NO_x gases or NaCN particulates to the air or CN^- and NH_3 or other nutrients to water.

At Orica's plant near Gladstone, effluent containing cyanide is acidified to release HCN, which is then converted to NaCN by reaction with NaOH and fed back to the process stream (Orica, 2002). The effluent is then treated to convert any remaining cyanide residues to cyanate, transferred to the site batch effluent systems and mixed with other effluents, tested analytically and discharged offsite to a tradewaste facility operated by the local shire council. Tail gas from the HCN absorber is fed to a burner and combusted to produce oxides of nitrogen (NO_x), which are subsequently 'denoxed' prior to emission via a stack. Air from the drier system is scrubbed in a caustic scrubber (recovering HCN as NaCN) before emission via a stack. Air and water emissions are reported to and managed by Queensland EPA and Calliope Shire Council.

At AGR's NaCN production plant at CSBP's Kwinana facility, process water from the solution manufacture plants is recycled within the process (CSBP, 2009). Stormwater collected from the plant area is captured, treated and tested prior to discharge. Evaporated water from the solid sodium cyanide plant is purified by ammonia stripping, reverse osmosis and hydrogen peroxide treatment before being tested and discharged. Waste gases from the solution plants are incinerated, and the heat produced used to generate electricity. Gaseous emissions from the solids plant are combined and vented through a two stage wet scrubber stack incorporating demisters to ensure that air emissions comply with Western Australian Department of Environment & Conservation licence conditions.

Waste waters from the NaCN plant (CN^- concentration limit = 1 mg/L) initially flow to the CSBP containment pond, where they mix with other effluent from the site to allow further dilution and degradation of cyanide and other nitrogen-containing substances before release. Water from the pond then flows through a nutrient stripping wetland before discharge. Initially a single wetland cell was constructed as a pilot. In 2008-09 two additional cells were constructed which are designed to be filled on alternate days and feed the original cell. The wetland is designed to remove nitrogen from waste water using nitrification and denitrification biological processes. Low level

concentrations of a number of metals are further reduced as water traverses the wetland. Marine discharge formerly occurred to Cockburn Sound, but discharge now goes to a common pipeline for ocean discharge from the Kwinana area, the Sepia Depression Ocean Outfall Landline (SDOOL). The Cockburn Sound discharge point is retained in case it is needed as an emergency outfall should SDOOL be unavailable. Daily concentration and load limits in effluent discharged from the site are specified in the Environmental Protection Act licence. The cyanide concentration limit is 0.1 mg free CN/L, and operation of the SDOOL occurs to a Monitoring and Management Plan which ensures that ANZECC/ARMCANZ (2000a) (Sections 9.8.2 and 11.9.1) 99% species protection guidelines for toxicants (with the exception of cobalt, for which the 95% species protection guideline will apply) will be met under both typical and 'worst-case' discharge concentrations at 100 m from the diffuser (Water Corporation, 2008).

7.2 Exposure during transport

Wildlife should not normally be exposed to cyanide during the transport, delivery and storage of NaCN, either in solid or in liquid form. However, aquatic and terrestrial wildlife could potentially be exposed to cyanide as a consequence of an incident during transport by rail or road, such as a traffic accident, leakage, or other misadventure. The extent of exposure would depend on the nature of the accident, limited by the quantities transported at one time and clean-up action taken. Incidents that have occurred in Australia and overseas are discussed in Section 5.4.2. Three incidents in Australia have involved significant spillage of NaCN. In one case, NaCN in solution was spilt into a culvert from which wildlife drank and were killed, demonstrating the need for prompt action when a spill occurs. At the other two incidents, emergency response measures contained and recovered the spilt material, and in the more recent incident also removed contaminated soil and water, and no harmful effects on wildlife or aquatic organisms were reported. However, some overseas incidents where significant release of NaCN occurred to water led to downstream environmental contamination and harm to aquatic organisms. NICNAS has not investigated the regulatory control measures that were in place in the various overseas jurisdictions at the time of these overseas incidents.

Various legislation, National Standards and Codes of Practice are in place to ensure safety and protect the environment during the handling, storage and transport of sodium cyanide, which is considered a Dangerous Good, as discussed in Section 11.3. As discussed in Section 5.4.2, the number of transport incidents in recent years is small compared to the large number of journeys over long distances by road and rail. Significant release of sodium cyanide has only occurred in three of those incidents, and harm to wildlife or aquatic life only arose in one of those incidents. However, due to concerns that some improvements are needed following a recent road transport cyanide spillage incident, the NT Government initiated a review of the regulatory regime applying to dangerous goods transport in the NT. Possible considerations arising from the incident include whether there is a need to have greater controls on the size of loads and vehicles that may be used for road transport with different types of container, to reduce the risks of such significant incidents occurring. Completion of clean-up and recovery was prolonged in this incident, hence an important issue is whether improvements are needed to the planning and implementation of response measures, so that recovery and clean-up operations are not delayed or prolonged, as delayed recovery increases the risk of environmental contamination spreading before clean-up is complete.

7.3 Exposure during use for gold beneficiation and recovery

7.3.1 Wildlife in the vicinity of TSFs and mine infrastructure

Although the TSFs and associated infrastructure that receive cyanide-containing waste materials from ore processing facilities (and heap leach operations) represent highly disturbed ecological areas, there is ample evidence to indicate that these facilities have the potential to provide habitat for wildlife such as birds, mammals, reptiles, amphibians and invertebrates (Henny, 1994; ERA Environmental Services, 1995; OSS, 1995; Eisler, 1991; Eisler et al., 1999; Donato, 1999; Donato, 2002; Donato et al., 2007, 2008; Adams et al., 2008a,b,c; Smith et al., 2008; Griffiths et al., 2009). Livestock may also use these areas (Donato, 2002). Anecdotal information indicates that most TSFs and other facilities used to contain cyanide solutions in Australia do not have perimeter fencing or overhead netting to prevent access by wildlife, but this has not been verified.

Donato (1999) identified 35 species of birds at gold mining TSFs in the NT (refer Appendix 2, Table A2-1). Salinity levels for these TSFs were not indicated by Donato (1999), but Adams et al (2008b) provided further information that indicated that one TSF was freshwater and six were presumably fresh, brackish or at most saline among the TSFs used in this study. It is likely that additional species would visit TSFs in the NT (e.g. finches, magpie geese, spoonbills, pied herons, pigeons, doves, cockatoos and parrots). Both nationally and internationally, protected wildlife have been observed at TSFs (Donato, 2002).

Over a four year period from 1992, Read et al. (2000) monitored bird populations in the Olympic Dam area in South Australia, which is located in an arid region and is characterised by low and temporally variable diversity and abundance of birds, as is the case in most arid regions. Olympic Dam is a copper/uranium/gold mine which has a peripheral discharge TSF and various dams and ponds. Cyanide is used to a minor degree to obtain gold, but investigations have shown it is present at undetectable concentrations in the tailings stream (S. Green, Western Mining Corporation, Pers. comm. 2005). Birds were monitored near (but not in the immediate vicinity) of the mine and processing plant, near a number of pastoral waterpoints, and at control regions with negligible mining or livestock grazing impacts. From a regional inventory of 172 species, 73 species were recorded during the study, which the authors noted was partly explained by the fact that most local species are nomadic or migratory and only inhabit the region when environmental conditions or seasons are appropriate. There were significant annual variations in population size of most species and greater abundance of most species in wet years. Habitat variables such as vegetation structure were also an important determinant of abundance of most species and tended to mask the impacts of land use.

Read et al. (2000) found that several bird species had benefited from the provision of permanent water at mining and pastoral sites (e.g. zebra finches, magpie-larks and crested pigeons), and other species utilised increased nesting or feeding opportunities associated with the mining operation (e.g. nankeen kestrels nesting on tall mining structures, red-backed kingfishers nesting in dune cuttings and stockpiles of soil or rock, and white-breasted woodswallows utilising magpie-lark nests) or increased food supply at the pastoral sites. Birds that are commensals of human habitation have also colonised or increased in abundance since development of the mine, such as house sparrows, magpie-larks and black kites. The principal bird species that were negatively correlated with mining were crested bellbirds and mixed-feeding flocks of small

insectivorous birds. The authors considered that this was possibly due to human intrusion and noise effects on territorial singing of the bellbirds, and noise, human disruption and predator effects on feeding flocks. Noise levels recorded in the study areas were generally more than 10 dB$_{\overline{7}}$ below the 80 dB threshold likely to disrupt the behaviour and movement of other bird species. Exposure to pollutants was not considered significant in this area, as evidenced by the successful breeding of sensitive bird species.

Some caution is necessary in extending Read's approach and results to TSFs containing cyanide, as cyanide at toxic concentrations is a fast-acting poison causing almost immediate debilitation, stupefaction and death. Therefore it is very unlikely that any impact on birds due to cyanide would be observed directly unless the tailings facility itself is monitored. Most bird species identified in studies by Donato as at-risk by exposure to cyanide do not breed in such locations, hence whether or not certain species breed in the vicinity of a mine is not necessarily an indicator of impact from cyanide (Donato, pers. comm. 2006). As with Read's research, natural temporal variation in bird diversity and abundance at arid locations also makes it difficult to infer conclusions about impacts such as depression of local bird populations over the timespan of such observations.

Read (1999) noted that artificial waters such as dams, sewage ponds, boredrains and mining waterbodies are used extensively by waterfowl in arid Australia, presumably as refugia during long distance movements. He commented that many waterfowl migrate at night and sometimes alight on unsuitable or even hazardous shiny surfaces, such as iron roofs, wet tarmac or toxic ponds, with the risk of not choosing appropriate waterbodies possibly compounded by hunger, thirst or exhaustion. Thus waterfowl deaths occur naturally due to birds failing to reach suitable waters, but sometimes this is due to interaction with the anthropogenic landscape.

The attraction of wildlife to TSFs and associated infrastructure may be due to the presence of suitable habitat features (resources/conditions) including surface waters for swimming, diving, foraging and protection from predators, embankments for roosting, foraging and breeding, beaches and slurry for foraging, sheltered areas and wide open spaces. Sources of food at TSFs may be primary (derived from the TSF environment itself) or secondary (prey and vertebrates and invertebrate carcasses in TSFs providing food for predatory and scavenging species) and TSFs provide a source of drinking water. Read et al. (2000) commented that birds may be attracted to mine sites by increased nesting and feeding opportunities (see above), and raptors use tall structures for perches and use updrafts associated with mining stockpiles for soaring. Donato (2002) indicated that birds are particularly attracted to shallow water (supernatant), wet slurry, bare ground and carcasses of vertebrates and invertebrates. Similar to their habitat use in natural areas, birds and other wildlife found at TSFs may be attracted to specific micro-habitats (e.g. terns and ducks: supernatant; shorebirds: supernatant and slurry interface; pratincoles: bare ground; and predatory birds: carcasses).

Donato (D. Donato, Donato Environmental Services, pers. comm. 2006) made the following comments. There is anecdotal evidence that some poorly managed tailings facilities provide conditions in the actual tailings cell that are conducive to the support of phytoplankton, zooplankton and some aquatic macroinvertebrate life, some of which provide food resources for birds. However, more detailed evidence from macroinvertebrate sampling at saline and hypersaline facilities in WA suggests that little or no aquatic macroinvertebrate life exists in the cyanide-bearing solutions at these facilities [According to Adams et al (2008b), the levels of salinity in fresh,

brackish, saline and hypersaline waters are 0-2000 mg/L TDS, 2000-14000 mg/L TDS, 14000-50000 mg/L TDS, and ≥50 000 mg/L TDS, respectively]. It is likely that in most cases birds that may acquire a primary food resource on or near the cyanide-bearing microhabitats at tailings facilities are preying on terrestrial and airborne insects. Much of this foraging occurs on relatively inert dry tailings surfaces, while many insects are taken as they become trapped in the wet tailings surfaces in beach habitats. Such foraging strategies are typical of the bird species involved. These include endemic waders such as Red-capped Plovers, Masked Lapwings and Black-fronted Dotterels. These are water-related species, however, they are considered to be at relatively low risk at tailings dams as their foraging strategy at the water's edge limits their contact with supernatant solutions and therefore does not represent a high-risk exposure pathway. Airborne insects are taken in the airspace above tailings facilities by swallows, martins, swifts and bat species. As these species take their prey while on the wing, they do not have prolonged intimate contact with cyanide-bearing substrates. These species are also considered at reduced risk for this reason, although many are known to drink while on the wing by scooping water from the surface.

Donato (pers. comm. 2006) observed that both routine (by on-site mine staff) and intensive monitoring (in research in the ACMER project 'Risk Assessment of the Effects of Cyanide-Bearing Tailings Solutions on Wildlife') has recorded visitations by reptiles and amphibians to tailings storage facilities. The reported rates of visitation by reptiles and amphibians and visitation by terrestrial mammals such as kangaroos are far outweighed by records of visitation by birds and even by bats. While birds can be more conspicuous than reptiles and amphibians, relative proportions reported are not considered to be unrealistic. One explanation proposed for this is that the spatial scale of inhospitable habitats surrounding most tailing facilities is more of a deterrent to animals such as reptiles and amphibians than to birds and bats, which can fly in. This is especially the case for TSFs of a heaped paddock design and heap leach pads, which often stand some tens of metres above the surrounding environment and offer little vegetation cover on the external walls. Such environments are similarly inhospitable to most ambulatory mammals, which have little motivation to traverse them if alternative water sources are available. However, he notes that mammals, reptiles and amphibians may represent a greater proportion of visitations to surrounding infrastructure such as groundwater intercept trenches that are closer to surrounding natural habitats and usually have lower cyanide concentrations.

Smith and Donato (2007) indicated that terrestrial mammal species which may be present include macropods (kangaroos and wallabies), dingos and introduced mammals such as wild dogs, cats, goats, rabbits and hares, but that larger mammals are generally only recorded at TSFs that are not adequately fenced or when gates are left open. Reptiles are rarely observed during wildlife monitoring at TSFs, but larger reptiles such as monitor lizards have been recorded at a range of gold mining TSFs in Australia. The authors state that amphibians (e.g. frogs and toads) are relatively common at TSFs, despite the fact that they are rarely recorded, and that mortality due to interaction with cyanide-bearing waters is relatively common. They comment that it is virtually impossible to exclude reptiles or amphibians from entering and interacting with TSFs or other water bodies containing cyanide.

Read and Pickering (1999) reported a comparative study of the presence of certain plant, lizard and arthropod species in control areas and in an island of remnant vegetation within a tailings retention system at Olympic Dam (a site with no significant cyanide in the waste stream, described above). Differences between the

impacted site and non-impacted areas (absence in the TSF area of hopbush, gecko (Gekkonidae) lizards and a common ant species, presence of colonising plant species, *Helea* beetles and scorpions, with dragon (Agamidae) and skink (Scincidae) lizard populations apparently unaffected) were attributed to acid spray, with radionuclide accumulation also observed in some species. Thus, like other waterbodies, reptiles and invertebrates may potentially be attracted to waters at TSFs and associated infrastructure, which may in turn attract predatory wildlife species (e.g. whiskered tern; Donato, 1999).

As wildlife interaction with TSFs is well documented at various sites, the presence of heavy metals, other chemicals and high or low acidity do not appear to stop wildlife interacting with or ingesting tailings solutions (Smith et al., 2007). These observations have included situations where solutions typically have a pungent and strong smell that is detectable to human olfactory receptors.

Donato et al. (2007) reported that the species at risk in tailings environments are those that interact (drink, feed or roost) with or on cyanide-bearing habitats in the tailings systems, and that species habitat preference and behaviour determine the expected cyanide dosage and consequent risks. Smith and Donato (2007) discuss the habitats favoured by various bird guilds, bats and other animals and thus the points in TSFs to which they may be attracted and risks associated with their behaviour at TSFs, and aspects of heap leach facility habitat contributing to the risk to wildlife, including likely susceptible species.

7.3.2 Recent wildlife interaction studies in arid/semi-arid areas of Western Australia

Further detailed data are now available from ACMER and MERIWA project reports (Adams et al., 2008a,b,c; Donato and Smith, 2007) and published papers (Smith et al., 2008; Griffiths et al., 2009) for recent evaluations at saline and hypersaline gold mine sites in the Coolgardie bio-geographic region of Western Australia. The results confirm and add to the above comments by Donato (made at an earlier stage of the work). These include Granny Smith Gold Mine, Kanowna Belle Gold Mine, St Ives Gold Mine (see Section 6.6.4), Sunrise Dam, and the Fimiston I and II tailings storage facility to the Fimiston Open Pit (Kalgoorlie 'Super Pit'). These studies were very thorough and considered wildlife seasonality, with ecological data being collected during various climatic seasons and migratory seasons for wader species. Studies have involved daily observations by on-site personal (according to prepared protocols), as well as intensive observations by the investigators. These comprehensively indicate visitation rates, abundance and species composition over time at the TSF sites and also at freshwater, saline and hypersaline sites of various sizes in the vicinity (Kalgoorlie-Boulder sewerage works, Kambalda Wetlands, and various freshwater, saline and hypersaline waterbodies sush as seepage trences, dams and ponds and lakes). Bird behaviour (e.g. feeding, drinking, preening, locomotion, resting/roosting or patrolling, including some observations of individual bird behaviour over 15 minute intervals) and habitat usage (e.g. supernatant, wet tailings, dry tailings, tailings stream, dry tailings/stream, beaches, aerial and walls) were also recorded. Aquatic macro-invertebrate sampling and aerial and terrestrial invertebrate sampling data were also collected. Thus the interaction of birds (and limited interaction by terrestrial mammals) with TSFs in arid regions of Western Australia is particularly well known.

For example, discussion drawn from Adams et al. (2008b,c) indicates the following - A cumulative total of 5710 wildlife visitations were recorded by on-site and third party

monitoring within the TSFs between 16 May 2006 and 31 May 2008. Guild composition was found to reflect the primary habitats present within the three TSFs, airspace over the TSF, tailings and supernatant. Diurnal wildlife visitations consist primarily of ducks (including Black Swan), endemic waders (primarily Red-capped Plover) and swallows. Swallows are common throughout the surrounding environment and were observed at most waterbodies surveyed. The comparative lack of ducks and other waterbirds despite the presence of supernatant is likely to be influenced by hypersalinity, absence of food and physical features of the TSF. Raptors and corvids were not common within the TSFs but are generally not common within the local environment. Raptors primarily used the TSFs for perching on walls or for flying over, at times to take advantage of the lift generated from heat rising from the TSF cells (primarily in summer). The small numbers of bush birds, granivores and terrestrial mammals (common in the surrounding environment) is a reflection of the lack of vegetation and hypersalinity within the TSFs. Most records of these guilds are either flying overhead or using TSF walls. Richards Pipit, which was recorded at all sites, is a bare ground specialist and works the walls of the TSFs.

In summary, the authors stated that the three TSFs can be described as ecologically and physically simple, being saline or hypersaline, devoid of complex habitats, devoid of vegetation, containing no aquatic macroinvertebrates and minimal terrestrial macroinvertebrate food resources for wildlife, and that the tailings systems can subsequently be described as low wildlife visitation and interaction systems.

The investigators concluded from their observations of the three sites that:

- wildlife recognised as at-risk are present;
- supernatant solutions are essentially devoid of live aquatic macroinvertebrates;
- terrestrial and aerial macroinvertebrates of varying class sizes are present on the TSFs and provide a limited food resource to wildlife (e.g. insects that have landed on, or have crawled or been blown onto and become embedded in the surface of supernatant, ponding, wet tailings and mud);
- the presence of wildlife is influenced by habitat and food provisions;
- hypersalinity inhibits wildlife drinking although some species can, under extreme conditions, tolerate some of the lower salinities recorded at the Granny Smith site (saline rather than hypersaline);
- hypersalinity influences the species that visit the TSFs; and
- vertebrate wildlife, primarily birds and bats, inhabit or interact with tailings solutions to a far lesser extent than they do at nearby fresh water bodies.

Thus very little or no food was available for species that obtain their food from within the water (for example ducks, terns and herons) and no wildlife were observed to successfully obtain food from the supernatant. However, some ducks, Black Swan and endemic waders were briefly observed attempting to forage. Terrestrial and aerial invertebrates were the main and possibly only source of food for vertebrate wildlife within the TSFs.

Foraging behaviour was consistently observed for Red-capped Plovers and Swallows when they were in the system, but was observed for other species as well. Food was continually present for Red-capped Plovers at the Granny Smith and Kanowna Belle sites, but foraging rates varied between the systems. While Red-capped Plover

numbers fluctuated, some individuals appeared to be actively foraging in these systems on all (or most) days and were considered to probably do so all year round. Swallows do not appear to live wholly in any TSF but to regularly visit and obtain food from all three systems on most days in all seasons.

The diversity of terrestrial invertebrates was simplified at the hypersaline TSFs compared with alternative water bodies, primarily due to lack of nearby vegetation, hypersalinity, and the facility being raised above the surrounding terrain. The abundance and composition of macroinvertebrate taxa was variable and expected to vary on a seasonal basis. Foraging behaviour was observed for many guilds at a number of alternative waterbodies. Red-capped Plovers and swallows were observed foraging at both fresh and hypersaline waterbodies.

Various species visit these areas at night (e.g. waterfowl and bats), when they may not be seen, but can be heard or detected by other means, e.g. audio recording devices/ echolocation data loggers. These log the frequency, number and time of bat calls and enable species to be identified and calls to be differentiated into navigation calls and foraging 'buzz' calls which can indicate feeding, drinking or social behaviour. Insectivorous bats were recorded in the airspace above all water bodies surveyed, but much less so over the TSFs evaluated than above noncyanide-bearing water bodies. The ratio of buzz/cruise calls at non-saline water bodies was also higher than that recorded at hypersaline supernatants, indicating that the level of feeding, drinking and social contact is less at hypersaline TSFs and water sources, compared to fresh water sources, consistent with the greater presence of food resources at freshwater bodies. However, whether there is some nocturnal interaction with tailings by bats or other avifauna could not be determined, though nocturnal interaction with TSFs by avifauna is expected.

The level and nature of the interaction at these freshwater bodies was dependent on physical features, presence of/distance to vegetation, water palatability (salinity), size and provision of food resources (vegetation and macroinvertebrates). Turkeys nest and stock dams (small farm-type dams) surrounded by vegetation that had few or no waterbird visitations but significant numbers of terrestrial birds, mammals and bats drinking from them. The larger waterbodies, containing aquatic plants and macroinvertebrates (particularly Kambalda wetland) often had waders, waterbirds and large numbers of ducks (several hundred) foraging and resting in them and terrestrial and aerial wildlife utilising them for food and drinking. Wildlife at alternative hypersaline waterbodies generally had considerably less wildlife diversity and abundance and a different guild composition than the freshwater bodies. Where hypersaline habitats mirrored those in the TSF, such as wet hypersaline mud at the saline wash and Lake Carey (both at Granny Smith), wildlife visitations were dominated by Red-capped Plovers with some migratory waders and swallows. Open pits that contain hypersaline water were generally dominated by aerial species and wildlife using the pit edge, with just four ducks in total recorded at the hypersaline waterbodies. The guild composition of the hypersaline waterbodies was similar overall to that of the TSFs. The Granny Smith seepage trench had a high diversity but many of these species were associated with vegetation on the trench walls.

Results at Sunrise Dam (Donato and Smith, 2007) and Fimiston (Smith et al., 2008; Griffiths et al., 2009) were comparable to the above.

7.3.3 Exposure of wildlife at tank leach operations

Mill and tank leaching sites

Continuous noise and human activity are likely to discourage most birds and animals from the immediate vicinity of an active mill and tank leaching facility, but they may visit or inhabit the area near active mine sites and may also enter areas when mines are temporarily or permanently closed. For example, birds may perch or nest on tall mining structures or nest in dune cuttings and stockpiles of soil or rock, or use updrafts associated with mining stockpiles for soaring (see above). Animals and birds could conceivably come into contact with cyanide residues in tanks or protected storage areas if appropriate clean-up and removal procedures have not been taken during closure and containment is subsequently breached. Similarly, aquatic organisms could be exposed in areas downstream of such a site through contaminated rainfall run-off.

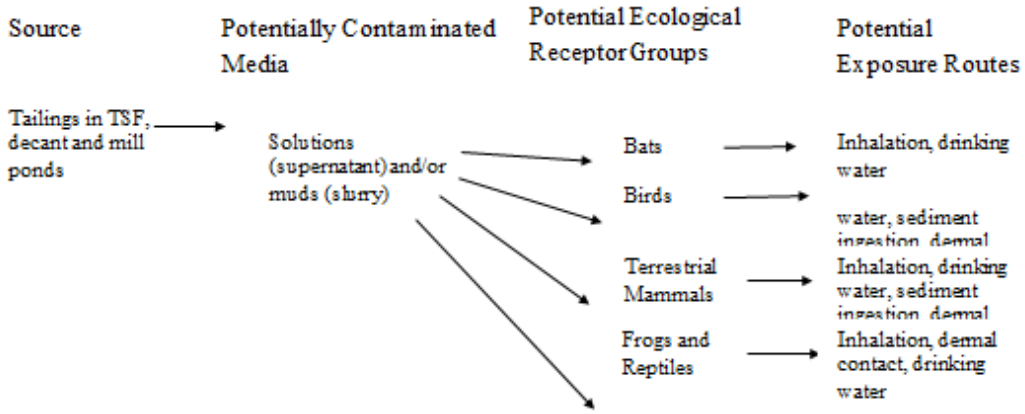
Tailings storage facilities and associated infrastructure

Birds and terrestrial organisms

Figure 7.1 provides a conceptual model of potential ecological receptors and exposure pathways at a generic TSF.

Exposure via multiple pathways, and to multiple forms of cyanide including free and various complexed cyanide forms, thiocyanate and cyanate, may occur concurrently if present together. In addition, wildlife may be exposed to a mixture of other chemical constituents in tailings.

Figure 7.1. Conceptual terrestrial wildlife exposure model for a generic TSF



Secondary exposure of predatory or scavenging wildlife could occur through the consumption of exposed prey. Metabolism within the animal together with the acute action of cyanide limit the concentrations that might be present in flesh with acute exposure. Similarly, with chronic exposure free and WAD cyanide compounds are unlikely to bioaccumulate in animal tissues (Eisler et al., 1999). Hence the risk of secondary exposure to predatory and scavenging wildlife is limited, though exposure could potentially occur to less toxic metabolites (e.g. thiocyanate) of cyanide, as well as cyanide that has not been metabolised to thiocyanate. Incidental exposure could occur through consumption of cyanide-contaminated gut contents or ingestion of solutions and/or sediment bound to prey and carcasses. As noted earlier, the presence of carcasses is also a potential factor in attracting scavengers to a TSF, where they may then receive primary exposure.

Exposure to cyanide in tailings in TSFs by wildlife may potentially result from:

- ingestion of waters containing cyanides (i.e. direct consumption as drinking water);
- incidental ingestion or contact with cyanides in water and sediment during feeding (e.g. filter-feeding waders and other benthic-foraging birds);
- inhalation of cyanide gas (i.e. HCN) or dust; and/or
- skin contact (dermal absorption) with cyanide-containing waters.

Adult birds that have been exposed orally (e.g. consumed waters or sediments) at TSFs may potentially expose their young to cyanide compounds during feeding (i.e. regurgitation of swallowed water/sediment).

It is evident (Section 6.6.4) that WAD CN concentrations in TSF discharge water, supernatant water and/or decant pond water can range widely, from as low as 1 mg WAD CN/L to well above 100 mg WAD CN/L (as high as ~600 mg WAD CN/L) at exceptional sites or under exceptional conditions. Within this range, there are data for a number of sites with ~100 mg WAD CN/L, i.e. significantly above the ICMC 50 mg/L standard (ICMI, 2006; Section 11.12.4). With increasing adoption of the ICMC, the majority of sites have or are likely to have a WAD CN concentration of 50 mg/L in the decant pond and other areas accessible to wildlife, with the possible exception of hypersaline sites (Section 9.9.2, Section 5.2.3). At sites in sensitive areas, e.g. in Tasmania, where potential aquatic exposure needs to be managed, cyanide is destroyed as far as possible, producing tailings discharge levels as low as 10 mg/L or less. Some sites may have an intermediate level of destruction due to government requirements, e.g. 20-30 mg/L in discharge, or may aim at achieving a limit such as 30 mg/L in the decant pond (e.g. to provide greater confidence that the 50 mg/L limit is consistently met).

Aquatic organisms and secondary exposure of terrestrial organisms through downstream flow

Exposure to aquatic organisms is not a concern in the TSF or associated dams and ponds used for storage of decant, process or drainage water on the site (any impacts on amphibians, which may be mobile between various ponds and waterbodies, would be expected to be localised to a small area), but is a possible concern if downstream areas were to be contaminated. Fish, aquatic invertebrates, algae and plants could then be exposed to cyanide residues, and this is also a possible secondary route by which birds and animals could be exposed.

Rainfall could produce excessive run-off or overflow from a TSF or associated facilities, potentially leading to downstream flow that may enter waterbodies or watercourses and lead to exposure of aquatic organisms to cyanide residues. Aquatic and terrestrial areas could also be potentially exposed to liquid and fine suspended solid material through failure of a TSF.

Many gold mines in Australia are located in arid regions, where the risk of cyanide contamination affecting aquatic organisms is low. However, other mines are located in temperate or sub-tropical and tropical areas, where rainfall may occur at various times during the year or predominantly in summer months. Even in arid areas, it is possible that storms could lead to run-off that could impact intermittent creeks or other areas containing vegetation and ground-dwelling animals, or areas with transient aquatic ecosystems, such as salt lakes in WA.

These events could produce a wide range of WAD CN concentrations, depending on the source and amount of dilution.

7.3.4 Exposure of wildlife at heap leach operations

The information available indicates that heap leach operations may attract wildlife principally due to the potential availability of surface water habitat for drinking and other purposes. Frogs may be attracted due to the presence of aquatic habitat, particularly after heavy rainfall. Operations providing wildlife with limited access to process solutions and drainage are unlikely to pose a risk to wildlife health under normal operations. While various incidents and impacts on wildlife have occurred overseas with heap leach operations (Sections 5.4.3 and 9.9.1), no reports of such incidents or impacts occurring in Australia have been seen. Figure 7.2 provides a summary of potential ecological receptors and exposure pathways at a generic heap leach operation. This provides a conceptual exposure model for wildlife at heap leach operations.

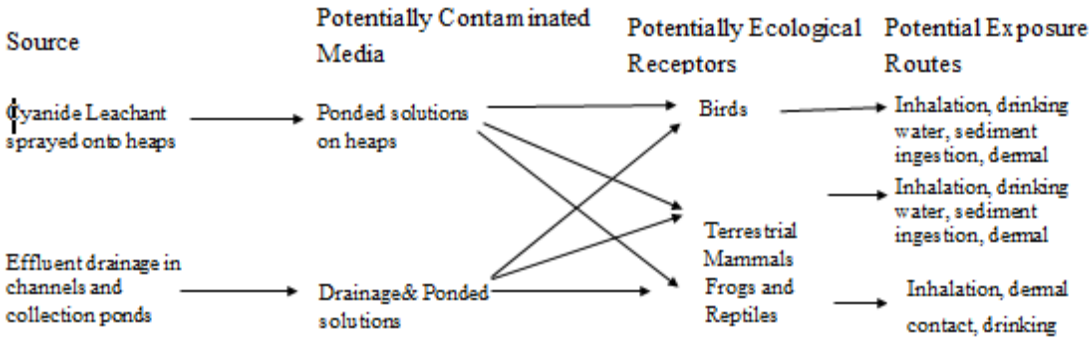
During cyanidation at heap leach operations, cyanide solutions are sprayed or sub-surface infiltrated onto the ore heaps. Ponding of cyanide solution on top of ore heaps has historically been reported, and wildlife mortality incidents have occurred after drinking this ponded solution (Henny et al., 1994). No data were available on the incidence of ponding in Australia.

Heap leach operations are relatively uncommon in Australia and much of the data available pertains to mines in the USA. Reported free cyanide concentrations in solutions added to ore piles or found in ponds at the top of ore piles range up to 1120 mg CN/L (Sparrow and Woodcock, 1988; Smith and Mudder, 1993; Henny et al., 1994; ERA Environmental Services, 1995; Staunton, 1991d), though typical levels are stated to be 250-500 mg/L by USEPA (1994). Ponding of cyanide solutions on ore heaps is not desirable operationally due to the potential for loss of cyanide and heap slumping (collapse).

WAD cyanide concentrations in heap leach drainage effluent, and the proportions of free and weakly complexed cyanide are likely to be variable (temporal and spatial) within and between different heap leach operations. Smith and Mudder (1993) reported concentrations of WAD cyanide in drainage channels of ~130 mg/L. ERA Environmental Services (1995) reported WAD cyanide concentrations in a pregnant liquor pond of 200 mg/L, and ~30 mg/L in a drainage channel. Laboratory-based soil column tests (Staunton, 1991c) suggest some soil types have 20% to 60% attenuation capacity for WAD cyanide, suggesting that discharges from ore heaps are generally likely to be $\leq$ 150 mg/L.

There are similar aquatic exposure and secondary wildlife exposure possibilities with heap leach facilities to those discussed above with TSF facilities, i.e. through run-off, overflow of ponds and dams, or collapse of the heap. Again, these events could produce a wide range of WAD CN concentrations, depending on the source, changes as the contaminated material moves downstream and amount of dilution.

Figure 7.2. Conceptual exposure model for terrestrial wildlife at a generic heap leach facility



7.3.5 Exposure from groundwater contamination

Depending on the receiving environment's hydraulic down gradient, ecological receptors potentially exposed to groundwater in the vicinity of TSFs and heap leach operations may include vegetation (via root contact) and other soil-dwelling organisms. Seepage may also discharge to surface waters inhabited by aquatic organisms and wildlife. Groundwater may also be extracted for a range of beneficial uses (e.g. livestock watering, irrigation).

However, generalisation of the potential for groundwater contamination is not possible for all TSF and heap leach operations in Australia due to the need to consider site-specific factors and operational controls at TSFs that limit seepage and contaminant migration in seepage. For instance, groundwater may or may not occur near to or discharge to the surface. The level of protection needed may also vary with the water quality, e.g. a lower level of protection is warranted where the natural groundwater is already hypersaline. Natural attenuation and degradation processes act upon cyanide compounds in soils. Operational and post-closure practices (e.g. engineering controls to intercept seepage and/or limit contaminant migration) will affect the potential for migration in seepage. Furthermore, groundwater monitoring is widely practiced to enable detection and rectification of contamination should it occur.

Results from groundwater monitoring at a range of Australian gold mines give a reasonable degree of confidence that total CN levels in groundwater are usually relatively low and restricted to the immediate vicinity of TSFs, with some cases where concentrations of total CN are higher, but controlled by active measures to limit spread of the groundwater (e.g. down slope or along old creek lines). In the worst cases, borefields with large numbers (up to scores) of recovery bores are in use to control groundwater depth and flow, but in all cases detections of WAD CN above background levels (0.01 mg/L) were restricted to at most 100-200 m around a facility, and generally much less, and movement of CN into the general groundwater was being satisfactorily limited. Sites generally showed a rapid decline in WAD CN (and total CN, where it was also recorded) with increasing distance from a TSF, and there was evidence that this was due to breakdown or fixation rather than dilution in moving groundwater.

The sites fell into the following general categories, which reflect the concentration of CN in the TSFs and other ponds, but evidently also reflect the adequacy of design of the storage facilities and local soil/lithography/geological etc conditions. At some sites there were differences between older and newer paddock TSFs, due to factors such as improved TSF design and steps to control CN levels in the slurry and/or dam, and between paddock TSFs and in-pit TSFs, e.g. due to greater difficulties in managing deposition into old pits where conditions favour seepage.

- Sites with very low WAD CN concentrations (<0.01 mg/L) in groundwater, even in close proximity to TSFs (e.g. a site where the INCO process was used).
- Sites with all samples always or almost always meeting the 0.5 mg/L WAD CN license limit at all bores surrounding paddock TSF and in-pit facilities. These sites varied widely in the extent to which measures such as trenches to intercept surface seepage and recovery bores to intercept water movement under the surface were required.
- Sites with some bores/piezometers in localised areas adjacent to a TSF somewhat exceeding the 0.5 mg/L WAD CN limit at times. These sites again varied widely in the extent to which measures such as trenches to intercept surface seepage and recovery bores to intercept water movement under the surface were required, but in all cases movement of cyanide further away from the vicinity of the TSF was adequately controlled.
- One case, where there was continually a very high CN concentration in the TSFs, leading to very high WAD CN levels (>100 mg/L) in groundwater near the TSFs, and where extensive measures (a borefield with numerous bores and with interception trenches) are needed to intercept seepage, limiting the high WAD CN concentrations to the vicinity of the TSF.

Overall, the data from these sites with active and/or closed TSFs indicate that cyanide is not impacting significantly on groundwater, though this may not have been the case without the ongoing, active protective measures in place to control groundwater. Lateral and downward movement of CN residues is evidently limited by degradation and fixation into insoluble forms (in some situations this may be affected by naturally acid conditions in groundwater). Where dam design and local hydrology/hydrogeology lead to significant seepage, excessive rising of the watertable and/or movement of seepage water is prevented by appropriately placed recovery bores, ranging from a few bores to large borefields, with the placement and number of bores guided by ongoing monitoring. There was evidence of declining levels after deposition to a TSF ceased, due to degradation in situ and dilution, rather than transport away. In comparison, there is evidence that other impacts of TSFs extend further and can be expected to take much longer to dissipate.

The value and necessity of installing and operating monitoring bores and the effectiveness, if needed, of interception bores is clearly demonstrated, though in most situations appropriate design and construction of TSFs should avoid the need for extensive interception operations. In addition to free CN and WAD CN, monitoring of total CN may be appropriate to detect movement of iron cyanides, and some monitoring may be appropriate for breakdown/reaction products such as thiocyanate, e.g. where ore conditions or tailings treatments may lead to significant concentrations being present; nor should it be assumed that groundwater movement will only occur down-gradient (Schulz, pers. comm. 2006).

The available data indicate measured levels in groundwater in the immediate vicinity of TSFs in Australia ranging from < 0.01 to > 100 mg/L WAD CN, but the measured concentrations fell to low levels by 100-200 m from the measured TSFs.

7.3.5 Exposure during release of HCN to the atmosphere

Apart from tailings slurry, emissions of cyanide from mine ore processing facilities are mostly directed to air as HCN, and overall the loss of HCN to air during processing is only very minor (~1%-2% - Section 4.4.2). Precautions such as personal and air monitoring devices are taken for human health reasons within hazardous areas of the mill facility, but in exposed areas HCN released to air rapidly dissipates to levels safe to human health. Run-off of water from the general mill area could occur following rain and could potentially impact downstream if not captured and directed to appropriate storage facilities, such as the TSF and associated dams or ponds. Incidents such as spills are managed promptly by recovery and re-use, or by detoxification with ferrous sulphate followed by collection and disposal to tailings. With temporary or permanent closure, under current legislation, state environmental agencies require mines to ensure areas of the mill which have potentially been contaminated with cyanide to be cleaned-up as part of the general site restoration, with treated waste most likely disposed of in tailings facilities, as occurred at Kidston Mine in Queensland (Environment Australia, 1998). Hence there is low potential for wildlife to be exposed to toxic levels of HCN, provided appropriate steps are taken to clean-up sites when mills are being closed.

Globally, Korte et al. (2000) suggested that the formation of open ponds should be avoided with the gold cyanidation process because of the large amount of HCN evaporating yearly from their surfaces, which they considered could accumulate in the atmosphere and may add to the contribution of other climate-active compounds in the air, such as CO_2 and methane. However, HCN is not currently listed among other gases in the atmosphere which are considered to have significant Global Warming Potential (USEPA, 2006a), and is not a significant source of other gases which are considered to be greenhouse gases (e.g. N_2O). HCN is also not considered likely to act significantly either directly or indirectly as an ozone depletor (Cicerone and Zeller, 1983; Lary, 2004).

HCN release to the atmosphere from gold mining use is also relatively minor compared to other sources, based on modelling of measured levels in the atmosphere (Section 6.3.3). There was a significant increase in use of sodium cyanide as a consequence of the rapid expansion during the 1980's in the amount of gold produced by heap leaching in the USA (Eisler and Wiemeyer, 2004), but any impact on HCN levels in the atmosphere as a consequence of this increase in use would therefore be expected to be very minor.

The estimated atmospheric lifetime for HCN is ~2-6 months (Section 6.3.3), consistent with comparisons of data over time which show an annual maximum thought to be associated with peak biomass burning emissions, e.g. fires in tropical savannah regions of Africa and South America during August to October (Rinsland et al., 2005). Data for tropospheric HCN above Kitt Peak, Arizona showed enhancement during the strong El Niños of 1982-1983 and 1997-1998 (associated with biomass burning), but there was no statistically significant long-term trend detected over the 22 year measurement period (Rinsland et al., 2001).

Thus it appears clear that annual and short term changes in tropospheric HCN concentrations are largely associated with differences in the extent of biomass burning over and between years, and that contributions from sodium cyanide use are very minor. Continuing gold mine use of NaCN is unlikely to lead to a significant increase in atmospheric HCN concentration or lead to harmful effects on climate or ozone depletion.

7.3.6 Total exposure for wildlife from gold mining use

Wildlife may potentially be exposed to one or more contaminated environmental media, and multiple exposures may occur concurrently (e.g. oral, inhalation and dermal). Donato (1999, citing *Reece, 1997) notes that it is known that cyanide is readily absorbed through skin, so birds wading or swimming in contaminated water may absorb quantities sufficient to be toxic. Cyanide is known to show ocular toxicity to mammals (Section 9.3.1) and therefore could presumably affect birds by that route also.

In general, the total exposure potential may be expressed using the following equation:

$$\text{Exposure}_{\text{total}} = \text{Exposure}_{\text{oral}} + \text{Exposure}_{\text{dermal}} + \text{Exposure}_{\text{inhalation}} \quad \text{(Eq. 1)}$$

Various body traits and behaviour differences between birds may affect the extent to which they are exposed to these different routes of exposure. For example, features such as oily fur and feathers and toughened skin, are likely to reduce the potential for skin contact with environmental media and absorption (Sample et al., 1996). Donato (pers. comm. 2006) suggests that the feet of floating or wading birds may be a potential area of uptake, but that many species can control the circulation to their feet so they can tolerate cold conditions, and this may help limit uptake. The observations by Read et al. (1999) that waterfowl remained on acid liquid evaporation ponds at Olympic Dam (Section 7.3.1) would appear to show a lack of sensitivity, but in that case there are bird deaths associated with the exposure even though birds do not drink the highly acidic water (pH < 1.5).

Birds differ in the types of habitat that they prefer for feeding, drinking, nesting or safety, and this affects whether or not they are attracted to a TSF or dam and the nature and extent of potential exposure that may follow (see Section 11.13). Species which dive or look under the water (e.g. grebes and hardhead (*Arytha australis*)) would be expected to have a greater skin surface and ocular exposure than other waterbirds (Donato, 1999; Read, 1999).

Bird species also differ in the potential nature of exposure according to their drinking behaviour. Species such as terns drink on the wing and do not remain for extended times on the water, while others may drink from the water's edge or from access points such as sticks. In contrast, waterfowl may remain for extended periods in a waterbody. Hence waterbirds may have significantly greater contact exposure to cyanide residues in water than other species. However, Donato (pers. comm. 2006) notes that his observations at gold mine TSFs suggest that birds need to drink from the water before they exhibit signs of cyanide toxicity and are not harmed if merely walking at the edge, and that it is more through intermittent drinking while floating on the water that waterfowl are affected, rather than simply skin contact (e.g. this is evident from observations of cyclical stupefaction: Section 9.2.1).

Although all potential exposure pathways have been considered in this assessment, the oral (i.e. drinking water) exposure route is considered the most likely and most

important pathway. Difficulties in quantifying wildlife exposure and uptake due to incidental ingestion of sediment, inhalation and skin or ocular absorption also limit the extent to which these potential exposure pathways could be evaluated in detail, but ingestion of supernatant is considered to present the greatest risk.

Daily exposure of wildlife to cyanide through the oral route, normalised to body weight, may be estimated using the following equation:

$$\text{Total Exposure } (E_j) = \left(\sum_{i=1}^{m} (I_i \times C_{ij} \times B_{ij})/bw\right) \qquad \text{(Eq. 2)}$$

Where:
E_j = total exposure to contaminant (j) (mg/kg-bw/day);
m = total number of media (e.g. surface water);
I_i = intake (ingestion/inhalation) for medium (i) kg/kg-bw/day or L/kg;
C_{ij} = concentration of contaminant (j) in medium (i) mg/kg;
B_{ij} = bioavailability of the contaminant (assumed 1 for free and WAD cyanide)
bw = body weight (kg wet weight).

Reported concentration ranges of cyanide compounds in TSFs and heap leach operation solutions range widely. Hence, values for C_j in the above equation will be based on the typical values described in Sections 7.3.1 and 7.3.4 (Table 10.1).

Table 7.1. Potential cyanide concentrations in mine site process solutions and wastes

Source	Potential concentration range (mg WAD CN/L)
Worst case	600
ICMC target	50
Current intermediate targets	20 to 30
Largely complete cyanide destruction	1

Values for intake factors (i.e. water ingestion rates; I_{water}) have been measured for few wildlife species. As such, exposure of wildlife species has been estimated using models based on allometric equations of intake parameters. Allometry is defined as the study of the relationships between the growth and size of one body part to the growth and size of the whole organism.

Drinking water intake rates

Sources of water for animals include free (drinking) water, metabolic water derived from the breakdown of food, and water moisture in food, and the total contribution of water intake may be derived from one or more sources concurrently.

Most Australian wildlife drink water from surface water bodies when available, but intake rates vary within and among species depending on individual requirements and the species' physiological adaptation to climatic conditions. However, few data are available on drinking water intake rates of Australian wildlife. Daily water requirements of wildlife depend on their rate of loss of water to the environment due to evaporation and excretion, which may vary spatially and temporally for individual animals or species. Water evaporation and excretion rates depend on several factors

including body size, ambient air temperature, and physiological and behavioural adaptations for conserving water. Many drier climate species have physiological adaptations to reduce drinking water requirements when conditions are harsh.

Taking into account dietary and metabolic water intake rates, Calder and Braun (1983) developed a general allometric equation for drinking water intake (I_{water}) by birds that is based on body weight as follows:

Avian Water Intake Rate (I_{water}; L/kg-bw/day) = $(0.059 \times bw^{0.67})/bw$ (Eq. 3)
Where bw = body weight (kg wet weight).

Calder and Braun (1983) obtained data from 21 northern hemisphere avian species of between 0.011 to 3.15 kg body weights to develop Equation 3. As an example, a 1 kg bird may drink ~60 mL of water each day. USEPA (1993) notes that this equation (and that for mammals below) is for drinking water, rather than total water available to the animal from the additional sources of metabolic water and water contained in food, which also help to balance the animals' daily water losses.

In general, birds drink more water at warmer ambient temperatures to make up for evaporative losses. Seibert (1949) found that Juncos (weighing 16-18 g) consumed an average of 11% of their body weight in water daily at an ambient temperature of 0°C, 16% at 23°C and 21% at 37°C. The white-throated sparrow increased water consumption from 18% of its body weight at 0°C to 27% at 23°C and 44% at 37°C.

Water consumption rates per unit body weight tend to decrease with increasing body weight within a species. In leghorn chickens, water intake is highest in young chickens (45% of body weight at 1 week old or ~62 g) to 13% at 16 weeks or ~2.0 kg. Water consumption also increases during the egg production period (Medway and Kare, 1959).

Based on measured body weights and drinking water intake from Calder (1981) and Skadhauge (1975), Calder and Braun (1983) developed an allometric equation for drinking water intake rates for mammals as follows:

Mammal Water Intake Rate (I_{water}; L/kg-bw/day) = $(0.099 \times bw^{0.90})/bw$ (Eq.4)
Where bw = body weight (kg wet weight).

Equations 3 and 4 are used in the USEPA Wildlife Exposure Factors Handbook (USEPA, 1993) and have been used to estimate drinking water intake rates for avian and mammalian wildlife species for this assessment. These water intake rates are considered estimates only and daily water intake by birds and mammals may be more or less than estimated, particularly depending on environmental conditions (e.g. temperature).

NTP (1993) reported that rats (0.225 kg average wet weight) consumed ~25 mL of drinking water per day under laboratory test conditions. This approximates the value estimated using Equation 4 (i.e. ~26 mL/day) for a mammal of similar body weight.

Drinking by wildlife may occur once or at a number of times during the day, and consequently the amount consumed at a particular time may be all or part of the total daily requirement. The frequency and time of drinking water depends on the individual (e.g. condition, gender, size, reproductive status), species and environmental conditions. Daily drinking frequency is critical to estimating risk to wildlife species from cyanide due to the potential for metabolism of small repeat doses without adverse effects. In addition, risk estimation is also influenced if an animal drinks from multiple

sources of surface water each day, the dose received is likely to be less than if the animal drank from only one source, assuming most sources are not contaminated with cyanide. For this assessment, it is assumed that the daily water requirements for wildlife are obtained only from the specific source types being evaluated (e.g. TSFs, decant ponds, heap leach facilities).

No cyanide-shyness or induced aversion has been assumed in this assessment when estimating exposure of wildlife to cyanide in environmental media. As discussed further below, animals do not appear to develop an aversion to cyanide despite experiencing harmful sublethal effects. There is some information to suggest that palatability of water to wildlife may be affected by high concentrations of cyanide or possibly other constituents in tailings waters (Section 9.2.2), but the extent to which this would limit consumption in the field cannot be determined and would presumably be affected by the availability of more attractive fresh water sources. Similarly, high salinity may limit the suitability of water for drinking. In particular, studies confirm that hypersalinity prevents consumption of tailings water containing cyanide residues (see Section 9.9.2), but in Australia that situation pertains only to certain areas of Western Australia where groundwater used for ore processing is hypersaline.

Field studies support the view that wildlife do inhabit areas containing cyanide solutions and that wildlife have been exposed to cyanide in these solutions. The behavioural traits of cyanide-shyness or induced aversion have not been demonstrated to occur in a representative range of wildlife species. Further consumption of contaminated water may occur even after a bird has been affected by an initial drink (Sections 9.9.2 and 9.2.1). Of the species assessed in cage and field studies (e.g. brushtail possums in New Zealand), a high proportion of individuals (up to 88%) did not exhibit cyanide-shyness when it was administered orally (60% w/w NaCN paste) and most possums subjected to sublethal oral doses of cyanide did not develop permanent cyanide aversion or avoid repeated exposure (O'Connor and Matthews, 1995; Warburton and Drew, 1994).

The apparent inability of cyanide to induce any learned aversion is supported by studies in rats (Ionescu and Buresova, 1977; Nachman and Hartley, 1975). O'Connor and Matthews (1995) suggest that induced aversion to cyanide in possums may be directly proportional to dose, and doses ≥5 mg/kg body weight resulted in >50% of surviving possums developing an aversion irrespective of route of exposure (intraperitoneal or oral) or type of cyanide formulation used (e.g. NaCN solution, NaCN paste, KCN pellet). However, variability of induced aversion amongst individuals was higher as dosage increased, and a proportion of possums did not develop any aversion. In an environment with multiple wildlife species, concentrations capable of inducing cyanide aversion in some animals may potentially induce greater adverse effects in more sensitive animals/species. Wildlife species may not have the time to develop an aversion to cyanide solutions (e.g. during migration) or the ability to avoid ingesting surface waters in areas where alternative surface waters are scarce.

The presence of heavy metals, other chemicals and high or low acidity also do not appear to stop wildlife interacting with or ingesting tailings solutions, including situations where solutions typically have a pungent and strong smell that is detectable to human olfactory receptors (Smith et al., 2007).

The allometric equations (Equations 3 and 4) and a range of environmental concentrations (based on Table 10.1) have been used to estimate the potential exposure of wildlife to cyanide in mine site facilities (Table 10.2).

Investigations of the drinking behaviour of various species were reviewed by Smith et al. (2007). Birds adapted to arid conditions in Australia that are reliant on standing water for drinking on a daily basis may drink up to four times per day in excessively hot or dry conditions (based on observations of only a single species, not indicated in the review). At many locations, some species did not drink every day despite hot and dry conditions. Among Australian Estrildid finches, many individuals visit water bodies to drink only once per day and there is evidence that Pictorella Mannikin and Gouldian Finch are able to imbibe most, if not all of their daily requirement in one drinking bout. Granivorous species are the most dependent on water, and they are also the most abundant avian group in the arid parts of Australia in localities where surface water is available. Nectivorous birds drink regularly, however, carnivorous and insectivorous birds are largely independent of water, and many small insectivorous birds appear never to drink. Thus, the worst case assumption that a bird may obtain all its daily water consumption on a single visit is not unrealistic.

Table 7.2. Summary of potential oral (drinking water) exposure to cyanide in mine site process solutions and wastes by wildlife (0.01-1.5 kg body weight)

Existing or target concentration	Potential concentration (mg WAD CN/L)	Estimated Dose (mg CN/kg-bw/day)	
		Mammals	Birds
Worst case	600	57-94	31-162
Common past practice	100	9.5-16	5.2-27
ICMC target	50	4.8-7.8	2.6-14
Intermediate targets	30	2.9-4.7	1.5-8.1
	20	1.9-3.1	1.0-5.4
	10	1.0-1.6	0.5-2.7
Largely complete cyanide destruction	1	0.1-0.2	0.1-0.3

7.4 Exposure from flotation use in base metal ore processing

Waste produced in base metal flotation processes flows to tailings dams, hence there are similar potential routes of environmental exposure to those arising from cyanide use for beneficiation in gold mines. From the limited information obtained, the quantities used annually at each site are much lower than is generally the case with gold mine use, though the concentrations used may range towards similar levels (50-250 g/t ore processed, compared to 100-500 g/t for gold). In most cases, a high percentage of the cyanide used is converted to insoluble metal complexes during use, whereas before further treatment, a significant amount of free cyanide may remain in tailings from goldmine use. Thus, significant exposure of wildlife to cyanide in the tailings appears less likely, and consideration of environmental exposure from goldmine use in tank leaching systems should adequately cover potential exposure resulting from base metal flotation use.

7.5 Exposure from electroplating, metal cleaning and metal surface treatment

These processes occur at enclosed industrial sites, generally with any unconsumed cyanide being treated to destroy it prior to disposal (Section 5.2.5). Hence, potential exposure of wildlife is limited to exposure to waste delivered to landfill or released to the sewer if the waste were not adequately treated prior to discharge.

7.6 Summary of environmental exposure assessment

Manufacture, transport and storage

Sodium cyanide manufacturing facilities in Australia are located in industrialised areas, where there is limited habitat for wildlife. These facilities must meet strict operational requirements managed by environmental agencies and/or local councils. There are licence limits on emissions of gases and particulates to the air or cyanide or nitrogen-containing substances formed from cyanide to water. To meet these, where possible cyanide is recovered and returned to the NaCN process, otherwise waste streams are treated to destroy cyanide residues. These measures are expected to prevent exposure of wildlife to harmful levels of cyanide.

Wildlife should not normally be exposed to cyanide during the transport, delivery and storage of NaCN. However, wildlife could potentially be exposed through an accident, leakage or other incident during transport. The extent of exposure would depend on the amount of cyanide released and the clean-up action taken. Delays in reacting to an incident and completing recovery/destruction of cyanide spills increase the risk of environmental contamination spreading or wildlife being exposed (e.g. by drinking pooled water, or contamination of a pond or stream).

Wildlife exposure through use in gold mining

Tailings Storage Facilities (TSFs) and associated infrastructure may provide habitat for wildlife and may also be accessed by livestock. Habitat in and around a TSF may be attractive to various species for swimming, diving, roosting, foraging, breeding and protection from predators. TSFs and their surroundings may provide various food sources, including terrestrial and airborne insects, live prey and carcases for raptors, and in poorly managed tailings facilities, potentially also phyto- and zooplankton and aquatic macroinvertebrates. TSFs and associated ponds may attract wildlife as a source of drinking water, particularly when there are few alternative water sources available, such as in arid areas. Poorly managed tailings facilities are therefore a major source of environmental exposure.

Studies have identified a large number of bird species at TSFs at gold mines or other mining operations, including species such as waterbirds and waders which spend significant time in or near water, ranging to species which fly in once or twice per day to drink, and including protected wildlife species. Various species visit at night (e.g. waterfowl and bats), when they are unlikely to be seen. Observations indicate that visitation by reptiles, amphibians and terrestrial mammals such as kangaroos are far outweighed by that by birds and by bats. Exposure to cyanide residues (concentrations from as low as 1 mg WAD CN/L to well above 100 mg WAD CN/L) at mining sites may occur via multiple pathways, including direct consumption of cyanide in drinking water, incidental ingestion or contact with cyanides in water and sediment during feeding, inhalation of HCN gas, and skin contact with cyanide-containing waters. Adult birds may potentially expose their young during feeding (regurgitation of

swallowed water/sediment). Secondary exposure of predatory or scavenging wildlife could also occur.

Exposure to aquatic organisms is not a concern in the TSF or associated dams and ponds, but is a possible concern if loss of cyanide residues occurs in runoff, overflow or seepage from a TSF, or in water draining from other areas of the site. Fish, aquatic invertebrates, algae and plants in downstream areas could then be exposed to cyanide residues, as could birds and animals consuming affected organisms or drinking contaminated water. Aquatic and terrestrial areas could also be potentially exposed through failure of a TSF. Exposure of vegetation (via root contact) and soil-dwelling organisms could potentially occur to groundwater in the vicinity of TSFs and heap leach operations. Groundwater also needs to be considered as it may be extracted for beneficial uses such as livestock watering and irrigation.

Groundwater contamination

Licences require the installation of bores at mining operations to monitor groundwater in the vicinity of structures such as TSFs, and these specify permissible limits for WAD CN (typically 0.5 mg /L). Available data indicate measured levels in groundwater in the immediate vicinity of TSFs in Australia range from < 0.01 to > 100 mg/L WAD CN, but the measured concentrations fell to low levels 100-200 m from the measured TSFs. In some situations dam design and local hydrology/hydrogeology lead to significant seepage. Excessive rising of the watertable and/or movement of seepage water must then be prevented by the use of recovery bores, ranging from a few to many bores. Ongoing monitoring is essential to ensure seepage is managed satisfactorily.

Release of HCN to the atmosphere

During gold ore beneficiation and processing some emission of HCN to air occurs, but overall the loss of HCN to air during these processes is only very minor (~1-2%). However, after material containing cyanide is deposited in tailings storage facilities, HCN emission to the atmosphere is expected as a significant means of dissipation. Some loss of HCN to the atmosphere may also occur from other mining and industrial uses.

While worldwide use of NaCN for gold ore processing may be a significant anthropogenic source of HCN in the atmosphere, on a global scale modelling using measured data suggests this is a minor source of release of HCN to the atmosphere compared to biomass burning. The estimated atmospheric lifetime for HCN is ~5 months, limiting the potential for long term increases in atmospheric concentration. Releases of HCN from gold industry or other uses of sodium cyanide are therefore considered unlikely to lead to significant increases in concentration of HCN in the atmosphere, and HCN is not considered to be of concern as a greenhouse gas or ozone depletor.

Modelling exposure of wildlife from gold mining use for risk assessment

While wildlife may be exposed to cyanide in a TSF by various means, for risk assessment purposes estimated exposure of wildlife to cyanide has been calculated based on the drinking water exposure route, as it is considered the most likely and most important pathway. As actual data on drinking water intake are limited, equations have been used which estimate drinking water intake rates for avian or mammalian wildlife species based on their bodyweight. These equations were developed from

actual data for northern hemisphere species ranging widely in bodyweight. The calculated water intake rates are considered estimates only and daily water intake by birds and mammals may be more or less than estimated, particularly depending on environmental conditions (e.g. temperature).

Drinking by wildlife may occur once or at a number of times during the day, and this is critical to estimate exposure to wildlife species from cyanide due to the potential for metabolism of small repeat doses without adverse effects. As a worst case scenario, it is assumed that even if multiple drinks are taken, all drinking water is obtained only from contaminated sources. Similarly, it is assumed that no aversion occurs due to sublethal cyanide exposure or other components in the water (e.g. salinity).

Calculations were made for various concentrations of WAD CN across the range reported in Australian TSFs (1-600 mg/L) for birds and small mammals (bodyweight ranging from 0.01-1.5 kg body weight).

Flotation use in base metal ore processing

Waste produced in base metal flotation processes flows to tailings dams, hence there are similar potential routes of environmental exposure to those arising from cyanide use for beneficiation in gold mines. However, available information indicates that in general a high percentage of the cyanide used is converted to insoluble metal complexes during use, with some loss as HCN. Significant exposure of wildlife to cyanide in tailings facilities therefore appears less likely than with gold beneficiation. Therefore consideration of environmental exposure from goldmine use in tank leaching systems should adequately cover potential exposure resulting from base metal flotation use.

Industrial uses

Electroplating, metal cleaning and metal surface treatment operations occur at enclosed industrial sites, generally with any unconsumed cyanide being treated to destroy it prior to disposal. Hence, potential exposure of wildlife is limited to exposure to waste delivered to landfill or released to the sewer if the waste were not adequately treated prior to discharge.

8. Kinetics and Metabolism in Animals

Many of the studies assessed in this chapter and Chapter 9 have been primarily summarised from the ATSDR (2006) review, though occasionally studies have also been summarised from the NTP (1993) review. However, primary sources of data were consulted where necessary. In addition, a comprehensive literature search was carried out of studies conducted from 1996 to date, for additional material of relevance to the hazard assessment, which has not been included in the ATSDR or other sourced reports or provided by importers or end-users of sodium cyanide and sodium cyanide products. References in the report that have not been sighted are marked with an asterisk(*).

Toxicokinetic data on sodium cyanide have been supplemented with data from other cyanogenic compounds. The basis for this approach is that cyanide (as hydrogen cyanide) originates in vivo following dissociation of cyanogenic compounds (e.g. sodium and potassium cyanide) or arising from catabolism of cyanogenic glycosides.

Human data are not considered in this report.

8.1 Absorption

Absorption of cyanide occurs rapidly through the gastrointestinal tract, lungs and skin. While data on *in vivo* absorption rates are not available, the extremely rapid onset of symptoms after exposure to cyanide (CN^-) makes it clear that cyanide is readily absorbed (NTP, 1993).

8.1.1 Inhalation

*Gettler and Baine (1938) reported that for dogs exposed to an unknown concentration of HCN, one dog reportedly absorbed 16.0 mg (1.55 mg/kg bw); the other dog absorbed 10.1 mg (1.11 mg/kg bw). These values correlated to fatal doses, with deaths occurring in 15 and 10 minutes, respectively. However, the accuracy of the reported values from such an old and briefly reported study is questionable.

8.1.2 Oral

The rate of absorption of cyanide from the gastrointestinal tract depends on the form of the cyanide and the presence of food in the tract (ATSDR, 2006). Food in the stomach delays the absorption of cyanide: dogs and cattle can be protected from the lethal effects of cyanide by the presence of carbohydrates in the stomach (*Couch, 1934; *Liebowitz and Schwartz, 1948). Conversely, cyanide can be released in lethal concentrations from cyanogenic glycosides in plants and foods; however, the uptake of cyanide in such cases is usually relatively slow, and the onset of symptoms is often delayed (*Towill et al., 1978). Absorption of cyanide from the gut across the gastrointestinal mucosa depends on the pH of the gut and the acid-base ionisation constant (pKa) and lipid solubility of the particular cyanide compound. HCN is a weak acid (pKa of 9.2 at 25°C), and the acidic environment in the stomach favours the non-ionised form (HCN) and facilitates absorption (ATSDR, 2006).

Rats excreted 47% of a cyanide dose in the urine during 24 hours following gavage treatment with 2 mg CN^-/kg as radiolabelled potassium cyanide (KCN), indicating that at least 47% of the cyanide was absorbed in 24 hours (Farooqui and Ahmed, 1982). NaCN has high acute oral toxicity in rats (LD50 = 2.7 - 8 mg CN/kg bw).

Three dogs were given lethal doses of cyanide. The amount absorbed was determined by the difference between the cyanide given and the cyanide left in the gastrointestinal tract (*Gettler and Baine, 1938). The dogs died 8, 21 and 155 minutes after treatment and absorbed 17%, 24% and 72% of the given dose respectively. Considering the methodology employed, the accuracy of these values from such an old and briefly reported study are questionable.

8.1.3 Dermal

Shaved and unshaved dogs were placed in a chamber in which their bodies, with the exception of the head and neck, were exposed to HCN vapour (*Walton and Witherspoon, 1926). No signs of toxicity were reported after exposure to 4975 ppm HCN for 180 minutes. Deaths occurred after exposure to 13 400 ppm HCN for 47 minutes and suggest dermal absorption, as do dermal LD50 values of 14.6 mg NaCN/kg bw, 22.3 mg KCN/kg bw and 7.0 mg HCN/kg bw (6.7 mg CN/kg bw) in the rabbit (Ballantyne, 1983).

Some cyanide compounds, such as KCN, have a corrosive effect on the skin that can increase the rate of dermal absorption (*NIOSH, 1976).

8.2 Distribution and macromolecular binding

Although the distribution of cyanide to the various tissues in the body is fairly uniform, the highest levels are typically found in the liver, lungs, blood and brain (NTP, 1993).

8.2.1 Inhalation

Once cyanide is absorbed, it rapidly distributes in blood throughout the body. In two dogs exposed to unspecified fatal concentrations of HCN, the highest cyanide levels were found in the lungs, blood, and heart (*Gettler and Baine, 1938). After inhalation exposure, the highest concentrations of cyanide in rats were found in the lungs, followed by the blood and the liver (*Yamamoto et al., 1982). Rabbits exposed to HCN at 2714 ppm for 5 minutes had blood and plasma cyanide levels of 170 and 48 µg/decilitre (dL). Wet tissue levels were 62, 54, 50, 6, 6 µg/l00 g and less than the detection level in the heart, lung, brain, kidney, spleen and liver respectively (Ballantyne, 1983).

8.2.2 Oral

Once cyanide is absorbed, it rapidly distributes in blood throughout the body. Combined data from rats that died 3.3 and 10.3 minutes after gavage doses of 7 or 21 mg CN/kg (as NaCN) showed average tissue concentrations of cyanide in µg/g (w/w) of 8.9, 5.8, 4.9, 2.1 and 1.5 in the liver, lung, blood, spleen and brain respectively (*Yamamoto et al., 1982). In rats treated with 4 mg CN/kg as KCN, cyanide levels 1 hour after exposure were 3380 µg/g in liver, 748 µg/g in brain, and 550 µg/g in kidney (*Ahmed and Farooqui, 1982). Similarly, rabbits administered 11.9 to 20.3 mg CN/kg as HCN by gavage had blood and plasma cyanide levels of 480 and 252 µg/dL respectively, and tissue levels (µg/100 g wet tissue) of 512, 107, 105, 95, 83 and 72 in

the liver, lung, heart, brain, kidney and spleen respectively at the time of death (Ballantyne, 1983). In a study using radioactively labelled KCN, the radioactivity detected in whole blood or plasma of rats decreased rapidly within 6 hours (*Farooqui and Ahmed, 1982).

Cyanide has the potential to form a variety of adducts in biological systems. A study of radiolabelled cyanide binding to regions of the brains of mice revealed that the hypothalamus accumulated more radiolabel than the cerebral cortex, hippocampus, or cerebellum (*Borowitz et al., 1994). Binding to certain tissue constituents may be important for decreasing the actions of cyanide and protecting cells from cyanide toxicity (*Devlin et al., 1989). However, cyanide has not been shown to accumulate in blood and tissues following chronic oral exposure to inorganic cyanides. Virtually no cyanide was found in plasma or kidneys of male and female rats that received HCN in the diet at approximately 10.4 mg CN/kg bw/day for 2 years, and only low levels were found in erythrocytes and liver: 1.97 and 0.97 µg/100 g respectively (Howard and Hanzal, 1955). At this dose level, levels of thiocyanate, a primary metabolite of cyanide, increased 3.5-fold in plasma, 3.3-fold in erythrocytes, 2.5-fold in kidneys and 1.3-fold in liver.

8.2.3 Dermal

Once absorbed, cyanide is distributed throughout the body, as shown in a study by Ballantyne (1983). Six rabbits administered 33.8 mg CN/kg as HCN had blood and plasma cyanide levels of 310 and 144 µg/dL, respectively. Wet tissue levels (µg/100 g) were 120, 110, 97, 66, 26 and 21 in the lung, heart, brain, kidney, liver and spleen respectively.

8.3 Metabolism/biotransformation

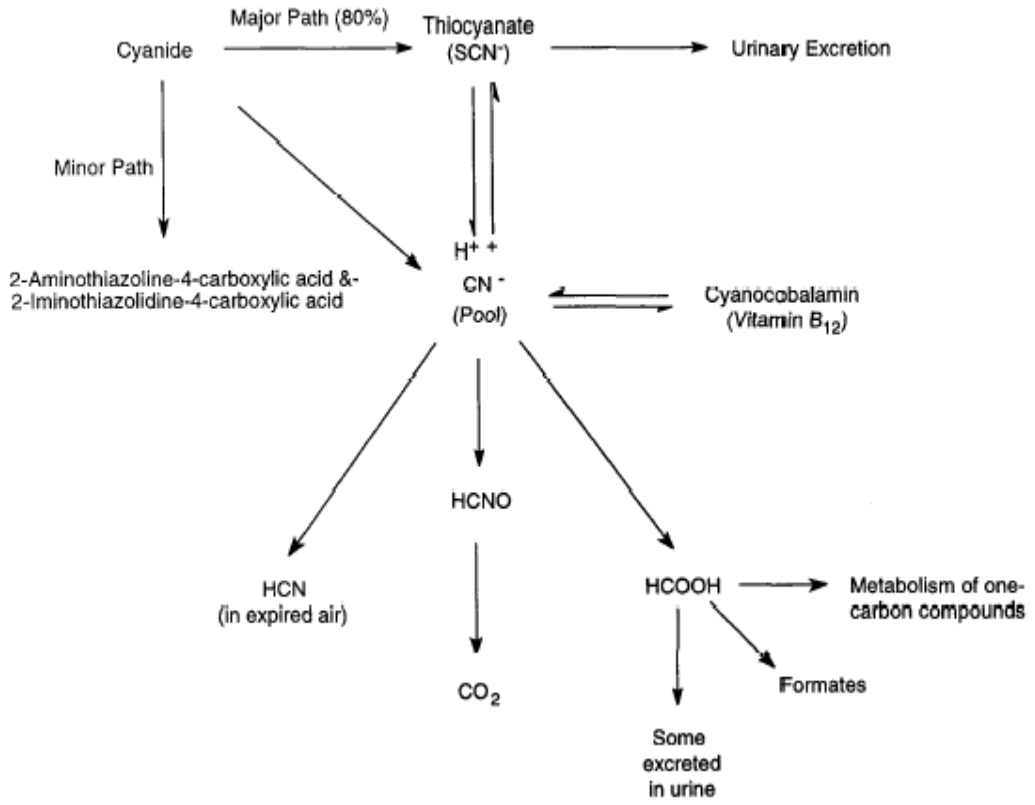
Although cyanide can interact with substances such as methemoglobin in the bloodstream, the majority of cyanide metabolism occurs within the tissues (NTP, 1993). The metabolism of cyanide has been studied in animals and one major route and several minor routes found, as illustrated in Figure 8.1 (ATSDR, 2006). It is suggested that these metabolic routes are potentially common to many animals including wildlife species; however, information is not available for all animal species, and thus it cannot be excluded that alternative metabolic processes may potentially occur.

The major metabolic pathway in animals is the conversion to thiocyanate by either rhodanese or 3-mercaptopyruvate sulphur transferase (*Wood and Cooley, 1956; Turner, 1969). In this metabolic pathway rhodanese catalyses the transfer of the sulfane sulphur of thiosulphate to the cyanide ion to form thiocyanate. Once thiocyanate is formed, it is not converted back to cyanide (ATSDR, 2006). Thiocyanate has been shown to account for 60% to 80% of an administered cyanide dose (*Blakley and Coop, 1949; *Wood and Cooley, 1956).

The tissue distribution of rhodanese is highly variable in different animal species (*Himwich and Saunders, 1948). In dogs, the highest activity of rhodanese was found in the adrenal gland, approximately 2.5 times greater than the activity in the liver. Monkeys, rabbits, and rats had the highest rhodanese activity in the liver and kidney, with relative low levels in the adrenals, and higher total rhodanese activity than in dogs. Low levels of rhodanese activity were found in the brain, testes, lungs, spleen and muscle among various species. In addition to rhodanese a number of other sulphurtransferases can metabolise cyanide; and albumin, which carries elemental

sulphur in the body in the sulfane form, may aid in the catalysis of cyanide to thiocyanate (*Westley et al., 1983). In brushtail possums, where cyanide is converted predominantly to thiocyanate, enzymatic activity (thiosulphate:cyanide sulphurtransferase) was ~50% lower in the liver of the possum than in dogs and may be higher in the kidney than liver (Turner, 1969).

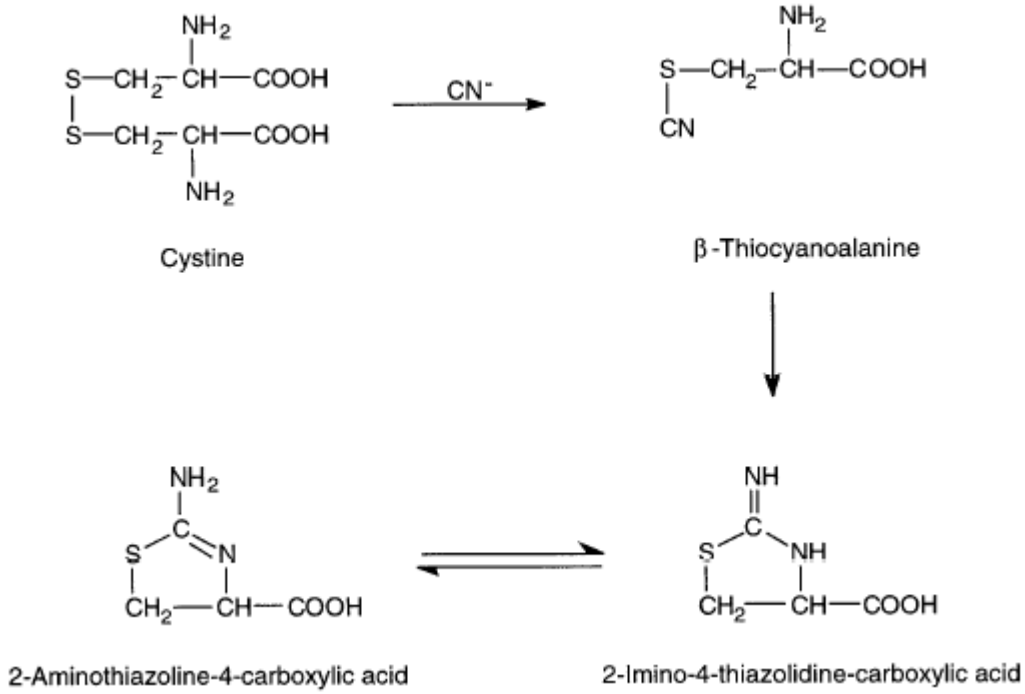
Figure 8.1. Basic processes involved in the metabolism of cyanide (ATSDR, 2006)



A species difference was seen in the metabolism of cyanide to thiocyanate in rats, pigs and goats following a single oral dose of 3.0 mg KCN/kg bw by gavage (Sousa et al., 2002). Maximum thiocyanate levels were detected in the plasma 3, 6 and 6 hours post dosing in the goat (55.2 µmol/L), rat (58.1 µmol/L), and pig (42.8 µmol/L) respectively. Over 24-hours post dosing, thiocyanate levels in rats were significantly higher than in pigs, and levels in goats were significantly higher than pigs at 3 and 18 hours. The biological half-life of thiocyanate in plasma was highest in the goat (13.9 hours).

Minor metabolic pathways that have been investigated include: conversion of cyanide to 2-aminothiazoline-4-carboxylic acid (*Wood and Cooley, 1956; Turner, 1969); incorporation into a 1-carbon metabolic pool (*Boxer and Rickards, 1952), or combining with hydroxocobalamin to form cyanocobalamin (Vitamin B12) (*Ansell and Lewis, 1970). Conversion to 2-aminothiazoline-4-carboxylic acid excreted in urine accounted for about 15% of an administered cyanide dose in rats (*Wood and Cooley, 1956). However, this compound was not detected in the urine of brushtail possums administered a solution by stomach intubation equivalent to a dose of 3 mg NaCN/kg bw (Turner, 1969).

Figure 8.2. Minor paths for the removal of cyanide from the body (*Ansell and Lewis, 1970)



The minor pathway for metabolism of cyanide in mammalian systems in which cyanide chemically combines with the amino acid cysteine is shown in Figure 8.2 (*Ansell and Lewis, 1970). This chemical reaction yields cysteine and β-thiocyanoalanine that is further converted to form 2-aminothiazoline-4-carboxylic acid and its tautomer, 2-iminothiazolidiene-4-carboxylic acid (ATSDR, 2006).

Reactions of cyanide with the salts or esters of some amino acids (e.g. pyruvate, α-ketoglutarate, oxaloacetate) led to the formation of cyanohydrin intermediates and their incorporation into intermediary metabolism (ATSDR, 2006).

The ability of cyanide to form complexes with some metallic ions such as cobalt is the basis for the reaction with hydroxocobalamin that yields cyanocobalamin (Vitamin B12). Cyanocobalamin, which contains cyanide and cobalt, is essential for the health of mammalian organisms (ATSDR, 2006).

8.4 Elimination/Excretion

Absorbed cyanide is mainly excreted as thiocyanate in the urine following oral administration; however, traces of cyanide may also be excreted unchanged or as a variety of metabolic products (e.g. carbon dioxide, β-thiocyanoalanine) in expired air, saliva, and sweat (*Friedberg and Schwarzkopf, 1969; Turner, 1969; *Hartung, 1982).

8.4.1 Inhalation

No animal studies are available investigating the elimination of cyanide following inhalation.

8.4.2 Oral

When rats were given 2 mg CN/kg as [^{12}C] KCN, urinary excretion of radioactivity reached 47% of the dose within 24 hours of administration (*Farooqui and Ahmed, 1982). When radiolabelled [^{14}C] NaCN was injected subcutaneously into rats at a level of 8.3 µmol, no difference in radioactivity eliminated was observed between a group pre-treated for 6 weeks with a diet containing 0.7 mg CN/kg as KCN and matching controls (*Okoh, 1983). Most (89%) of the radioactivity was detected in the urine by 24 hours, and thiocyanate was the major metabolite. About 4% of the radioactivity was expired via the lungs, mostly as carbon dioxide.

In brushtail possums administered a single dose of cyanide solution by stomach intubation equivalent to a dose of 3 mg NaCN/kg bw, urinary excretion of thiocyanate accounted for 62%-76% of the administered dose in the first 6 days, with most in the first 2 days (Turner, 1969).

8.4.3 Dermal

No studies are available investigating the elimination of cyanide following dermal exposure.

8.5 Summary of kinetics and metabolism in animals

Rapid onset of symptoms after exposure to cyanide through the gastrointestinal tract, lungs and skin indicates that cyanide is readily absorbed via these routes. Sodium cyanide has high acute oral toxicity (LD50 = 2.7 – 8 mg/kg bw) in rats and high acute dermal toxicity (LD50 = 14.6 mg/kg bw) in rabbits.

Distribution of cyanide in various body tissues is fairly uniform with highest levels found in the liver, lungs, blood and brain in rats and rabbits.

The majority of cyanide metabolism occurs within tissues in animals. The major metabolic pathway is the conversion of cyanide to thiocyanate by either rhodanese or 3-mercaptopyruvaten sulphur transferase. The distribution of rhodanese in tissues is highly variable in different animal species. Monkeys, rabbits and rats had the highest rhodanese activity in the liver and kidneys, with relatively low levels of activity in adrenals. In dogs, the highest activity of rhodanese was in the adrenal gland. The total rhodanese activity in dogs was lower compared to monkeys, rabbits and rats. The rate of metabolism of cyanide to thiocyanate depends on the species. The biological half-life of thiocyanate in plasma was highest in the goat (~14 h).

Absorbed cyanide is mainly excreted as thiocyanate in the urine. Traces of cyanide may also be excreted unchanged or as a variety of metabolites in expired air, saliva and sweat.

9. Environmental Hazard Assessment

This chapter discusses available ecotoxicity data for cyanide to terrestrial and aquatic species. These data indicate the nature and extent of the hazard presented by cyanide to various organisms and enable suitable toxicity endpoints to be determined for subsequent risk assessment.

Data on sodium cyanide have been supplemented with data from other cyanogenic compounds, as cyanide (as hydrogen cyanide) originates in aqueous environments, such as in vivo, following dissociation of cyanogenic compounds (e.g. sodium and potassium cyanide) or arising from catabolism of cyanogenic glycosides. The use of such data is considered well founded for systemic effects, but may not be suitable for any effect that may occur on local contact. Therefore endpoints that involve local reactions at the initial site of contact (e.g. irritation, and sensitisation in this instance) have been evaluated with data on sodium cyanide.

For an environmental risk assessment, it is a standard practice to use data from tests carried out according to standard guidelines with standard test species as surrogates for wild local species. However, for cyanide, much of the available data for terrestrial and avian species are with tests that do not meet current guidelines, and several of the avian studies are with non-standard species, including wild species from North America. No data are available specifically for Australian mammals or birds, but there are some data for Australian aquatic species.

References in the report that have not been sighted are marked with an asterisk (*).

9.1 Mode of action of cyanide toxicity

The main toxic effects of cyanide are attributed to the disruption of energy metabolism. Cyanide inhibits mitochondrial cytochrome c oxidase by binding with the ferric ion of cytochrome a_3, the terminal oxidase of the respiratory chain, leading to cytotoxic hypoxia and respiratory system failure (Ballantyne, 1987). A two-step process for inhibition of cytochrome c oxidase has been proposed: initial penetration of cyanide into a protein crevice of cytochrome c oxidase (*Stannard and Horecker, 1948) followed by binding to the trivalent iron ion of the enzyme (*Van Buuren et al., 1972). This blockage to the electron transfer chain and cessation of aerobic metabolism causes a shift to anaerobic metabolism and depletion of energy rich compounds such as adenosine triphosphate (ATP) and results in the accumulation of pyruvic and lactic acid, that leads to respiratory arrest and death (*Rieders, 1971; *Way, 1984).

In addition to binding to cytochrome c oxidase, cyanide also binds to catalase, peroxidase, methemoglobin, hydroxycobalamin, phosphatase, tyrosinase, ascorbic acid oxidase, xanthine oxidase, and succinic dehydrogenase. These reactions may also contribute to cyanide toxicity (*Ardelt et al., 1989; *DiPalma, 1971; *Rieders, 1971).

Cyanide affects a range of organs including the CNS, cardiovascular and/or respiratory system, thyroid, reproductive organs, gastro-intestinal tract, skin, liver and kidneys (Isom, 2002; *Okalie and Osagie, 1999; Faust, 1994; Kamalu, 1993; Ballantyne, 1987; *Palmer and Olson, 1979; Philbrick et al, 1979). Due to its high dependency on

oxidative metabolism and limited anaerobic capacity, the CNS is particularly vulnerable to cyanide intoxication (*Way, 1984). Blindness is common in cyanide-treated animals and is considered to be a result of persistent anoxia in the brain (NTP, 1993).

Exposure to a high sublethal dose of cyanide may have long-term consequences. In humans, these have included cerebellar and sub-cortical disturbances with concomitant impairment of co-ordination and movement and Parkinsonian-like symptoms (Fischbein et al., 2000; *Rosenow et al., 1995; *Valenzula et al., 1992; *Grandas et al., 1989). Parkinsonian-like effects have also been recorded in animals (*Rosenberg et al., 1989).

Cyanide is a neurotoxin that produces selective brain degeneration (lesions). In intraperitoneal studies in mice, cyanide resulted in two distinct brain (doperminergic neuron) lesions: non-gliotic lesions in the motor cortex, and gliotic lesions in the substantia nigra (Mills et al., 1999). These are thought to be due to two distinct modes of cell death: necrosis (substantia nigra region) and apoptosis (cortical region). Oxidative stress is considered a common activator of the lesions.

9.2 Effects on avian species

This sub-section describes the toxicity to birds, and most of the studies have been sourced from the Eisler (1991) review. No toxicity data were available for reptiles (e.g. snakes, lizards, tortoise). Data from mammals and birds are considered indicative in the absence of reptilian data, as it has been suggested that there is little difference in the interspecies sensitivity to acute doses of cyanide between modern eutherian carnivores and endemic species (Marks et al., 2002). However, the limited details reported reduce the reliability that can be attached to this qualitative statement. Nevertheless, a wide-range of wildlife species are susceptible to the effects of cyanide (Adams et al., 2008a,b; Donato et al., 2007; Smith et al., 2007; Donato, 2002; Eisler et al., 1999; Donato, 1999; ATSDR, 2004; Sinclair et al., 1997; Wiemeyer et al., 1986) and toxicity data show little variation in the acute toxicity of cyanide to various animals.

Data available for birds include acute inhalation, oral and repeat oral studies. These studies are presented below.

9.2.1 Acute toxicity

Inhalation

No studies are available with NaCN. A single study is available with HCN. *Barcroft (1931) investigated acute toxicity in three bird species: domestic chickens (*Gallus domesticus*), rock doves (i.e. common pigeon - *Columba livia*) and canaries (*Serinus canarivus*) were all exposed to 120 mg HCN/m^3 (equivalent to 107 ppm cyanide v/v). All chickens were reported to have survived for at least 60 minutes, while all rock doves and canaries died within 10 and 3 minutes respectively.

Oral

Acute lethality to birds

Wiemeyer et al (1986) conducted acute oral toxicity studies with NaCN and a range of bird species. One purpose of this study was to collect data on cyanide residues in the

blood of birds dying from cyanide poisoning to assist the interpretation of post mortem investigations (including a dead Californian condor that had been exposed to NaCN from a baiting device). Hence some of the tests were not actually designed to determine an LD50, and the species tested included several wild species, rather than simply standard test species. One reason for the focus on raptor species is that bird exposure to cyanide was associated with the use of baits and fumigants for pest mammals, and use in gold mining was not mentioned. Domestic chickens (*Gallus domesticus*) were used for an initial range-finding study, as they are similar in weight to the turkey vulture (*Cathartes aura*), which was described as the 'primary experimental model'. The turkey vultures were only tested for blood residue investigation purposes. Acute oral LD50 studies were conducted with black vultures (*Coragyps atratus*), American kestrels (*Falco sparverius*), eastern screech-owls (*Otus asio*), European starling (*Sturnus vulgaris*), and Japanese quails (*Coturnix japonica*).

An acute oral LD50 study was also conducted with mallard ducks (*Anas platyrhynchos*), reported by Henny et al. (1994), with further data evidently relating to this study presented by Hagelstein and Mudder (1997a). Mallard ducks were used for this study because waterfowl and shorebirds constituted over 70% of avian mortality at Nevada gold mines, and no data were available for aquatic bird species.

In these studies, sodium cyanide was administered to the birds in a single dose by gelatin capsule (as 99.4% reagent grade for the Wiemeyer et al., 1986 study and 96.7% technical grade for the Henny et al., 1994 study). The experimental methods used for the LD50 studies were based on those described by Hill and Camardese (1984), who referred to the (then) avian single-dose oral LD50 (median lethal dose) protocol of the US Federal Insecticide, Fungicide and Rodenticide Act (FIFRA, US Environmental Protection Agency, 1978). LD50 values were estimated by probit analysis.

Of the avian toxicity test data available, only the mallard duck (*Anas platyrhynchos*; a close relative of the local Pacific Black Duck) is a standard OECD test species for oral toxicity tests. Data are occasionally generated on the Japanese quail, an alternative OECD test species, whereas the starling and domestic chicken are generally considered to be relatively insensitive species. Thus, the available data includes species known to range widely in sensitivity from toxicity studies conducted with other chemicals, and also included several raptor species not normally tested in such studies.

Thus, these studies were based on a satisfactory guideline and were analysed by an appropriate statistical procedure. They are considered acceptable, but cannot be considered fully reliable as:

- in most cases, only 3-5 birds per dose level were used, whereas current guidelines (USEPA 850.2100) specify a minimum of 10;
- important information is lacking from the available reports, including the actual doses tested in several studies, various other details of the methods and details of the results, so that endpoints cannot be independently confirmed;
- the birds used in the Wiemeyer et al. (1986) study were in several cases wild caught, non-standard test species, with no indication as to how they were habituated to the test facilities or how they reacted to the stresses involved in capture, handling and dosing;

- while the Wiemeyer et al. (1986) study related to sodium cyanide, its purpose and design related to baiting uses of the substance rather than gold mining, though various raptor species are also present at mine sites.

The available data on the methods used and results of these studies are summarised in Table 9.1.

Vomiting soon after dosing is a potential problem in oral toxicity studies as it can reduce the dose received. Wiemeyer et al. (1986) commented that neither passerine (including starlings) nor galliform (including quail and domestic chickens) bird species have well developed vomiting reflexes. They stated that even though vomiting was noted in two black vultures that eventually survived exposure, its prevalence was difficult to ascertain in these studies because birds were deprived of food before exposure, but presumably regurgitation of the capsule casing would have been readily evident. Mallard ducks are a species where the gagging reflex is sometimes observed in toxicity studies, but Henny et al. (1994) do not mention this occurring, though they did observe the treated birds (which were fasted overnight before dosing) continuously for 1 hour after dosing. Vomiting did need to be allowed for in studies with pigeons by Cooper (2003), but in that case liquid was delivered to the birds rather than a capsule.

Wiemeyer et al. (1986) noted that the black vultures, kestrels, owls and quail reacted much more violently to NaCN exposure than did the chickens or starlings. The first signs of toxicosis (i.e. illness resulting from exposure to a toxic substance, in this case cyanide) at nearly all dosages occurred between 30 sec and 5 min post exposure, and death usually followed in 15-30 min. Birds alive at 1 hour usually recovered, e.g. surviving black vultures were standing and reasonably alert at 1 hour after dosing. LD50 values from their study ranged from 4.0 to 21 mg/kg bw (equivalent to 2.1 to 11.1 mg CN/kg bw) in the species tested. There were no sex differences in the two species where this was tested (quail and starlings). Marked differences in acute toxicity of NaCN were found, with the three flesh eaters being more sensitive than the three plant material consumers, and species differences in sensitivity to NaCN were not related to body size. As expected, the chickens and starlings were relatively insensitive compared to the quail (Table 9.1).

The results for mallard duck from the Henny et al. (1994) study indicated it to be the most sensitive bird species of those that have been tested in acute oral studies with NaCN (LD50 = 2.7 mg/kg bw, equivalent to 1.4 mg CN/kg bw). This result is considered acceptable, though not fully reliable, as only 6 birds per dose were tested and the full study report is not available. It is consistent with that of 2.9 mg NaCN/kg bw (equivalent to 1.5 mg CN/kg bw) reported by Clark et *al* (1991) in a study that is available as an abstract only and hence cannot itself be evaluated adequately.

Data to indicate the NOEL values for lethal effects ($NOEL_{mortality}$) are available for some species in the above studies. These data indicate $NOEL_{mortality}$ values ranging from 0.53 mg CN/kg bw for mallard ducks to 6 mg CN/kg bw for domestic chickens, with the corresponding LOELs being 1.1 mg CN/kg bw and 12 CN/kg bw, respectively (Table 9.1). A higher $NOEL_{mortality}$ value for mallards (the most sensitive species for which data are available) of 0.8 mg/kg bw was obtained in the biochemical studies by Pritsos and Ma (1997) and Ma and Pritsos (1997) discussed below (Table 9.2).

Acute lethality to mallard ducks

Smith and Mudder (1991) and Hagelstein and Mudder (1997ab) briefly reported an unpublished study by *Fletcher (1986) on the acute toxicity, measured as mortality, of

cyanide in tap water and mine effluent solution to mallard ducks. The original study reports were not available and few details of test methodologies and data were presented. The following discussion draws on these secondary sources.

In the first *Fletcher (1986) study, different sets of five male and five female 20 week-old mallard ducks were exposed to a range of concentrations of free cyanide in tap water (0-265 mg/L) in a single dose (it is not clear whether this was administered by gavage, or was in fact simply provided on a single occasion for a limited period in drinking water). Following administration of the single dose, the ducks were observed for a period of seven days. The LC50 value for this single dose exposure for the combined male and female ducks was 181 mg total CN/L. Assuming a bodyweight of 1.0 kg per duck, this was stated to equate to an LD50 of 2.5 mg NaCN/kg (the calculated figure is stated to be the 'acute oral toxicity of cyanide in the tap water or the actual mining solution when expressed in terms of mg/kg', but is then compared directly to the other toxicity values for NaCN presented in Table 9.1). Expressed in terms of total CN, this LD50 would be 1.3 mg/kg.

In a second similar study with mallard ducks by *Fletcher (1986), solution collected from an effluent holding pond at a gold mining operation in Nevada was used instead of tap water. The total cyanide levels were adjusted through the addition of NaCN to produce concentrations ranging from 107-332 mg/L. The result, again provided as a LC50 value following a single dose, was calculated to be 212 mg total CN/L. Assuming a bodyweight of 1.0 kg per duck, this equated to an LD50 of 3.2 mg NaCN/kg, or 1.7 mg CN/kg.

All of the mortalities occurred within the first three hours following treatment and all surviving birds appeared normal after seven days. Smith and Mudder (1991) noted that the effluent pond result was similar to that obtained with tap water and suggested that the overall results indicated that cyanide (rather than other toxins) was the primary concern with toxicity from mining solutions. Hagelstein and Mudder (1997a) noted that in general, the mallard tolerates slightly higher concentrations of cyanide when it is in solution with other effluent or process solution ions. However, there is inadequate evidence to confirm this from the slightly lower LC50 value for the effluent pond water in this single comparison. It is also evident that the way in which the solutions were prepared left much of the cyanide present as free CN.

If in fact provided as a direct single dose, these studies (*Fletcher, 1986) appear to have been conducted based on standard USEPA acute toxicity guidelines, though the results have unconventionally been expressed as LC50 values. It may also be that in fact they were short term exposure drinking water studies, which would explain the presentation of the results as LC50 values and the lack of certainty as to the volume received by each bird. Without the original reports to verify the actual procedures used and the full results, including the measured concentrations and dose volumes given, actual bird weights, and sublethal effects, these data cannot be confirmed or fully interpreted. With a 'single dosing' regime it is likely that the experimenters were able to achieve the concentrations stated, whether administered by gavage or in drinking water. However, the conversions of the LC50 data to LD50 values appear to be approximations, as the bodyweights used were evidently approximations, and if administered voluntarily via drinking water, the volume taken was also uncertain. Hence these studies are considered as supplementary information rather than reliable or acceptable toxicity studies.

However, the LD50 results for mallard ducks inferred from these studies are supportive of the LD50 result for mallard duck obtained by Henny et al. (1994) discussed above. The latter value will therefore be used as the endpoint for that species, i.e. 1.4 mg CN/kg.

The volume of solution given per bird or assumed to have been consumed by each bird in the *Fletcher (1986) studies was stated to be ~10 mL, but this is not fully consistent with the calculated results. Using the corresponding LC50 and LD50 figures (correcting the LD50 value from NaCN to total CN), back calculations indicate that the average doses or assumed intake for these studies were ~7.3-8.0 mL per bird (i.e. ~0.25 US fl oz). This is approximately one eighth of the estimated daily drinking water consumption of ~60 mL for a bird weighing 1 kg using the allometric Avian Water Intake Rate equation of Calder and Braun (1983) (Section 7.3.6). This was evidently envisaged by the researcher as representative of water consumption by mallard duck in a single drinking event. Studies by Pritsos and Ma (1997), Ma and Pritsos (1997), Cooper (2003), Brasel et al. (2003) and Cooper and Pritsos (1999) with mallard ducks and homing pigeons (below) used a similar strategy, with forced gavage of 10 mL of test solution varying in concentration intended to represent exposure to a single drink of CN-contaminated water in investigations of sub-lethal effects.

The LC50 results are also considered acceptable as an indication of the concentration of cyanide which is toxic to mallards from a single drinking event. However, some caution in interpreting these single event LC50 concentrations is necessary, as field and laboratory observations make it clear that individual birds within a species differ significantly in their drinking behaviour (see 'Short term oral and contact exposure' discussion below), as well as there being wide differences between species. In particular, mallards are a waterbird which can be expected to drink at several times over a day and therefore to take a smaller proportion of their daily water intake with each drink. In contrast, species which visit a waterbody on one to a few occasions per day to drink would be expected to take a larger proportion of their daily consumption on each occasion they visit. Caution is also necessary in interpreting how the results from a single exposure event apply to continuing exposure after an initial drink, as there may be cumulative effects due to incomplete detoxification and recovery between drinking events, and/or a decrease in the ability of detoxification mechanisms to operate. The LC50 results are somewhat higher than the LC50 of 115 mg CN/L from the brief test with 2 h exposure described below, which could be a result of greater water ingestion and/or additional means of exposure in the test below.

An evaluation of the mortality from the *Fletcher (1986) studies together with those by *Fletcher (1987) (Section 9.2.2) was used to estimate a LC1 (concentration in the water necessary to kill 1% of the birds) for free CN of ~50 mg/L. This was stated to be equivalent to ~0.73 mg/kg bodyweight in a single dose, i.e. below reported LD50 values in the literature (Table 9.1). Note that if a 1 kg duck consumes 8-10 mL of a 50 mg WAD CN/L solution, this would result in a body dose of 0.4-0.5 mg CN/kg, which is at or below the lowest NOEL for lethal effects to mallard ducks of 0.5 mg CN/kg (see Table 9.1: evidently from the Henny et al., 1994 study).

Table 9.1. Avian acute oral toxicity studies with sodium cyanide

Species	Sex	Median weight (g)	Dosages tested[a]	Other comments	Results (as NaCN unless indicated otherwise)	Reference
Domestic chicken (*Gallus domesticus*)	F	1610	0, 6, 12, 24 and 48 mg NaCN/kg bw, 3 birds/dose	Range finding study for a species similar in weight to the turkey vulture.	LD50 = 21 mg/kg bw (11.1 mg CN/kg bw) 95% CI 12-36 mg/kg bw At 6 mg/kg bw (3.2 mg CN/kg bw), responses commenced about 10 min after exposure and were comparatively mild and clearly sublethal. At 48 mg/kg bw (25.4 mg CN/kg bw), signs of toxicosis were also observed from about 10 min post exposure, but the signs intensified over time and several birds died. There were intermediate results at the other concentrations. Surviving birds were killed after 30 min observation for blood monitoring purposes. The LD50 was estimated from observed deaths and projected deaths based on clinical signs at the time of killing.	Wiemeyer et al. (1986)
Turkey vultures (*Cathartes aura*)	M/ F	~2100	25 and 36 mg/kg bw (13.3 and 19.1 CN/ kg bw), 1 and 15 birds respectively.	Wild-trapped birds – not an LD50 test, primarily for blood studies.	The bird at the lower dose died in 27 min and those at the higher dose in 8-41 min. Early toxic signs were slight incoordination, rapid eye-blinking, head-bowing, and wing droop, followed by loss of coordination and convulsions resulting in the birds lying in various positions and exhibiting tail fanning and opisthotonos. Breathing became increasingly deep and laboured, followed by gasping, shallow intermittent breathing, and death.	Wiemeyer et al. (1986)
Black vulture (*Coragyps atratus*)	M/ F	2215	3, 4.5, 7 and 36 mg NaCN/kg bw, 3 birds each, except 4 at 4.5 mg/kg bw	Wild-trapped birds	LD50 = 4.8 mg/kg bw (2.5 mg CN/kg bw) 95% CI 4.4-5.3 mg/kg bw. 3 mg/kg bw (1.6 mg CN/kg bw): no deaths in 60 min, 4.5 mg/kg bw (2.4 mg CN/kg bw): 1 death, time to death 30 min, 7 mg/kg bw (3.7 mg CN/kg bw): 3 deaths, time to death 14-18 min, 36 mg/kg bw (19.1 mg CN/kg bw): 3 deaths, time to death 8-14 min. In a preliminary study, individual birds died in 11 min at 16 mg/kg bw and 8 min at 25 mg/kg.	Wiemeyer et al. (1986)

Species	Sex	Median weight (g)	Dosages tested[a]	Other comments	Results (as NaCN unless indicated otherwise)	Reference
Andean condor (*Vultur gryphus*)	-	-	36 mg/kg bw (19.1 CN/ kg bw), 1 bird	-	Died	*Krynitsky et al. (1986)
American kestrel (*Falco sparverius*)	M/ F	118	4 dosages (not specified), 5 birds in each	Captive colony	LD50 = 4.0 mg/kg bw (2.1 mg CN/kg bw) 95% CI 3.0-5.3 mg/kg bw	Wiemeyer et al. (1986)
Eastern screech-owl (*Otus asio*)	M/ F	185	4 dosages (not specified), 5 birds in each	Captive colony	LD50 = 8.6 mg/kg bw (4.6 mg CN/kg bw) 95% CI 7.2-10.2 mg/kg bw	Wiemeyer et al. (1986)
European starling (*Sturnus vulgaris*)	M/ F	75	Analysis for both sexes together	Wild-trapped birds	LD50 = 17 mg/kg bw (9.0 mg CN/kg bw) 95% CI 14-22 mg/kg bw	Wiemeyer et al. (1986)
	M	78	5 dosages (not specified), 5 birds in each		LD50 = 17 mg/kg bw (9.0 mg CN/kg bw) 95% CI 9-32 mg/kg bw	
	F	72	5 dosages (not specified), 5 birds in each		LD50 = 18 mg/kg bw (9.5 mg CN/kg bw) 95% CI 11-30 mg/kg bw	
Japanese quail (*Coturnix*	M/ F	130	Analysis for both sexes together	Captive colony, reproductively active at the time	LD50 = 9.4 mg/kg bw (5.0 mg CN/kg bw) 95% CI 7.7-11.4 mg/kg bw	Wiemeyer et al. (1986)

Species	Sex	Median weight (g)	Dosages tested[a]	Other comments	Results (as NaCN unless indicated otherwise)	Reference
japonica)	M	124	5 dosages (not specified), 10 birds in each for each sex	of dosing (the other species in Wiemeyer et al., 1986 were not)	LD50 = 10.3 mg/kg bw (5.5 mg CN/kg bw) 95% CI 7.5-14.1 mg/kg bw	
	F	148			LD50 = 8.5 mg/kg bw (4.5 mg CN/kg bw) 95% confidence intervals 5.9-12.2 mg/kg bw	
Mallard (*Anas platyrhynchos*)	M/F	1260	0, 1.0, 2.0, 2.8, 4.0 and 5.7 mg NaCN/kg bw, 3 M and 3 F birds/dose	Reproductively quiescent, 6 month old birds from a captive flock.	LD50 = 2.7 mg/kg bw (1.4 mg CN/kg bw) 95% CI 2.2-3.2 mg/kg bw 1 mg/kg bw (0.53 mg CN/kg bw): no deaths, 2 mg/kg bw (1.1 mg CN/kg bw): about 6% dead, 2.4 mg/kg bw (1.3 mg CN/kg bw): about 33% dead	Henny et al. (1994) Hagelstein and Mudder (1997a)
	-	-	-	Limited information	LD50 = 2.9 mg/kg bw (1.5 mg CN/kg bw)	Clark et al. (1991) (abstract)
	M/F	Evidently ~1000 g	0-265 mg CN/L as NaCN in tap water in a 7.5 mL dose[b]	20-week old ducks	2.5 mg NaCN/kg bw (1.3 mg CN/kg) based on an approximate bodyweight of 1.0 kg	*Fletcher (1986) (cited by Smith and Mudder, 1991)
	M/F	Evidently ~1000 g	107-332 mg total CN/L in effluent pond water in a 7.5 mL dose		3.2 mg CN/kg bw (1.7 mg CN/kg) based on an approximate bodyweight of 1.0 kg	

(a) It is clear from the Wiemeyer et al. (1986) paper that there was a control for the chickens, but not for the vultures. It is not explicitly stated, but controls were presumably included in the other tests by Wiemeyer et al. (1986). (b) Actual volume uncertain, and may have been an acute drinking water exposure study rather than an acute oral study with dosing by gavage.

Comparative acute toxicity for different forms of cyanide

A paper by Link et al. (1996) relates the data for the acute oral toxicity of NaCN to mallard ducks from the study by Henny et al. (1994) discussed above to the acute oral toxicity of KCN, CuCN, $Hg(CN)_2$ and $CH_2(CN)_2$ (malonitrile). The latter toxicants were compared against this baseline study, using only 14 test birds per toxicant. These birds were administered an amount equal in terms of the CN content to the LD50 from the baseline study, which used 72 birds (the purpose of the paper was to describe a statistically assessable protocol for minimising resources used to make such comparisons). Presumably other test conditions were very similar to the original NaCN study, but details were not provided. Nine of the 14 birds dosed with KCN at 1.5 mg CN/kg bw died, whereas no birds died with the other toxicants. Hence, with acute oral exposure, CuCN, $Hg(CN)_2$ and $CH_2(CN)_2$ were significantly less toxic than NaCN, whereas KCN had comparable toxicity.

A similar procedure was used for water exposure in a study conducted by Hill and Henry (unpublished) which Link et al. (1996) discussed. Individual mallard ducks (12 for each of 5 test concentrations) were exposed to contaminated water for a 2 hour period (few test details were provided). The estimated LC50 from this study was 115 mg CN/L (Table 9.3). However, this result is difficult to interpret fully without more experimental details to indicate the extent to which birds were exposed by various routes (e.g. how much water they drank in this short time period) and without information on other observations, such as sublethal effects. This result was then compared with other toxicants in similar fashion to the tests conducted with acute oral exposure (above), but with one toxicant differing, i.e. $Na_2Cu(CN)_3$ rather than CuCN. Six of the 14 birds dosed with KCN at 115.1 mg CN/L died, compared to 13 birds with $Hg(CN)_2$, 1 bird with $Na_2Cu(CN)_3$ and no birds with $CH_2(CN)_2$. Thus with this means of exposure, KCN had comparable toxicity to NaCN, $Hg(CN)_2$ was significantly more toxic (surprisingly different to the acute oral result), and $CH_2(CN)_2$ was significantly less toxic.

Short term oral and contact exposure

Henny et al. (1994) reported a brief experiment conducted to examine differences in susceptibility to CN exposure in water between individual birds (presumably related to drinking behaviour). It also provides a description of the unpleasant symptoms of CN poisoning which resulted. Differences in behaviour affecting susceptibility to CN are also evident in the field (Section 9.9.1). Henny et al. (1994) described a similar sequence of symptoms in ducks in the field, and the symptoms described are comparable with those seen in studies of pigeons by Cooper (2003), described below.

Adult mallard ducks were exposed for 4 h in tanks to water containing 115 mg CN/L as NaCN (i.e. as free CN). The water was adjusted to pH 10.5 with calcium oxide, and control mallards were exposed to either water at pH 6.5 or calcium oxide-adjusted water at pH 10.5. Some individuals exposed to CN began exhibiting lateral bill shaking within seconds to a few minutes exposure, and repeated this response after most apparent drinking bouts. This response was not exhibited by either set of control birds, hence the water pH was evidently not the cause of the response. After the initial bill shaking response in CN-exposed birds, some birds remained alert, others were stupefied, and others arched their neck with the bill pointing upward and appeared to gasp. Often the latter response was associated with wing extension and a burst of powerful flapping that would abruptly cease with death or a stupefied appearance. During stupefaction, the head often drooped into the water and sometimes remained

submerged without struggle until death. Stupefied birds that did not die usually aroused in 15-30 minutes, appeared alert, began drinking, and generally repeated the above sequence of behavioural responses. Many birds survived more than one period of stupefaction, and if they survived the initial two exposures, death rarely occurred after three cycles (i.e. after about 1.5 h of the 4 h trial).

Sub-lethal effects following acute oral exposure

Data are also available from studies that investigated acute sublethal biochemical effects of potassium cyanide (KCN) in adult female mallards (Pritsos and Ma, 1997; Ma and Pritsos, 1997) and homing pigeons (Brasel et al., 2006; Cooper, 2003; Brasel et al., 2003; Cooper and Pritsos, 1999 – these are a MSc thesis of which relevant portions were available, a conference abstract and a conference poster). A summary of the results of these studies is also presented in Table 9.2. The treatments differed in concentration rather than the volume gavaged, and the concentrations used were comparable to WAD CN concentrations that may be found in TSFs: the range of doses tested was 0.25-2.0 mg KCN/kg bw, or 0.1-0.8 mg CN/kg, and this was obtained using solutions ranging in concentration from 10-80 mg/L CN^- to birds weighing ~1 kg, in each case with the amount gavaged being 10 mL on a single occasion (cf. the *Fletcher, 1986 study discussed above). The biochemical studies involved administration of the test solution, followed by euthanasia 2 or 24 hours later, depending on the measurements being made, so that blood and tissue samples could be taken.

Visible signs

Cooper (2003) indicated that initial signs of toxicosis appeared soon after treatment for all but the lowest dosages (>0.5 mg KCN/kg bw, i.e. 0.2 mg CN/kg bw) in preliminary treatments conducted with both pigeons and mallard ducks. These signs included panting and laboured breathing, eye-blinking, head-bowing, tremors, lethargy, incoordination and convulsions. Animals with the latter two symptoms either became unresponsive or lay down in atypical poses. These comments indicate a NOEL = 0.2 mg CN/kg bw, LOEL = 0.4 mg CN/kg bw for both mallards and pigeons, though Brasel et al. (2003) stated that doses used for the homing pigeon flight studies were at levels which did not produce outward observable adverse effects.

Biochemical studies

Mallards were dosed with KCN solution at up to 0.8 mg CN/kg bw (Pritsos and Ma, 1997; Ma and Pritsos, 1997). Serum creatine kinase levels and rhodanese and 3-mercaptopyruvate sulphurtransferase (3-MPS) activity were then determined in the heart, liver and brain 24-hours post-dosing, along with mitochondrial respiratory control ratio (RCR; a measure of mitochondrial integrity and ability to synthesize ATP) and ATP levels in the heart, liver and brain 2-hours post dosing. Additionally, ATP levels in the heart, liver and brain were determined at 6, 12 and 24-hours post-dosing following administration of 0.4 mg CN/kg bw. Compared to controls, effects were seen at the lowest doses tested: a significant decrease in ATP levels in liver and brain at 0.1 mg CN/kg bw; a significant decrease in respiratory control ratios (RCRs) in liver, brain and heart at 0.2 mg CN/kg bw; and a significant increase in serum creatine levels, rhodanese and 3-MPS enzyme activity in the brain at 0.4 mg CN/kg bw. In the time course study, ATP levels had returned to normal in the heart, liver and brain by 24-hours post-dosing. The results from these studies are presented in Table 9.2.

Cooper (2003; also reported in Brasel et al., 2003) also investigated the biochemical effects of cyanide (as KCN) on trained homing pigeons (*Columba livia*) and mallards. Initially, pigeons and mallards were dosed at 0.8 mg CN/kg bw and measurements were made of enzyme production and lipid peroxidation. These tests proved inconclusive except for the superoxide dismutase (SOD) assay. SOD was higher in treated than control birds for brain, heart and liver tissue in both species, though not always significantly so at the 5% level. There was a very highly significant increase in SOD in pigeon liver tissue. The effects of KCN on pigeons were also assessed using mitochondrial RCR assays. Brain and heart tissue exhibited greater sensitivity to cyanide than liver tissue by this measure, with a reduction in treated birds which was significant at the 5% level for brain tissue and approached 5% significance in heart tissue.

Cooper (2003) also discussed the results of ATP studies with female mallard ducks reported by Pritsos and Ma (1997), in comparison with similar results for pigeon tissues. For mallards, there was an additional dose point at 0.1 mg CN/kg bw which produced a significant reduction in ATP in liver tissue sampled 2 h after administration. There were similar findings with the homing pigeon studies, with significant differences from controls at doses of 0.4 mg CN/kg bw for brain and liver tissue. In terms of ATP responses to cyanide exposure, there was some evidence that the mallards may have been more sensitive to cyanide than homing pigeons.

Pigeon flight time studies

As a reduction in ATP levels in avian species could result in compromised flight due to depressed energy metabolism, the sublethal effects of cyanide were then determined using the homing pigeon model, where flight times were measured in treated and untreated birds (Brasel et al., 2006; Cooper, 2003). Through successive trainings, return times were established and flight paths ingrained in the homing pigeons. Initially, untreated pigeons were set free *en masse* or in groups of ≤6 on several occasions from distinct liberation points to establish flight times. Return time was clocked by electronic scanner, which recorded individual bird bands at the loft (destination) entrance. Flight distances between liberation and destination points varied between 65-200 miles (105-322 km).

For the flight tests, randomly selected pigeons from this trained group were dosed with KCN solution at 0.0, 0.4, 0.5, 0.8 mg CN/kg bw, allowed to recuperate for 15-20 min, and then released. The recuperation period allowed treated birds to overcome the initial effects of cyanide poisoning including lethargy, laboured breathing, incoordination and tremors. Birds regurgitating or vomiting the dose of KCN in the flight trials were not included in the trial and were replaced. Both of these actions were observed during the studies with mallards and homing pigeons. Measures taken to reduce the potential for regurgitation and vomiting of doses included administration of a small dose volume and gently holding the beak of the bird until the animal no longer indicated a gag reflex. Flight trials were repeated 8 times between August-October 1999, with a fresh randomisation on each occasion.

The test results show that for the two shorter distance flights, ≤150 miles (242 km), untreated birds dominated the earliest return times. In longer trials, a dose dependent response was found, with significantly longer flights for both the 0.5 and 0.8 mg CN/kg bw doses. Some birds in the highest treatment dose took up to 4.1 times longer to fly the same distance as the fastest untreated bird, and comparison of pooled data indicated that the median times to fly the same distances for the two highest treatments

were ~1.6 and 1.8 times longer, respectively, than for the untreated birds. Extension of flight times in treated birds is attributed to disorientation, severe toxicosis or energy depletion due to cyanide, i.e. effects consistent with the biochemical effects discussed above.

Cooper and Pritsos (1999) briefly reported a similar study to the above, except that homing pigeons were administered one of 2 doses of NaCN (not stated). As for KCN, flight times of homing pigeons increased with increasing cyanide dose, and with flight distance.

Conclusions regarding sublethal effects

The studies reported by Pritsos and Ma (1997), Ma and Pritsos (1997) and Cooper (2003) indicate a range of biochemical effects to mallards at doses of 0.1-0.8 mg CN/kg bw, using 10 mL doses at a concentration of 10-80 mg CN/L per bird on a single occasion. The extent of any short or long term biological impact from these doses cannot be predicted from the biochemical effects alone, but it is noteworthy that for mallards, these effects occur down to levels approximately one tenth of the acute LD50 value. Pritsos and Ma (1997) concluded that 50 mg CN/L is not a 'safe' level for some migratory birds, and that even at 20 mg CN/L, significant biological insults are occurring.

Biochemical studies by Cooper (2003) with pigeons suggest a comparable level of toxicity to those with mallards in some measures and greater sensitivity in mallards in others. His study with pigeon flight times indicated significant effects at doses of 0.5-0.8 mg CN/kg bw, i.e. 10 mL doses at a concentration of 50-80 mg CN/L per bird on a single occasion.

Ma and Pritsos (1997) indicate that from USEPA (1993 – cf. Section 7.3.6), an average female mallard would drink 0.055 g water/g bw/day, or ~55 mL per day for a 1000 g bird. They considered their administration of cyanide in 10 mL water was therefore not an unreasonable representation of water by these birds at any one time. However, comparable exposure may occur at lower concentrations if >10 mL is consumed in one event or at closely spaced intervals.

9.2.2 Repeat dose/dietary toxicity

Oral

Three unpublished repeat oral studies of limited quantitative value have been undertaken with cyanide salts or mining effluent in drinking water (*Fletcher 1987; Wildlife International Ltd, 1993ab). There is little information on cyanide exposure in the diet, except for a study with cyanogenic glycosides.

Mine effluent and tap water studies

Smith and Mudder (1991) and Hagelstein and Mudder (1997ab) briefly reported an unpublished study by *Fletcher (1987) on the acute toxicity, measured as mortality, of cyanide in tap water and mine effluent solution to mallard ducks. As with the *Fletcher (1986) study (above), the original study report was not available and few details of test methodologies and data were presented.

In the *Fletcher (1987) study, mallard ducks were exposed to a cyanide-containing process solution as the sole source of drinking water for a period of seven days (longer than the standard 5 days). The cyanide concentration (evidently total CN) in the

process solution was 83 mg/L, and this was adjusted by NaCN addition (or presumably, tap water dilution) to produce several test concentrations ranging from 37.5-300 mg/L total cyanide. Five male and five female 19-24 week old mallard ducks were exposed to the range of test concentrations, with buffered tap water as the control solution. Mortalities occurred at concentrations above 75 mg/L total CN, with all but three mortalities occurring on the first day of exposure. The LC50 value was calculated to be 158 mg/L as total CN, or 136 mg/L as free CN.

There are significant difficulties in considering this drinking water study, particularly in view of the difficulties in achieving and maintaining the nominal test concentrations evident in the drinking water tests discussed below, or of estimating cumulative drinking water exposure. There was no indication that the test solutions were renewed or replaced during the study, hence the absence of deaths after the first day could reflect declining CN concentrations as the solutions aged. There were no water consumption data to enable total exposure to be estimated. Without the original reports to verify the actual procedures used and provide data such as measured concentrations recorded over the exposure period and the full results for lethal and sub-lethal effects on the birds, the reported results for this study cannot be confirmed or adequately interpreted and therefore, considered unreliable.

The LC50 values obtained are similar to those found with acute single dose drinking water exposure. They therefore provide limited support for the argument that the birds' metabolism and detoxification of cyanide enable them to tolerate repeated dosing, rather than succumbing to cumulative doses as they take further drinks of contaminated water, as was also evident in the observations of short term exposure discussed above (Section 9.2.1).

Drinking water exposure studies

Bobwhite quail

Fourteen day old northern bobwhite quail (*Colinus virginianus*), housed in laboratory pens (10 per treatment concentration), were exposed to sodium cyanide provided in drinking water *ad libitum* for 5 days, followed by 3 days post-exposure monitoring where birds were exposed to cyanide-free drinking water (Wildlife International Ltd, 1993a). Test methods were based on procedures described by USEPA (1982, 1991), OECD (1984) and ASTM (1987). Drinking water was prepared by dissolving sodium cyanide (~99% purity) of varying amounts (0.025, 0.0445, 0.079, 0.1405 and 0.25 g) in water (250 mL) deionised by reverse osmosis that was first adjusted to pH 10.5 with calcium oxide (CaO). This pH was used in an effort to simulate gold mining process solution (see Section 4.4.2).

Test and control water was prepared and presented daily during the exposure period. Drinking water was presented in water containers with a 1.3 cm wide drinking space to minimise surface area and loss through evaporation. Average ambient temperature was 19.4±1.8°C (humidity 21±8%). The test photoperiod was 16 hours light (~300 lux) to 8 hours darkness. Birds were acclimated from hatching to test initiation, and birds exhibiting abnormal behaviour during the acclimation period were not used in the tests. During the tests, birds were observed twice daily for mortality, toxicity and abnormal behaviour.

Table 9.2. Sublethal acute oral avian toxicity studies with potassium cyanide

Substance/ Bird species	Dose levels	Result	Reference
KCN Female mallards (*Anas platyrhynchos*)	0, 0.25, 0.5, 1.0 or 2.0 mg/kg bw (0, 0.1, 0.2, 0.4 and 0.8 mg CN/kg bw)	No deaths were seen at any dose level. 0.1 mg CN/kg bw: significant reduction was seen in ATP levels in liver (53%) and brain (23%) 2-hours post-dosing (RCR levels not determined). 0.2 mg CN/kg bw: significant reduction was seen in ATP levels in liver (38%) and brain (25%) and RCR in liver (18%), brain (37%) and heart (29%) 2-hours post-dosing. 0.4 mg CN/kg bw: significant reduction was seen in ATP levels in liver (63%) and brain (57%) and RCR in liver (25%), brain (44%) and heart (38%) 2 hours post-dosing, and a significant increase in serum creatine kinase (235%) and rhodanese (57%) and 3-MPS activity (33%) in the brain 24-hours post-dosing. ATP levels had returned to normal in the liver, brain and heart by 24-hours post dosing. 0.8 mg CN/kg bw: significant reduction in ATP levels in liver (59%) and brain (85%) and RCR levels in liver (41%), brain (41%) and heart (38%) 2-hours post dosing, and a significant increase in serum creatine kinase (234%) 24-hours post-dosing (rhodanese and 3-MPS activity not determined).	Pritsos and Ma (1997); Ma and Pritsos (1997)
KCN Homing pigeons (*Columba livia*)	0.0, 1.0, 1.25 or 2.0 mg KCN/kg bw (0, 0.4, 0.5 and 0.8 mg CN/kg bw)	Significant dose dependent relationship between dose and flight duration to fixed destinations for doses ≥1.25 mg KCN/kg bw. For the two highest doses, median flight times increased by ~1.6 and 1.8 times that of untreated pigeons.	Cooper (2003)

Nominal treatment concentrations were 100, 178, 316, 562 and 1000 mg NaCN/L. Samples of drinking water were analysed on day 0 and day 5 to verify test concentrations using a cyanide ion specific electrode. Nominal and actual concentrations of the cyanide ion in the drinking water were 83.4%-115% of nominal with the exception of the 151 mg/L test concentration, which on day 5 was only 13.4% of nominal even though the treatment solution was prepared daily (Wildlife International Ltd, 1993a), indicating that the reported nominal test concentrations are not reliable, given the absence of measured data for days 2-4. Unreliable nominal treatment concentrations were evident in another test with sodium cyanide by Wildlife International Ltd (1993b; refer below).

Bird body weights, water and food consumption rates were monitored on Day 0, 5 and 8. Average estimated water consumption and food consumption rates were determined daily for each test and control group for the exposure period (days 0-5) and for the post-exposure period (days 6-8). Water and food consumption rates were determined by measuring the change in weight of the water (accounting for evaporation) or food presented to the birds over a given time period. However, both water and food consumption rates include an unknown component of wastage/spillage by the birds, which could not be avoided. Hence it is impossible to reliably estimate the volumes of water actually ingested per day from the apparent consumption data.

Food consumption/wastage was variable among groups and no clear concentration-dependent effect was evident. However, there was a significant reduction in weight gain with increasing cyanide concentration in the water presented to the birds. This reduction in weight gain is attributed to a reduction in water consumption. Apparent daily water consumption on the first day of exposure was 7-8 g/bird in the control, but fell from 6-7 g/bird at nominal concentrations of 100 and 178 mg/L to 4, 2 and 1 g/bird at 316, 562 and 1000 mg/L, respectively. A similar pattern was evident on successive days during the 5 day exposure period, but there was little difference evident in the post exposure period (e.g. 11-13 g/bird on the first day of that period in control birds, 10-14 g/bird in birds that had received 100-562 mg/L, all birds dead at 1000 mg/L). Water consumption in the control birds was approximately double that predicted by avian drinking water consumption modelling (USEPA, 1993; Section 7.3.6). This estimates daily consumption of ~4 g for an 18 g bird, as the control quails were at the start of the test, and ~5.5 g for a 29 g bird, as the control birds were at the end of exposure.

Thus the control birds evidently wasted some water, while birds at the highest water concentrations consumed less than they would be expected to consume and may have spilt very little. This could be a result of reduced palatability with increasing NaCN concentration, but an alternative explanation may simply be that the birds were suffering sub-lethal effects from the cyanide that reduced their ability to drink or interest in drinking, such as lethargy (see below). Learned aversion to mine process waters from gold mines (which are alkaline and contain cyanide residues, though they are probably below pH 10.5) has not been found to reduce exposure (Section 7.3.6), but a possible factor is differences in palatability associated with the presence of other substances in the process water and/or in the forms of cyanide present. Effects on water consumption of mallards were seen in a similar study, discussed below. A sodium cyanide drinking water study with rats also showed reduced

consumption at ≥ 100 mg NaCN/L in the absence of clinical signs of NaCN administration or dehydration, which the authors attributed to poor palatability (NTP, 1993). Reduced water consumption was also seen with rats dosed with KCN in drinking water at concentrations adjusted based on consumption to give ≥ 40 mg KCN/kg bw/day (Leuschner et al., 1991 – Section 9.3.2).

There were no overt signs of toxicity at a nominal concentration of 100 mg/L and such signs did not appear with the 178 mg/L treatment until the afternoon of day 3. At 316 mg/L (nominal), one bird showed some signs of toxicity on the afternoon of day 0, but no clinical signs then occurred until the morning of day 3. At 562 mg/L, signs of toxicity were noted on the afternoon of day 0 and were absent the following afternoon, but reappeared on day 2, with the single death found on the morning of day 6. Signs of toxicity at these concentrations continued until day 7. At 1000 mg/L, signs of toxicity appeared on the afternoon of day 0 and continued until day 4, with deaths occurring from day 0 and all birds dead by day 4. Signs of toxicity included wing droop, lethargy and a ruffled appearance at 178 mg/L, plus depression at 316 mg/L, worsening with increasing concentration to include reduced reaction to external stimuli, loss of coordination, and at the highest concentration, prostrate posture.

A single mortality (1/10 birds) occurred at 562 mg/L, while all birds died at 1000 mg/L, with a LC50 value of 705 mg NaCN/L (95% CI 562-1000) reported for this study based on nominal concentrations (Wildlife International Ltd, 1993a). However, this reported LC50 value is clearly above that from the *Fletcher (1987) study and is likely to significantly underestimate toxicity due to uncertainty in the actual treatment concentrations to which the birds were exposed. The doses actually received are highly uncertain both because of this and because of the uncertainty in water consumption as opposed to spillage. For example, if the apparent consumption data are considered together with the nominal concentration data, the mid-range treatment (316 mg/L nominal) actually resulted in the highest total consumption of CN, but no mortality was observed in this group.

Thus there were clear worsening trends with increasing dose in clinical signs and mortality, and the declining trend in apparent water consumption probably indicated both reduced wastage-causing activity as well as a reduction in actual water consumption. The estimated LC50 value based on nominal concentration data is unreliable. When the LC50 value is converted on the basis of the CN^- content in NaCN, the value of 374 mg CN/L appears very high compared to measured WAD CN concentrations in TSFs where known mass bird death events have occurred, as well as minor or individual bird impacts (Section 9.9). It is also much higher than predicted from acute oral LD50 data with Japanese quail (see below). The estimated LC50 values are quite unreliable and this study is considered unacceptable.

Mallard ducks

Wildlife International Ltd (1993b) undertook a study using methods similar to the above, but with 7 day old mallards (10 per treatment). Stock solution was prepared by dissolving sodium cyanide (6.6 g; ~99% purity) in 2200 mL of water deionised by reverse osmosis and adjusted to pH 10.5 with CaO. To prepare the test concentrations (100, 178, 316, 562 and 1000 mg NaCN/L), amounts of stock solution (100, 178, 316, 562, 1000 mL) were diluted in 3000

mL deionised, pH adjusted water. Mallards were provided drinking water containing the test material via a nipple water system. Despite this, reported values for apparent water consumption indicate a large amount of wastage occurred with control birds, e.g. at the start of the exposure period mean control bird weights were 86-93 g, yet they consumed 192-243 g/water each on the first day, whereas avian drinking water consumption modelling (USEPA, 1993; Section 7.3.6) indicates they would be expected to consume ~12 g/bird/day.

Analytical determination of CN using a cyanide ion specific electrode indicated that actual treatment concentrations on day 0 were only ~5%-8% of nominal and on day 4 concentrations were ~6%-8% of nominal, even though the solutions were prepared daily. Re-analysis of day 0 and day 4 test solutions gave concentrations of ~11%-27% and 15%-23% of nominal. The analytical results suggest that the mallards were exposed to concentrations much lower than the estimated nominal concentrations reported, with further uncertainty due to the absence of data for the other days of exposure.

From the first day of the exposure period continuing through the post exposure period, there was a clear reduction in water use by mallards exposed to the NaCN solutions, with a generally decreasing trend with increasing concentration. For example, on the first day of exposure, water consumption was 95, 32, 46, 25 and 9 g/bird at nominal concentrations of 100, 178, 316, 562 and 1000 mg NaCN/L, respectively. On the third day, the corresponding values were 110, 65, 32, 4 and 7 g/bird, compared to 174-218 g/bird in the control groups. Thus, as with the quail study, apparent consumption somewhat exceeded expected drinking water consumption at the low test concentrations (though not nearly as much as in the controls), and fell short of expected consumption at the highest concentrations. There were also reduced weight gain and reduced feed intake with increasing treatment concentration, and even the lowest test concentration led to lower feed consumption and weight gain compared to the control.

As with the above quail study, the earliness of onset and severity of clinical signs increased with increasing dose, and these effects may have been a contributing factor to reduced water use. However, no clinical signs were evident at the 100 and 178 mg/L nominal concentrations. This may indicate a palatability factor with NaCN, or possibly in this test the control water was not brought to a pH of 10.5 with CaO and it is the alkalinity of the water that discouraged use.

Of the ten birds in each treatment group, four birds died at a nominal concentration of 316 mg/L, and all birds died at the two higher concentrations. A LC50 value of 340 mg NaCN/L (95% CI 316-562) was reported for this study based on the nominal concentrations (Wildlife International Ltd, 1993b). This converts to 180 mg CN/L, i.e. comparable to the results of the *Fletcher (1987) study (above). However, this LC50 value substantially underestimates toxicity, as actual treatment concentrations were significantly less than nominal. If the available measured CN^- data (reanalysed data set) are used instead of the nominal values, an LC50 estimate of ~42 mg CN/L is obtained. This value is similar to or below levels known to cause minor or individual bird death incidents at TSFs (Section 9.9), and comparable to values predicted from acute oral LD50 data with mallard ducks and other birds (Table 9.4). However, the uncertainties in the concentrations of CN^- to which the birds were actually exposed are still too great for either LC50 estimate to be considered reliable. This study is therefore considered unacceptable.

Table 9.3. Avian water exposure cyanide toxicity studies

Species	Nature of test	Comments	Results	
Mallard ducks (*Anas platyrhynchos*)	LD50 acute exposure tests based on a single dose of tap water or process water containing a range of free CN concentrations, with the results expressed as an acute LC50	Tap water	Acute drinking water exposure LC50 = 181 mg/L free CN in a single dose (evidently of 7.5 mL)	*Fletcher (1986)
		Effluent pond water	Acute drinking water exposure LC50 = 212 mg/L free CN in a single dose (evidently of 7.5 mL)	
	LC50 dietary exposure test based on drinking water exposure for 7 d	Process solution adjusted with NaCN	7 d LC50 = 158 mg/L total CN 7 d LC50 = 136 mg/L free CN (evidently initial concentrations, without replenishment)	*Fletcher (1987)
Bobwhite quail (*Colinus virginianus*)	Drinking water exposure for 5 days based on dietary test guidelines	14 d old birds, initial weight ~18 g	LC50 = 705 mg NaCN/L (probit-based CI not available), equivalent to 374 mg CN/L (nominal concentrations, not reliable)	Wildlife International (1993a)
Mallard ducks (*Anas platyrhynchos*)		7 d old birds, initial weight ~86-93 g	LC50 = 340 mg NaCN/L (probit-based CI not available), equivalent to 180 mg CN/L (nominal concentrations, not reliable) LC50 based on measured data = ~42 mg CN/L (still not reliable)	Wildlife International (1993b)
Mallard ducks (*Anas platyrhynchos*)	Individual ducks were placed in pens with contaminated water and exposed for a 2 h period. Test concentrations were 0, 40, 56, 80, 112 and 160 mg CN/L as KCN, with 12 ducks per dose.	No details available, but presumably similar to the LD50 study of Henny et al. (1994)	Short term (2 h) water exposure LC50 = 115 mg CN/L (95% CI = 88.4, 173)	Link et al. (1996)

Dietary studies

There appear to be no dietary studies with cyanide salts and birds, but there is a study by *Gomez et al, (1988 – reported in IPCS, 2005 and Hagelstein and Mudder, 1997a) with diets containing cyanogenic glycosides, which release CN^- in the gut (Section 5.1.1). In two experiments, one day old chickens were fed diets containing up to 30% cassava root meal (CRM) or cassava foliage meal (CFM) for 56 or 63 days. The cassava meal itself contained 300 (CRM) or 156 (CFM) mg total CN/kg. Increased quantities of dietary cassava cyanate from either source were associated with increased blood serum thiocyanate. Diets with CRM failed to adversely affect broiler survival, performance or feed efficiency. The CFM diets led to increased mortality, decreased weight gain and decreased feed efficiency, but these effects were ascribed to aflatoxin contamination rather than the presence of cyanogenic glycosides. Thus, the study showed that broilers were tolerant of relatively high levels of dietary cyanogenic glycosides. As stated above, domestic fowls are known to be a relatively insensitive species to chemical toxicity.

LC50 values estimated from LD50 data

Using the LD50 values and corresponding median bird weights indicated in Table 9.1 and the drinking water estimation approach discussed in Section 7.3.6, worst case LC50 values for each species can be calculated assuming an entire day's water consumption occurs within a short period, i.e. a worst case situation which is likely to be rather different to normal field behaviour for many species. The resulting values are shown in Table 9.4 (95% confidence intervals have not been shown).

9.2.3 Toxicologically significant forms of cyanide to birds

Hagelstein and Mudder (1997b) presented a discussion of factors affecting the toxicological significance of different forms of cyanide when ingested by birds.

They note that the primary toxic constituents in mining process solutions are the WAD forms of cyanide, including free CN and the weakly bound metal complexes of copper, nickel and zinc, and not other constituents of total cyanide such as iron complexes. They claim that free cyanide is rapidly absorbed from the avian digestive tract, while its formation and absorption from the dissolved metal complexes are comparatively slow, even at low pH. As evidence of the stability of metal cyanide complexes, they note that conditions needed for laboratory analyses of WAD CN are somewhat more rigorous than the stomach of an animal, though it should be noted that the stomach pH of raptors is lower than that used to determine WAD CN (Section 3.3.1).

They argue that metal complexed cyanides have been demonstrated to be less toxic individually than is free cyanide, as a result of which an organism can tolerate a higher level of complexed cyanide than free cyanide, since its detoxification mechanisms rapidly convert slowly forming free cyanide to thiocyanate. Furthermore, under acidic conditions below a pH of 4, such as in the stomach, WAD CN complexes partially dissociate to free CN and an insoluble neutral metal cyanide complex which precipitates, as for copper and nickel cyanides in the following equations:

$Cu(CN)_3^{-1} + H^+ = Cu(CN)_2\ (s) + HCN$

$Ni(CN)_4^{-2} + 2H^+ = Ni(CN)_2\ (s) + 2HCN$

Table 9.4. Estimated LC50 values for NaCN to various bird species, based on LD50 data and median bird bodyweights in the corresponding studies

	LD50 (mg CN/kg)	Median weight (g)	Estimated daily water consumption (g)	Estimated LC50 (mg/L)
Domestic chicken (*Gallus domesticus*)	11.1	1610	81.2	220
Black vulture (*Coragyps atratus*)	2.5	2215	101	55
American kestrel (*Falco sparverius*)	2.1	118	14.1	18
Eastern screech-owl (*Otus asio*)	4.6	185	19.0	45
European starling (*Sturnus vulgaris*)	9.0	75	10.4	65
Japanese quail (*Coturnix japonica*)	5.0	130	15.0	43
Mallard (*Anas platyrhynchos*)	1.4	1260	68.9	26

They add that in order to break down the neutral metal cyanide complexes a much lower pH was needed, together with an extended period of vigorous agitation. Hence it was likely that as detoxification in the animal to thiocyanate is relatively rapid, it is unlikely that very slow release of additional free cyanide, if it occurs, would contribute to long term chronic or sublethal toxicity.

Hagelstein and Mudder (1997b) then gave as an example what they considered typical composition of a 50 mg/L WAD CN solution associated with a cyanidation solution after treatment or recovery and prior to its discharge into a TSF:

> Copper cyanide 30 mg/L as CN, zinc cyanide 10 mg/L as CN, nickel cyanide 5 mg/L as CN, and free cyanide 5 mg/L.

With this solution, free CN could eventually increase to about 25 mg/L as about one third of the copper cyanide breaks down, one half of the nickel and zinc cyanides break down, and the remaining neutral metal cyanides precipitate. Therefore, at most only about half of the measured WAD CN content would become available.

While these arguments may apply to some degree in various circumstances, evidently where steps have been taken to destroy free cyanide, it is noted that the actual composition of tailings effluent may vary widely. Measured data show that high concentrations of free CN may still remain in tailings effluent (Section 6.6.4), though it is likely that these values are overestimates because of sampling and methodology difficulties with determining free CN (Schulz, pers. comm. 2006). Thus in practice, it appears reasonable to conclude that in many cases the actual composition of the WAD CN will result in somewhat lower toxicity than an equivalent concentration of free cyanide. However, the extent of these effects is dependent on the conditions at individual sites, which are also likely to change over time, and any such effects are likely to be less significant in species such as raptors with a low stomach pH.

9.3 Effects on mammalian species

9.3.1 Acute toxicity

Sodium cyanide is very toxic by all the routes of exposure investigated. The LD50 values for NaCN together with LC50 values for hydrogen cyanide in various species are reported in Table 9.5, along with studies investigating acute toxicity.

Inhalation

No studies are available for NaCN, which is not volatile but which may occur in dusts. A number of studies are available for HCN, with exposure durations ranging from 10 seconds LC50 = 3778 mg/m^3) to 1 hour LC50 = 158 mg/m^3 for HCN.

In a series of experiments, Ballantyne (1983a; *1984) determined LC50 values for HCN for a number of exposure periods starting from 10 seconds and longer in rats and 45 seconds and longer in rabbits. For each test 6 to 10 female animals per dose, and a minimum of 4 dose levels, were used. No further experimental details are available. The results from this study, together with a number of additional studies cited in the ATSDR (2006) review are presented in Table 9.5. In this table, all values have been converted from HCN to cyanide (CN) and are presented as ppm and mg/m^3.

In a rat inhalation study with cyanogen [$(CN)_2$], asphyxia was observed in animals exposed to a concentration equivalent to 125 ppm (140 mg/m^3) cyanide from 7.5 minutes exposure. At 500 ppm (562 mg/m^3) eye irritation was observed from 7.5 minutes exposure, and restless and panic movements, poor coordination, tremor, and lethargy from 1.5 minutes (*McNerney and Schrenk, 1960).

Data are also available from old, poorly reported studies investigating histopathological changes to the central nervous system (CNS) and brain following exposure to cyanide (*Hirano et al., 1967: *1968; *Levine, 1969; *Levine and Stypulkowski, 1959). However, the limited details available, including information on exposure levels, mean no reliable conclusion can be drawn from the data. Similarly, although *Hartung (1982) reported clinical signs of toxicity in cats and dogs at additional exposure levels of HCN to those reported in Table 9.5, as well as experiments in rabbits, the absence of information on exposure duration means these data are of limited value. Hence, they are not discussed further in this review.

A recent study is available investigating the potentiation of noise-induced hearing loss by low concentrations of HCN in rats (Fechter et al., 2002). The combined exposure to loud noise and HCN caused a dose-dependent compound action potential (CAP) threshold impairment that exceeded the noise exposure alone. It is suggested by the authors that this impaired auditory function with HCN plus noise is due to oxidative stress in the cochlea. However, the significance of these findings to wildlife is unclear, as animals are unlikely to be exposed to a combination of HCN and a loud continuous noise for a substantial length of time.

Oral

Studies are available for NaCN, as well as other cyanide salts. For NaCN, LD50 values ranging from 5.1 to 15 mg/kg bw (equivalent to 2.7 to 8.0 mg CN/kg bw) have been reported in the rat (Smyth et al., 1969; Ballantyne, *1984; 1988). Additionally values of LD50 values of 8.7 and 28 mg NaCN/kg bw are available for the mouse (Clark et al., 1991), along with 5.1 and 5.7 mg NaCN/kg bw in the rabbit (Ballantyne, 1983), 8.4

mg NaCN/kg bw in brown bats (*Myotis lucifugus*; Clark et al., 1991) and 8.66 mg NaCN/kg bw for brushtail possums (*Trichosurus vulpecula*; Bell, 1972).

In a series of experiments by Ballantyne (1983), 6 to 10 female rabbits per dose, and a minimum of 4 dose levels, received NaCN, potassium cyanide (KCN) or HCN. Two series of experiments were conducted and LD50 values of 5.1 and 5.7 mg NaCN/kg bw, 5.9 and 7.5 mg KCN/kg bw, and 2.5 and 4.2 mg HCN/kg bw were obtained. No further details are available. In a later study also by Ballantyne (1988), 10 female rats and 10 female New Zealand rabbits per dose were administered 4.5 to 6.3 mg/kg bw and 4.0 to 6.4 mg/kg bw NaCN respectively, and observed up to 7 days post-dosing. LD50 values of 5.7 and 5.1 mg NaCN/kg bw were obtained in the rat and rabbit respectively. Clinical signs of toxicity, in order of their development, included rapid breathing, weak movements, tremors, respiratory distress, severe spasms and convulsions, shallow breathing and coma.

The majority of studies investigating acute oral toxicity are old and/or contain limited or no information on methodology, such as, Ferguson (1962), Smyth et al (1969) and Clark et *al* (1991), which are only available as an abstract, or are of limited value as only a single dose level was employed (Christel et al., 1977).

The results from all the above studies along with studies cited in Ballantyne (1987) are presented below in Table 9.6. In this table, doses and LD50 values with NaCN are also reported as mg CN/kg bw, while other cyanide salts are reported as mg CN/kg bw only.

Information on acute cyanide poisoning is also available in wildlife and livestock.

Bell (1972) investigated the acute oral toxicity of NaCN to wild-caught Australian brushtail possums (*Trichosurus vulpecula*), a pest species in New Zealand (Morgan and Hickling, 2000; Eason et al., 2000; Gregory et al., 1998; O'Connor and Matthews, 1995; Warburton and Drew, 1994; Turner, 1969). NaCN was dissolved directly in distilled water (4000 mg/L) and ≤5 mL was administered orally to each possum via a size 4 enterogastric catheter within 24 hours of capture. Five dosages were assessed (7, 8, 9, 9.5 and 10 mg/kg bw; 8 or 16 per treatment). After dosing, possums were placed in individual cages and mortality was monitored. Mortality in the lowest and highest doses was 19% and 100%, respectively, with 50% mortality at a dose of 9.5 mg NaCN/kg bw. An LD50 value of 8.66 mg NaCN/kg bw (95% CI 8.17-9.60) was calculated by probit analysis (4.6 mg CN/kg bw, 95% CI 4.3-5.1).

In a New Zealand study, Gregory et al. (1998) investigated the spontaneous and response behaviour of brushtail possums exposed orally to a single dose of cyanide. In the spontaneous behaviour study, 22 possums (14 male, 8 female) were used. Mean live weight was 3.03±0.48 kg (range 1.45-4.03 kg). Four possums were given 0.4 g of a 600 g/kg of a commercial sodium cyanide paste and 18 possums ate 20±8 mg/kg of KCN in the encapsulated form (pellet). Pellets (5-6 mm diam.) consisted of KCN encased in a water-insoluble, acid-resistant coating which has to be broken mechanically (e.g. chewing action) before HCN can be produced in the gut. After consumption, possums were observed for effects until death. There were no obvious differences in effects in animals receiving the paste or pellet. Four behavioural phases were observed over time:

- Normal behaviour (2 mins 13 s);

Table 9.5. Acute inhalation toxicity studies with hydrogen cyanide and mammals

Species (strain)	Exposure duration	Endpoint	Results	Reference
Rat	10 secs	LC50	3237 ppm (3637 mg CN/m^3)	Ballantyne (1983)
	1 min	LC50	1260 ppm (1416 mg CN/m^3)	
	5 min	LC50	422 ppm (475 mg CN/m^3)	
Rat (Wistar)	5 min	LC50	483 ppm (543 mg CN/m^3)	*Higgins et al (1972)
Rat	30 min	LC50	129 ppm (145 mg CN/m^3)	*Ballantyne (1984)
Rat	30 min	LC50	148 ppm (166 mg CN/m^3)	Ballantyne (1983)
	1 h	LC50	136 ppm (153 mg CN/m^3)	
Mouse	1 to 2 min	'Fatal'	1252 ppm (1406 mg CN/m^3)	*Hartung, (1982)
Mouse (ICR)	3 min	Mortality	90% mortality in males at 400 ppm (449 mg CN/m^3)	*Hume et al (1995)
Mouse (ICR)	5 min	LC50	310 ppm (348 mg CN/m^3)	*Higgins et al (1972)
Mouse (Swiss-Webster)	30 min	Respiration LD50	Respiratory rate depressed by 50% (RD50) at 60 ppm (67 mg CN/m^3) 150 ppm (169 mg CN/m^3)	*Matijak-Schaper and Alarie (1982)
Mouse	45 min	'Fatal'	106 ppm (119 mg CN/m^3)	*Hartung, (1982)
	2.5 to 4 h	'Fatal'	43 ppm (49 mg CN/m^3)	
Rabbit	45 secs	LC50	2084 ppm (2341 mg CN/m^3)	Ballantyne (1983)
	5 min	LC50	350 ppm (393 mg CN/m^3)	
	25 min	LC50	178 ppm (200 mg CN/m^3)	
Monkey (*Cynomolgus*)	30 min	Various	Severe dyspnea, disrupted respiration, bradycardia, arrhythmia, T-wave abnormalities, semi-consciousness and electroencephalogram changes at 96 ppm (108 mg CN/m^3)	*Purser et al (1984)
Dog	2 to 10 min	Various	Motor incoordination, muscular rigidity and coma from 149 to 633 ppm (167 to 711 mg CN/m^3)	*Haymaker et al (1952)
Dog	1 h	'Tolerated'	87 ppm (97 mg CN/m^3) may be 'tolerated' during exposure, however, deaths seen after exposure.	*Hartung, (1982)
Cat	6 to 7 min	'Markedly toxic'	120 ppm (135 mg CN/m^3)	*Hartung, (1982)

- Ataxia: impaired balance and co-ordination, but remained upright or standing (lasting ~1 min);
- Recumbent with intermittent spasms: prostrate and unable to support their weight on their limbs with some having mild to moderate episodes of hyperpnoea or dyspnoea, limb movements, spasms, body turning whilst recumbent, convulsions, and breathing movements. Convulsive episodes included dorsiflexion with chin and forelimbs extended, forelimb padding and running movements, hindlimb tonic flexion, tail flailing and apnoea and tachypnoea after convulsions had subsided; and
- Recumbent with limited activity: prostrate with little physical activity other than breathing movements. This was the longest phase accounting for 52% of the time between consumption and death.

Average time to death was 14 min 8 s (up to 21 min 45 s). None of the possums showed any salivation, retching or vomiting at any stage.

In a second trial by Gregory et al. (1998), 20 possums (14 male, 6 female), were offered 21±5 mg/kg of KCN in the pellet form. After consumption, the responsiveness of the possums to external stimuli was observed. External stimuli included auditory (a loud noise), visual (a threatening gesture by moving a hand rapidly towards the face of the possum), somatosensory and pain (pinching the ear, foot and tail). An overt physical response to an external stimulus was recorded as a positive result. The righting response and jaw muscle tension was also tested. On average, the possums ate 90% of the pellet administered (~19 mg KCN/kg bw). Abnormal behaviour (imbalance) was noted after 3 min 15 s. Over time (5-6.5 mins), the possums were unable to respond to each of the stimuli or from being handled. Convulsive episodes were followed by death after ~17.9 mins (average). None of the possums showed any salivation, retching or vomiting at any stage. The first faculty that showed obvious signs of depression was balance, followed by reduced responsiveness to auditory and visual stimuli. Loss of responsiveness to somatosensory and potentially pain varied temporally with different parts of the body, and the response to pinching the ear was lost before the foot pinch and tail pinch. Possums exposed to external stimuli (i.e. more physically active) took slightly longer on average to experience brain dysfunction and die.

Red foxes poisoned orally by sodium cyanide in meat baits via a gelatine capsule (1 gram NaCN) generally exhibited a short period of head shaking followed by a period (45-60 seconds) of immobility immediately after eating the bait (Marks and Gigliotti, 1996). The cyanide was mildly irritating yet no obvious signs of distress were apparent. Some foxes tried to continue feeding before immobilisation occurred. Dosed animals then exhibited a sudden short burst of uncoordinated activity (e.g. staggering, running 5-12 seconds), prior to collapse. Within 3 minutes of head shaking, all dosed foxes showed a lack of corneal reflex, corresponding to brain death. A rapid and strong heartbeat was always apparent for at least 2 minutes after brain death. Periodic muscular contractions would occur spontaneously for up to 10 minutes after death.

Table 9.6. Acute oral toxicity to mammals of sodium cyanide, potassium cyanide and hydrogen cyanide

Substance	Species (strain)	Number of animals/dose level	Endpoint	Results	Reference
NaCN	Female rat	10	LD50	2.7 and 3.0 mg CN/kg bw	Ballantyne (*1984; 1988)
	Rat		LD50	8.0 mg CN/kg bw	Smyth et al (1969)
	Mouse		LD50	4.6 mg CN/kg bw	Clark et *al* (1991)
	White-footed mouse		LD50	14.8 mg CN/kg bw	
	Female rabbit	6-10	LD50	2.7 and 3.0 mg CN/kg bw	Ballantyne (1983)
	Red fox	10 animals fed 530 mg CN in meat bait	Mortality	All animals died	Marks and Gigliotti (1996)
	Little Brown Bat		LD50	4.4 mg CN/kg bw	Clark et *al* (1991)
	Brushtail possum	8-16 per dose administered by enterogastric catheter 7.0-10.0 mg NaCN/kg bw.	LD50	4.6 mg CN/kg bw	Bell (1972)
KCN	Female rat		LD50	3.0-3.9 mg CN/kg bw	*Ballantyne (1984)
	Male rat (Sprague-Dawley)	3	LD50	~4.0 mg CN/kg bw	Leuschner et al (1991)
	Rat (Sprague-Dawley)	4 mg CN/kg bw	Mortality	19/20 animals died	Ferguson (1962)
	Male rat		LD50	4.0 mg CN/kg bw	Ballantyne (1987)
	Female rabbit		LD50	2.3 mg CN/kg bw	Ballantyne (1987)
HCN	Female rat		LD50	3.5-4.0 mg CN/kg bw	*Ballantyne (1984)
	Female rabbit	6-10	LD50	2.4-4.0 mg CN/kg bw	Ballantyne (1983)

Livestock exposed to cyanide usually show effects within minutes, with symptoms including excitability (initially) then muscle tremors, salivation, lachrymation, defaecation, urination and dyspnoea (shortness of breath), followed by muscular incoordination, gasping and convulsions. Death may occur quickly, depending on the dose received (*Towill, et al., 1978; Cade and Rubira, 1982). Livestock are mostly exposed to cyanide through consumption of certain forage plants (e.g. some varieties of sorghum).

Dermal

In a series of experiments Ballantyne (1983a; 1988) investigated the acute toxicity of NaCN, as well as other cyanide salts, in the rabbit. LD50 values equivalent to 4.1 to greater than 106 mg CN/kg bw were obtained depending on the experimental conditions employed. In the earlier study by Ballantyne (1983), 6 to 10 female rabbits per dose (a minimum of 4 dose levels), received NaCN, KCN or HCN. LD50 values were 14.6 mg NaCN/kg bw (equivalent to 7.7 mg CN/kg bw), 22.3 mg KCN/kg bw (8.9 mg CN/kg bw) and 7.0 mg HCN/kg bw (6.7 mg CN/kg bw). No further experimental details are available.

In a later study by Ballantyne (1988), 6 to 12 female New Zealand rabbits per dose were administered NaCN at 7.0-20 mg/kg bw to moist skin, 5.0-10.0 mg/kg to abraded skin and 200 mg/kg bw to dry skin, for a 6 hour exposure period. LD50 values of 11.8 mg NaCN/kg bw (6.3 mg CN/kg bw) and 7.7 mg NaCN/kg bw (4.1 mg CN/kg bw) were obtained for moist and abraded skin respectively. Signs of toxicity seen in animals with moist or abraded skin, in order of their development, included rapid breathing, weak movements, tremors, respiratory distress, severe spasms and convulsions, shallow breathing, and coma. For animals with dry skin no signs of toxicity or deaths were seen at the only dose tested, hence, the LD50 was greater than 200 mg NaCN/kg bw (greater than 106 mg CN/kg bw).

Deaths occurred also in guinea pigs when administered HCN, however, the doses used could not be quantified from these old poorly reported studies (*Fairley et al., 1934; *Walton and Witherspoon, 1926). Hence, they are not discussed further in this review.

Ocular

Data are available in the rabbit that show cyanide is very toxic following a single instillation to the eye (Ballantyne 1983a; 1988). The data indicate that NaCN, KCN and HCN are more toxic to rabbits via the ocular than the dermal route of exposure.

In the earlier study by Ballantyne (1983), 6 to 10 female rabbits per dose, and a minimum of 4 dose levels, received NaCN, KCN or HCN. LD50 values were 5.0 mg NaCN/kg bw (equivalent to 2.7 mg CN/kg bw), 7.9 mg KCN/kg bw (3.2 mg CN/kg bw) and 1.1 mg HCN/kg bw (1.0 mg CN/kg bw).

In the later study by Ballantyne (1988), 3.18 to 9.96 mg/kg bw NaCN powder was instilled into the conjunctival sac of 10 female New Zealand rabbits per dose and animals observed for signs of toxicity, including local eye injury, over a 7 day post-instillation period. A LD50 value of 4.5 mg NaCN/kg bw (2.4 mg CN/kg bw) was determined. Signs of toxicity seen, in order of their appearance, were rapid breathing, weak and ataxic movements, convulsions, irregular shallow breathing, and coma. Deaths occurred within 4 to 12 minutes.

Irritation

No standard skin studies are available for NaCN, as it is very toxic to rabbits by the dermal route of exposure following a single application, as discussed above. In the study by Ballantyne (1988), however, the author reported that irritation was promptly seen following instillation of NaCN powder to the rabbit eye, and consisted of marked lachrymation, moderate conjunctival hyperemia, and mild chemosis. In survivors, the conjunctival hyperemia became progressively more severe and, by 24 hours post-instillation, there was mild to moderate corneal opacification and mild iritis. Conjunctival redness and lachrymation slowly resolved after 24 hours, but mild inflammation (no further details) was still present at the end of the observation period: day 7 post instillation. Although keratitis had resolved in a few animals by day 7, in the majority there was a persistent mild to moderate keratitis.

Sensitisation

No data are available.

9.3.2 Repeat dose toxicity

Inhalation

No studies are available for NaCN. Studies are available for cyanogen [$(CN)_2$] and HCN. More detailed study summaries and evaluation of the data are presented in Table 9.7.

The toxicity of sub-chronic exposures to $(CN)_2$ was investigated in both rats and dogs in a 6-month study by Lewis et al (1984). Male rats were exposed to 0-25 ppm $(CN)_2$, equivalent to approximately 0 to 50 ppm cyanide respectively. Plasma T_3 and T_4, hematocrit values and haemoglobin concentration were determined, along with lung moisture content and gross and microscopic examination performed on the heart, liver, kidney, cerebellum, cerebrum, lungs, thyroid, spleen, and bone marrow. The only treatment related effect seen was a statistically significant decrease in body weight gain at 50 ppm cyanide compared to controls.

Male rhesus monkeys were exposed to 0 to 25 ppm $(CN)_2$ for 6 months, equivalent to approximately 0 to 50 ppm cyanide (Lewis et al., 1984). Behavioural tests, lever-pressing responses taught on a reinforcement schedule (one reinforcement for each response) were conducted on all animals as were electrocardiograms. Plasma T_3 and T_4, hematocrit values and haemoglobin concentration were determined, along with lung moisture content and gross and microscopic examination performed on the heart, liver, kidney, cerebellum, cerebrum, lungs, thyroid, spleen, and bone marrow. For behavioural testing, an increase in mean response was seen for all dose levels. The increase at 50 ppm was marginally statistically significant though transitory, as the rate returned to control levels before exposures were terminated. Compared to controls, a statistically significant decrease in lung moisture content was reported in animals exposed to 22 and 50 ppm cyanide.

In a 20-day study in male rats (*O'Flaherty and Thomas, 1982), increased cardiac-specific creatinine phosphokinase activity was detected in the blood of rats exposed to 200 ppm (225 mg/m^3) HCN, equivalent to 192 ppm (216 mg/m^3) cyanide.

In a 28 to 96 day study (*Valade, 1952), clinical signs of toxicity and histopathological changes to the brain and CNS were seen in dogs exposed to 45 ppm (50.6 mg/m^3) HCN, equivalent to 43 ppm (48.6 mg/m^3) cyanide.

Oral

A limited number of studies are available in the rat and dog with NaCN along with studies that used sources of cyanide other than NaCN. More detailed study summaries and evaluation of the data are presented in Table 9.8.

Studies with NaCN are presented below.

In a well conducted and comprehensive 13-week study (NTP, 1993), male and female rats and mice were administered NaCN in drinking water at concentrations up to 300 ppm: equivalent to approximately 12.5, 12.5, 24.3 and 28.8 mg CN/kg bw/day in male and female rats, and male and female mice, respectively. Animals were evaluated for histopathology, clinical chemistry, haematology, urine chemistry and reproductive toxicity, as well as sperm motility and vaginal cytology examinations.

In rats water consumption was reduced at the top two dose levels. A slight decrease in body weight gain was seen in males at 12.5 mg CN/kg bw/day. At 12.5 mg CN/kg bw/day a slight though statistically significant reduction was seen in cauda epididymal weight and in the number of spermatid heads per testis. A marginal decrease was also seen in sperm motility in all treatment groups compared to controls, which was statistically significant at 12.5 mg CN/kg bw/day. In females, a significant increase was seen in time spent in proestrus and diestrus relative to estrus and metestrus at 4.9 mg CN/kg bw/day and above.

In mice water consumption was reduced at the top two dose levels. A slight decrease in body weight gain was seen in females at 28.8 mg CN/kg bw/day. In males, a slight reduction was seen in cauda epididymal weight at 24.3 mg CN/kg bw/day.

In a 14-week study (Kamalu, 1993), dogs were fed either a control diet containing rice as the carbohydrate source, cassava that was expected to release 10.8 mg HCN/kg cooked food (equivalent to 10.4 mg CN/mg bw/day), or a control diet containing a level of NaCN expected to release 10.8 mg HCN/kg cooked food. Haematological and biochemical investigations along with urinalysis were conducted throughout the study, and histological examination conducted on the liver, kidney, myocardium, testis and adrenal gland.

For animals administered NaCN (10.4 mg CN/kg bw/day), a statistically significant increase in urinary protein excretion with a decrease in serum albumin was seen. A changed plasma-free amino acid profile was seen along with histological changes in the kidney, adrenal gland and testes, and an effect on spermatogenesis.

Table 9.7. Summary of repeat-dose inhalation toxicity

Species	Exposure	NOAEC	Result	Comment	Reference
Rats (Sprague-Dawley, 30 males per group)	0, 11, 25 ppm (CN_2) 6 h/day, 5 days/wk for 6 months (approx 0, 22, 50 ppm CN)	22 ppm CN	Decrease in body weight gain (13%) at 50 ppm CN. No deaths, clinical signs of toxicity, haematology, clinical chemistry or histopathological changes seen.		Lewis et al. (1984)
Monkeys (Rhesus, 5 males per group)	0, 11, 25 ppm (CN_2) 6 h/day, 5 days/wk for 6 months (approx 0, 22, 50 ppm CN)	50 ppm CN	Significant, but transient changes in behaviour at 50 ppm cyanide and a statistically significant decrease in lung moisture content at 22 and 50 ppm cyanide, in the absence of histopathological changes to the lung. No deaths, clinical signs of toxicity, haematology or clinical chemistry changes seen.	Behavioural changes and decreases in lung moisture content are considered to be of questionable biological significance.	Lewis et al. (1984)
Rats (Long-Evans, males)	200 ppm (HCN) 12.5 mins at 4-day intervals for 20 days (approx 192 ppm CN)	< 192 ppm CN	Increased cardiac – specific phosphokinase activity in blood in the absence of histological changes to the heart.		*O'Flaherty and Thomas (1982)
Dogs	45 ppm (HCN) 30 mins at 2-day intervals for 28-96 days (approx 43 ppm CN)	---	Dyspnea, tremors, stiffness, ataxia, vomiting, tenesmus and diarrhoea observed, along with vasodilation, haemorrhage and atrophy in Purkinje cells of the brain and glial cells of the CNS.	Dogs have very low levels of rhodanese, an enzyme used to detoxify cyanide.	*Valade (1952)

For animals administered cassava in the diet (10.4 mg CN/kg bw/day), a statistically significant increase in urinary protein excretion and decrease in plasma albumin, calcium and potassium was seen. A changed plasma-free amino acid profile was seen, along with histological changes in the liver, kidney, adrenal gland, heart and testes.

In a 14.5 month study (*Hertting et al., 1960), degenerative changes in ganglion cells of the CNS and cloudy swelling of epithelial cells of the renal tubules were seen in dogs administered NaCN in capsules at dose levels of 0.27 to 1.68 mg CN/kg bw/day. It is also reported that chronic intestinal inflammation was observed in dogs administered 20.3 mg CN/kg bw/day.

Studies that used sources of cyanide other than NaCN are presented below.

Rat

In a 15-day study (Sousa et al., 2002), male rats were administered KCN daily in drinking water at dose levels up to 9.0 mg KCN/kg bw/day (equivalent to 3.6 mg CN/kg bw/day). Animals were evaluated for clinical chemistry and histopathology conducted on the kidney, thyroid and liver. A statistically significant decrease in body weight gain was seen throughout the study at 3.6 mg CN/kg bw/day. A statistically significant increase in clinical chemistry parameters were seen from the lowest dose tested (0.12 mg CN/kg bw) though decreases were seen at 3.6 mg CN/kg bw. Histopathological changes to the kidney were seen at 1.2 mg CN/kg bw/day and above, the liver at 3.6 mg CN/kg bw/day, and the thyroid in a dose dependent manner in all treated groups.

In a 13-week study (Leuschner et al., 1991), male rats were administered KCN in the drinking water at dose levels up to 140 to 160 mg/kg bw/day (equivalent to 56 to 64 mg CN/kg bw/day). The top dose level of 64 mg CN/kg bw/day was reduced to 56 mg CN/kg bw/day at the beginning of week 12 of exposure as a total of 11 animals had died. A statistically significant decrease was seen in water consumption from 16 mg CN/kg bw and body weight gain from 32 mg CN/kg bw/day, along with an increase in food consumption at 56 to 64 mg CN/kg bw/day.

In a 13-week study (*Gerhart, 1986), male and female rats were administered copper cyanide (CuCN) by gavage up to dose levels equivalent to 7.8 mg CN/kg bw/day. Clinical signs of toxicity were seen at all dose levels. Deaths were seen at 14.5 mg CN/kg bw/day along with an increase in testes weight. Clinical signs of toxicity, a decrease in haemoglobin concentration, and decrease in body weight gain in males and liver necrosis in females were seen at 4.35 mg CN/kg bw/day.

In a further 13-week study (*Gerhart, 1987), male and female rats were administered potassium silver cyanide ($KAg(CN)_2$) at dose levels up to 7.8 mg CN/kg bw/day for 13 weeks. Clinical signs of toxicity were seen at all dose levels. Deaths, reductions in body weight gain, increased testes weight and corneal opacity were seen at 2.6 mg CN/kg bw/day, and haematological effects and increased spleen weight at 7.8 mg CN/kg bw/day.

In a briefly reported 13-week study (*Olusi et al., 1979), female rats were fed a standard laboratory diet, a 50% gari diet (a form of cassava meal), raw cassava or 50 or 100 g KCN/kg standard diet. Haemoglobin (Hb) concentration, packed cell volume (PCV), thyroid, thymus and spleen organ weight, and T_3 and total protein levels were determined. Clinical signs of toxicity and a reduction in body weight were seen in animals receiving the cassava and KCN diets and effects were seen in the parameters

assessed. However, the limited experimental details prevent any reliable estimation of the dose in mg CN/kg bw/day. Consequently, this study is not discussed further in the review.

In a 3-month study (Soto-Blanco et al., 2002a), male rats were administered up to 0.6 mg KCN/kg bw/day daily by gavage, equivalent to 0.24 mg CN/kg bw/day. Animals were evaluated for clinical chemistry and histological examination was conducted on the CNS, pancreas and thyroid. At 0.24 mg CN/kg bw/day a statistically significant decrease in cholesterol was seen and a neuronal loss in the hippocampus that was described as more 'intense'. Histological changes were seen in the spinal cord for all treatment groups, and the brain at 'higher' doses.

In a 11.5-month study (Philbrick et al., 1979), male weanling rats were fed a normal diet or a semi-purified diet with and without 1500 ppm KCN, equivalent to 30 mg CN/kg bw/day. Plasma thyroxine and thyroxine secretion rates (adjusted for bodyweight) were determined at 4 and 11 months. A significant decrease in body weight gain was seen in the complete and restricted diet with KCN. A significant, but transient decrease was seen in plasma thyroxine levels in KCN treated rats, along with a significant increase in relative thyroid weight. Modest myeloid degeneration was also seen in the spinal cord white matter of rats receiving the restricted diet, the restricted diet plus KCN and the normal diet plus KCN.

In the same study (Philbrick et al., 1979), male rats were administered 2400 ppm potassium thiocyanate (KSCN) (equivalent to 67 mg CN/kg day) following the same methodology. Effects seen on thyroxine levels, thyroid weight and spinal cord with KCN were also seen with KSCN.

In a 2-year dietary study, groups of rats were fed a standard diet fumigated with HCN to give doses up to 300 ppm HCN (Howard and Hanzal, 1955). Food was prepared fresh every two days and placed in special feeding jars in order to keep the HCN concentrations at approximately designated levels. Haematological parameters were determined and histological examination was conducted on the heart, lungs, liver, spleen, stomach, small and large intestine, kidneys, adrenal thyroid, testes or uterus and ovaries, cerebrum and cerebellum of the brain. Dietary intake of HCN was determined to be approx 0, 5.0 and 11.2 mg HCN/kg bw/day (equivalent to 0, 4.3 and 10.4 mg CN/kg bw/day respectively). No effects were seen in HCN treated animals.

Rabbit

In a 40 week dietary study (*Okalie and Osagie, 1999), male rabbits (6 per dose) were administered KCN in the diet at a level estimated to be equivalent to 8 mg CN/kg bw/day. The cyanide-exposed group had reduced food intake efficiency and weight gain, and focal necrosis was noted in the liver and kidney at necropsy.

Pig

In a 24-week study (Jackson, 1988) fasted male (castrated) and female juvenile miniature pigs were administered KCN daily by gavage at dose levels up to 1.2 mg CN/kg bw/day. Daily behavioural determinations were made on a range of performance measures and learning events along with plasma T_3, T_4 and glucose levels. Two behavioural trends were observed at 0.4 mg CN/kg bw/day and above, along with a statistically significant decrease in plasma T_3 and T_4 and increase in fasting glucose levels. Clinical signs of toxicity were seen from 0.7 mg CN/kg bw/day and above.

Table 9.8. Summary of repeat-dose oral toxicity

Species	Exposure	NOAEL	Result	Comment	Reference
Rats (F344, 10 per sex per group)	0, 3, 10, 30, 100 or 300 ppm (NaCN) in drinking water for 13 wks (approx 0, 0.2, 0.5, 1.4, 4.5, 12.5 mg CN/kg bw/day in males and 0, 0.2, 0.5, 1.7, 4.9, 12.5 mg CN/kg bw/day in females)	4.5 mg CN/kg bw/day for effects on male reproductive organs.	A slight decrease in body weight gain (5%) was seen in males at 12.5 mg CN/kg bw/day, along with a statistically significant reduction in cauda epididymal weight (13%) and in the number of spermatid heads per testis. A marginal decrease was also seen in sperm motility in all cyanide treatment groups. In females, a significant increase was seen in time spent in proestrus and diestrus relative oestrus and metestrus at 4.9 and 12.5 mg CN/kg bw/day.	Minor changes in haematological, clinical chemistry and urinalysis parameters along with marginal decreases seen in sperm motility were not considered to be biologically significant. Similarly, the lack of a dose response for effects on the oestrus cycle suggests this is a chance finding.	NTP (1993)
Mice ($B6C3F_1$, 10 per sex per group)	0, 3, 10, 30, 100 or 300 ppm (NaCN) in drinking water for 13 wks (approx 0, 0.3, 1.0, 2.7, 8.6, 24.3 mg CN/kg bw/day in males and 0, 0.3, 1.1, 3.3, 10.1, 28.8 mg CN/kg bw/day in females)	8.6 mg CN/kg bw/day for effects on male reproductive organ weight	A slight decrease in body weight gain (7%) was seen in females at 28.8 mg CN/kg bw/day. In males, a slight reduction was seen in cauda epididymal weight (18%) at 24.3 mg CN/kg bw/day.	Haematological, clinical chemistry and urinalysis revealed minor changes that are not considered to be biologically significant. No histological changes seen or effect on spermatogenesis.	NTP (1993)
Dogs (6 per group)	Standard diet, standard diet plus NaCN or cassava for 14 wks (approx 0, 10.4, 10.4 mg CN/kg bw/day)	<10.4 mg CN/kg bw/day	NaCN diet: changed plasma-free amino acid profile that indicated amino acids were accumulating and not being utilised, and statistically significant increase in urinary protein excretion. Nephrosis, adrenal gland hyperplasia and hypertrophy, marked testicular germ cell sloughing and degeneration, and a significant reduction in testicular tubules in stage 8 of spermatogenic cycle. Cassava diet: effects seen as with NaCN diet except that no effect seen on spermatogenesis. Comparison with the NaCN diet indicates that the additional	The dog has very low levels of rhodanese, an enzyme used to detoxify cyanide.	Kamalu (1993)

Species	Exposure	NOAEL	Result	Comment	Reference
			histopathological changes are not entirely due to cyanide.		
Dogs (3 in total)	Daily administration of capsules containing NaCN at dose levels of 0.27 – 1.68 mg CN/kg bw/day for 14.5 months		Degenerative changes in ganglion cells of the CNS and cloudy swelling of epithelial cells of renal tubules in all treated animals.	The small number of animals in the study means that no reliable conclusions can be drawn from the data.	*Hertting et al. (1960)
Rats (Wistar, 6-10 males per group)	0, 0.3, 0.9, 3.0, 9.0 mg KCN/kg bw/day in drinking water, daily for 15 days (approx 0, 0.12, 0.36, 1.2, 3.6 mg CN/kg bw/day)	1.2 mg CN/kg bw/day for effects on body weight gain and liver.	Dose-related increase in the incidence of reabsorption vacuoles was seen in the thyroid in all treated groups. A statistically significant increase in plasma aspartate amino transferase levels was seen at 0.12-1.2 mg CN/kg bw/ along with a decrease at 3.6 mg CN/kg bw/day. Congestion and cytoplasmic vacuolisation in epithelial cells of the proximal tubules of the kidney was seen at 1.2 CN/kg bw/day and above. At 3.6 mg CN/kg bw/day, a statistically significant decrease in body weight gain (70%) was seen along with a decrease in plasma alanine aminotransferase levels and degeneration of liver hepatocytes.	The lack of a dose response for observed changes in clinical chemistry parameters and limited evidence on the histopathological changes in the thyroid and kidney (i.e. quantitation of incidence and severity of effect) limits the significance that can be attached to these data.	Sousa et al. (2002)
Rats (Sprague-Dawley, 26-40 males per dose)	0, 40, 80, 140 –160 mg/kg bw/day KCN in drinking water for 13 wks (approx 0, 16, 32, 56-64 mg CN/kg bw/day)	16 mg CN/kg bw/day for effects on body weight gain.	Significant dose related decrease in body weight gain at $\geq$ 32 mg CN/kg bw/day ($\geq$1 5%) in presence of a dose related decrease in water consumption at 16 mg CN/kg bw/day ($\geq$17%), and increase in food consumption (22%) at 56-64 mg CN/kg bw/day.	Decreases seen in water consumption are considered to be due to a lack of palatability.	Leuschner et al. (1991)

Species	Exposure	NOAEL	Result	Comment	Reference
Rats (Sprague-Dawley, males and females, numbers not reported for all dose levels)	CuCN by gavage daily for 13-wks (approx 0.14, 1.45, 4.35, 14.5 mg CN/kg bw/day)		Hypoactivity and hunched posture seen at 0.14 mg CN/kg bw/day and above. At 4.35 mg CN/kg bw/day laboured respiration and a decrease in haemoglobin concentration was seen along with a decrease in body weight gain in males (12%) and liver necrosis in females. At 14.4 mg CN/kg bw/day deaths were seen in 23/40 rats along with an increase in testes weight in males. Deaths were attributed to haemolytic anaemia from copper toxicity.	The liver necrosis in females at 14.5 mg CN/kg bw/day was seen in the absence of effects on haematology parameters, and is thus considered probably due to the toxicity of copper rather than cyanide The unknown contribution of copper to the observed effects prevents identification of a reliable NOAEL for cyanide.	*Gerhart (1986)
Rats (Sprague-Dawley, males and females, numbers not reported for al dose levels)	$KAg(CN)_2$ by gavage daily for 13-wks (approx 0.8, 2.6, 7.8 mg CN/kg bw/day)		Laboured respiration was seen at 0.8 mg CN/kg bw/day. At 2.6 mg CN/kg bw/day deaths were seen in 9/40 rats along with corneal opacity and a decrease in body weight gain (21%) and increase in testes weight in males. Convulsions and lethargy were seen at 7.8 mg CN/kg bw/day along with increased mean corpuscular volume, corpuscular haemoglobin concentration and spleen weight.	As for the study with CuCN, the unknown contribution of the metal ion, in this case silver, to the observed effects prevents identification of a reliable NOAEL for cyanide.	*Gerhart (1987)
Rats (Weanling, 10 males per group)	Normal diet or semi-purified diet (that contained methionine, vitamin B12 and iodine) with and without 1500 ppm KCN (approx 30 mg CN/kg bw/day) or 2400 ppm KSCN (approx 67 mg CN/kg day) for 11.5 months	< 30 mg CN/kg bw/day	KCN: Body weight gain was significantly reduced in the both diets with KCN (magnitude not reported). Significant decrease in plasma T_3 levels at 4, but not 11.5 months, and increase in relative thyroid weight, in both KCN diets. Modest myeloid degeneration was seen in the spinal cord white matter of rats receiving the restricted diet and both KCN diets. KSCN: Effects seen on thyroxine levels, thyroid weight and spinal cord with KCN were also seen with KSCN.	The transient decrease in plasma thyroxine levels and increase in relative thyroid weight in KCN treated rats is suggestive of an adaptive response.	Philbrick et al. (1979)

Species	Exposure	NOAEL	Result	Comment	Reference
Rats (Wistar, 6 – 7 males per group)	0, 0.15, 0.3, 0.6 mg KCN/kg bw/day daily by gavage (approx 0, 0.06, 0.12, 0.24 CN/kg bw/day) for 3 months		An effect was seen on a single clinical chemistry parameter: statistically significant decrease in cholesterol (44%) was seen at 0.24 mg CN/kg. No effects were seen on serum glucose, T_3 or T_4 levels. No histopathological changes were seen in the liver or pancreas. The authors reported neuronal loss in the hippocampus that was more 'intense' in animals at 0.24 mg CN/kg bw/day. In the spinal cord, a dose related increase in spheroids was reported in white matter for every experimental group. In the cerebellum, damaged Purkinje cells and loss of cerebellar white matter were reported in animals that received 'higher' cyanide doses.	The minimal detail provided on the histopathological changes seen (i.e. incidence and severity) limits the significance that can be attached to these results.	Soto-Blanco et al. (2002a)
Rats (10 per sex per group)	Standard diet fumigated with 0, 100 and 300 ppm HCN for 2-years. Doses determined to be 0, 5.0 and 11.2 mg HCN/kg bw/day (approx 0, 4.3 and 10.4 mg CN/kg bw/day)	10.4 mg CN/kg bw/day	No clinical signs of toxicity, effect on survival rate, haematology parameters or histological changes were seen in treated animals.	Food, prepared fresh every 2-days, was placed in special feeding jars in order to keep the HCN concentration at the designated levels. However, it cannot be excluded that the actual dose may be lower due to evaporation of HCN from the food.	Howard and Hanzal (1955)
Rabbits (New Zealand, 6 males per group)	KCN in the diet for 40 weeks. Dose estimated to be approx 20 mg KCN/kg bw/day (approx 8 mg CN/kg bw/day)	< 8 mg CN/kg bw/day	Reduced food intake efficiency and weight gain, along with focal necrosis in the liver and kidney was seen in treated animals.		*Okalie and Osagie (1999)

Species	Exposure	NOAEL	Result	Comment	Reference
Juvenile Pigs (Pittman Moore miniature, 5 females and 7 castrated males)	KCN daily by gavage for 24-weeks at doses equivalent to 0, 0.4, 0.7, 1.2 mg CN/kg bw/day		Two behavioural trends were observed at 0.4 mg CN/kg bw/day and above, and a statistically significant and dose related decrease was seen in serum T_3 and T_4 and increase in fasting glucose levels during the 'latter weeks' of the study. Vomiting was seen in animals at 0.7 mg CN/kg bw/day and above along with an increase in shivering in animals receiving 1.2 mg CN/kg bw/day.	No reliable conclusions/NOAEL can be identified from the data as animals were experimentally compromised: they were starved.	Jackson (1988)
Goats (Alpine-Saanen, 6 – 8 weanling males per group)	In a 5-month study, 0, 0.3, 0.6, 1.2, 3.0 mg KCN/kg bw/day (approx 0, 0.12, 0.24, 0.48, 1.2 mg CN/kg bw/day) in milk until weaning and then drinking water: KCN administered half in the morning half in the evening.		Congestion was seen in the cerebellum, spheroids and axonal swelling in the grey matter of the spinal cord and focal congestion in the pons at 0.48 mg CN/kg bw/day, along with haemorrhage and gliosis in all three tissues. At 1.2 mg CN/kg bw/day damage and loss of Purkinje cells was seen in the cerebellum, spheroids, gliosis and spongiosis in the pons, spheroids, axonal swelling, gliosis, and spongiosis in the medulla oblongata, and spheroids in the ventral horn of the spinal cord. Transient signs of generalised muscle tremors and ataxia were seen in a single animal at 1.2 mg CN/kg bw/day. No evidence of apoptosis was detected in the CNS.	Limited evidence on the histopathological changes in the CNS (i.e. incidence and severity of effect) limits the significance that can be attached to these data.	(Soto-Blanco et al., 2002b)
Lactating Goats (mixed bred, 1-3 years old)	In a 3-month study, 0, 1.0, 2.0, 3.0 mg KCN/kg bw/day (approx 0, 0.4, 0.8, 1.2 mg CN/kg bw/day) in drinking water during lactation days 0 to 90. 7-11 animals per treatment group. KCN administered half in the morning half in the evening.		No clinical signs of toxicity or serum changes (glucose, cholesterol, AST, ALT, γGT, PUN, creatinine, T3, T4), changes in body weight or lesions of the pancreas or brain. One goat died in the highest treatment group on day 55 of lactation. Cyanide and thiocyanate in dams presented a dose and time-dependant increase in all treatments, and thiocyanate levels on kids were increased dose-dependently and peaked on day 30. Cyanide was present in kids from day 30 and 60, but not at day 90. In the mothers, there were an increased number of		Soto-Blanco and Gorniak (2003)

Species	Exposure	NOAEL	Result	Comment	Reference
			reabsorption vacuoles on the colloid of the thyroid follicles, moderate hepatocellular vacuolisation and degeneration and mild cytoplasmic vacuolisation of the tubular epithelial cells, but not in the glomular cells, of the kidney. In the kids, there was an increased number of reabsorption vacuoles on the colloid of the thyroid follicles with cytoplasmic vacuoles in the epithelial cells of these follicles, mild cytoplasmic vacuolisation of the tubular epithelial cells of the kidneys, and moderate but more severe than in mothers, hepatocellular vacuolisation and degeneration with loss of acinar architecture, nuclear pyknosis in some hepatocytes, and fibrinoid deposition in the periportal region. Lesions were more intense in the highest dose group.		

Goat

In a 5-month study (Soto-Blanco et al., 2002b), male goats were administered KCN from weaning twice daily for a daily total dose of up to 1.2 mg CN/kg bw/day. Histological examination was conducted on the CNS and immunohistochemistry undertaken for the presence of apoptosis and gliosis (an excess of astroglia in damaged areas of the brain). Histological changes were reported in the brain and spinal cord, along with gliosis at 0.48 mg CN/kg bw/day and above. Transient signs of clinical toxicity were seen in a single animal at 1.2 mg CN/kg bw/day.

Female goats orally dosed with KCN (0.4, 0.8 and 1.2 mg CN/kg bw/day) in tap water twice daily from lactation days 0 to 90 showed clinical signs of maternal toxicity in the highest treatment (Soto-Blanco and Gorniak, 2003). Both cyanide and thiocyanate were present at increased levels in mothers and kids from the treatment groups indicating maternal transfer. Microscopic lesions, but without alteration of serum parameters, were found in the thyroid, liver and kidneys of both mothers and kids. The pancreas and central nervous system sections (including the cortex, hippocampus, brain stem, cerebellum, and spinal cord) were unaffected by the cyanide treatment. Long-term exposure to cyanide is responsible for several degenerations of the central nervous system in both humans (Wilson, 1987) and male goats (Soto-Blanco et al., 2002b); however, in this study an absence of brain lesions is attributed to cyanide and thiocyanate elimination by lactation and thus protecting the lactating animal, and the levels of these chemicals in milk were not sufficient to promote lesions in the kids.

Dermal

No data are available.

9.3.3 Mutagenicity

In vitro

In the only study available with NaCN (tested from 0.3 to 333 μg/plate), a negative result was obtained in a well conducted Ames test with *Salmonella typhimurium* strains TA 97, TA 98, TA 100 and TA 1535 with and without metabolic activation (NTP, 1993). Cytotoxicity was clearly seen in all strains except *S. typhimurium* TA 97 and positive controls gave results that confirmed the validity of this test.

Data are also available with cyanide salts other than NaCN. Some of the summaries presented below have been sourced from the ATSDR (2006) review.

In Ames tests with KCN, a negative result was obtained in *S. typhimurium* strains TA 98, TA 100, TA 1535. TA 1537 and TA 1538 with and without metabolic activation (*De Flora, 1981), and strains TA 82 and TA 102 with activation (*De Flora et al., 1984). Negative results were also obtained for KCN with and without metabolic activation in a DNA repair test in *Escherichia coli* strains WP67, CM871 and WP2 (*De Flora et al., 1984) and a DNA synthesis inhibition assay in HeLa cells (*Painter and Howard, 1982).

In a study investigating DNA fragmentation, freshly isolated rat thymocytes and a baby hamster kidney (BHK-21) cell line were exposed to 1.25 to 10 mM KCN for 1 to 24 hours (Bhattacharya & Rao, 1997). KCN induced both time and dose dependent DNA fragmentation accompanied by cytotoxicity in hamster kidney cells and rat thymocytes, though a statistically significant increase in DNA fragmentation was seen for a single dose and time point in the absence of cytotoxicity with rat thymocytes: 5

mM KCN after 2 hours exposure. The dose response relationship between fragmentation-DNA double strand breaks (DSB)-and cytotoxicity was investigated in A549, a human epithelial like lung carcinoma cell line treated with KCN (Vock et al., 1998). Induction of DSB was only seen after cell viability was reduced to less than 60%, indicating that observed DNA damage was a secondary consequence of cytotoxicity.

For HCN a positive response was reported in an Ames test without metabolic activation. The addition of metabolic activation decreased the induction of reverse mutation by 40% of non-activated levels to give a 'weakly' positive result (*Kushi et al., 1983).

In vivo

No standard studies are available. In a non-standard study, no testicular DNA-synthesis inhibition was detected in mice after a single oral dose of KCN, equivalent to 1 mg CN/kg bw (*Friedman and Staub, 1976).

9.3.4 Carcinogenicity

No data are available for NaCN. Although oral studies of up to two years duration are available in the rat with other cyanide salts, the small group sizes mean no reliable conclusions can be drawn from the data of these relatively old studies.

9.3.5 Fertility

No fertility study is available with NaCN.

In the only fertility study available, which was briefly reported (Olusi et al., 1979), female rats, 10 per group, were fed a standard laboratory diet, a 50% gari diet (a form of cassava meal), raw cassava or 50 or 100 g KCN/kg standard diet for 2 weeks then mated 1:1 with males fed the standard laboratory diet. Sperm positive females were returned to their designated diet until weaning. Compared to controls, a statistically significant decrease in body weight gain was seen in females fed the gari diet, while rats fed raw cassava lost body weight during pregnancy. Results for body weight gain are not reported for females receiving KCN in the diet. Compared to 9/10 pregnant control rats, only 8/10, 4/10, 0/10 and 0/10 females became pregnant receiving the gari, cassava and low and high KCN dose diets respectively. While this study suggests qualitatively that effects on fertility are only seen in the presence of severe systemic toxicity in females, the limited results provided mean no reliable quantitative conclusions can be drawn from the data.

Data are also available from repeat oral studies that investigated effects on the reproductive organs, spermatogenesis and/or oestrus cycling.

In a well conducted and comprehensive study (NTP, 1993), F344 rats and B6C3F$_1$ mice, 10 per sex per group per species, were administered NaCN in drinking water at concentrations of 0, 3, 10, 30, 100 or 300 ppm for 13 weeks. Doses were equivalent to approximately 0, 0.2, 0.5, 1.4, 4.5, and 12.5 mg CN/kg bw/day in male rats, 0, 0.2, 0.5, 1.7, 4.9 and 12.5 mg CN/kg bw/day in female rats, 0, 0.3, 1.0, 2.7, 8.6 and 24.3 CN/kg bw/day in male mice, and 0, 0.3, 1.1, 3.3, 10.1 and 28.8 CN/kg bw/day in female mice. In males, a slight though statistically significant decrease was seen in cauda epididymal weight (13%) and number of spermatid heads per testis at 12.5 mg CN/kg bw/day. A marginal decrease was also seen in sperm motility in all treatment groups

compared to controls, but was not considered by the authors to be biologically significant. These limited effects were seen in the presence of mild systemic toxicity: a slight (5%) reduction in body weight gain in males at 12.5 mg CN/kg bw/day. In females, a significant increase was seen in time spent in proestrus and diestrus relative estrus and metestrus at 4.9 and 12.5 mg CN/kg bw/day. This effect on the time spent in each estrus stage is of questionable biological significance.

In male mice, a slight reduction was seen in cauda epididymal weight at 24.3 mg CN/kg bw/day (18%) in the absence of an effect on sperm. No adverse effect was seen on oestrous cyclicity in female mice.

In studies by *Gerhart (1986; 1987), male and female Sprague-Dawley rats, number per sex per dose not reported, were administered CuCN or $KAg(CN)_2$ daily by gavage for 90 days at doses equivalent to 0.14, 1.45, 4.35 and 14.5 mg CN/kg bw/day and 0.8, 2.6 and 7.8 mg CN/kg bw/day, respectively. Increased testes weight was seen in male rats at 14.5 mg CN/kg bw/day as CuCN and at 2.6 mg CN/kg bw/day and above as $KAg(CN)_2$ in the absence of histopathological changes to the testes. Increases were seen in the presence of systemic toxicity: significant reductions in body weight gain (i.e. >10%) were noted. No effects were seen on female reproductive organ weight with CuCN or $KAg(CN)_2$.

Six dogs per group were fed either a control diet containing rice as the carbohydrate source, cassava that was expected to release 10.8 mg HCN/kg cooked food (equivalent to 10.4 mg CN/mg bw/day), or a control diet containing a level of NaCN expected to release 10.8 mg HCN/kg cooked food (Kamalu, 1993). Compared to controls, marked testicular germ cell sloughing and degeneration were seen along with a statistically significant reduction in the frequency of testicular tubules in stage 8 of the spermatogenic cycle in animals fed NaCN. However, the absence of information on systemic toxicity (i.e. effects on body weight gain) limits the significance that can be attached to these data in determining whether it is a direct effect on the reproductive organs or a secondary consequence of systemic toxicity. While for animals fed cassava, observed histological changes to the testes were considered not to be entirely due to cyanide.

9.3.6 Developmental toxicity

A single developmental study, sourced from the ATSDR (2006) review, is available with NaCN. In this study, it is reported that subcutaneous infusions of NaCN to pregnant hamsters increased the incidence of neural tube defects (*Doherty et al., 1982). However, the route of administration is not a relevant route of exposure.

Data are also available from studies that used sources of cyanide other than NaCN.

Rat

Pregnant Wistar rats were fed a cassava-based diet that contained 12 mg HCN/kg diet or the same diet containing 500 ppm KCN from the day of breeding and throughout gestation and lactation (Tewe and Maner, 1981a). Doses were equivalent to approximately 0.5 and 52 mg CN/kg bw/day. No significant effect was seen on mortality, litter size, birth weight or body weight gain of pups during lactation.

In a study sourced from the ATSDR (2006) review, increased embryonic deaths, microcephaly with open eyes, limb defects and growth retardation were reported in rats fed a diet containing 80% cassava powder during gestation (*Singh, 1981). However, the author indicated that the results should be viewed with caution due to the preliminary nature of the report, and also indicated that the effects could have been due to the low protein content of the cassava diet.

Hamster

In studies sourced from the ATSDR (2006) review, reduced foetal body weight and delayed ossification were seen in the offspring of Syrian hamsters fed a cassava diet containing 1.0 mg CN/kg bw/day on days 3 to 14 of gestation (*Frakes et al., 1986) and also for hamsters fed the cyanogenic glucoside linamarin during pregnancy (*Frakes et al., 1985). In both studies reduced body weight gain was seen in the pregnant females. Similarly, developmental effects (encephalocele and rib abnormalities) were only seen at maternally toxic dose levels following a single oral dose of amygdalin (*Willhite, 1982).

Pigs

In a dietary study (Tewe and Maner, 1981b), groups of 6 pregnant pigs (Yorkshire) were fed a cassava diet containing 0, 250 or 500 mg cyanide (as KCN) per kg of cassava from the day after breeding to parturition. Total cyanide concentration received was 30, 277 and 521 mg CN/kg diet and doses were determined to be 0.9, 7.8 and 17.3 mg CN/kg bw/day. On day 110 of gestation, two gilts per group were sacrificed and histopathological examination undertaken on selected organs. Following parturition, diets were changed to a standard based feed for the 56-day lactation period. At necropsy, proliferation of glomerular cells of the kidney was seen in 1/2, 1/2 and 2/2 gilts at 0.9, 7.8 and 17.3 mg CN/kg bw/day respectively. Both gilts fed 17.3 mg CN/kg bw/day also had thyroid glands with epithelial follicular cells that were low in height and had an accumulation of colloid. Compared to the low dose group, foetal spleen and heart relative organ weights were significantly decreased at 17.3 mg CN/kg bw/day: 21% and 10% respectively. No effect was seen on litter size, foetal body weight or body weight gain during lactation.

9.4 Effects on terrestrial plants

Eisler (1991) and more recently Larsen et al. (2004) provide a review of cyanide phytotoxicity. No phytotoxicity data were available for plants exposed to cyanide in air, although when HCN is used as a fumigant (concentrated), it may produce adverse effects on fruits due to acidity (refer below). The issue of phytotoxicity is complicated as many plant species contain organocyanide forms, (glucosides) for chemical defence (Larsen et al., 2004). Many species of plants, such as cassava, sorghum, flax, cherries, almonds, and beans, contain cyanogenic glycosides that release HCN when hydrolysed (Towill et al., 1978). Furthermore, all vascular plants and certain fungi and algae produce cyanide as a by-product in the synthesis of the plant hormone and pheromone ethylene (Peiser et al., 1984). Cyanogenesis has an important role in plant defence against predatory herbivores. This herbivore-plant interaction is not simple; the degree of selectivity by herbivores varies among individuals and by differences in hunger and previous diet (Jones, 1988). Cyanide poisoning of livestock by forage sorghums, such as Sudan grass and various hybrid cultivars, is well known (Cade and Rubira, 1982) and has led to the development of several variations of sorghums that have a reduced capability of producing cyanide poisoning (Egekeze and Oehme, 1980).

Although mitochondria in plants possess a cyanide-resistant alternative oxidase system (Shugaev, 1999), higher plants contain enzymes that are irreversibly damaged by cyanide (Larsen et al., 2004). Cyanide affects enzymes associated with respiration (through iron complexation in cytochrome oxidase) and ATP production and other processes dependent on ATP, such as ion uptake and phloem translocation, eventually leading to death (Towill et al., 1978). Cyanide produces chromosomal aberrations in some plants, but the mode of action is unknown (Towill et al., 1978). At lower concentrations, effects include inhibition of germination and growth, but cyanide sometimes enhances seed germination by stimulating the pentose phosphate pathway and inhibiting catalase (Towill et al., 1978; Solomonson, 1981). The detoxification mechanism of cyanide is mediated by the rhodanese enzyme, which is widely distributed in plants (Solomonson, 1981; Leduc, 1984).

USEPA (2006c) lists brief results for phytotoxicity tests with the grass species alkali sacaton (*Sporobolus airoides*) and creosote bush (*Larrea tridentata*) and sodium cyanide in water at a pH of 10.5. Eighty seeds were sown per pot (3 pots per treatment) placed in a growth chamber, with exposure to the cyanide solution by irrigation. In both tests, germination was poor, mortality was >50% after 2-3 months, with chlorosis and necrosis evident. However, the concentration of sodium cyanide tested was not specified and the high pH may also have influenced phytotoxicity.

Larsen et al. (2004ab) investigated the phytotoxicity of cyanide (KCN) to basket willows (*Salix viminalis*). In aqueous solutions, 2 mg CN/L depressed transpiration after 72 h by about 50% and all died after 3 weeks exposure. Trees exposed to 0.4 mg CN/L in aqueous solution initially showed a depression of transpiration, but recovered after 72 hours. As this depression was also evident in the control due to lack of nitrogen in the nutrient solution, the effect was not significant. Doses of 8 and 20 mg CN/L in aqueous solution quickly resulted in mortality (<1 week) to the trees. At the end of the test, almost all cyanide had disappeared from the solutions. Levels of cyanide in plants were related to the toxicity, with no elevated levels of cyanide in plants exposed to 0.4 mg CN/L. Willows grown in sand showed no toxic effects when irrigated with cyanide solutions at 10 mg CN/L, but after 96 h transpiration was reduced to ~50% at 20 mg CN/L and to <20% at 30-50 mg CN/L. Accumulation of CN in plant tissue was observed at 40 and 50 mg CN/L, up to ~4 mg/kg in leaves and ~15 mg/kg in roots. Mathematical modelling predicted that at <10 mg CN/L, the cyanide would be rapidly metabolised, whereas at higher doses uptake would occur more rapidly than metabolism and cyanide would accumulate in the plant tissue. Plants in sand survived irrigation with 20 mg CN/L, but those treated with ≥30 mg/L died. The roots of the surviving willows were able to consume about 10 mg CN/kg (fresh weight)/hour.

Vascular plants possess the enzymes beta-cyanoalanine synthase and beta-cyanoalanine hydrolase, which convert free cyanide to asparagine, an amino acid important for nitrogen storage (Larsen et al., 2004; Miller and Conn, 1980). The synthase combines HCN with L-cysteine to produce beta-cyanoalanine (Blumenthal et al., 1968). Larsen et al. (2004a) investigated the in-vivo phytoremediation capacity of willow and other woody plants (poplar, elder, rose and birch) to remove cyanide from growth media. Tests were performed with detached leaves and roots in KCN solutions of different concentrations. The highest removal capacity was obtained for basket willow hybrids (*Salix viminalis x schwerinii*). The *Michaelis–Menten* kinetics was determined. Realistic values of the half-saturation constant, K_M, were between 0.6 and 1.7 mg CN/L; the maximum metabolic capacity, v_{max}, was around 9.3 mg CN/kg (fresh

weight)/hour. Larsen et al. (2004a) estimated that with a v_{max} of 14.5 mg/kg/hour, about 1100 kg of free cyanide could potentially be removed by 1 hectare of willows during a growth period of 200 days.

Effect of cyanide complexation

Cyanide phytotoxicity decreases with cyanide-metal complexation and associated stabilisation, particularly iron-complexed cyanides (Shifrin et al., 1996; Trapp and Christiansen, 2003). Phytotoxicity tests performed with iron-complexed cyanide and cyanide-polluted gasworks soil found that complexed cyanide was taken up less efficiently than free cyanide, and concentrations of 1000 mg/L were non-toxic to poplars. Willows survive in gasworks soils containing >1000 mg CN/kg (Trapp and Christiansen, 2003).

9.5 Effects on terrestrial arthropods

Hydrogen cyanide was one of the first fumigants to be used extensively under modern conditions. Its use for treating trees under tents against scale insects was developed in California in 1886 (Woglum, 1949). The use of HCN has been declining in recent years, but it is still important in certain fields of application. HCN is one of the most toxic of insect fumigants. The fact that it is very soluble in water has considerable bearing on its use in practice. Thus, it may produce injury on moist materials, such as fruit and vegetables, because the solution of HCN in water is a dilute acid. Not only does this acid render these materials unpalatable and possibly hazardous for human consumption, but also its action, by causing burning, wilting or discoloration, may make them unmarketable.

HCN has been widely used for fumigating dormant nursery stock that is sufficiently dry. It may be used for some living plants if they can be washed with water immediately after treatment to prevent burning by the acid. HCN may be employed for fumigating many dry foodstuffs, grains and seeds. Although HCN is strongly sorbed by many materials, this action is usually reversible when they are dry, and, given time, all the fumigant vapours are desorbed. With many foodstuffs little, if any, chemical reaction occurs, and there is no detectable permanent residue. Because of the high degree of sorption at atmospheric pressure, HCN does not penetrate well into some materials. It was largely because of this that vacuum fumigation was adopted (Bond, 1984).

Among the commonly used fumigants, HCN is one of the most toxic to insects. It also has a rapid paralysing effect on most insect species. This action is an important consideration in dealing with insects, because sublethal concentrations may bring about apparent death and after exposure to the fumigant, the reversible action of the poison may permit the insect to recover. This reaction has been referred to as protective stupefaction (Lindgren, 1938). It is important from the practical point of view because it means that the maximum recommended concentration should be attained as quickly as possible during the application of the fumigant (Bond, 1984).

Highly toxic substances, such as cyanides, are sometimes feeding cues and stimulants for specialised insects (Eisler, 1991). For example, instar larvae of the southern armyworm (*Spodoptera eridania*) strongly prefer cyanogenic foods, such as foliage of the lima bean, a plant with comparatively elevated cyanide content (up to 31 mg CN/kg in some varieties in the form of linamurin; Brattsten et al., 1983). Feeding was stimulated in southern armyworms at dietary levels up to 508 mg KCN/kg (208 mg

CN/kg) for first to fourth instar larval stages, and between 1000 and 10 000 mg KCN/kg diet for fifth and sixth instar larvae (Brattsten et al., 1983). Sixth instar larvae pre-exposed to diets containing 5000 mg KCN/kg showed no adverse affects at dietary levels of 10 000 mg KCN/kg; however, previously unexposed larvae showed reversible signs of poisoning at 10 000 mg CN/kg diet, including complete inhibition of oviposition and 83% reduction in adult emergence (Brattsten et al., 1983). Experimental studies with southern armyworm larvae and thiocyanate, one of the in vivo cyanide metabolites, showed that 5000 mg thiocyanate per kilogram diet reduced pupation by 77%, completely inhibited oviposition, and reduced adult emergence by 80% (Brattsten et al., 1983), strongly suggesting that thiocyanate poisoning is the primary effect of high dietary cyanide levels in southern armyworms.

Resistant species, such as southern armyworms, require injected doses up to 800 mg KCN/kg bw (332 mg HCN/kg bw) or diets of 3600 mg KCN/kg for 50% mortality (Brattsten et al., 1983), but data are scarce for other terrestrial invertebrates. Exposure to 8 mg HCN/L air inhibits respiration in the granary weevil (*Sitophilus granarius*) within 15 min and kills 50% in 4 hours.

9.6 Effects on micro-organisms

Eisler (1991) indicated that some species of bacteria exposed to cyanide may exhibit decreased growth, altered cell morphology, decreased motility, mutagenicity, and altered respiration (Towill et al., 1978). However, not all micro-organisms are affected by cyanide and there is evidence for natural biodegradation through the use of cyanide (Barclay et al., 2002; CSIRO, 1997; Hagelstein and Mudder, 1997a; White and Markwiese, 1994; Kjeldsen, 1999). This process has been advanced for treatment of cyanide in wastewaters (Gaudy et al., 1982; Knowles, 1988; Boucabeille et al., 1994). Mixed microbial populations capable of metabolising cyanide and not previously exposed to cyanide were adversely affected at 0.3 mg HCN/kg; however, these populations can become acclimatised to cyanide and can then degrade wastes with higher cyanide concentrations (Towill et al., 1978).

Acclimatised microbial populations in activated sewage sludge can often completely convert nitriles to ammonia, sometimes at concentrations as high as 60 mg total cyanides/kg (Towill et al., 1978). Cyanide can be degraded by various pathways to yield a variety of products, including carbon dioxide, ammonia, beta-cyanoalanine, and formamide (Knowles, 1988). Several species of fungi can accumulate and metabolise cyanide, but the products of cyanide metabolism vary. For example, carbon dioxide and ammonia are formed as end products by *Fusarium solani*, whereas α-amino butyronitrile is a major cyanide metabolite of *Rhizoctonia solani* (Towill et al., 1978). Cyanide compounds are formed as secondary metabolites by many species of fungi and some bacteria by decarboxylation of glycine (Knowles, 1988).

Certain rhizobacteria may suppress plant growth in soil through cyanide production. In one case volatile metabolites, including cyanide, from fluorescent pseudomonad soil bacteria prevented root growth in seedlings of lettuce (*Lactuca sativa*; Alstrom and Burns, 1989). Not all cyanogenic isolates inhibit plant growth. Some strains promote growth in lettuce and beans by 41%-64% in 4 weeks versus 49%-53% growth reduction by inhibitory strains (Alstrom and Burns, 1989). Kjeldsen (1999) indicated that aerobic biodegradation of cyanide may occur by isolated bacterial strains or mixed cultures, where cyanide provides nitrogen, and in some instances, a carbon source. Bacteria isolated from a cyanide-contaminated soil degraded simple cyanides by 70%

of the initial concentration (100 mg CN/kg to 30 mg CN/kg) within 120 hours. Typical by-products include ammonia, carbon dioxide and sulphate.

A limit for effective anaerobic biodegradation was found under laboratory conditions by Coburn (1949; cited in Chatwin et al., 1987) to be 2 mg/L. Above this concentration, the cyanide was apparently found to be inhibitory to the anaerobic microbial culture tested. At concentrations below 2 mg/L, Coburn (1949) reported evidence of denitrification of certain soluble cyanides yielding N_2 gas, potentially due to nitrates under limited free O_2 conditions, and particularly in the presence of available sulphur compounds. Further test details were not available.

9.7 Effects on aquatic organisms

Applicants to this assessment provided very few aquatic toxicity tests or data, and a range of literature sources were reviewed for this assessment. The effects of cyanide on fish and other aquatic organisms have been reviewed by the US Environmental Protection Agency (USEPA, 1985), the Canadian Council or Resource and Environment Ministers (CCREM, 1987), Eisler et al. (1999) and the Australia and New Zealand Environment and Conservation Council (ANZECC/ARMCANZ, 2000a). ANZECC/ARMCANZ (2000a) provide a most recent and thorough summary of aquatic toxicity data for cyanide. Data for cyanides are also listed in the very comprehensive US EPA ECOTOX database (http://www.epa.gov/ecotox/), and this source was consulted to augment the data from the above reviews, both to add more information where details were unclear and to check for more recent data that may not have been considered by them.

The toxicity classification of cyanide to aquatic organisms according to the Globally Harmonized System (GHS) for Hazard Classification and Communication (UNECE, 2005) is discussed in Appendix 3. Australian water quality guidelines for the protection of aquatic ecosystems have been presented in Section 11.9.1.

9.7.1 Freshwater aquatic toxicity data

Aquatic toxicity data for freshwater fish, invertebrates, algae, and macrophytes have been described in Table 9.9. In general, the data have been peer reviewed prior to publication (e.g. Low and Lee, 1981; USEPA, 1981, 1985; ANZECC/ARMCANZ, 2000a), and data in ANZECC/ARMCANZ (2000a) have undergone rigorous scientific review.

9.7.2 Marine aquatic toxicity data

Aquatic toxicity data for marine fish, invertebrates, algae and coral species have been presented in Table 9.10. In general, the data presented have been peer reviewed prior to publication, and most of the data have undergone rigorous scientific review by ANZECC/ARMCANZ (2000a).

Data available for anemones and corals (Chalker and Taylor, 1975; Barnes, 1985; Jones and Stevens, 1997; Cervino et al., 2003) refer to acute tests involving very short duration (1-60 minutes) exposures to cyanide in seawater, indicative of the exposure duration experienced during illegal cyanide fishing practices rather than those of standard laboratory methods.

Table 9.9. Summary of selected freshwater aquatic toxicity data for cyanide

Taxa	No. of Species	Endpoint / Data	Value (µg CN/L)	Reference
Fish	22	24 to 96 h LC50.	40 to 1200[(a)]	ANZECC/ARMCANZ (2000a)
		Lowest 24 h LC50 (Atlantic salmon, *Salmo salar*)	40	
		90 d EC50 (reproduction; brook trout, *Salvelinus fontinalis*)	7.8	USEPA (1984)
		256 d EC50 (reproduction; Fathead minnow, *Pimephales promelas*)	16	
Crustaceans	9	24 to 96 h LC50	90 to 2200 [(b)]	ANZECC/ARMCANZ (2000a)
Insects	5	48 to 96 h LC50	432 to 2490	
Molluscs	8	48 to 96 h LC50	791 to 1080	
Other freshwater invertebrates		48 h LC50 (Oligochaete *Aeolosoma headleyi*)	9 to 160[(c)]	
		48 h LC50 (*Aeolosoma headleyi*; <10°C)	9 to 10	
		48 h LC50 (*A. headleyi*; >15°C)	>120	
		96 h LC50 (Platyhelminthes *Dugesia tigrina*)	2100	
		24 h LC50 (Rotifer *Brachyonus calyciflorus*)	62 400	
		6 d chronic NOEC (population growth) (Hydra *Hydra viridissima*)	67	
Protozoans	1	48 h LC50 (*Spirostomum ambiguum*)	2040	Nałęcz-Jawecki and Sawicki (1998)
Diatoms	1	50% reduction in cell division (96 h EC50; *Navicula seminulum*)	277 to 491	USEPA (1985).
Green algae	2	96 h EC50 (cell number increase; *Scenedesmus quadricauda*)	160	Eisler (1991), USEPA (2005).
		LOEC (7 d growth rate; *S. quadricauda*)	30	USEPA (1985), USEPA (2005).
		10 d NOEC (growth rate; *Chlamydomonas* sp.)	10 to 100	

Taxa	No. of Species	Endpoint / Data	Value (µg CN/L)	Reference
Cyanobacteria	1	90% cell *mortality* (24 h; *Microcystis aeruginosa*)	8000	Fitzgerald et al. (1952)
		LOEC (growth rate, *M. aeruginosa*)	75	USEPA (1985).
Macrophytes	3	Decreased potassium uptake (120 h; Duckweed *Lemna gibba*)	26 000	Kondo and Tsudzuki (1980)
		32 d EC50 (root weight) (Eurasian milfoil *Myriophylium spicatum*)	22 400	USEPA (1985).
		Non-phytotoxic in 72 hours (Water Hyacinth *Eichornia crassipes*) [(d)]	300 000	Low and Lee (1981).

(a). Fish: 17 of the 22 spp had values <470 µg CN/L.

(b) Crustaceans: Most values ranged between 100 to 500 µg CN/L. Low outlying values of 1 and 3 µg CN/L were reported for *Daphnia pulex* (Cairns et al., 1978), which were reported for the highest temperature 25°C, while lower temperatures of 20°C gave higher LC50 values. Chronic (5 d) LOEC and NOEC (reproduction) for waterfleas (*Moinodaphnia macleayi*) were 67 µg CN/L and 20 µg CN/L respectively (Rippon et al., 1992).

(c) Oligochaete: figures obtained below 10°C were 9000−10 000 µg CN/L, and at 15°C and above were ≥120 000 µg CN/L.

(d) Water Hyacinth accumulated 6.7 g CN/kg dry weight of plant matter when exposed to 300 mg CN/L for 72 h (Low and Lee, 1981).

Table 9.10. Summary of selected marine aquatic toxicity data for cyanide

Taxa	No. of Species	Endpoint / Data	Conc. (µg CN/L)	Reference
Fish	2	96 h LC50 (Black bream, *Acanthopagrus butcheri*) 96 h LC50 (Australian bass, *Macquaria novemaculata*) 289 d LC50 (Sheepshead minnow, *Cyprinodon variegatus*)	70 109 in range 29 to 45	Pablo et al. (1996); ANZECC/ARMCANZ (2000a)
Crustaceans	6	48 to 96 h LC50 96 h LC50 (Shrimp *Penaeus monodon*)	110 to 250 110	Pablo et al. (1997a)
		24 h LC50 (Brine shrimp *Artemia salina*) (a non-marine salinity-tolerant species).	6970	ANZECC/ARMCANZ (2000a)
Sea anemone	1	*Aiptasia pallida* (Caribbean sea anemone, 10 animals), 1-2 minutes exposure. 3 died, 7 lived after 12 weeks. High mitotic index, lower alga density (with abnormalities), mild bleaching, swollen tentacles.	50 000	Cervino et al. (2003)
Molluscs	2	96 h LC50 (Mussel *Mytilus edulis*)	36 000	ANZECC/ARMCANZ (2000a)
		14 d LOEC, 14 d LC20 (Mussel *Mytilus edulis*)	18, 100	Eisler (1991)
		48 h EC50, 48 h NOEC (Doughboy scallop *Mimachlamys asperrima*, abnormality in the development of embryos into shelled, D-veliger larvae).	29, 5	Pablo et al. (1997b)
Annelids	1	96 h LC50 (*Dinophilus gyrociliatus*)	5940 to 7570	ANZECC/ARMCANZ (2000a)
Diatoms	1	72 h EC50 (growth rate, *Nitzschia closterium*) NOEC (growth rate, *N. closterium*)	57 10-31	Pablo et al. (1997c)
Green algae	1	Respiration inhibition (glucose oxidation; *Prototheca zopfii*) 35% respiration inhibition (2 h) and 45% respiration inhibition (2 h)	 260 and 2600	Webster and Hackett (1965)
		95% NADH oxidase inhibition	26 040	
Red algae	1	Reduced tetrasporophyte growth (*Champia parvula*). Reduced tetrasporangia production Reduced growth EC100 (reproduction; *C. parvula*).	16 25 11 11	USEPA (1985)
Corals	4	Inhibition of photosynthesis and calcification following exposure for 1	260	Chalker and Taylor (1975) and Barnes

Taxa	No. of Species	Endpoint / Data	Conc. (µg CN/L)	Reference
		h, with evidence that this was associated with effects on zooanthellae (symbiotic algae) rather than the host (Staghorn corals *Acropora cervicornis* and *A. formosa*).		(1985)
		NOEC (Photosynthesis and calcification; *Pocillopora damicornis*)	52 000	Jones and Stevens (1997)
		Discoloration in 12 h and 100% mortality within 24 h following 10-30 mins exposure (*P. damicornis*).	5 200 000	
		Discoloration in 24 h following 5 mins exposure (*P. damicornis*).	5 200 000	
		Discoloration following 10-30 mins exposure (*P. damicornis*).	520 000	
		90% reduction in respiration at 7.5 mins exposure (*P. damicornis*).	2 600 000	
		10% to 20% reduction in respiration at 2.5 mins exposure (*P. damicornis*).	52 000	
		Acropora millepora (9 colonies), 1-2 minutes exposure. 4 died, 4 lived after 4 weeks. High mitotic index, lower alga density, mild bleaching, tissue detachment, swollen tissue.	50 000	Cervino et al. (2003)

9.7.3 Chronic effects on fish and invertebrates

Fish are a cyanide-sensitive group of aquatic organisms (Eisler, 1991; Eisler et al., 1999). Under conditions of continuous exposure for prolonged periods (early life stage, partial life cycle and life cycle studies with test durations of 28-256 d), adverse effects on fish ability at swimming and reproduction usually occur at concentrations between 5 and 7 µg CN/L and on survival between 20 and 76 µg CN/L. Other adverse effects on fish from chronic cyanide exposure include susceptibility to predation, disrupted respiration, osmoregulatory disturbances, and altered growth patterns (Table 9.11). Free cyanide concentrations between 50 and 200 µg CN/L are fatal to the more sensitive fish species over time, and concentrations >200 µg CN/L are rapidly lethal to most species (USEPA, 1980). Cyanide-induced pathology in fish includes subcutaneous haemorrhaging, liver necrosis and hepatic damage. Exposure of fish to 10 µg CN/L for 9 days was sufficient to induce extensive necrosis in the liver, although gills showed no damage. Liver histopathology intensification was evident at exposure concentrations of 20 to 30 µg CN/L and exposure periods up to 18 days (Leduc, 1984).

Table 9.11. Symptoms of cyanide exposure in freshwater fish

Activity or Organ Affected	Nature of Effect	Concentration (µg CN/L)
Spawning	100% inhibition	5
Egg production	42% reduction	10
Egg viability	100% egg infertility	65
Spermatogenesis	Permanent reduction	20
Abnormal embryonic development	Severe deformities	70
Hatching	Up to 40% failure	10 to 100
Swimming	90% reduction at 6°C	15

Source: Ingles (1982).

Cyanide has a strong, immediate and long-lasting inhibitory effect on the swimming ability of fish (Leduc, 1984). Free cyanide concentrations as low as 10 µg CN/L can rapidly and irreversibly impair the swimming ability of salmonids in well-aerated waters (Doudoroff, 1976). This may potentially be due to respiratory and neurological effects, as observed in higher order organisms (e.g. mammals, birds).

Cyanide affects fish reproduction by reducing both the number of eggs spawned, and the viability of the eggs by delaying the process of secondary yolk deposition in the ovary (Lesniak and Ruby, 1982; Ruby et al., 1986). Vitellogenin (Vtg), a glyco-lipophosphoprotein present in plasma of fish during the process of yolk formation, is synthesised in the liver under stimulation of oestrogen and subsequently sequestered in the ovary. Vitellogenin is essential for normal egg development. Exposure of naturally reproducing female rainbow trout (*Oncorhynchus mykiss*) to 10 µg CN/L for 12 days during the onset of the reproductive cycle produced a reduction in plasma vitellogenin levels and a reduction in ovary weight. The loss of vitellogenin in the plasma removed a major source of yolk (Ruby et al., 1986). There is uncertainty as to whether this effect of cyanide in fish is related to an effect on hormone(s) of the endocrine system.

Reproductive impairment in adult bluegills (*Lepomis macrochirus*) occurred following exposure to 5.2 µg CN/L for 289 days (USEPA, 1980). Newly fertilised eggs are usually resistant to cyanide prior to blastula formation; however, delayed effects

occurred at 60 to 100 µg CN/L, including birth defects and reduced survival of embryos and newly hatched larvae (Leduc, et al., 1982). Concentrations of 10 µg CN/L or greater have caused developmental abnormalities in embryos of Atlantic salmon (*Salmo salar*) after extended exposure (Leduc, 1978). These abnormalities, which were absent in controls, included yolk sac dropsy and malformation of eyes, mouth and vertebral column (Leduc, 1984). Dropsy is a distension of the abdomen, giving the fish a 'pot belly' appearance. This is a strong indicator of disease problems, which may include swelling of internal organs (liver, spleen or kidney), build up of body fluids (oedema, ascites), parasite problems, or other unknown cause. Dropsy is a common element in many of the serious diseases, since it is commonly associated with systemic disruption of osmoregulation due to blood-cell or kidney damage.

Osmoregulatory disturbances recorded in fish exposed to 10 µg CN/L may affect migratory patterns, feeding and predator avoidance (Leduc, 1984).

Increased levels of cortisol (indicating a stress response) and increased susceptibility to the pathogen *Saprolegia parasitica* were found in rainbow trout exposed to cyanide at 70 µg/L for 24 h (Carballo et al., 1995).

Sodium cyanide has stimulatory effects on oxygen-sensitive receptors in lungfish, amphibians, reptiles, birds and mammals (Smatresk, 1986). Facultative air-breathing animals appear to rely on air breathing when external chemoreceptors are stimulated. Obligate air-breathing fish are more responsive to internal stimuli (Smatresk, 1986).

Several authors (Eisler et al., 1999; Leduc, 1984; Clark, 1937) suggest a potential stimulatory effect on growth (hormesis) in animals when exposed to very low, sub-lethal concentrations; however, no test data were presented to support this hypothesis.

Eisler et al. (1999) indicate that among aquatic invertebrates, adverse non-lethal effects occur with exposure to cyanide concentrations between 18 to 43 µg CN/L, and lethality between 30 and 100 µg CN/L, although some amphipod (*Gammarus pulex*) deaths occurred at exposure concentrations between 3 and 7 µg CN/L.

USEPA (1984) noted that both freshwater and saltwater plant species (algae and macrophytes) show a wide range of sensitivities to cyanide, with the saltwater red macroalga algae *Champia pulvula* the most sensitive species listed (growth and reproductive effects at 11 to 25 µg/L). More recent research has shown that the saltwater diatom species *Nitzschia closterium* is similarly sensitive (growth rate NOEC = 10-31 µg/L). While some other algal species showed harmful effects at cyanide concentrations <100 µg/L, the available data indicate that other algal and aquatic macrophyte species are much less susceptible (effects at cyanide concentrations of 3000 to 30 000 µg/L).

9.7.4 Factors affecting the aquatic toxicity of cyanide

Factors affecting cyanide toxicity to aquatic organisms include water pH, temperature, cyanide species, oxygen content, life stage, species sensitivity, co-associated chemicals, as well as physiological condition (Eisler et al, 1999).

However, some caution is necessary in comparing these data, as differences in the conduct of laboratory tests may have led to apparent differences between species or test conditions that are not necessarily real. For example, USEPA (1984) noted that most of the aquatic invertebrate species tested were considerably more resistant to cyanide than fishes (though *Daphnia* sp. and *Gammarus pseudolimnaeus* were

comparable in sensitivity), but also observed that about half of the tests with invertebrates were under static conditions and the test concentrations were not measured, whereas many of the tests with fish were under flow-through conditions (likely to maintain more stable concentrations) and in which free cyanide concentrations were measured.

Water pH

The equilibrium of the chemical in water at a specific pH governs the amounts of the different forms of the chemical. These different chemical forms have different chemical properties and hence exhibit different degrees of toxicity. Cyanide equilibrium in water involves the neutral species hydrocyanic acid (HCN) and ionic form cyanide (CN). In general, low pH can increase the toxicity of cyanide (Collier and Winterbourn, 1987, Alabaster and Lloyd, 1982, CCREM, 1987). At lower pH, the proportion of HCN in solution increases (Section 6.3.1). The neutral form (HCN) is more toxic as it is able to cross biological membranes more readily than the ionic form. Solution pH levels in the range of 6.8 to 8.3 have little effect on cyanide toxicity to aquatic organisms, but toxicity is enhanced at more acidic pH (Eisler et al., 1999).

Water temperature

Temperature affects cyanide toxicity differently depending on the aquatic species. The toxicity of cyanide to rotifers, snails and water fleas (*Daphnia* spp.) increased with an increase in temperature (Cairns et al., 1978). The 48-h LC50 for the snail *Nitocris* sp. decreased from 13 600 µg CN/L at 5°C to 7000 µg CN/L at 25°C (toxicity increased). Similar 2-fold increases in toxicity with increasing temperature were reported for *Daphnia magna*, *D. pulex* and a rotifer. The increase in toxicity of cyanide at higher temperature was explained in part by increased metabolism of the organism (Cairns et al., 1978). In contrast, the oligochaete (*Aeolosoma headleyi*) showed the opposite trend with 48 h LC50 values of 9000 to 10 000 µg CN/L at 10 and 5°C, compared to 120 000 µg CN/L at 15°C and 160 000 µg CN/L at 20°C and 25°C. Similarly, toxicity to several crustaceans was around 2 times higher at temperatures above 31°C, but temperature did not appear to affect toxicity to insects or molluscs under similar conditions.

Season and exercise modify the lethality of HCN to juvenile rainbow trout (McGeachy and Ludec, 1988). Cairns et al. (1978) did not report any effect of temperature on cyanide toxicity to 5 species of fish, but they did notice a variation with different species. Brown (1968) found that cyanide was more toxic to rainbow trout fry at 3°C than at 13°C. Smith et al (1978) examined the effects of temperature on cyanide toxicity to fathead minnows (*Pimephales promelas*) collected as field stock and found that juvenile fish were more sensitive at lower temperatures and at oxygen levels below 5 mg/L. The 96 h LC50 varied from 53 µg CN/L at 4°C to 143 µg CN/L at 18°C. Toxicity to several fish species was around 4 times higher (lower LC50) at 31.4°C than at 26.5°C (Sarkar, 1990). Ingles (1982) indicated that cyanide toxicity to fish tested increased 3-fold with a 12°C decrease in temperature. 96-hour LC50 values for rainbow trout at 6.3°C, 12.3°C and 18.0°C were 28, 42, and 68 µg CN/L, respectively.

Temperature effects on algal sensitivity to cyanide are inconclusive (Cairns et al., 1978).

Dissolved oxygen

At reduced dissolved oxygen (DO) concentrations it is known that many compounds become increasingly toxic, including cyanide (Eisler et al., 1999). EIFAC (1973) reported that the acute toxicity of several common toxicants roughly doubled as the DO concentration was halved from 10 mg O_2/L to 5 mg O_2/L.

Life stage, species and co-associated chemicals

USEPA (1984) stated that certain life stages and species of fish appear to be more sensitive to cyanide than others. There is general agreement that juveniles and adults are the most sensitive life stages and embryos, and sac fry the most resistant (Eisler et al., 1999 citing Smith et al., 1978, 1979; USEPA 1980; and Leduc 1984). However, this may not be the case with aquatic invertebrates: e.g. comparison with the data from other mollusc tests suggests high sensitivity at the embryo/larva life stage of the doughboy scallop (Pablo et al., 1997b; Table 9.9 and Table 9.10).

Substantial interspecies variability exists in sensitivity to free cyanide (Eisler et al., 1999; ANZECC/ARMCANZ, 2000a), though it is highly toxic to most species (LC50/EC50 < 1000 µg/L), as shown in Table 9.9 and Table 9.10. Eisler (1991) concluded that fish were the most sensitive aquatic organisms tested under controlled conditions and algae and macrophytes were comparatively tolerant, but more recent data makes it clear that some species of aquatic invertebrates and algae are also very sensitive. Toxicity to freshwater and marine organisms appears broadly comparable, as evidenced by the similar marine and freshwater trigger values of 4 µg/L and 7 µg/L, respectively, derived by ANZECC/ARMCANZ (2000a) using statistical analyses of acute toxicity data.

Ingles (1982) indicated that cyanide toxicity, in terms of survival duration, increases with chloride ion concentration. Eisler et al. (1999) reported that ammonia or arsenic act synergistically with cyanide.

Cyanide forms, complexes and other products

While data on acute toxicity of free cyanide are available for a wide range of species, fewer data are available for metal-cyanide complexes (Doudoroff, 1976; Mudder, 1995, 1997). Nevertheless, the different forms of cyanide have different chemical properties, and hence different degrees of toxicity to aquatic organisms (refer Table 9.12 for general guidance). The free cyanide present or derived from dissociation of complexed or bound cyanides are the principal toxic forms (Doudoroff et al., 1966, Broderius et al., 1977), the former being more toxic because it is able to cross biological membranes.

Pablo et al. (1996) investigated the relative toxicities of cyanide (as NaCN) and iron-cyanide complexes including $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ to two Australian marine fish species (Australian bass *Macquaria novemaculeata* and black bream *Acanthopagrus butcheri*). The 96-hour LC50 values (in µg CN/L) have been summarised in Table 9.13.

As indicated in Table 9.12 and Table 9.13, aquatic toxicity decreases with iron complexation of free cyanide. The toxicities of the iron-cyanide complexes were consistent with the significant toxic component being free cyanide, and the toxicity of the iron-cyanide complexes correlates well with free (rather than total) cyanide toxicity (Doudoroff, 1976). The difference in toxicity of ferricyanide and ferrocyanide is attributed to differences in the extent of dissociation to free cyanide, as affected by

reaction thermodynamics and kinetics, photolysis and HCN losses through volatilisation (Pablo et al., 1996).

Table 9.12. Aquatic toxicity (LC50) to fish of metal-cyanide complexes and compounds and cyanide breakdown products

Term	Species or Compound	Toxicity to Fish [(a)] (lowest LC50) mg CN/L (unless stated otherwise)
Free cyanide	CN	~0.1
	HCN	0.05 to 0.18
Simple Compounds		
a) Readily soluble	KCN(solid)	0.02 to 0.08
	$NaCN.2H_2O$ (solid)	0.4 to 0.7
	$Ca(CN)_2$ (solid)	-
b) Relatively insoluble	CuCN (solid)	-
	$Zn(CN)_2$ (solid)	-
	$Ni(CN)_2$ (solid)	-
Weak complexes	$Cd(CN)_4^{2-}$	-
	$Zn(CN)_4^{2-}$	0.18
Moderately strong complexes	$Ni(CN)_4^{2-}$	0.42
	$Cu(CN)_2^-$	-
	$Cu(CN)_3^{2-}$	0.71 (24 hours)
	$Cu(CN)_4^{3-}$	-
	$Ag(CN)_2^-$	-
Strong complexes	$Fe(CN)_6^{4-}$	35 (light); 860 to 940 (dark)
	$Fe(CN)_6^{3-}$	35 (light); 860 to 1210 (dark)
	$Au(CN)_2^-$	-
Thiocyanate	SCN	50 to 200 mg/L
Cyanate	OCN	34 to 54 mg/L
Ammonia	NH_3	Strongly pH dependent, 0.8 mg/L
Nitrate	NO_3	23 mg/L

Sources: ANZECC/ARMCANZ (2000a); Environment Australia (1998), Beck (1987), Richardson (1992), MCA (1996), Hagelstein and Mudder (1997a).

(a) Comparative data for fish only; however, fish are less sensitive to ammonia than aquatic invertebrates (ANZECC/ARMCANZ (2000a).

Formation of a nickel-cyanide complex markedly reduced the toxicity of both cyanide and nickel at high concentrations in alkaline pH. At lower concentrations and acidic pH conditions, nickel-cyanide solutions increase in toxicity by more than 1000 times, owing to dissociation of the metallocyanide complex to the more toxic form HCN (Towill et al., 1978).

Table 9.13. Comparison of toxicity data (96-h LC50 or 72-h EC50) for free and complexed cyanide (mg/L) to two Australian fish species, one marine microalga and one marine mollusc

Fish Species	NaCN	$K_3Fe(CN)_6$	$K_4Fe(CN)_6$	Test
Australian bass	109	2830	285 000	96 h LC50
Black bream	70	1730	20 500	96 h LC50
Doughboy scallop	29	128	686	48 h EC50
(*Mimachlamys asperrima*)	5	15	40	48 h NOEC (larval development)
Marine diatom (*Nitzschia closterium*)	57	127	267	72 h EC50 (growth rate inhibition)

Sources: Pablo et al. (1996, 1997b, 1997c)

9.8 Toxicity reference values (TRVs)

9.8.1 The TRV approach and summary of the TRVs determined

Oral Toxicity Reference Values (TRVs) derived for the assessment of risks from exposure to cyanide by mammals and birds and the aquatic TRV have been presented in Table 9.14. TRV is equivalent in general terminology to the term Predicted No Effect Concentration (PNEC), but the United States Army Center for Health Promotion and Preventative Medicine (USACHPPM, 2000) reference discussed below uses the term TRV.

A high level of confidence of wildlife health protection is afforded by the derived TRVs for cyanide. Rationales for these values are presented in the following section.

No published wildlife TRV for cyanide based on recent research was available. In an ecological risk assessment of a site in the United States, Tetra Tech EM Inc (2002) adopted an avian TRV of 0.04 mg/kg bw based on the acute oral toxicity data for American kestrel of Wiemeyer et al. (1986). In that instance, the acute LD50 of 4 mg/kg bw was divided by an uncertainty factor of 100 (as in Table 9.15). However, as discussed later, this factor is considered to be unnecessarily conservative.

A TRV for reptiles could not be derived due to a lack of toxicity data, however the derived wildlife TRV is probably also protective of reptiles.

The approach used by the United States Army Center for Health Promotion and Preventative Medicine (USACHPPM, 2000) has been adapted for this assessment for both mammals and birds. Using the Approximation Approach, TRVs may be derived by extrapolating from a range of toxicity test endpoints (LC50, acute LOAELs) to derive two TRVs: a chronic NOAEL-based TRV and a chronic LOAEL-based TRV. As TRVs that are protective of wildlife health are required, only NOAEL-based TRVs have been derived for this assessment.

Table 9.14. Derived mammalian, avian and aquatic TRVs for cyanide

Taxa and Toxicity Data	Reference	AF	Derived TRV
Mammals			
Acute LD50 (rabbits): 2.3 mg CN/kg bw	Ballantyne (1987) /Table 9.6	10	0.23 mg CN/kg bw
Birds			
Acute LD50 (mallard ducks): 1.4 mg CN/kg bw	Henny et al. (1994) /Table 9.1	10	0.14 mg CN/kg bw
Aquatic species			
	Based on ANZECC/ARMCA NZ (2000a)		4 μg/L (freshwater) 7 μg/L (marine)

AF = Assessment Factor (refer Table 9.15).

USACHPPM (2000) has recommended the assessment factor (AFs i.e. safety or uncertainty factors) for use to derive NOAEL-based TRVs listed in Table 9.15. The methodology is scientifically based, and is an important internationally published guide that describes the rationale and methods for deriving wildlife TRVs, particularly for situations such as site environmental risk assessments. Assessment (or uncertainty, or safety) factors are intended to account for potential differences in response between species, and differences in response due to exposure duration (e.g. acute vs chronic) and endpoints (e.g. LD50 vs NOAEL). They also account for differences between the controlled laboratory conditions under which toxicity tests are conducted and the generally harsh environmental conditions in which wildlife live.

However, the assessment factors proposed in USACHPPM (2000) are applicable to small sets of toxicity data (the example given in the reference has a single bird toxicity study), whereas the avian and mammalian toxicity data for cyanide are somewhat larger and include a diversity of studies, though not large enough for probabilistic assessment and not all reliably meeting standard guidelines. It is therefore considered that lower assessment factors can be argued on a weight of evidence basis. Furthermore, cyanide is a highly acute poison and the acute to chronic toxicity ratio is likely to be relatively low compared to many other toxicants. Also, some of the species for which there is greatest concern (migratory birds) are likely to receive acute rather than chronic exposure.

In general, the capacity for cyanide metabolism in animals means that a single, lethal dose of cyanide may not have lethal effects if that same quantity is ingested in smaller portions over time (Section 7.3.6). It is likely that a greater cumulative dose would be required for lethality. However, sublethal effects could also harm the bird's subsequent survival, e.g. through the energy effects determined in biochemical studies and the effects on bird flight observed with pigeons (Section 9.2.2), or through greater predation susceptibility. For this assessment, it has been assumed for worst case exposure assessment that the animals evaluated consume all of their daily water requirements in one event. This is considered relevant to at least some species or individual animals in the environment.

Table 9.15. NOAEL-based AFs for use in deriving wildlife TRVs

	AF to approximate a TRV that is:	
Type of Datum Available	**NOAEL-Based AF [(a)]**	**LOAEL-Based AF [(a)]**
Chronic NOAEL	1	na
Chronic LOAEL	10	1
Sub-chronic NOAEL	10	na
Sub-chronic LOAEL	20	4
Acute NOAEL	30	na
Acute LOAEL	50	10
LD50	100	20

Source: USACHPPM (2000). The type of datum available (e.g. sub-chronic LOAEL) is divided by the assessment factor (AF) to derive a chronic NOAEL-based TRV. NOAEL = No observed adverse effect level. LOAEL = Lowest observed adverse effect level.
(a) Sourced from Ford et al. (1992) except for the chronic LOAEL.
na: not applicable.

For aquatic organisms, the freshwater and marine trigger values from the Australian water quality guidelines for the protection of aquatic ecosystems (ANZECC/ARMCANZ, 2000a, Section 11.9.1) will be used as the TRVs.

9.8.2 Selection of Toxicity Reference Values (TRVs)

Relevant forms of cyanide

The forms of cyanide relevant to this environmental assessment include free and metallocyanide complexes (e.g. WAD forms) of varying biological availability. It is considered relevant to environmental conditions that the derived TRVs for mammals and birds for cyanide are based on toxicity studies where cyanide was administered in a salt form rather than as organically-bound cyanide (e.g. diets of plants containing cyanogenic glycosides).

The avian and mammalian TRVs presented below refer to doses administered in free cyanide forms (e.g. NaCN), and free cyanide is recognised as the most toxic and readily available form of cyanide. Very limited reliable toxicity data were available for metallocyanide complexes (e.g. WAD forms), which is particularly relevant due to the predominance of these types of complexes in tailings discharges at mining operations. Although there may be some environmental conditions where cyanide is present in metallocyanide complexes where the cyanide concentrations may not be as readily correlated to hazard due to lower bioavailability and delayed effects, many metallocyanide complexes (e.g. WAD cyanide) have been demonstrated to be biologically available to varying degrees and thus of toxicological relevance. Therefore, the extrapolation of TRVs based on free cyanide to environmental conditions involving free and available forms of metallocyanide complexes is considered applicable in the absence of chemical or site-specific data. In some instances, data suggest that the WAD CN component of tailings may be comprised of very high proportions of free CN (refer Section 6.6.4), but free CN content in the original water sampled may be significantly overestimated due to sampling and methodology difficulties (Schulz, pers. comm. 2006). Exposure to the dissolved metal may pose an additional hazard in these circumstances, but this review is focused on cyanide toxicity, and not on that of other components.

Avian toxicity data

Drinking water toxicity studies where birds were exposed to NaCN solutions at similar pH to gold mine process water were provided and would have been the studies of choice for selecting a TRV if they had not been so unreliable (Section 9.2.2). Similarly, a study with exposure to a range of cyanide concentrations in actual process water has been conducted, but the study report was not available and may or may not have been reliable. No other acceptable studies with dietary exposure of birds were available.

The most useful studies for birds were acute oral exposure studies, which were generally conducted to a standard guideline, but are considered as acceptable rather than reliable, due to deficiencies in their design and reporting (Section 9.2.1). These covered a range of seven species, including two standard test species, three raptors, and two species known to be relatively insensitive to chemicals. Of these, mallard ducks were found to be the most sensitive. Data were available from additional studies with mallard ducks exposed to a single dose of tap or effluent pond water with various concentrations of cyanide or provided with contaminated water for a short period. Too few study details are available to be certain of the results and their interpretation and therefore, considered unreliable. Because of the availability of data for several species and additional data for the most sensitive species, and the nature of toxicity of cyanide as an acute toxin, it is considered that a satisfactory assessment factor for the avian toxicity endpoint is 10, rather than 100, as would be required according to Table 9.15. Use of the 1.4 mg/kg bw LD50 value from Henny et al. (1994) and an AF of 10 for the purposes of this risk assessment results in the derivation of an avian TRV of 0.14 mg/kg bw.

Sublethal toxic effects from the available acute oral toxicity studies have been studied in special studies with mallard ducks and pigeons, as well as being reported for LD50 studies. Ma and Pritsos (1997) indicated that tissue taken from mallard ducks killed two hours after they were dosed with 0.25 mg KCN/kg bw (0.1 mg CN/kg bw) showed statistically significant biochemical effects (i.e. brain and liver tissue ATP reduction) compared to untreated birds. However, these biochemical data cannot be related directly to effects of ecological relevance, and differences evident at 2 h post dosing were no longer evident at 24 h. Work by Cooper (2003) indicated that homing pigeon flight time was significantly increased when pigeons received a single oral dose of ≥ 1.25 mg KCN/kg bw (≥ 0.5 mg CN/kg bw) when compared to untreated control pigeons. Cooper (2003) also indicated that a single oral dose of ≥ 0.5 mg KCN/kg bw (≥ 0.2 mg CN/kg bw) produced no observed signs of toxicity in mallards and pigeons, whereas there was an early onset of such signs at doses ≥ 1.0 mg KCN/kg bw (≥ 0.4 mg CN/kg bw), in mallards at least. Hence, based on observable signs, the lowest reported NOEL value was 0.2 mg CN/kg bw for mallards, the most sensitive species of those tested based on acute oral toxicity. The TRV derived above is below the lowest NOEL for observable effects from this sequence of studies, though comparable to levels causing short term biochemical effects.

Mammalian oral toxicity data

Both single and repeat dose oral toxicity data were available for mammals. Although the study data with pigs from Jackson (1988), with group sizes of only three (Table 9.8, Section 9.3.2), suffers from a lack of statistical power, the data were used by the World Health Organisation (WHO) to derive the tolerable daily intake (TDI) for cyanide in WHO drinking water guidelines (WHO, 1996). The data were also used by

the National Health and Medical Research Council (NHMRC) to derive the current Australian drinking water guideline value of 0.08 mg/L for cyanide (NHMRC, 2004), based on the NOAEL of 1.2 mg/kg bw/day in pigs. However, the study by Jackson (1988) is not considered acceptable as the test animals were experimentally compromised (starved) during the tests. As such, the most reliable repeat dose toxicity study available is considered to be from NTP (1993), with a NOAEL (effects on reproductive organ) for male rats of 4.5 mg/kg bw/day, which was provided in drinking water at 100 mg NaCN/L (53 mg CN/L). IPCS (2004) also criticised the Jackson (1988) study and that with goats by Soto-Blanco et al. (2002b – Table 9.8), and used the NOAEL from NTP (1993) to derive an intermediate exposure minimal risk level for humans.

Acute oral studies with mammals were available for 6 species with NaCN, including a marsupial species (brushtail possum) as well as mice, white-footed mice, rats, and foxes. Further studies with some of these species were available with KCN and HCN. Thus there is a good body of data for acute oral exposure, though not enough species to warrant a probabilistic assessment approach. The lowest acute oral toxicity value is the LD50 for KCN to rabbits of 2.3 mg/kg bw (Ballantyne, 1987). Because of the availability of data for several species and the nature of toxicity of cyanide as an acute toxin where recovery occurs from sublethal doses, it is considered that a satisfactory assessment factor for the mammal toxicity endpoint is 10, rather than 100, as would be required according to Table 9.15. Use of the 2.3 mg/kg bw LD50 value and an AF of 10 for the purposes of this risk assessment results in the derivation of a mammalian TRV of 0.23 mg/kg bw.

Aquatic toxicity data

Australian water quality guidelines for the protection of aquatic ecosystems were published in 2000 (ANZECC/ARMCANZ, 2000a). The guidelines provide a decision-tree framework for the assessment of surface water quality, with provision for screening-level and more detailed levels of investigation, if required, to assess risks from substances in surface waters.

The guidelines provide trigger values for free cyanide for the protection of aquatic life from screened acute toxicity data from tests conducted at different pHs (6.5 to 8.6) and temperatures (5°C to 30°C). The toxicity data used by ANZECC/ARMCANZ (2000a) to derive water quality trigger values were subjected to rigorous quality checks and review prior to adoption. Minimum data requirements were specified, leading to reliability estimates for the trigger values derived. All toxicity values were first converted to concentration as un-ionised HCN using the reported pH and temperature. The Australian freshwater and marine trigger values for cyanide of 7 µg CN/L and 4 µg CN/L, respectively, were calculated from LC50 values using a statistical distribution method allowing for a theoretical protection level of 95% of species, and an acute to chronic ratio (ACR) of 8.45 (rather than an AF of 10). These trigger values, which are appropriate for screening-level environmental assessments, are considered by ANZECC/ARMCANZ (2000a) to be of moderate reliability for protecting aquatic ecosystems. It is noted that both these values are above natural background levels (Section 10.3), as would be expected for them to be practicable.

These values have therefore been adopted as the aquatic TRV values, as the exposure scenarios relate to situations where such screening level assessments are made, such as environmental impact assessments for NaCN manufacturing facilities and TSFs. The corresponding values to protect 99% of species were 4 µg CN/L and 2 µg CN/L: these

values provide more protection for sub-lethal effects (see Table 9.11) and could be used for protection of highly valued aquatic ecosystems or species.

9.9 Field observations of terrestrial and aerial wildlife mortality at gold processing facilities

Wildlife deaths involving cyanide have occurred due to exposure to gold ore process solutions (e.g. at heap leach operations), and to solutions disposed in tailings storage facilities and associated waterbodies, such as decant ponds.

9.9.1 International data on wildlife impacts

Incidents and monitoring data involving wildlife mortalities at TSFs and heap leach facilities have been reported by several investigators (e.g. Eisler et al., 1999; Henny et al., 1994; Eisler, 1991; Clark, 1991). Reported deaths were mostly thought due to wildlife gaining access to, and consumption of, solutions containing elevated concentrations of cyanide.

Henny et al. (1994) reported on data from the Nevada Department of Wildlife which indicated that between 1986 and 1991, cyanide in mill tailings ponds and heap leach solutions at 95 gold operations in Nevada had killed numerous wildlife (>9500 individuals, mainly migratory birds) as described in Table 9.16. The list of species from the Nevada sites included coyote (*Canis latrans*), badger (*Taxidea taxus*), beaver (*Castor canadensis*), mule deer (*Odocoileus hemionus*), blacktail jackrabbit (*Lepus californicus*), and kit fox (*Vulpes macrotis*), as well as skunks, chipmunks, squirrels, and domestic dogs, cats and cattle (Eisler et al., 1999). Deaths were reported at concentrations of WAD CN of 62 mg/L, 81 mg/L and higher, however no deaths were noted at concentrations below 59 mg/L WAD CN.

Henny et al. (1994) also reported inspections conducted in 1990 by the US Fish and Wildlife Service at 16 mines in Nevada (mostly single visits, with one mine revisited under different detoxification procedures). Concentrations of WAD CN at the point of discharge ranged from 8.4-216 mg/L, with a pH of 9.3-11.4 in most cases (in one case the mine was using acidification in an attempt to dissipate CN as HCN into the atmosphere, where the pH was as low as 6). Several of the mine operators were using steps such as ferrous sulphate addition to the TSF to reduce wildlife hazard. Cyanide concentrations generally decreased from the discharge pipe to the reclaim (decant) area. The tailings pond sizes ranged from 1-150 ha.

Birds were present at tailings dams at 13 mines, but not at those with the three highest CN concentrations at discharge (138- 216 mg/L WAD CN), one of which was using hazers (humans with shell-crackers). Bird mortality was evident at only two mines, with TSF discharge concentrations of 59 and 62 mg WAD CN/L. A dead white-footed mouse was found in one pond with 26 mg/L WAD CN at discharge, but it is not clear what concentration of WAD CN the mouse was actually exposed to, and its death may have been due to other causes. The death of one bird (sandpiper) was also reported where the concentration of cyanide in the tailings pond water near the dead bird was 16 mg/L. However, the pond had previously contained higher cyanide concentrations and the exposure concentration could not be determined, and other effects may have caused the death of this bird. Henny et al. (1994) also reported bird deaths at heap leach pads where birds were exposed to puddled cyanide solution containing 79 and 120 mg WAD CN/L.

Table 9.16. Selected incidences of wildlife mortality from cyanide at Nevada Gold Mine TSFs (1986 to 1991)

Category	Proportion	No. of Species	Groups	Category Totals
Birds	91%	91	Waterfowl	38%
			Shorebirds	35%
			Perching birds	24%
			Other [a]	3%
Mammals	7%	28	Rodents and rabbits	62%
			Bats	25%
			Carnivores	7%
			Other [b]	6%
Amphibians & Reptiles	3%	6	Amphibians	70%
			Reptiles	30%

Source: Henny et al. (1994); a: Includes 15 raptorial species and 5 gallinaceous spp.; b: 2 ungulate spp.

Henny et al. (1994) also reported observations on differences in behaviour between species and individuals affecting their susceptibility to cyanide poisoning. For example, at one tailings pond 13 ducks of various species were observed to swim near a reclaim area where the WAD CN concentration was 19 mg/L for 2 h without evidence of intoxication. Five cinnamon teal were then observed to land on the same pond in the delta area near the discharge point (WAD CN 62 mg/L). One of these drank earlier and more liberally than the others and soon began showing signs of toxicity, before losing consciousness and dying by ~30 minutes after arrival. The other four birds showed no signs of harm, flew off when disturbed and were thought to have survived.

At the Ridgeway Mine (a tank leach facility with an 80 ha tailings pond) in South Carolina, USA between December 1988 and December 1990, Clark (1991) reported that cyanide poisoning resulted in the death of 271 vertebrate animals. Taxa included birds (86%), mammals (13%), reptiles and amphibians (1%). Of the 35 mammals, 29 were bats, including 12 red bats found in September and October, suggesting a link to their migration regime (this was also evident in data showing seasonal trends in bat deaths). Clark (1991) indicated that bat deaths occurred at the Ridgeway Mine TSF when the mine reported cyanide concentrations of <20 mg/L in the TSF, but original sources and data to enable this claim to be evaluated were not provided in this article.

Clark (1991) noted that the reported wildlife deaths are likely to have been minimum estimates, particularly for bats, which are small and dark and therefore difficult to find and identify, and which drink in flight over open water and may disappear into the pond rather than land. A further difficulty is that they fly at night and hence their presence near TSFs is not readily observable. Clark et al. (1991) noted that experimental dosing of little brown bats (*Myotis lucifugus*) with sodium cyanide resulted in delayed mortality that took place over much longer periods than in birds and mice. Hence they suggested relatively more bats may die away from tailings areas, where they are less likely to be found and reported.

Smith and Mudder (1991) noted records for a Nevada mine where WAD CN levels were reduced over a six-day period from 500 mg/L to <50 mg/L when a hydrogen peroxide CN destruction process was introduced. There was a dramatic drop in bird mortalities which persisted in subsequent years, with the 29 mortalities occurring in 1989 being a 97% drop from those occurring in 1986.

Hagelstein and Mudder (1997b) noted that different species of migratory birds have been found dead within and adjacent to unnetted or uncovered tailings impoundments in which the total cyanide levels exceeded 200 mg/L, but that injured birds that were found still alive after 60 minutes of exposure to the same concentration levels often survived (citing Clark and Hothem (1991) and Wiemeyer et al. (1986)). Thus birds can survive short term exposure to such high concentrations, provided they do not continue to be exposed and are not predated upon while vulnerable.

Clark and Hothem (1991) noted that searches and counts of dead animals had been limited to immediate mine sites and wildlife that escaped from these sites were assumed to be unharmed. However, in 1989 a single red-breasted merganser (*Mergus serrator*) was found dead 20 km from the nearest known source of cyanide, the Cyprus Copperstone mine in western Arizona. The pectoral muscle tissue of this bird tested positive for cyanide. Considering this incident, Clark and Hothem (1991) suggested a possible mechanism by which cyanide-induced mortality may occur away from cyanide solutions despite the acute toxicity of cyanide. They proposed that an animal might drink cyanide solutions and avoid immediate death if the level of free cyanide were low enough, but may die later when additional cyanide from WAD cyanide (such as that bound to copper) is liberated by stomach acid. Thus retarded absorption of CN because of gradual dissociation of metal-CN complexes present in WAD CN may cause delayed mortality, though it may also reduce the peak concentration of free CN in the gut (see Section 9.2.3). The amount of mortality occurring away from mine sites has still not been conclusively demonstrated, but there appear to be no other similar reports linked to cyanide use in mining apart from the above red-breasted merganser incident. It should also be noted that the presence of cyanide in the tissues of the merganser does not necessarily prove the death was due to cyanosis. While evidently not a factor in this incident, it should also be noted that there are other anthropogenic and natural sources of cyanide that can cause the death of birds and mammals as discussed below.

The US Geological Survey (USGS) Field Manual of Wildlife Disease (USGS, 1999) indicates that from 1986–95, more than 3000 cyanide-related mortalities involving about 75 species of birds representing 23 families were reported to the National Wildlife Health Center (NWHC). Waterbirds and passerines represented the greatest number of species affected. Exposure to cyanide used in gold mining accounted for almost all of the mortalities. Bait and trigger devices which release sodium cyanide into the mouth of an animal when triggered have also been documented as the cause of mortality of non-target bird species in the USA, such as eagles and other scavengers (e.g. see Acute toxicity, Oral: Section 9.2.1). Only one bird in these submissions (a bald eagle, evident from fluorescent marking produced when the device triggers) was killed by sodium cyanide from one of these devices, which are used to kill mammalian predators of livestock (specifically coyotes and other canids).

Natural sources of cyanide (*Cotoneaster pyracantha* (firethorn) shrubs) have also been linked to the deaths of hundreds of songbirds (cedar waxwings) over several years recently in South Dakota, USA (USGS, 2004). Choke cherry (*Prunus virginiana*) seeds also contain chemical compounds that release cyanide if the seed capsule is

broken during digestion, and songbirds have been killed by cyanide poisoning from eating these seeds (USGS, 1999).

AngloGold Ashanti (2004, 2005) discuss wildlife impacts at the Yatela gold mine in Mali (West Africa) and the actions taken to minimise them. This was a heap leach facility, and high free CN concentrations were likely to have been present on the surface of the heap – Section 7.3.4). In the first dry season (2001), 554 bird fatalities were recorded, including swifts, swallows, nightjars, buzzards, goshawks and hobbys. Bird fatalities decreased to 40 in 2002, 16 in 2003, and 2 each in 2004 and 2005, as a consequence of the following measures:

- construction of a series of shallow drinking ponds around the periphery of this heap leach facility, to provide alternative watering points;
- use of noise deterrents, including propane cannons, recorded bird alarm calls, and regular patrols to scare away birds;
- covering of ponded areas with shade-cloth, while puncturing these surface ponds with long metal rods to allow the solution to infiltrate into the heap;
- covering of solution trenches on either side of the leach pads with shade-cloth, to prevent birds from accessing this stream of process solution; and
- floating a large number of HDPE balls ('bird balls') on the surface of the open water process ponds, technology which covers and disguises all exposed water and prevents birds landing on the pond or perching on the balls.

AngloGold Ashanti (2005) and Johnson and Donato (2005) discussed wildlife impacts at the Sadiola Hill Gold Mine in Mali, an open pit mine with a TSF. From 1997 (when operations commenced) to 2001 no wildlife fatalities were observed. However, as transition from oxide ores to deeper sulphide ores occurred, an increased rate of cyanide addition was required and WAD CN levels increased to > 200 mg/L in the tailings decant pond. In a nine-week period in March-May 2002, 197 birds died at the silt trap, the return water dam and the tailings decant pond. Action taken included temporary halting the sulphide ore treatment and installing a hydrogen peroxide plant at the tailings decant pond to destroy cyanide, followed by construction of a permanent cyanide destruction system using sodium metabisulfite, as the initial facility was found to be inadequate.

While these measures prevented further fatalities in 2002 and continued to maintain WAD CN concentrations in the tailings decant pond below 50 mg/L, 77 bird fatalities occurred at the TSF silt dam and return water dam in April 2003. Toxicological tests conducted at Onderstepoort Veterinary Institute in South Africa were inconclusive, but it was tentatively suggested that the fatalities were due to toxicosis from WAD CN, with a potential synergistic effect caused by cyanate/thiocyanate. Cyanide toxicosis to birds roosting near a discharge spigot was determined to be the cause of 17 deaths during December 2003.

Further investigations were made when 107 fatalities were recorded in May 2004, again while WAD CN concentrations in the tailings decant pond were < 50 mg/L. After dismissing toxicity due to cyanide and ruling out natural causes such as extreme heat, starvation or disease, and toxicity from heavy metals, it was determined that sodium ion toxicosis was the likely cause. Sodium levels in the brain tissue of two bird species were found to be 2218 and 2255 ppm, above the 1900 ppm threshold for sodium toxicosis, and a review of water quality monitoring revealed that dissolved

sodium concentrations in the return water dam were higher than in previous years (800-1400 mg/L over the period in which the mortalities occurred, with a strong seasonal trend due to evaporation and precipitation). A similar conclusion was reached for five bird mortalities that occurred in 2005. Measures taken to minimise further impacts included increased bird hazing operations, habitat modification to make it less attractive to wildlife, construction of 30 fresh-water ponds to lure birds away from process ponds, and a program of routine wildlife monitoring and pond inspections. At the time of reporting, monitoring had indicated that the number of bird species frequenting the process ponds has decreased from 50 to 15 and the frequency of visits has also reduced.

9.9.2 Wildlife poisoning incidents in Australia

Major incidents recorded in previous decades

Anecdotal information suggests that wildlife poisoning incidents at TSFs have occurred at least since the early 1980s in Western Australia (WA) and the Northern Territory (NT) (Donato, 2002). Holmes (1998) stated that there are several anecdotal reports of thousands of finches dying around mine pondages near Croydon (in north Queensland) in the 1970s. Ryan and Shanks (1996) reported that a major bird death incident had occurred in 1985 at Windara, north of Kalgoorlie in WA, when 60 000 budgerigars were killed at a tailings dam: this information is anecdotal, as no further details or source for this report were indicated, but it was also noted in the Australian Senate the previous year (Hansard, 1995). NT DBIRD indicates that guidance was developed in response to a major incident that occurred in the 1990s in Tennant Creek, when tens of thousands of finches died – a combination of fires and other stresses made a dam look attractive at a time when the processing plant was experiencing problems with a difficult ore and CN levels were abnormally high.

A well-publicised mass bird death incident occurred in Australia in mid 1995, at the TSF at the Northparkes Gold Mine, central western NSW (Sinclair et al., 1997; Environment Australia, 1998; OSS, 1995). This mine used tank leaching during the initial stage of the project. Towards the end of this stage of mining, a build-up of high levels of toxic copper-cyanide complexes in the tailings dam developed due to a change to a higher copper content in the ore being encountered, necessitating additional cyanide use in the mill to extract the gold from the ore. This had not been detected, as there was no routine monitoring of WAD CN (there was no statutory requirement). Initially ~100 dead birds were seen by mine staff, and when a count was made 8 days later, this had grown to 2700 birds, as birds ingested high concentrations of available cyanide compounds. Species killed included black duck, grey teal, swans, and seagulls. WAD cyanide levels in the tailings dam reached over 380 mg/L (>500 mg/L total cyanide).

In late August, steps were taken to reduce the WAD CN concentrations in the dam by using hydrogen peroxide (H_2O_2), which resulted in a fall in WAD CN from ~350 mg/L to <50 mg/L by early October. During this time, bird mortality and cyanide levels were monitored closely and the overall trend showed that by controlling cyanide levels to <50 mg/L WAD CN there was a corresponding and dramatic decrease in bird mortality. Use of cyanide has ceased in Stage 2 of the project, with the exhaustion of oxidised ores with higher gold grades and the transition to sulphidic copper ore with lower gold grades – this ore is processed by flotation methods and transported off-site for further processing.

On-going minor incidents

The above occasional mass bird poisoning incidents appear to be due to high levels of cyanide in tailings waters at a time when flocks of birds are strongly attracted to them, e.g. because of drought. Various data, including some gold processing site records, show that smaller incidents of increased wildlife mortality due to cyanide poisoning have occurred on an intermittent, ongoing basis. Deaths of terrestrial species such as kangaroos are also recorded, but these are often determined to be due to the animals becoming bogged in the mud, rather than cyanosis.

Donato (2002) discussed wildlife and livestock incidents at TSFs and associated infrastructure in Australia, indicating that representatives from a range of species, including birds (e.g. waterfowl, seabirds, predatory and shorebirds), cattle, goats, pigs, frogs, lizards, mice and small marsupials, wallabies and kangaroos, have been poisoned by cyanide at these facilities. Bats may also be attracted to TSFs and associated infrastructure (Henny et al., 1994; Clark, 1991), but there are limited Australian data available on bat utilisation or effects. Birds are generally the most frequently affected fauna (Donato, 2002; OSS, 1995).

Examples of such incidents from available data are discussed below. Records show intermittent deaths of individual birds or small groups, and occasional more significant incidents. From the limited data available, there is clear evidence of improved management of wildlife safety in declining trends in cumulative mortality per year at individual sites.

Ryan and Shanks (1996) discussed bird deaths at the Mt Todd Gold Project, 230 km South East of Darwin in the Katherine Region of the Northern Territory (NT), which had been a heap leach operation and was initiating a new stage where tank leaching would be used and a 130 ha tailings storage facility would ultimately be in use. Citing a letter received by Bird Observation & Conservation Australia (BOCA) from the Office of the Supervising Scientist on behalf of the then Minister for the Environment, they claimed the company involved had reported 91 bird carcasses had been found in a 12-month period in 1994-95. While none of these had included the endangered Gouldian Finch (known to breed in close proximity to the mine) or other small birds, the company was also said to have noted that small bird carcasses may be quickly scavenged by predatory species or be covered by tailings sediment and so go undetected. Ryan and Shanks (1996) also claimed they were “reliably informed” of an incident late in 1995 where 200 pratincoles landed on the leach heap and subsequently died, but no further details or source for this report were provided.

Donato (2002) reported that for a six month period in 1999 at one mining operation in Western Australia (WA), 313 deaths were recorded.

The WA DoE commented that animal deaths may be attributed to CN when in fact they are due to drowning and starving. WA DoIR noted that even a single macrofauna death is reportable to them, whether due to cyanosis or drowning. Seventeen kangaroo deaths had been recorded in three years prior to 2004, most due to becoming stuck in mud, with some due to traffic at the site. They were not aware of any aquatic ecosystems being affected. Three incidents involving wildlife potentially being exposed to cyanide-containing tailings at TSFs were reported to the DoIR in 2000-2001. Separately, these involved the deaths of 6 swans, 2 kangaroos and an unidentified mammal, and 24 whiskered terns. These occurred in 2000-2001.

NT DBIRD noted an incident in 2001 (evidently at a time when seasonal lakes were drying up and the number of birds had increased) where birds were sighted landing on a decant pond and were seen to look sick within 5 minutes. The environmental department was alerted straight away, but by the time the officer reached the pond, ~40-50 birds were dead, with the rest of the flock flying off (species not stated). Dead birds were removed and destroyed to prevent scavenging.

Responses from a survey of gold processing facilities showed that monitoring programs to detect trapped, distressed or dead/dying birds and animals vary from once daily or once per 12 h shift as an incidental check to a formal check once every 6 h plus informal/incidental check every 3 h. Some responses indicated provisions for reminding observers of the things needing checking and for recording such incidents in a consistent fashion; some sites referred to relevant training of operators; and some sites evidently have trained environmental staff on duty. It is evident that several sites have formal plans in place for wildlife observation training and procedures, and this is likely to improve with adoption of the ICMC. One point that did not appear to be general practice is whether or not carcasses were removed – access to the surface of TSFs may not be possible without equipment such as hovercraft, but recovery of carcasses is recommended by documents such as NTDME (1998), so as not to attract raptors and carnivores. Unpublished reports provided for this assessment by Australian gold processing sites also indicate that affected birds are sometimes rescued and may recover from cyanide poisoning (one report mentions providing oxygen to the rescued birds to assist this). However, the merits of this need to be balanced against considerations of human safety and practicality and the likelihood of success (e.g. there is a limited likelihood of secondary poisoning of predators arising from this means). Recovery of corpses for autopsy may not provide a conclusive result and is considered unnecessary, unless potential causes other than cyanide need to be evaluated: in the absence of other conclusive evidence, cyanide should be assumed to be the cause of death.

Information from these unpublished reports for one site in the Northern Territory in recent years indicated that bird deaths occurred periodically on the in-pit tailings facilities & that the decant water is sampled in these instances to determine if the death may be CN-related. Reports were provided for 11 incidents involving the deaths of 30 birds over 2002-2004, ranging from 1-9 birds of various species in each incident (magpie larks, black ducks, mudlarks, black swans, red necked avocets, black & little black cormorants, kestrels, egrets, and unknown species due to partial burial). The incident reports noted action in some cases such as hosing down a cement surface to remove potential CN residues, continuation of visual inspections, bird deterrents/scaring away, and installation of netting.

An earlier report indicated a generally declining trend in bird deaths, from ~305 in 1995-96 to ~20 in 1996-97, 235 in 1997-98, ~140 in 1998-99 and 65 in 1999-2000. The report attributed this decline to a specific strategy to minimise bird access to the tailings storage, by minimising the volume of water stored on the tailings surface, patrolling the tailings storages during the high season, and irregularly firing gas cannons.

In 1995, ERA Environmental Services undertook a questionnaire survey of avian use of TSFs and incidents at selected Australian mines. This was reported in the Cowal Gold Project draft environmental impact statement (ERA Environmental Services, 1995). A summary of the data is presented in Table 9.17. Caution is necessary in evaluating these data as they lack clarity and details, and at the time wildlife impacts

are likely to have been underestimated (Section 9.9.3). A significant number of bird deaths occurred in the first year of operations at the second site listed in Table 9.17, but it is not clear what the typical concentration of WAD CN to which the birds may have been exposed was in that first year.

Table 9.17. Avian incidents at TSF and heap leach areas at five gold mines in the Top End of the Northern Territory based on a survey by ERA Environmental Services (1995).

Reported Cyanide Concentration and location (presumably WAD CN)	Number and Types of Birds Affected	Other comments
100 mg/L on a heap leach pad (ponded waters)	During and after heavy rainfall events, frogs appear in the leach pad, to which cormorants and small birds are attracted. Kites and other predatory birds wheel above the leach pad, preying on the smaller birds. This situation led to 22 observed bird mortalities in 1993.	Devoid of vegetation and does not usually attract birds.
Typically <10 mg/L (it is not clear whether this was the case in the 1st year) in a 45 ha decant dam	50 to 60 bird deaths, all black-tailed kites occurred in the 1st year of operations, subsequently limited to 1-2 ducks or terns per year, stated to be most likely due to lower CN concentrations in the water.	Periodically a small flock of pelicans lands on the water: within 16 h of sighting gunshot noise is used.
Typically <30 mg/L in the tailings dam, and 0.5 mg/L in the decant pond	Bird activity in this 1st year of operation was minimal and restricted to waterhens and ducks on the TSF.	No deaths recorded
200 mg/L in the pregnant liquor pond, ~10 mg/L in the barren liquor pond, ~30 mg/L in a storm pond.	4 raptors found dead on the heap leach stockpile; 1 cormorant dead in the pregnant liquor pond; and 2 kingfishers were retrieved from the plastic lined storm pond launder channel, and while distressed, recovered within 15 minutes and were released.	
30-100 mg/L in several large evaporation ponds, and in decant ponds and other CN-bearing waterbodies on the minesite; 25 mg/L in the TSF; there is also a large mine dewatering pond that resembles a natural billabong.	Bird activity consists of an itinerant bird population on the ore heaps and shorebirds searching for invertebrates around ponds; waterbirds roost on sparsely vegetated ponds and seek food from vegetated ponds on the minesite; observations of bird activity around the tailings dam have been restricted to small wader footprints along its edges: 2 raptors found dead, over a 12 month period (Whistling & Black-tailed kites, location not specified)	Hazing techniques have not been found necessary as the birds are easily disturbed, e.g. by an approaching vehicle.

Source: ERA Environmental Services (1995).

Smith and Donato (2007) noted that reports of wildlife deaths are often unconfirmed, underestimated, poorly measured and exceed estimates made by the Minerals Council of Australia based on a questionnaire conducted in 1996 (MCA, 1996). Donato et al. (2007) noted that the latter estimated that there were 1000 deaths per annum at the 200 operational tailings dams in Australia and reported the following conclusions (comments by Donato et al. (2007) are italicised):

- 72% of tailings dams in Australia are rarely or never used by wildlife *(since shown to be incorrect)*,
- 65% of gold mines in Australia recorded <5 deaths per year *(likely to have been a result of inadequate methods used rather than an accurate representation of impacts)*,
- 74% of mining operations never experienced 10 deaths in a week *(possibly a result of methods used rather than an accurate representation of impacts)*,
- migratory birds were not an issue to the extent reported in the USA *(but various migratory species may be present and there are conservation concerns for these species - Section 11.10.1)*;
- anecdotal evidence from Australian TSFs is that birds tend to come and go as these features offer only some roosting habitat *(much more is now known about different types of habitat present in TSFs)*; and
- there are a number of cases of high WAD CN levels where significant bird deaths have not occurred *(since shown to be accurate in regard to hypersaline situations – see below)*.

The industry now has a much greater understanding and awareness of wildlife issues at gold mine facilities, as evident in the data discussed below and in Section 7.3, and of the action needed to ensure wildlife safety, as developed in the ICMC. This has included recognition of the importance of ensuring monitoring is appropriately conducted (Section 9.9.3).

Systematic study on wildlife impacts of gold mine tailings dams in the Northern Territory

A study by the Northern Territory (NT) Bird Usage of Tailings Storage Facilities Group (Donato, 1999) involved trained observers monitoring wildlife activity and mortality at TSFs in the NT over 13 months in 1996-97. Three of the seven mining operations monitored were in the Centre (South of latitude 15ºS, primarily an arid climate) and four in the Top End (North of 15ºS, a tropical climate with distinct wet and dry periods). Salinity levels for these TSFs were not indicated by Donato (1999). Adams et al. (2008b,c) provided additional discussion of the common methodology used in these and subsequent studies, and presented further data for one site which they identified as a freshwater site.

The observers recorded a total of 220 bird species on the case study mining leases, of which 77 species were seen on TSFs. A total of 930 deaths were recorded during the study period, and an additional 929 deaths were indicated from anecdotal information for the two years prior to the study. Observations were not made of exposed wildlife that moved off-site and beyond view. The composition of avian mortalities was 20% duck species, 5% whistling kite and black kite, 15% wader species, 7% Australian and

oriental pratincole, 36% tern species, and 17% others. Further details of the species present and effects on them are provided in Appendix 2, Table A2-1.

The findings of the study regarding the concentrations of WAD CN present where mortalities occurred were consistent with those reported by Henny et al. (1994). Few mortalities (four, 0.02 mortalities per observation day) were recorded at ≤50 mg/L WAD CN in open impoundments, with no mortalities at two sites that consistently operated at <50 mg/L WAD CN, whereas significant mortality events occurred at >50 mg/L WAD CN. When tailings discharge concentrations were between 50 and 100 mg/L, bird deaths occurred at a rate of 1.90 deaths per observation day, and at >100 mg/L (where other interventions were made) the avian death rate was 1.69 deaths per observation day. Most birds visited between September and March in the Centre, whereas in the Top End no significant difference was evident in bird visitations in the dry (April to September) and the wet (October to March), except for the passage of pratincoles in December.

An important insight is obtained from data presented in Adams et al. (2008b,c) for a site in the Donato (1999) study which was identified as freshwater (salinity anecdotally recorded below TDS 1500 mg/L). When bird visitations and mortalities at one site were plotted over time together with changing WAD CN concentration data, it is clear that while WAD CN concentrations remained below 50 mg/L in January to April 1997, no mortalities occurred, despite bird visitations reaching over 20 per day. As WAD CN concentrations built up in April-May and reached 50 mg/L, mortalities became evident and continued into June. No visitations or mortalities were shown over June to September, but visitations then resumed (WAD CN ~100 mg/L) and mortalities again became evident.

As a result of this study, the value of 50 mg WAD CN/L has been adopted by the Northern Territory Department of Minerals and Energy (NTDME, 1998) in their Best Practice Guidelines for Reducing Impacts of Tailings Storage Facilities on Avian Wildlife in the Northern Territory of Australia. As evident from the above, the emphasis of the recommended cyanide concentration is therefore placed on the absence of significant acute wildlife mortality.

Data from unidentifed sites in Australia and Africa were evaluated graphically and statistically by Donato et al. (2008). At one site WAD CN concentrations were always above 50 mg/L, but mortalities declined over time and appeared to be related to a decline in the area of supernatant over time. At another, the data were found to support the hypothesis that the relationship between 'cyanide intake and bird-deaths is not linear and that relationship is characterised by a threshold at approximately 50 mg WAD CN per litre of tailings waste'.

Saline and hypersaline mine site studies in Western Australia

The salinity level of water can be described according to the concentration of Total Dissolved Solids (TDS) present as fresh (0-2000 mg/L TDS), brackish (2000-14 000 mg/L TDS, saline (14 000-50 000 mg/L TDS) or hypersaline (>50 000 mg/L TDS) (Adams et al, 2008b). The salinity level of water in TSFs or at heap leach facilities in the studies described above was generally not indicated. However, groundwater used as a source for the process water at WA gold processing facilities in the Kalgoorlie/Laverton area it is often saline or hypersaline.

While various field data indicate WAD CN concentrations >50 mg/L may cause bird deaths and relatively few deaths occur at concentrations below 50 mg/L, Donato et al.

(2004) noted that anecdotal evidence suggested that WAD CN discharge at up to 150 mg/L may be safe to wildlife under hypersaline conditions experienced in some regions of Australia. This has since been explored in major studies undertaken at hypersaline and saline gold mine sites in Western Australia (further described in Sections 6.6.4 and 7.3.2), as discussed below.

In studies reported by Adams et al. (2008a,b,c) there were no recorded cyanide-related wildlife deaths either by on-site monitoring for 1319 days or by the authors for 91 days with more intensive observations, despite WAD CN concentrations generally exceeding 50 mg/L. Detailed observations were made of behaviour, and no comments on adverse effects noted (presumably they would have been added to the behaviour categories listed if observed).

At the Fimiston TSF near Kalgoorlie, tailings discharge concentrations exceeded the 50 mg/L level episodically and wildlife were known to interact with habitats where exposure was likely. Thus again wildlife impacts may have been expected, yet none were recorded (Griffith et al., 2009).

Similarly, at the hypersaline Sunrise Dam Central Tailings Discharge (CTD) site, concentrations of WAD CN in discharge averaged 62.4 mg/L during the sampling period (2004-2006), and exceeded 50 mg/L on 72% of sampled days (Donato and Smith, 2007). Nonetheless, on 1096 visitations and no cyanide-related deaths of wildlife were recorded on the CTD (TDS ~158 000 mg/L at discharge), and 748 visitations and no cyanide-related wildlife deaths were recorded on the stormwater/decant pond (TDS ~134 000 mg/L at discharge).

As discussed in Section 6.6.4, Kanowna Belle and St Ives tailings systems are described as hypersaline and are substantially more saline than seawater, with approximately 50 000 mg/L TDS at St Ives and 200 000 mg/L TDS at Kanowna Belle. during the course of this study and historically. Adams et al. (2008b) indicate that drinking of these undiluted solutions is beyond the physiological capabilities of all vertebrate wildlife. Birds may be adapted to consume saline water by specialised adaptations in the form of salt glands located in the nasal passages that filter salt from the blood producing a highly concentrated sodium chloride solution which is then expelled (as in marine species). Some species of birds can excrete salt in their urine (e.g. Zebra Finch) (Smith et al., 2007). However, the maximum recorded salinity an Australian animal is capable of drinking is 47 000 mg/L TDS for a Zebra Finch, equivalent to 116-133% of seawater (35 000 mg/L TDS).

Therefore wildlife would not be expected to drink hypersaline water. This was confirmed by observations: from a total of 5710 wildlife records within the TSFs at St Ives, Kanowna Belle and Granny Smith, there were just two apparent drinking observations (Adams et al., 2008b). Both observations were made following substantial rainfall within the previous 24 hours and were interpreted as drinking from a freshwater lens sitting on top of the saline supernatant solution, although some diluted supernatant may have been ingested. No impact was observed in either case. Indications are that despite the lower salinity at Granny Smith (at times not saline, dipping intermittently to as low as ~7000 mg/L TDS), wildlife were drinking elsewhere. In contrast to wildlife behaviour at the three TSFs, drinking behaviour was commonly observed at a number of alternative fresh water bodies but not at alternative hypersaline waterbodies. It is clear that at all sites terrestrial and aerial birds and mammals drink from fresh surface waters when available in preference to saline TSF supernatants.

From these observations on drinking water, plus observations of wildlife interactions and the extent of food resources present at these three facilities (Section 7.3.2), the following findings regarding the lack of mortalities were made:

- No wildlife species can drink hypersaline tailings solutions in excess of 50 000 mg/L TDS because of osmotic regulatory (water balance) requirements.
- The few species of wildlife that interact or forage within the TSFs limit ingestion of saline and hypersaline solutions to avoid ingestion of salt and therefore dehydration. The dosage of cyanide-bearing solutions received by wildlife from interaction with hypersaline tailings solutions is therefore limited to small amounts of solution ingested inadvertently by birds pecking out terrestrial macroinvertebrates from dry tailings, wet tailings and supernatant solutions. The dosage of cyanide received is insufficient to cause wildlife mortalities at the salinity level and cyanide concentrations recorded, as demonstrated by zero mortalities.
- The presence (number and composition) of wildlife species visiting and interacting with tailings solutions is strongly influenced by lack of aquatic food provisions, which are limited by hypersalinity, metal and cyanide concentrations. Very limited interaction occurs from wildlife that feed on aquatic invertebrates. Wildlife presence is also strongly influenced by abundance of terrestrial and aerial invertebrates, which are present to some degree at all TSFs.
- TSF habitats are unattractive to the great majority of wildlife (especially bush birds and granivorous birds), partly due to the physical features and lack of vegetation within the systems.

It was concluded that:

- Hypersalinity (>50,000 mg/L TDS) provides a natural barrier for wildlife exposure to WAD cyanide contained in tailings solutions because at this salinity the solutions are outside the physiologically safe drinking range of wildlife and wildlife seek to avoid its ingestion while foraging.
- Salinity (>14,000 mg/L TDS) provides a partial barrier for wildlife exposure to WAD cyanide contained in tailings solutions because at this salinity wildlife are either unable to drink solutions or preferentially drink fresh water if it is available.

9.9.3 Issues regarding monitoring of wildlife at TSFs

Field-based surveys of wildlife at TSFs and the correlation of mortality to cyanide concentrations to which the animals were exposed are subject to practical problems. There are also issues regarding the adequacy of routine wildlife monitoring at TSFs.

In most cases, data on numbers of wildlife deaths in TSFs and other cyanide containing facilities have been considered to be minimum estimates (Donato, 2002; Donato et al. 2007), due to:

- inadequate monitoring frequency and procedures at individual sites, including no monitoring on the assumption that there are no wildlife deaths;
- lack of observer skill;
- poor observability of animals (small size and camouflage) relative to large size of TSFs, and difficulty in collecting and counting carcasses;

- dispersion following exposure, where mortality or other adverse effects occurs away from the site of exposure and detection;
- rapid scavenging of small carcasses of cyanide-killed fauna prior to detection;
- submergence in liquor or supernatant or carcasses being covered by sediment;
- taxonomic errors (incorrect identification of species); and
- emphasis on monitoring specific wildlife (e.g. birds), but not other groups (e.g. ground-dwelling mammals, nocturnal avifauna and bats, snakes, lizards, tortoises, invertebrates).

To address the issue of the adequacy of monitoring in the MERIWA project, small blue and black party ballons were filled with water and thrown into the supernatant to simulate typical small carcasses such as waders or small ducks. Black balloons were obvious and easily detected with binoculars against the white saline tailings at each of these sites. A total of 195 balloons were set on 18 occasions with 171 balloons being detected by on-site staff, in all cases on the next scheduled wildlife monitoring. At each site only the dedicated wildlife observers with field binoculars (and training) detected the presence of balloons. This supports the above comments on underestimation with past practices and illustrates the necessity for monitoring to be conducted by staff using binoculars and with appropriate training.

Detection of cyanide in cyanide-affected wildlife through sampling and analytical testing is difficult due to metabolic processes. Assigning effects or mortality due to cyanide is more difficult when the initial effect of cyanide is compounded by secondary factors that may be enhanced after the effects of cyanide have ameliorated such as loss of condition, bogging/miring in tailings, drowning, infectious disease and predation. Comments recorded with data from some individual sites suggest that there is a misapprehension among some of those making routine observations that if WAD CN concentrations in water near where a carcass is found are <50 mg/L, the death must not have been due to cyanide.

Clark (1991) and Clark and Hothem (1991) suggested that some birds or bats might not die immediately following drinking a lethal dose of cyanide-containing water, but may fly away before adverse effects occur. Animals that are affected sublethally or that die due to cyanide toxicity in locations out of view of fauna surveyors are generally not included in surveys at TSFs or heap leach facilities, and off-site mortalities in remote areas may be difficult to detect. However, while there are sound arguments for sublethal effects and/or gradual liberation of cyanide in the stomach causing mortalities away from the site of exposure, there appears to be very limited evidence that this does occur (see Section 9.9.1).

Smith et al. (2007) report personal observations regarding bird deaths which suggest that delayed effects may occur, with other factors possibly contributing to mortality (the authors do not indicate the WAD CN concentration in the situations described). However, it appears that all the birds they observed remained where they were exposed until death, though predator aversion is likely to have been affected and many predatory species apparently occupy TSFs for this reason: ‘Some larger birds have been observed to survive incapacitated for over 12 hours after initial ingestion of supernatant containing tailings before dying (Smith, G, pers. obs.). Whether cyanide was the sole cause or led to secondary factors such as shock, from which birds often don’t recover, is unknown. Many birds that survived an initial dose of cyanide have

been observed to continue to drink mine waste solutions at regular intervals and gradually lose condition resulting in death (Donato, D, pers. obs.). Wildlife that suffer lethargy from non-lethal doses may drown if they are unable to keep their heads above the water (Donato, D, pers. obs.)'.

In the evaluations at hypersaline sites in Australia by Adams et al. (2008) discussed above, the possibility that wildlife did not die *in situ* but flew away and died elsewhere was specifically considered. However, this hypothesis was dismissed based on the argument that no deaths attributable to cyanide were observed at any of the three study sites, yet if deaths were occurring literature expectations would be that some (if not all) carcasses would be recorded *in situ.*

There are also practical problems in correlating wildlife mortality to cyanide concentration reported in the field. In laboratory ecotoxicity studies, the dose administered to animals can be accurately controlled and monitored, particularly when animals are gavaged. However, field studies do not have this level of control and animal exposure may be subject to wide variability. Furthermore, the determination of the concentration of cyanide in the environmental media is also subject to wide variability due to sampling and analytical error. There is a potential for error between the concentration of cyanide analytically measured and that to which wildlife are actually exposed. The dose-response relationship for cyanide is acute, and effects assessment is sensitive to small increments of dose and it is known that the concentration of cyanide in TSFs varies spatially and temporally due to changes in ore quality, operational use of cyanide, discharge concentration and volatilisation (Adams et al., 2008a,b,c; Donato, 1999; Henny et al., 1994). For scientific analysis, statistically robust sampling is required for analysis from the area where and when wildlife are exposed.

While the needs of scientific investigation differ from those of routine monitoring, it is evident that improvement in how routine monitoring has been conducted is needed. The industry is well aware of this, and Standard of Practice 4.9 in the ICMC is 'implement monitoring programs to evaluate the effects of cyanide use on wildlife, surface and ground water quality' (ICMI, 2006). Appropriate guidance for wildlife and habitat monitoring have been developed to meet compliance requirements for the ICMC (Smith and Donato, 2007; Donato, 2002, 2005; Donato et al.,, 2004, 2007).

9.9.4 Toxicity of other tailings components

Smith et al. (2007) indicate that cyanide is the most significant contaminant in gold mining that influences wildlife mortality, but that tailing solutions often contain a range of metals, metalloids and chemicals, many of which are toxic to wildlife at various concentrations. They note that harmful effects may occur in animals from exposure to heavy metals and metalloids, with metals such as mercury, lead and cadmium able to bioaccumulate, and heavy metals known to negatively effect survival and reproduction success in birds. Thus where additional constituents are present at or approach toxic levels within the tailings this may have an impact on the toxicity of cyanide and the tailings facility as a whole. However, as noted by Henny et al. (1994), no other component present in tailings from the gold milling process causes immediate death, except for cyanide.

Johnson and Donato (2005) discussed evidence from evaluations of bird mortalities that occurred in 2004 and 2005 at the Sadiola Hill Gold Mine in Mali (Section 9.9.1) that sodium levels may reach sufficiently high that birds may die. They postulated that

species which were affected such as grasshopper buzzard, herons and egrets were susceptible to sodium concentrations in the order of 800-1000 mg/L, whereas species which are permanently resident in the area and were not found among the observed mortalities are adapted to higher sodium concentrations (note that the water was not hypersaline). The 800 mg/L level was adopted as a conservative target for the site if decisions were being made to regulate sodium levels in process waters, and as a trigger for intensifying bird-hazing measures during the dry season. Johnson and Donato (2005) note that significant bird mortalities have also been recorded at impoundments associated with brine extraction of salt, and at base metal mining operations in the United States and Australia, and Smith et al. (2007) discussed these reports in more detail.

9.10 Summary of environmental hazard assessment

Nature of cyanide toxicity

Ecotoxicity data for sodium cyanide and other cyanogenic compounds show that cyanide has very high acute (e.g. single dose) toxicity to aquatic and terrestrial animals and is also toxic to plants and certain micro-organisms. It is also toxic via chronic (e.g. long term or repeat dose) exposure, such as adverse impacts on egg production and spawning in fish.

Once in the bloodstream of an animal, cyanide rapidly forms a stable complex with enzymes involved in cellular respiration, resulting in cytotoxic hypoxia or cellular asphyxiation. The lack of available oxygen causes a shift from aerobic to anaerobic metabolism, leading to the accumulation of lactate in the blood. These effects lead to depression of the central nervous system (CNS) that can result in respiratory arrest and death. A range of other enzymes and systems are also affected by cyanide. In general, effects from non lethal doses tend to be reversible over time due to metabolic cyanide degradation processes; however, fitness is likely to be impaired during recovery. There is a range of debilitating signs of cyanosis.

Toxicity of different forms of cyanide

WAD CN is generally considered the most appropriate measure of 'biologically available' cyanide because it includes free cyanide and various forms of cyanide which may release free cyanide once consumed by an animal, but not forms of cyanide that are unlikely to release free cyanide to an animal. From arguments which have been presented regarding the availability of weakly bound metal complexes of copper, nickel and zinc at the pH of a bird's stomach, it appears reasonable to conclude that in many cases the actual composition of the WAD CN will result in somewhat lower toxicity than an equivalent concentration of free cyanide. This is because formation and absorption of free CN from the dissolved metal complexes occur comparatively slowly, and because complexes may partially dissociate to free CN together with an insoluble neutral metal cyanide complex which precipitates and is unavailable. However, the extent of these effects is dependent on the conditions at individual sites, which are also likely to change over time. WAD CN determinations may also underestimate bioavailable cyanide in species such as raptors, which have a stomach pH lower than that used to determine WAD CN.

Toxicity to birds

Laboratory studies have been conducted where birds were exposed to cyanide in drinking water, which is expected to be the most significant exposure route at mines.

Drinking water studies based on standard test guidelines indicated avian LC50 values for bobwhite quail and mallard ducks of 374 mg CN/L and 180 mg CN/L, respectively. However, these studies were considered as unreliable due to uncertain actual concentrations and exposure. The toxicity of cyanide in mine effluent and tap water with single or repeated exposure of mallard ducks has also been investigated, with LC50 values of 181-212 mg WAD CN/L and 136-158 mg WAD CN/L respectively. The results were interpreted as indicating an overall LC01 (1% mortality) of 50 mg/L for repeat exposure, which appears to be a further basis for selection of 50 mg WAD CN/L as a protective value. However, the original reports have not been seen, very limited information on the studies was available and the results are considered to be unreliable.

Other brief exposure (2-4 h) studies with mallards indicate a short exposure LC50 of ~115 mg WAD CN/L, which is consistent with field observations on acute mortality. An assessment factor of 10 could be applied to these, suggesting a concentration of ~12 mg WAD CN/L would be safe to protect mallards from any lethal effects with short term exposure. However, in extending these results to other species with different drinking behaviours and bodyweights, the relative size of a single dose would need to be considered (e.g. a dose of ~8-10 mL used for the ~1 kg mallards is relative to a total day's consumption of ~60 mL. Mallards would be expected to take six or more drinks per day, whereas a bird weighing ~50 g would consume around 10 mL water per day, and depending on the species, may only arrive to drink once or twice per day).

The most reliable data available for toxicity for birds were from acute oral toxicity tests with seven bird species, with the acute LD50 to mallard ducks of 1.4 mg CN/kg bw the most sensitive value. Modelling based on these limited results estimated a Predicted No Effect Concentration (PNEC) of ~1 mg/L. The use of acute toxicity data for assessment of toxicity from drinking water consumption requires interpolation of the results using estimated daily water consumption. As birds (and animals) may be able to detoxify cyanide if sufficient time elapses between the intake of sublethal doses, assumptions also need to be made regarding the proportion of daily water consumption that birds would ingest in each dose. As a worst case, ingestion of the entire day's consumption in a single dose has been considered. This is appropriate for species that arrive at water sources only once or twice per day, but is clearly conservative for species such as waterbirds (e.g. mallards) which take several drinks over the day. Such differences in drinking behaviour between species make it difficult to extrapolate toxicity results from one species to another.

There are also studies of biochemical effects and effects on pigeon flight time from cyanide exposure which indicate effects at relatively low doses. Expressed as the concentration given in a single dose of 10 mL (compared to an expected approximate daily water consumption of ~50-60 mL), significant biochemical effects occurred at concentrations as low as 20 mg free CN/L, and significant pigeon flight time effects at 50-80 mg free CN/L. The metabolism of the birds may recover from such doses, but while affected, birds may be more likely to succumb to predators or suffer reduced flying capacity. However, there is no conclusive evidence from observations or incident reports that these effects occur in the field, although in any case they would be very difficult to detect because they would occur at diffuse locations distant from the site where exposure occurred.

Observations also indicate that birds do not avoid drinking cyanide-contaminated mine waste water and may remain in a pond and take further drinks, potentially leading to a cumulative toxicity effect. Depending on drinking behaviour (e.g. species differences)

a bird may also take in a greater relative dose. However, it is also noted that birds are averse to drinking hypersaline water. Consequently, cyanide intake is reduced where the water is hypersaline and field studies show mortalities do not occur at hypersaline conditions even at WAD CN concentrations exceeding 50 mg/L.

Toxicity to mammals

Similarly, the most reliable toxicity data for mammals were acute oral toxicity studies, with the acute LD50 of 2.3 mg CN/kg bw the most sensitive value for rabbits. Modelling based on these results and drinking water consumption tables again estimated a Predicted No Effect Concentration (PNEC) of ~1 mg/L.

No toxicity data were available for reptiles (e.g. snakes, lizards, tortoise), but data from mammals and birds are considered indicative in the absence of reptilian data.

Toxicity to terrestrial plants

Many plant species contain organocyanide forms, (glucosides) for chemical defence, and cyanide is also produced as a by-product in the synthesis of the plant hormone ethylene. Higher plants contain enzymes that are irreversibly damaged by cyanide, but have other enzymes that can detoxify it. Experimental data with basket willows conducted to explore their use in phytoremediation found that when plants were grown in aqueous solutions doses of 8 and 20 mg CN/L in aqueous solution resulted in mortality in <1 week. When the plants were grown in sand, there were no toxic effects with irrigation by cyanide solutions at 10 mg CN/L; at 20 mg CN/L transpiration was reduced by 50%, but plants survived; while at 30, 40 and 50 mg/L transpiration was greatly reduced and the plants died. It should be noted that other components of tailings also influence phytotoxicity, including the resulting pH and salinity.

Toxicity to aquatic organisms

For aquatic assessment, a range of acute and chronic toxicity data are available with free cyanide for a range of fresh water and marine species, including fish, invertebrates, algae and aquatic macrophytes. The ANZECC Water Quality Guidelines trigger value for cyanide for protection of 95% of aquatic organisms is 0.007 mg free CN/L at the boundary of freshwater mixing zones, or 0.004 mg free CN/L at the boundary of mixing zones if release is to coastal waters.

Toxicity to terrestrial arthropods

Hydrogen cyanide has been used as a fumigant to treat various arthropod pests in some countries. As a fumigant, HCN has a rapid paralysing effect on most insect species. Sublethal concentrations may bring about apparent death, but if exposure is insufficient stupefied insects may recover. However, susceptibility of species varies, and insects which prefer cyanogenic food sources (e.g. lima bean foliage) may be highly tolerant of cyanide in their diet, with cyanide a feeding cue and stimulant to them.

Toxicity to micro-organisms

Some species of bacteria exposed to cyanide may exhibit decreased growth, altered cell morphology or other harmful effects, but not all micro-organisms are affected by cyanide and microbial populations can become acclimatised to cyanide and can then degrade wastes with higher cyanide concentrations. Microbes can degrade cyanide by various pathways to yield a variety of products. Several species of fungi can

metabolise cyanide, and cyanide compounds are formed as secondary metabolites by many species of fungi and some bacteria by decarboxylation of glycine.

Incidents of wildlife poisoning in Australia and overseas and field observations

There have been incidents in Australia where hundreds or thousands of birds have been killed within a relatively short period at a single gold ore processing site through exposure to cyanide residues in a TSF or associated facilities. Records indicate smaller numbers of birds have died on an intermittent, ongoing basis at gold ore processing site TSFs and heap leach facilities in Australia and the USA. Field data from the past need to be viewed with some caution due to various practical difficulties in obtaining field observation data, and it is likely that the extent of impacts has been significantly underestimated in the past.

Reliable corresponding information on WAD CN concentrations in areas to which the dead animals were exposed is not always available. However, there is now a body of evidence from scientific observations, anecdotal sources and incident reports at mine sites which indicates that where significant mortalities are observed, WAD CN concentrations are > ~50 mg WAD CN/L. Scientific studies observed relatively few or no mortalities at lower WAD CN concentrations, and the observed mortality at concentrations < 50 mg WAD CN/L in those studies may or may not have been associated with cyanide toxicity. There are some brief published reports indicating mortalities at cyanide concentrations ~20 mg/L, but there is insufficient information for these to be considered reliable – e.g. the animals may have been exposed to higher WAD CN concentrations at an earlier time or different point to where samples were obtained, or died from other causes. Thus field studies give a general indication that 50 mg WAD CN/L is protective of significant bird death incidents, while 1 mg WAD CN would be unnecessarily low, but some caution is needed because field observations to determine the extent of sublethal effects are lacking.

10. Environmental Risk Characterisation

This chapter provides an assessment of the risks to the environment through use of sodium cyanide based on the conceptual models and exposure assessment presented in Chapter 7 and the toxicity assessment presented in Chapter 9.

Environmental risk assessment of industrial chemicals in Australia is conducted according to the "Environmental Risk Assessment Guidance Manual for Industrial Chemicals", available at http://www.ephc.gov.au/taxonomy/term/75. The manual has been endorsed by the Environment Protection and Heritage Council (EPHC) and accords to international best practice.

10.1 Risks during manufacture and transport

Manufacture

Cyanide-containing wastewaters from plants manufacturing sodium cyanide are discharged to wastewater treatment/detoxification systems or to publicly-owned trade waste/sewerage treatment plants (TW/STPs), with protective limits placed on concentrations of cyanide and its breakdown products at various points in the discharge stream and/or receiving waters.

Transport

Large quantities of sodium cyanide are transported around Australia for the mining industry, and aquatic and terrestrial organisms could potentially be exposed to cyanide as a consequence of an incident during transport by rail or road (Sections 7.2 and 5.4.2). Transport incidents in Australia and overseas indicate the nature of such events and their possible consequences, particularly where spilt material cannot adequately be recovered or contained and destroyed, e.g. major spills into flowing water that may affect aquatic organisms (Section 5.4.2). Risk is likely to be low if prompt emergency response such as appropriate clean up and recovery processes are undertaken in the event of an accident. Appropriately trained drivers to handle spills/transport incidents will minimise risk of environmental exposure. Various legislation, National Standards and Codes of Practice are in place to ensure safety and protect the environment during the handling, storage and transport of sodium cyanide, which is considered a Dangerous Good, as discussed in Section 11.3.

As discussed in Section 5.4.2, in Australia the number of transport incidents in recent years is small compared to the large number of journeys over long distances by road and rail. Significant release of sodium cyanide has only occurred in three of those incidents, and harm to wildlife or aquatic life only arose in one of those incidents, in the Tanami Desert in February 2002. In that case, a spill of liquid occurred along a road, from which wildlife drank and were harmed before measures were taken to remove the hazard. Recommendations arising from the incident investigation were directed towards product inventory management at the mine, improvements to the StoL emptying process, locking of input and outlet valves on isotainers, driver training in dangerous good management and better government departmental co-ordination of chemical spill incidents.

While no wildlife were harmed in an accident in the Northern Territory in February 2007 (Section 5.4.2), completion of clean-up and recovery was prolonged in this second incident, increasing the risk of environmental contamination had a significant rainfall event occurred before clean-up is complete. However, in response to this incident, the NT Government initiated a wider review of regulatory regimes governing the transport of dangerous goods in the Northern Territory (NT Government, 2007) (Section 5.4.2).

10.2 Risks to wildlife with use in gold mines

10.2.1 Risk quotients for drinking water exposure based on laboratory data

The following risk assessment is based on laboratory studies with acute oral exposure, which were considered to be the most reliable data available for toxicity for both birds and mammals (Section 9). As explained in Section 9, there are various deficiencies or limitations in other laboratory data, including drinking water studies. Two drinking water studies (*Fletcher, 1986, 1987) are repeatedly referred to via citation of Hagelstein and Mudder (1997a) or Smith and Mudder (1991) to support a 50 mg WAD CN/L level as safe (e.g. Adams et al., 2008a,b; Donato et al., 2007; Johnson and Donato, 2005; Donato, 2002, 2005). However, these studies or further information about them could not be obtained, therefore those data are considered unreliable. The alternative approach of considering field data for risk assessment is discussed in Section 10.2.3.

A risk quotient (RQ) approach has been used based on laboratory data to predict the risks to mammalian and avian wildlife using gold mine TSFs or heap leach ore piles or their associated ponds. A TRV is normally used in conjunction with an exposure prediction to estimate ecological risk (USACHPPM, 2000). However, exposure may range very widely, as discussed in Sections 5.2.3, 6.6.4, 6.7.1 and 7.3.1. Consequently, risk assessment will be based on a range of potential WAD cyanide concentrations, as shown in Table 7.2 (Section 7.3.6). To predict a low environmental risk, the RQ needs to be 1 or less (i.e. RQ $\leq$1). A RQ value that exceeds 1 does not mean that adverse effects will necessarily occur, but that certain circumstances may potentially pose an adverse risk, and further investigation is required before a more definitive assessment of impacts can be made.

Wildlife exposure modelling results have been presented in Table 10.1 for birds, and Table 10.2 for mammals.

Birds

The wildlife risk assessment modelling indicates RQ values in excess of 40 for birds via oral (drinking water) exposure at WAD CN concentrations of $\geq$ 100 mg/L, which would be expected from reports of significant bird death incidents at TSFs at such concentrations (Section 9.9). At the ICMC target level of 50 mg/L WAD CN, the risk quotient estimated from the available data is still unacceptable at 19-100. By these figures, the risk quotient does not actually fall to an acceptable level until the WAD CN levels are $\leq$1 mg/L (Table 10.1).

In the absence of soundly conducted and reported bird drinking water studies with bird species differing in drinking behaviour, this assessment must rely on the available acute toxicity data. An even more conservative assessment factor (AF) could in fact be justified because the avian acute toxicity studies were incompletely reported and at

best are considered acceptable rather than reliable, but a lower AF has been used on the basis of the weight of evidence from these and other data, including the sublethal effects studies. Using acute exposure data, it is then very difficult to mitigate the effects of bird drinking behaviour, given large differences between individuals and species (see below). A further factor is that the lower gastric pH of raptors means that more of the total cyanide present may be available compared to other birds or than indicated by standard WAD CN analyses. Furthermore, high temperatures may increase water consumption above the assumed figures.

Table 10.1. Estimated risk quotients for birds (0.01-1.5 kg bw) potentially exposed to cyanide solutions

Existing or target concentration	Potential Exposure Concentration (mg WAD CN/L)	Dose (estimated)[a]	TRV[b]	Risk Quotient Range
		mg CN/kg bw/day		
Worst case	600	31-162	0.14	221-1157
Common past practice	100	5.2-27	0.14	37-193
ICMC target	50	2.6-14	0.14	19-100
Intermediate targets	30	1.5-8.1	0.14	11-58
	20	1.0-5.4		7.1-39
	10	0.5-2.7		3.6-19
Largely complete cyanide destruction	1	0.1-0.3	0.14	0.7-2.1

(a) Refer Table 7.2, Section 7.3.6;
(b) TRV (Toxicity Reference Value – Oral), Refer Table 9.14, Section 9.8.1.

Noting the levels in Water Quality Guidelines, it is acknowledged that the AF approach makes these levels highly protective, meaning that at ~1 mg/L even the bird species known to be most sensitive should show no harmful effects from drinking water exposure, such as may impair flying ability or predator susceptibility (see below). It might be argued that some level of acute mortality or delayed mortality due to initially sublethal effects is acceptable for most bird species (e.g. other than threatened species). However, even if the AF of 10 is not used and a direct comparison is made between the LC50 values estimated in Table 9.4 (Section 9.2.2) and the concentrations shown in Table 10.1, it is evident that a high percentage of most of the species tested would die at a concentration of 50 mg/L WAD CN, with ~50% of the two most susceptible species tested dying at 18 and 26 mg/L according to the assumptions made.

The indication that WAD CN concentration should be below ~1 mg/L for bird safety appears to be very conservative compared to actual observations of birds at TSFs (Section 9.9). General observation data seem to indicate that keeping WAD CN somewhat below the 50 mg WAD CN/L level provides a significant degree of protection to birds, at least in terms of readily observed mortality. As discussed, the assumptions made in this assessment are worst case, particularly the assumptions that the birds consume their entire day's drinking water within a short period (i.e.

comparably to acute oral dosing) and that the toxicity of TSF and associated waters is similar to that of NaCN solutions.

Waterbirds appear to be among the most susceptible species based on acute oral dosing, but the fact that they are likely to consume their day's water in several small doses over the day is likely to significantly reduce the concentrations which cause death. Birds may survive potentially lethal concentrations because the sublethal effects cause them to cease drinking for a sufficient period that the ingested cyanide is detoxified, as described for ducks in both the laboratory and field (Section 9.2.1). If birds are assumed to drink on 6-8 occasions (i.e. similar to mallard ducks consuming doses of ~8-10 mL per occasion) and total detoxification is assumed between drinks, the risk quotient would fall to an acceptable level at ~3-20 mg/L, depending on bodyweight (i.e. assuming daily drinking water consumption $1/6^{th}$ to $1/8^{th}$ of the estimated daily water consumption derived from allometric equations – Section 7.3.6). This is consistent with results from brief exposure (2-4 h) studies with mallards. These indicate a short exposure LC50 of ~115 mg WAD CN/L, from which an assessment factor of 10 indicates a concentration of ~12 mg WAD CN/L as protective of mallards from lethal effects with short term exposure. However, cumulative toxicity is likely to be somewhat greater than this, as detoxification between drinks may not be complete and the capacity of detoxification mechanisms may decline with repeated short term exposure.

Only a two-fold increase in concentration could be applied to species which drink twice daily, assuming they take in approximately equal amounts morning and night and do so over a short period. Most at risk would be species such as finches, which might for example visit once in the middle of the day, staying by the water for a relatively short period while they drink (Section 7.3.6). Thus levels which may be safe for waterbirds may be harmful to other species.

One factor which may contribute to differences between field toxicity in practice and that predicted from laboratory studies is the composition of the WAD CN present. This is likely to result in slower or reduced availability of cyanide from an animal's gut (Section 9.2.3). Thus in practice, it appears reasonable to conclude that in many cases the actual composition of the WAD CN will result in somewhat lower toxicity than an equivalent concentration of free cyanide. However, the extent of these effects is dependent on the conditions at individual sites, which are also likely to change over time. Any such effects are likely to be less significant in species such as raptors with a low stomach pH. It has also been suggested that the contribution from slowly available forms of cyanide could lead to delayed toxicity (Section 9.9.1).

There are also studies of single dose cyanide exposure to mallard ducks and pigeons which explored sublethal effects. Expressed as the concentration given in a single dose of 10 mL (compared to an expected approximate daily water consumption of ~50-60 mL for birds of the same size), significant biochemical effects occurred at concentrations as low as 20 mg free CN/L, and significant pigeon flight time effects at 50-80 mg free CN/L. While the birds would be expected to recover from such doses, temporary impacts on flying capacity could affect the ability of migratory species to fly on safely to the next waterhole, and birds may also be more susceptible to predators (e.g. while in a stupefied or weakened state).

Mammals

Similarly, the risk assessment modelling for mammals indicates RQ values which are still at unacceptable levels at the ICMC target of 50 mg WAD/CN/L, with acceptable

levels not reached until WAD CN is ≤1 mg/L (Table 10.2). Similar comments apply to the worst case assumptions made regarding the nature of mammalian drinking water exposure at TSFs and similar facilities.

Table 10.2. Estimated risk quotients for mammals (0.01-1.5 kg bw) potentially exposed to cyanide solutions

Existing or target concentration	Potential Exposure Concentration (mg WAD CN/L)	Dose (estimated)[a]	TRV[b]	Risk Quotient Range
		mg CN/kg bw/day		
Worst case	600	57 to 94	0.23	248 to 409
Common past practice	100	9.5-16	0.23	42-68
ICMC target	50	4.8-7.8	0.23	21-34
Intermediate targets	30	2.9-4.7	0.23	13-20
	20	1.9-3.1	0.23	8.3-14
	10	1.0-1.6	0.23	4.3-7.0
Largely complete cyanide destruction	1	0.1-0.2	0.23	0.4-0.9

(a) Refer Table 7.2, Section 7.3.6;

(b) TRV (Toxicity Reference Value – Oral), Refer Table 9.14, Section 9.8.1.

10.2.2 Other factors influencing the risk to wildlife

Any impacts on reptiles would be limited to the vicinity of the TSF, as they would not be likely to move far or to be attracted from long distances, but could ultimately repopulate the area once the TSF has been closed. There is more concern with bats and native marsupial species such as kangaroos, which are likely to be more mobile and to be attracted from longer distances. There is greater concern for birds, which can fly in from larger distances. The greatest concerns are for migratory birds, which may be attracted to TSFs while flying long distances during their migration flights, and for threatened species utilising the local habitat.

Of the potential exposure routes evaluated, ponding of cyanide solution on heap leach pads would appear to pose the greatest risk to wildlife due to the potentially high concentration of cyanide used (section 7.3.4), and also because those solutions contain free cyanide rather than the products of reactions of minerals. However, the much lower frequency of heap leach operations in Australia relative to tank-based mining operations with TSFs that potentially provide a larger habitat for wildlife than heap leach operations, make tank-based operations of relatively higher overall risk to wildlife than heap leach operations.

Factors other than cyanide concentration may also influence risks to wildlife at certain facilities containing cyanide solutions, which may be reflected in the species at risk or the absence of effects on wildlife. Recent research (Adams et al., 2008a,b,c; Donato and –Smith, 2007 and Griffiths et al., 2009) has confirmed anecdotal observations that cyanide toxicity is avoided where waters are hypersaline, primarily as wildlife do not drink hypersaline water. Resources and conditions suitable for wildlife habitat may vary among sites and over different seasons and years. Habitats at some sites may be spatially larger, more suitable and more diverse at some facilities, such as large TSFs

and drainage ponds with large free water surfaces, which may potentially attract a greater diversity of species and abundance of animals. In other locations, wildlife utilisation may be very rare due to geographic isolation from habitats. Geographical location of facilities with respect to wildlife migration routes and wildlife habitats will also influence the risk to specific wildlife populations, but such routes are not necessarily fixed over time and are not completely known. One means by which harm occurs to animals is physical entrapment (bogging) in the soft surface of a TSF, and animals may potentially be exposed to toxicants other than cyanide and its derivatives (Section 9.9.4).

10.2.3 Risk to wildlife based on field data

General situations

As discussed above, there are various factors which may affect the extent to which exposure to available cyanide actually occurs in the field, hence it is important to also examine data from field records and observations of wildlife impacts and there association with cyanide concentration, which is most appropriately based on WAD CN evaluation (Section 3.3.1).

In Australia, wildlife monitoring data and incident reports from TSFs and associated infrastructure have generally been unavailable, as formal records are non-existent, very limited or confidential. Such data if available are usually lacking in important detail (e.g. reliable concentration data corresponding to mortality reports), and older data have generally not been obtained using reliable monitoring procedures and are likely to have underestimated mortalities (Section 9.9.3). Similar comments pertain to older reports for incidents that have occurred overseas (Section 9.9.1). However, as apparent from Sections 9.9, there are relatively few comprehensive and reliable reports for mortality incidents, thus relatively poor quality and anecdotal reports should be noted.

From Section 9.9, substantial reliable data are now available for arid areas in Western Australia in addition to previously published data for areas in the Centre and Top End of the Northern Territory, for which some more details have been made available in the reports by Adams et al. (2008a,b) (Section 9.9.2). These satisfy rigorous wildlife monitoring program requirements, together with corresponding data for TSF WAD CN concentrations, with very detailed data available for the Western Australian sites. Scientifically based guidance/protocols for wildlife monitoring at TSFs and heap leach facilities have been developed from these investigations and have been conveyed to the industry (Smith and Donato, 2007), thus future monitoring for individual mine sites should be much more reliable.

The following international and Australian reports clearly show that significant wildlife mortalities were observed at WAD CN concentrations >50 mg/L, but that relatively few or no mortalities were observed at lower WAD CN concentrations:

- observations at mills tailings facilities and heap leach sites in the USA reported by Henny et al. (1994);
- studies of bird usage and impacts at seven gold mining sites in the Northern Territory (Donato, 1999, with additional detail provided in Adams et al, 2008a,b);
- data presented by Donato et al. (2008), but the identity and actual location of the site are not identified and limited details were provided.

Observations which have been reported for some sites indicate that serious mortality incidents were alleviated as WAD CN concentrations were treated to reduce them below 50 mg/L:

- a report by Smith and Mudder (1991) regarding a Nevada mine;
- the report by Sinclair et al. (1997) of an incident at the North Parkes mine in NSW;

The description of mortality incidents at the Sadiola Hill Gold Mine in Mali (AngloGold Ashanti, 2005 and Johnson and Donato, 2005) partially support 50 mg WAD CN/L as a safe level, but mortalities occurred in April 2003 at WAD CN concentrations <50 mg/L. At the time, this was tentatively ascribed to toxicosis from WAD CN with a potential synergistic effect caused by cyanate/thiocyanate. When mortalities recurred in 2004, investigations suggested that the likely cause was sodium toxicity, with elevated sodium levels partially contributed to by one of the reagents used to lower WAD CN levels. Provided this argument is accepted, the observations continue to support 50 mg/L as a safe level, but raise the need to be conscious of other potential toxicants associated with cyanide use.

The Donato (1999) report indicates that some, albeit very few, mortalities occurred while WAD CN concentrations were <50 mg/L, but there is very little information regarding the extent to which sublethal effects occur to wildlife in the field in association with WAD CN concentrations below 50 mg/L. It should be noted that there is a level of background mortality due to other causes, and in the studies where deaths occurred below 50 mg WAD CN/L the mortality may have been due to various causes and may or may not have been associated with cyanide toxicity. Some reports of wildlife mortality incidents do not indicate the WAD CN concentration to which the animals were exposed.

There is one concerning report by Clark (1991), who stated that bat deaths at the Ridgeway Mine TSF in Carolina USA had occurred when the mine reported cyanide concentrations <20 mg/L in the TSF. However, there are very few details to inform this observation and there may be uncertainty in the stated concentration value – e.g. this may be referring to free cyanide rather than WAD CN, and concentrations may have varied over time or been higher in other areas. Findings of a single dead white-footed mouse and a sandpiper noted by Henny et al. (1994) at WAD CN concentrations of 16 and 26 mg/L may have been due to other causes, or due to exposure to an earlier, higher concentration or in the area where exposure actually occurred. Observations of occasional dead animals noted in unpublished records provided by the industry and reported in scientific studies (e.g. Adams et al., 2008b) were sometimes ascribed to other causes, such as physical injuries or entrapment. Clearly, not all wildlife deaths occurring at goldmine operations are due to cyanide toxicity, and it may be difficult to reliably determine the cause of death.

The above assessment (Section 10.2) considered a worst case situation of species which only drink on a single occasion per day, as is the case with Estrildid finches (Section 7.3.6). Estrildid finches do not appear among mortalities recorded in the study in the Northern Territory by Donato (1999) (see Appendix 2), but they were not observed to be drinking from the observed TSFs. At the time, the investigators assumed this was because of the lack of vegetation in the vicinity of the TSF to provide sufficient cover from predators to allow safe drinking (Donato, pers comm 2009).

There is very little information recorded on harmful effects on wildlife from cyanide observed in the field, and no field observations reported of sublethal effects without mortalities (e.g. sick birds some of which died and others flew off, or an affected bird which subsequently died). Where sublethal effects were observed, WAD CN concentrations were >50 mg /L or concentrations were not indicated.

Hypersaline situations

Observations in field studies indicated below and conducted in Western Australia in recent years found no mortalities occurred at WAD CN concentrations at sites where the waters in which cyanide was present were hypersaline (≥50 000 mg/L TDS).

- the St Ives and Kanowna Belle hypersaline sites and Granny Smith saline site in studies reported by Adams et al (2008a,b,c);
- the Sunrise Dam hypersaline site evaluated by Donato and Smith (2007);
- the Fimiston site evaluated by Smith et al (2008) and Griffiths et al (2009)

This is because the birds did not drink the hypersaline water. Similar results were observed at a saline site, but this was considered to be only partially protective, as consumption by some species may occur under some circumstances.

Site specific situations

There may be site specific factors other than hypersalinity for which scientific argument can be presented to allow a higher limit to apply in certain areas of a specific site without adverse effects to wildlife. For example, DES (2009) argue that maintaining WAD CN levels below 50 mg/L in the tailings stream flowing from the spigot is not necessary for a TSF at the Waihi Gold Mine in New Zealand, as there are protective mechanisms specific to the flowing tailings streams at this site. In that situation, potential exposure at that point is minimised by a combination of the behaviour and morphology of wildlife present at this site, and the turbulence and physical chemistry of the tailings stream. However, DES (2009) notes that the maintenance of suspended solids and turbulent flowing tailings streams is critical to these protective mechanisms, and that this case is specific to the site ("brief turbulent flowing tailings streams with WAD cyanide concentration above 50 mg/L, discharging essentially direct into supernatant that is well below 50 mg/L, is not an operating practice representative of industry norms").

Conclusions

It is concluded that significant wildlife mortalities are likely if wildlife are exposed to WAD CN concentrations exceeding 50 mg/L, with the exception of sites where water is hypersaline and animals do not consume the cyanide-containing waters. Based on available field data, significant wildlife mortalities are unlikely to occur at WAD CN concentrations below 50 mg/L, but the available field data do not confirm zero mortalities at WAD CN concentrations below 50 mg/L. However, there is a level of background mortality due to other causes, and from available information the contribution of cyanide toxicity to overall deaths at WAD CN levels below 50 mg WAD CN/L cannot be determined with certainty.

The 1 mg/L WAD CN level arrived at using a risk quotient approach is clearly conservative, but the 50 mg WAD CN/L level is also well above the levels of 20 mg free CN/L found to cause signs of toxicity in mallard ducks and pigeons with acute exposure similar to consumption that may occur in the field (i.e. administered in 10

mL water - Section 9.2.1). This concentration level (50 mg WAD CN/L) is also approaching 50% of that found by Henny et al. (1994) to cause mortality or serious sublethal effects to mallard ducks, which was a single test concentration of 115 mg free CN/L (Section 9.2.1). Therefore caution is still essential in considering 50 mg WAD CN/L as a safe level, especially as these data are reasonably representative of actual exposure. Adequate monitoring to ensure that harmful effects are not occurring is therefore essential and the adequacy of the 50 mg/L level should be reconsidered if harmful effects are observed in the field at lower concentartions.

The results for hypersaline situations clearly indicate the importance of exposure in causing cyanide toxicity, with avoiding consumption of water the prime means of protection. Reduced habitat attractiveness, limited food sources and the availability of alternative waterbodies also contribute to wildlife protection (Section 9.9.2). Studies in the Northern Territory and Western Australia indicate the importance of habitat in determining the abundance and composition of wildlife present. The benefit of measures to reduce habiat attractiveness, limit access to cyanide-containing waters and provide alternative water sources is clearly demonstrated in the report by AngloGold Ashanti (2004) for the Yatela gold mine in Mali (Section 9.9.2). A reduction in mortalities associated with reducing the area of supernatant was indicated by Donato et al. (2008).

Thus to ensure the risk to wildlife is acceptable, even if WAD CN concentrations are maintained below 50 mg/L additional measures should be taken to reduce the risks of wildlife being exposed to cyanide. The use of other measures to replace or support concentration controls is discussed in Section 11.13.

10.3 Risks to aquatic life

Background levels of cyanide in natural waters are generally very low, but may be significantly higher near sources of contamination. IPCS (2004) discusses data from various USA sources, including the US Environmental Protection Agency's (EPA) comprehensive STORET database and Agency for Toxic Substances and Disease Registry (ATSDR) HazDat Database. The mean cyanide concentration in most surface waters in the USA is < 3.5 µg/L. Data from the late 1970s to early 1980s indicated that the levels are higher only in limited areas, where they may exceed 200 µg/L. Cyanides (HCN and various metal cyanides, including NaCN) were detected in surface water samples at 70 of 154 hazardous waste sites investigated, and have also been detected in groundwater samples at 191 of 419 waste sites studied and in leachate samples at 16 of 52 sites studied. The median concentrations in the positive samples were 160 µg/L for groundwater, 70 µg/L for surface water, and 479 µg/L for the leachates.

Environmental discharges of solutions containing cyanides are typically treated prior to effluent discharge to Australian natural surface water bodies. Discharges are managed and monitored in accordance with statutory requirements and environmental permits, as noted in Section 5.3. Discharge limits are generally based on ensuring the ANZECC/ARMCANZ (2000a) trigger values or site-specific limits are not exceeded in the mixing zone downstream of the discharge points. Various forms of accidental discharge could also lead to aquatic exposure from which potentially harmful effects can be assumed, hence there are mechanisms in place to minimise these risks and respond to such events if they should arise (Refer Chapter 11).

Concentrations of cyanide in managed, artificially constructed facilities associated with ore processing (e.g. TSFs, decant ponds, leach pad drains and collection ponds, etc) contain elevated concentrations of cyanide. While concentrations in discharge to TSFs have typically been in the range 10-100 mg WAD CN/L, they may be as high as ~600 mg WAD CN/L in exceptional cases. These residues may potentially be very harmful to aquatic life if they were to reach natural waters, but are not a concern when collected in specific structures, except for potential localised impacts on amphibians moving in from other nearby aquatic areas (Section 7.3.1).

Controlled release of treated solutions is necessary in situations such as high rainfall areas or where site assessment shows that heavy rainfall may lead to overflow of TSFs into downstream areas. The concentration of initial cyanide discharge to TSFs is then reduced to low levels by cyanide destruction techniques, eg to ≤10 mg WAD CN/L in Queensland, or as low as 1-2 mg WAD CN/L in Tasmania. Water may then flow through further ponds to allow natural degradation, with protective limits placed on concentrations of cyanide and its breakdown products (e.g. thiocyanate and ammonia) ultimately released to streams or natural water bodies (refer Sections 6.6.4, 6.7.1, 7.3.3 and 7.3.4).

More generally, exposure of and risk to aquatic organisms in downstream areas could occur through accidental or uncontrolled release of contaminated solutions from mine sites to natural water bodies (e.g. from overflow of the storage facility, run-off from the processing site or TSF areas, or through contaminated seepage and groundwater returning to the surface). Harmful effects on aquatic organisms could follow, depending on the amount and concentration released, and on dilution effects. As well as releasing freshly deposited material which may still contain free cyanide, release to aquatic areas following failure of a storage facility or heap leach ore pile could expose tailings containing cyanide products to the air and to sunlight, potentially mobilising cyanide and HCN that would otherwise have remained safely immobilised in forms such as metal cyanide complexes. Harmful effects on aquatic organisms and other wildlife could be expected from cyanide, other toxic components, and from physical effects from the large volume of material potentially released. Hence it is important that TSF and other facilities are properly designed, operated, monitored and maintained. Measures in place to ensure this are discussed in Chapter 11.

10.4 Risks to vegetation

The risk to vegetation from cyanide use in gold mining operations pertains mainly to the potential impacts of surface run-off, seepage and groundwater containing cyanide residues, e.g. in the areas surrounding a TSF and along creeks or other drainage lines. Thus the growth or species composition of vegetation may be altered if these waters are not adequately controlled. However, measures taken to protect other wildlife and groundwater contamination are likely to minimise any potential impact on plant life and toxic levels of cyanide would not be expected to persist in soil (Section 6). Furthermore, it appears likely that in contrast to birds and mammals, in many situations other components of these waters may be comparable or higher in toxicity to plants than those related to cyanide, e.g. salinity and pH, and there may also be waterlogging effects where groundwater is elevated or seepage is occurring.

Trees and other vegetation in the immediate vicinity of TSFs may be deliberately removed to avoid the habitat being attractive to birds or other wildlife, additional to clearance for structural and access reasons. Appropriate vegetation is re-established as part of mine closure management requirements, hence it is important that residues in soil on and around TSFs or heap leach ore piles do not inhibit this process. Modern environmental plans for mining operations address this from the start, with removal and stockpiling of topsoil, and subsequent restoration of a suitable layer of topsoil for replanting (EPA, 1995b; MPD, 2004; DITR, 2007).

Consequently, long term impacts from cyanide on vegetation in the vicinity of TSFs or heap leach piles, or when these areas are restored and revegetated after use has ceased, are not expected and existing controls (refer Section 11) sufficiently mitigate risks to vegetation. However, maintenance

10.5 Risks to wildlife with use for flotation

Where NaCN is used for flotation at base metal mines, delivery to a TSF of cyanide as free cyanide or various other forms of WAD CN would present similar risks to the environment to those from use in the gold industry. While it appears likely from available information that cyanide concentrations potentially arising in tailings storage facilities from this use are very low and that free cyanide is largely destroyed in the process, there were no measured data available to confirm this for Australian ore processing facilities.

10.6 Risks from industrial uses

Waste from industrial sites and laboratories is detoxified by treatment on the site and/or subsequently released to TW/STPs or landfill (Section 7.5). TW/STPs typically have water quality intake criteria for cyanide to protect against toxicity to beneficial micro-organisms in the plant, and discharge concentrations limits managed under license agreements with environment protection agencies. Processes within WW/STPs and landfills are likely to degrade any remaining free cyanide (Sections 5.3, 6.8 and 6.9).

Consequently, existing controls (refer Chapter 11) sufficiently mitigate risks to aquatic organisms.

10.7 Summary of risk characterisation

Manufacture and transport

Cyanide releases from sodium cyanide manufacturing facilities are unlikely to pose an adverse risk to the environment because residues in air from the manufacturing facility are scrubbed to minimise release of HCN to the atmosphere. Cyanide in this or other water from the plant is recovered or destroyed, and residues remaining in water are treated to destroy cyanide and passed through subsequent effluent treatment processes before release. Discharges to waters and sewers of cyanide and its breakdown products are managed under environmental protection license agreements with state and territory environment protection agencies.

In the case of transport of cyanide around the country, the large total quantities in circulation for the mining industry are of concern in the event of accident or misadventure. Transport incidents in Australia and overseas indicate the nature of such events and their possible consequences, particularly where spilt material cannot adequately be recovered or contained and destroyed, e.g. major spills into flowing water (Section 5.4.2). However, the Australian Tanami Desert incident listed also indicates that terrestrial/avian wildlife may be exposed under some circumstances. In that case, a spill of liquid occurred along a road, from which wildlife drank and were harmed before measures were taken to remove the hazard. Measures are necessary to minimise the risks of accidents, leakage or other incidents occurring and to respond promptly with appropriate cleanup and recovery procedures in the event that an incident occurs.

Risks to terrestrial animals and birds at mines

In general, without mechanisms to control wildlife habitation or controls on cyanide concentrations in solutions in areas that are accessible to wildlife, the concentrations of cyanide reportedly contained in gold ore processing infrastructures (e.g. TSFs, decant ponds, heap leach pads and drainage channels) in Australian mining facilities have the potential to adversely affect wildlife health, particularly through the oral (drinking water) route. The gold mining industry appears to be trending towards the adoption of the International Cyanide Management Code, which advises various strategies for risk management including a threshold guideline value of 50 mg WAD CN/L in tailings to minimise the potential impact of TSF and related facilities on wildlife.

However, consideration of the available data in a risk quotient-based assessment approach using acute oral avian toxicity data from laboratory studies indicates that this level is not adequately protective of most bird species, with some mortality possible at concentrations well below 50 mg/L. To assure protection of sensitive avian species from acute mortality and from harmful sublethal effects that might lead to delayed mortality, such as greater susceptibility to predators or reduced flying ability of migratory birds, assessment based on the available data indicates that the concentration of WAD CN in water available to birds would need to be ≤1 mg/L.

This is a highly conservative figure and is likely to be impracticable to implement in many situations. It is recognised that the assessment has been based on assumptions that may not always be the case, particularly that the birds consume their entire day's drinking water within a short period (i.e. comparably to acute oral dosing) and that the toxicity of TSF and associated waters is similar to that of NaCN solutions. However, this approach has been necessary to protect individual species that might be heavily exposed due to their drinking behaviour and due to the poor quality of the data available. It should also protect against potentially greater availability of total cyanide to raptors, or contributions through other routes of exposure (e.g. dermal) which were assumed to be relatively minor and were not considered. Laboratory data more directly related to the nature of exposure (drinking water studies, and use of mining effluent rather than simply NaCN solutions) were not considered acceptable for the purposes of risk assessment, and they only related to mallard ducks, which being waterbirds take several drinks of water per day.

Field observation data from a range of sources are available, ranging from anecdotal or unpublished information to major scientific studies. International and Australian evaluations show that significant wildlife mortalities were observed at WAD CN concentrations >50 mg/L, but that relatively few or no mortalities were observed at

lower WAD CN concentrations. Observations have also been reported for some sites which indicate that serious mortality incidents were alleviated as WAD CN concentrations were treated to reduce them below 50 mg/L. There is very little information regarding the extent of wildlife mortalities or sublethal effects occurring in association with WAD CN concentrations below 50 mg/L. Some reports of wildlife mortality incidents of varying scales do not indicate the WAD CN concentration to which the animals were exposed. There is one brief report of bat deaths occurring at a time when the mine reported cyanide concentrations <20 mg/L in the TSF, but the report lacks details to confirm the actual form and concentration of cyanide to which the affected bats were exposed. Another published paper noted individual animals had been found dead where WAD CN concentrations were 16 and 26 mg/L, but again limited information was available. Not all wildlife deaths occurring at goldmine operations are due to cyanide toxicity, and it may be difficult to reliably determine the cause of death. In areas of Western Australia where groundwater used for ore processing is hypersaline (>50 000 mg/L TDS), field evaluations have confirmed that no mortalities occurred despite WAD CN concentrations exceeding 50 mg/L, as minimal exposure via drinking water or other sources occurred.

It is concluded that significant wildlife mortalities are likely if wildlife are exposed to WAD CN concentrations exceeding 50 mg/L, with the exception of sites where water is hypersaline and animals do not consume the cyanide-containing waters. Based on available field data, significant wildlife mortalities are unlikely to occur at WAD CN concentrations below 50 mg/L. However, some caution is needed in the extent to which this is considered a safe value because field observations to determine the extent of sublethal effects are lacking. Lower concentration control levels may therefore be appropriate for species which need high protection.

Detailed consideration of other risk mitigation strategies to protect birds from harm to exposure to cyanide at these facilities is therefore essential. In particular, these include measures to reduce or prevent access by birds, bats and terrestrial vertebrates to the contaminated water, and measures to keep the habitat unattractive to wildlife in areas where contamination may be present. A combination of such measures could be applied, together with a concentration-based approach. As part of such an approach, it would also be important to monitor cyanide concentrations in water accessible to wildlife as well as monitoring for the presence of wildlife, impacts on wildlife, and presence of habitat attractive to wildlife. Active measures could then be applied, including hazing to deter birds while a risk is present, and correction of conditions making harmful concentrations of cyanide present in areas attractive and/or accessible to wildlife.

Risks to wildlife during use for flotation is low as cyanide concentrations arising in TSFs from this use are very low.

Risks to aquatic organisms

For the natural aquatic environment, reported cyanide concentrations in some ore processing facility solutions and tailings generally exceed water quality guidelines for cyanide for the protection of aquatic life and pose a risk should an environmental release to natural waters occur. However, these facilities are designed and constructed specifically to contain cyanide tailings and discharges to natural waters are not anticipated within operational designs, unless the water is first treated to destroy the cyanide present. Where seeps or leaks do occur, corrective measures are typically implemented.

Long term impacts from cyanide on vegetation in the vicinity of TSFs or heap leach piles, or when these areas are restored and revegetated after use has ceased, are not expected and existing controls sufficiently mitigate risks to vegetation.

Industrial users

Industrial users of sodium cyanide, excluding mining operations, mostly discharge waste from processes using it to landfill and/or to wastewater treatment facilities and/or sewage systems that are managed under licenses based on aquatic ecosystem protection and administered by state and territory environment protection agencies. In many cases, cyanide wastes are treated on site before they are discharged from the site. As such, discharges of cyanide solutions from these facilities are unlikely to pose an adverse risk to the environment under these regulatory arrangements.

11. Current Environmental Risk Management

This chapter discusses measures that have been implemented or are being implemented to reduce the likelihood of adverse environmental effects from exposure to sodium cyanide and its products. The inherent hazards of cyanide are generally well known and there is a range of established government and industry environmental controls covering the lifecycle of sodium cyanide from manufacturing, storage, handling, transportation and uses through to waste management (including waste emplacement facilities). In addition to measures applying in Australia, international and overseas legislation are also discussed, where appropriate.

The following topics are discussed in this chapter:

(a) National and state/territory regulatory controls for the storage, handling and transport of dangerous goods;

(b) Measures to protect the environment from contamination during use and waste disposal;

(c) Guidelines to protect aquatic organisms;

(d) Legislation and policies to protect wildlife and conserve biodiversity;

(e) Voluntary industry measures pertaining to sodium cyanide manufacture, transport and use for gold mining;

(f) Measures to protect wildlife which have been or may be used at various mine sites.

References in the report that have not been sighted are marked with an asterisk(*).

11.1 General environmental controls and monitoring

In Australia, the activities involving manufacturing, procurement, industrial use, storage, handling, transportation and discharge of sodium cyanide to the environment are controlled by state and territory regulations. These regulations pertain to major hazard facilities, dangerous goods, safety and emergency procedures, emissions, waste management and protection of the environment, and are enforced by means of a system of conditional permits, licenses and warrants.

In addition, the major industry groups, such as chemical manufacturers and mining and metal extraction industries, have established self-regulating programs for occupational safety and environmental protection. These include environmental management systems (EMS) (e.g. Ticor, 1996) under ISO 14000 or equivalent, quality assurance/control (QA/QC) systems, safety and environmental management (SEM) systems, Standards and Codes of Practice. Within the industry, and there is a general philosophy of continuous improvement through the Responsible Care® program and other industry initiatives.

11.2 Major hazard facilities (MHF)

Major Hazard Facilities (MHF) are one of seven priority hazard issues identified by the Commonwealth Government for which the Safe Work Australia (formerly the Office of the Australian Safety and Compensation Council (OASCC) or the National Occupational Health and Safety Commission (NOHSC)) maintains a national standard and a national code of practice. These are the *National standard for the control of major hazard facilities* [NOHSC:1014(2002)] and the *National code of practice for the control of major hazard facilities* [NOHSC:2016(1996)], both initially declared in 1996 (NOHSC, 2002a).

A MHF is an area where an activity takes place involving specified materials nominated in Schedule 1 of the National Standard by NOHSC (1996a). Facilities that manufacture, store, handle or use >20 tonne per annum of NaCN (solid or liquid form) or HCN are classified as MHFs. This means that the MHF legislation includes not just the two Australian sodium cyanide manufacturing facilities, but also extends to storage facilities, and most ore processing sites using NaCN.

There has been existing legislation to protect employees, the community and the environment from the hazards associated with normal industrial operations, but the operation of a MHF can create hazards of a scale and type which was not necessarily covered by existing legislation. Hence there was a need for controls designed to eliminate the underlying and immediate causes of major accidents and to limit their consequences (NOHSC, 2005ab). In 2001, Workplace Relations Ministers Council (WRMC) endorsed five strategies (and three related actions) to achieve national consistency in MHF regulation and assigned responsibility for progressing achievement to OASCC. The strategies are:

- facilitating a consistent regulatory framework in all jurisdictions (including reviewing and updating Schedule 1 of the National Standard on MHF Control);
- facilitating the sharing of expertise among jurisdictions;
- developing practical guidance and training material;
- facilitating the mutual recognition of safety case assessments; and
- developing performance indicators to compare safety outcomes.

The related actions include consistency in who regulates MHFs, monitoring implementation in each jurisdiction, and risk based cases for exemption.

To address the WRMC strategies, a Major Hazards Facilities Implementation Reference Group (MHFIRG) was formed consisting of representatives of the state, territory and Commonwealth jurisdictions and employer and employee representatives. To provide guidance, a review of key differences between states, territories and the Commonwealth at the time was undertaken (NOHSC, 2002b).

Implementation of legislation/regulations giving effect to the National Standard for the Control of Major Hazard Facilities is complete or well advanced in all states and in the Northern Territory. Priority is being given to other regulations under the *Dangerous Substances Act 2004* in the ACT, where there are currently no facilities which would be classified as MHFs.

11.3 Dangerous goods management

The *National standard for the storage and handling of workplace dangerous goods* [NOHSC:1015(2001)] and *National code of practice for the storage and handing of workplace dangerous goods* [NOHSC:2017(2001)], the *Australian code for the transport of dangerous goods by road and rail* (7th edition) (ADG 7), and some Australian Standards provide national guidance on storage, handling, transport and labelling of dangerous goods, including sodium cyanide, in Australia.

11.3.1 Storage and handling of dangerous goods

National Standard applying to storage and handling

The *National standard for the storage and handling of dangerous goods* [NOHSC: 195(2001)] sets out requirements to ensure the effective control of the storage and handling of dangerous goods, including NaCN, so as to protect the safety and health of workers and the public as well as the protection of property and the environment.

This standard was also produced by the OASCC/NOHSC. As with other national standards and codes of practice produced by the OASCC, these are guidance and advisory documents only, and may be adopted by governments in the state and territory regulations to make up part of their Occupational Health and Safety (OHS) framework (http://www.ascc.gov.au/ascc/AboutUs/LegalFramework/ accessed May 2007). The introduction to the documentation for this Standard (NOHSC, 2001a) explains the nature of the Standard as follows:

> In terms of managing the storage and handling of dangerous goods, the national standard marks a significant change in approach. The national standard replaces current prescriptive requirements with a performance-based approach incorporating the principles of hazard identification, risk assessment and risk control. This approach includes a storage and handling system which covers the risks associated with the premises where any dangerous goods are stored and handled, as well as the risks associated with the use of any container, tank, vehicle or freight container, spill containment system, plant and fire fighting and fire protection systems used on premises, in connection with the storage and handling of dangerous goods.
>
> The national standard provides a framework within which individual Commonwealth, state and territory regulatory authorities can develop workplace regulations so that a nationally consistent regulatory regime can be achieved. To that end OASCC established two administrative mechanisms to facilitate the development of a nationally consistent regime:
>
> 1. An implementation group that can include representatives of all relevant regulatory authorities and industry partners; and
> 2. An annual review of the national standard implementation that will report on the extent of consistent adoption.
>
> Traditionally, dangerous goods legislation has extended beyond the workplace to address public safety and the environment. OASCC recognises that for non-workplaces the performance and duty-based approach applied to various hazards in the workplace may not be appropriate. Therefore, in declaring this national standard, OASCC states that it intends that for non-workplaces, the performance-based approach will be only the framework within which regulation of non-workplaces will operate. It is envisaged that individual jurisdictions may need to supplement the requirements of the national

standard with more prescriptive requirements to ensure public safety where dangerous goods are stored and handled in non-workplaces.

The *National standard for the storage and handling of dangerous goods* is accompanied by the *National code of practice for the storage and handling of workplace dangerous goods* [NOHSC: 2017 (2001)] (NOHSC, 2001b), which provides practical advice on compliance for those who have duties under the national standard. The *National code of practice for the storage and handling of dangerous goods* also provides the information and guidance for the storage and handling of dangerous goods as minor quantities, and as consumer packages supplied by retailers.

Each Australian state and territory provides statutory controls on storage, handling and transport of dangerous goods. Table 11.1 provides a list of primary state and territory legislation and guidance.

Australian Standard applying to storage and handling

Requirements and recommendations for the safe storage and handling of toxic substances that are classified as Class 6.1 in the ADG Code in Australia (e.g. sodium cyanide) are also covered by Australian Standard AS/NZS 4452:1997: *The storage and handling of toxic substances* (Standards Australia, 1997). This Standard applies in locations that are generally industrial, commercial or rural in nature, and also includes laboratories where the provisions of this Standard are additional to those of AS 2243.10:2004 (*Safety in laboratories-storage of chemicals*). It provides more specific guidance for specific aspects important to environmental protection during storage of dangerous substances than the NOHSC standard, such as bunding, containers,

This Standard is referred to by various regulations, codes of practice and other guidance pertaining to the storage and handling of NaCN. For example, the Standard is referred to as one of various secondary codes of practice incorporated as part of the draft WA Storage and handling of Dangerous Goods Code of Practice (WA DCEP, 2006), and in regard to bunding and spill management, the NSW DECC (NSW EPA, 2005) indicates that 'where applicable, the construction of bunds must comply with the requirements of AS/NZS 4452:1997: *The storage and handling of toxic substances'.*

This Standard does not apply to the transport on land of toxic substances, which is covered by the ADG Code, or storage in port areas. Storage of dangerous goods in port areas is covered by Australian Standard AS 3846-2005 *The handling and transport of dangerous cargoes in port areas*. Each state and territory provides legislative controls in accordance with AS 3846-2005.

11.3.2 Transportation of dangerous goods

The Department of Infrastructure, Transport, Regional Development and Local Government (formerly the Department of Transport and Regional Services -DOTARS) works with the states and territories, and the National Transport Commission (NTC), to promote best practice and internationally harmonised legislation for the land transport of dangerous goods in Australia. The NTC is a body established under an Inter-Governmental Agreement with a charter to develop, monitor and maintain uniform or nationally consistent regulatory operational reforms relating to road, rail and inter-model transport. It is funded jointly by the Australian Government, states and territories.

The NTC is responsible for maintaining regulations on the transport of dangerous goods by land within Australia. In developing policy and legislation relating to the transport of dangerous goods by road and rail, the NTC has been advised by a representative group of industry sectors and appropriate government regulatory authorities. The NTC produces model legislation which is then copied or referenced by jurisdictions to produce operational law in their respective States and Territories. The NTC also has responsibility for the production of the Australian Dangerous Goods Code. This Code is a reference document setting out detailed technical and procedural requirements for a range of activities performed in the day-to-day preparation for and transportation of dangerous goods by either road or rail.

The 6th Edition of the Australian Dangerous Code (ADG 6) has been reviewed and the technical requirements in the latest version (ADG 7) brought up to date with the 15th edition of the United Nations Recommendations on the Transport of Dangerous Goods, Model Regulations (NTC, 2007). ADG 7 is supported by a revised legislative framework consisting of a Model Act, and a model set of regulations (or Model Subordinate Law). The Model Act on the Transport of Dangerous Goods by Road or Rail replaces the *Road Transport Reform (Dangerous Goods) Act 1995* (Commonwealth). The Model Subordinate Law on the Transport of Dangerous Goods by Road or Rail replaces the existing Road Transport Reform (Dangerous Goods) Regulations 1997 and the Rail (Dangerous Goods) Rules and underpins the Code.

ADG 7 has been implemented in most jurisdictions this year (as of August 2009), with a transitional period of up to 12 months, and is expected to be implemented by the remaining jurisdictions by the end of 2009 (Department of Infrastructure, Transport, Regional Development & Local Government, pers. comm., 2009).

Technical advice on the application of the ADG Code is obtained through the 'Competent Authority' appointed in each state or territory for road and rail, air, or sea transport (NTC, 2008b). If a matter covers more than one state or is for an extended period, it will normally be referred to the Competent Authorities Panel (CAP).

Land transportation of dangerous goods

As indicated above, each state and territory stipulates controls on the transportation of dangerous goods, typically including licensing of transporters, guidance on dangerous goods transport safety, offences and penalties (Table 11.1). Commonwealth legislation (i.e. *Road Transport (Dangerous Goods) Act 1995* and Road Transport Reform (Dangerous Goods) Regulations 1997) and the ADG Code make provision for safety in the transport of dangerous goods by road as part of the system of nationally consistent road transport laws.

Australian Standard AS 1678.6.0.002-1998 (Standards Australia, 1998) provides emergency procedures for the management of incidents that may occur during domestic land transportation of sodium cyanide. The Standard describes the chemicals hazards, protective clothing, emergency procedures, and first aid in the event of a transportation accident involving sodium cyanide.

Due to the potential human and environmental health risks during transportation, major transportation issues are incorporated within state and territory environmental impact assessment legislation, such as the Transportation Route Study Review by the Western Australian Environment Protection Authority (EPA WA, 1987).

The National Road Transport Commission (NRTC, 2003) has prepared guidance for the preparation of transport emergency response plans to identify the necessary resources, personnel and logistics which allow for a prompt, coordinated, and rational approach to a transport incident. In addition to such a plan, it is stressed that continual appraisal using table-top and simulation exercises, regular updating of equipment, contact lists, and training of personnel are needed to improve the capability to successfully respond to transport emergency situations, and that liaison and communication with emergency and security services along the transport route is a critical element in the development of the plan.

Northern Territory WorkSafe have indicated that the principal transporters of sodium cyanide in Australia no longer use triple road-trains for the transport of solid sodium cyanide in containers. The mode of road transport used currently is either double road-trains with end-loading containers or road-trains with tank containers on drop decks. Tank containers are transported as triples. They note that both of these configurations would be considered lower risk

Further comments on road transport in WA

With road transport of NaCN in WA, typically two isocontainers (liquid form) or two seatainers each containing 20 CIBCs (solid form) are transported on trucks with two trailers (i.e. B-doubles with one container per trailer), except where trucks are limited to a single container (G. Peirce, CSBP Chemicals, pers. comm. 2007). However, this appears not to be a legislative requirement and some use of triple trailers may occur on roads where their use is permitted. Similarly, in other states some transport may occur on triple trailers, e.g. the recent truck accident in the NT involved a road train with 3 trailers. Road access arrangements for road trains are a state/territory matter and are not indicated in ADG 7 (Department of Infrastructure, Transport, Regionsal Development and Local Government, pers. comm., 2009).

Under EPA requirements in WA, wherever possible transport of liquid NaCN from the Kwinana factory is required to be by rail, except where goldmines cannot be serviced practicably and/or efficiently by rail from Kwinana, or rail services are temporarily unavailable (EPA WA, 2004). Thus for the Eastern Goldfields, sodium cyanide is transported from the factory to Kalgoorlie by rail and then distributed by road, but transport may occur directly by truck to northern areas.

Various requirements have been in place as part of the conditions for the transport of sodium cyanide from the Kwinana manufacturing site (EPA WA, 2004). These have included liaison with Local Government Authorities, relevant government departments, state emergency authorities and local emergency management advisory committees, including setting up emergency plans and training programs, consistent with the recommendations of NRTC (2003) discussed above. Vehicles are equipped with means of 2-way communication, equipment and materials in accordance with an approved emergency response plan, and provision and maintenance of stocks of neutralising agent at the manufacturing plant and along the main transport routes at agreed locations for use in emergencies. Ferrous sulphate is recommended as the preferred neutralising agent for offsite incidents and hydrogen peroxide for use within the plant, but information in EPA WA (2004) indicates that sodium hypochlorite may be used under strict direction from the manufacturer.

The legislation under which these provisions have applied in WA has changed with the introduction of national ADG legislation (EPA WA, 2004). Similar measures apply to varying degrees in other states and territories through their respective legislation

complementing the ADG legislation. However, the WA requirements appear more comprehensive and detailed.

Air transportation of dangerous goods

The transportation of dangerous goods by air is administered by the Civil Aviation Safety Authority (CASA). Sodium cyanide is generally not transported by air in Australia; however, small quantities are imported by airfreight as a minor component of electroplating solution.

Sea transportation of dangerous goods

A large component of sodium cyanide manufactured domestically (~40%-60%) is exported by ship to many countries, and a much smaller quantity is imported by ship into Australia for domestic uses.

The Australian Maritime Safety Authority (AMSA) is responsible for the management of the transportation of dangerous goods by ship. Shipping safety and pollution from ships is managed at a National level by AMSA.

Australia is a member of the International Maritime Organisation (IMO), and a signatory to the International Convention for the Prevention of Pollution from Ships 1973, as modified by the Protocol of 1978 (MARPOL 73/78; Department of Foreign Affairs and Trade, 1988a) that controls operational pollution and introduces measures to mitigate the effects of marine pollution. MARPOL 73/78 covers pollution by chemicals. The International Maritime Dangerous Goods (IMDG) Code, published by the International Maritime Organisation (IMO, 2000), provides guidance and standards for transport of dangerous goods by sea. IMO's Intervention Convention affirms the right of a coastal state to take measures on the high seas to prevent, mitigate or eliminate danger to its coastline from a maritime casualty. The 1990 International Convention on Oil Pollution Preparedness, Response and Co-operation (Department of Foreign Affairs and Trade, 1995) provides a global framework for international co-operation in combating major incidents or threats of marine pollution. Sodium cyanide has an IMO classification of 6.1.

11.3.3 Packaging specifications for dangerous goods

Specifications and standards, including the ADG Code (ADG 7), apply to containers used for packaging dangerous goods to minimise the risk of incidents during storage, handling and transportation. Sodium cyanide is approved for transport in specified drums, intermediate bulk containers (IBCs), portable tanks and in road tankers (for liquids).

ADG 7 provides specifications for intermediate bulk containers (IBCs) for the transport of dangerous goods. IBCs for containing and transporting dangerous goods must comply with these specifications and other legislative requirements.

Composite IBCs as used for NaCN are packed in freight containers, providing several layers of protection for the contents. For example, CIBCs used by CSBP's Kwinana plant contain NaCN briquettes in a polythene bag which is contained in a hermetically sealed plastic liner in a plywood outer box, and the CIBC has to meet specifications such as a drop test (Fozdar pers. Comm. 2005; Peirce, pers. comm. 2006). Under EPA requirements in WA, isotainers used by CSBP to transport liquid NaCN are manufactured to meet Australian and international codes and are comprised of a tank mounted in a steel frame. These are fitted to flat-top rail wagons (2 per wagon on

standard gauge rail) or road trailers (a single isotainer per trailer) by twistlocks designed to ensure that in the event of a derailment the container will remain secured to the wagon. They are provided with safety features including the use of top loading and discharge, a pressure relief device, an integral ruggedised steel frame enclosure and additional strengthening around the loading/discharge point to provide roll-over protection (EPA WA, 2004).

The StoL containers developed by Orica for transport of solid NaCN for sparging at the point of delivery (Section 4.2.2) have also been designed to Australian and International standards and the ADG and IDMG Codes (http://www.orica-miningchemicals.com accessed May 2007).

Other Australian Standards also relate to containers used for the transport of dangerous goods and may therefore apply to sodium cyanide, including AS 2809.1-2008 (Road tank vehicles for dangerous goods - General requirements for all road tank vehicles) and AS 2809.4-2001 (Road tank vehicles for dangerous goods - Tankers for toxic and corrosive cargoes), and AS ISO 16106-2007 (Transport packages for dangerous goods - Dangerous goods packagings, intermediate bulk containers (IBCs) and large packagings - Guidelines for the application of ISO 9001).

11.3.4 Complementary state/territory legislation

Each state and territory has an established regulatory system for licensing of dangerous goods storage facilities. The following legislation is likely to have been replaced with the latest revision of the ADG Code.

Table 11.1. Primary dangerous goods legislation and guidance

State/Territory	Relevant Dangerous Goods Legislation/Guidance
Australian Capital Territory	Road Transport (Safety and Traffic Management) Act and related regulations and amendments
New South Wales	Dangerous Goods (Road and Rail Transport) Act 2008 Dangerous Goods (Road and Rail Transport) Regulation 2009
Queensland	Dangerous Goods Safety Management Act (2001) Dangerous Goods Safety Management Regulation (2001) Transport Infrastructure (Dangerous Goods by Rail) Regulation (2001) Transport Operations (Road Use Management - Dangerous Goods) Regulation (1998)
Northern Territory	Dangerous Goods Act (1996) Dangerous Goods Regulations (1996) Dangerous Goods (Road and Rail Transport) Act (2004) Dangerous Goods (Road and Rail Transport) Regulations (2004)
Western Australia	Dangerous Goods (Transport) Act (1998) Dangerous Goods (Transport) (Road and Rail) Regulations (1999)

State/Territory	Relevant Dangerous Goods Legislation/Guidance
	Explosives and Dangerous Goods (Dangerous Goods Handling and Storage) Regulations (1992) Water Quality Protection Guidelines for Mining and Mineral Processing – Above-ground fuel and chemical storage (Water Quality Protection Branch, WRC, 2000a)
South Australia	Dangerous Substances Act (1979) Dangerous Substances Regulations (2002)
Victoria	Dangerous Goods Act (1985) Road Transport (Dangerous Goods) Act (1995) and amendments Dangerous Goods (Storage and Handling) Regulations (2000) Dangerous Goods (Transport by Rail) Regulations (1998) Dangerous Goods (Transport) Regulations (1987)
Tasmania	Dangerous Goods Act (1998)

11.3.5 Procurement of sodium cyanide

Throughout Australia, procurement (purchase) of sodium cyanide is illegal without a license issued by state and territory Health Departments under various regulations pertaining to poisons including:

- *Medicines, Poisons and Therapeutic Goods Act 2008*, and regulations (ACT);
- *Poisons and Therapeutic Goods Act 1966*, and Poisons and Therapeutic Goods Regulation 1994 (NSW);
- *Health Act 1937*, and Health (Drugs and Poisons) Regulation 1996 (Qld);
- *Poisons and Dangerous Drugs Act 1999*, and regulations (NT);
- *Poisons Act 1964*, and regulations (WA).
- *Controlled Substances Act 1984*, and Controlled Substances (Poisons) Regulation 1996 (SA);
- *Drugs, Poisons and Controlled Substances Act 1981* (Vic); and
- *Poisons Act 1971* (Tas).

Control of procurement provides a means for minimising the risk of sodium cyanide being obtained and used inappropriately. No incidents of inappropriate acquisition in Australia were identified during this assessment.

11.4 Hazard communication

11.4.1 Labelling and hazard warning systems

The Australian Code for the Transport of Dangerous Goods by Road and Rail (ADG Code) establishes an environment protection-based labelling system.

In Australia, hazardous substances must be sold in containers that are appropriately labelled. Appropriate labelling communicates to users information on the appropriate use and disposal of the chemical, thus minimising risks to the environment from improper practices. All states and territories have adopted a uniform system for labelling which seeks to ensure that appropriate information about the hazardous substance is conveyed to the user via standardised phrases and symbols.

Under the ADG Code, sodium cyanide is assigned a dangerous goods class of 6.1, with United Nations (UN) numbers of 1935 ("cyanide solution N.O.S." [30% alkaline solution] – HAZCHEM 2X, HIN 66/60) and 1689 (solid – HAZCHEM 2X, HIN 66). The number in the HAZCHEM code (Hazchem Emergency Action code) refers to firefighting extinguishing media, and the 2 denotes 'fine water spray'. The following letter denotes the nature of hazards presented by the substance - X indicates no risk of violent reaction or explosion; recommended personal protective equipment is liquid-tight chemical protective clothing and breathing apparatus; and appropriate measures are to contain, and that spillages and decontamination runoff should be prevented from entering drains and watercourses. The HIN (Hazard Identification Number) of 66 indicates 'highly toxic substance' and 60 indicates 'toxic or slightly toxic substance' (Appendix C in NTC, 2007).

Classification under the OECD Globally Harmonised System for Classification and Labelling of Chemicals (GHS; UNECE, 2005) is indicated in Appendix 3.

Guidance is also available to accompany the *National code of practice for the storage and handling of dangerous goods* (NOHSC, 1990).

11.4.2 Material safety data sheets (MSDS)

Revised MSDS code

In general, the material safety data sheet (MSDS or safety data sheet (SDS)) describes the chemical and physical properties of a material and provides advice on its safe handling and use. Under the OASCC *National model regulations for the control of workplace hazardous substances* (NOHSC, 1994a) and the corresponding state and territory legislation, suppliers of a hazardous chemical for use at work are obliged to provide a current MSDS to their customers. Employers must ensure that a current MSDS is readily accessible to employees using or having a potential for exposure to the chemical. The MSDS is also accessed by emergency services personnel who may need to deal with a chemical in an emergency situation.

The *National code of practice for the preparation of material safety data sheets, 2nd edition*, published by the National Occupational Health and Safety Commission (NOHSC, 2003), provides minimum requirements for information in SDSs to ensure their relevance and applicability to occupational, public and environmental safety. The revision of the MSDS Code addressed various technical elements and facilitates Australia remaining consistent with international approaches to hazard communication, i.e. with the Globally Harmonised System for the Classification and Labelling of Chemicals (GHS). The major focus of the revised MSDS Code is to incorporate the GHS information provisions of the *National standard for the storage and handling of workplace dangerous goods* [NOHSC:1015(2001)]. The revised MSDS Code came into effect on 24 April 2006.

Provision of ecological information (so far focussing on aquatic toxicity) is a requirement of the GHS, under Section 12 of the 16 header MSDS format that will

become the international standard. The availability of information on ecotoxicity, persistence, degradability and mobility in the SDS is intended to assist the evaluation of the environmental impact of the material if it is released to the environment. It can assist in handling spills, and evaluating waste treatment practices. At the time of publication of the revised MSDS Code, there was no consistent national requirement under the Commonwealth, state and territory hazardous substances regulations to provide this aquatic ecotoxicity information. However, under Dangerous Goods regulation, some states and territories have required this information.

MSDS for sodium cyanide

Several MSDSs were provided by both of the sodium cyanide manufacturers in Australia, which included both solid and liquid (30% NaCN) forms. A further seven importers or formulators also provided MSDSs for the cyanide forms they import and distribute. These MSDSs provide a range of information, generally including health hazards, physical/chemical properties, ingredients, first aid procedures, antidotes and advice to doctors, exposure standards, engineering controls, personal protective equipment (PPE), storage and transportation requirements and spill response in the event of a spill or leak incident.

In general, most of the MSDSs comply with the national code of practice concerning the consideration of accidental environmental release (spill response) measures. With respect to spill response, treatment and disposal, most of the MSDSs available emphasise the following key requirements:

- Immediate action, Communication, and Evacuation/Access Restriction;
- Trained spill response personnel and Personal Protective Equipment;
- Spill Source Control and Containment;
- Cleanup Procedures and Neutralisation/Detoxification; and
- Disposal/Recycling.

All MSDS advise contacting the manufacturer in the event of a major spill incident. Spill response procedures have been described in Appendix 4.

At least one MSDS recommended using hydrogen peroxide to detoxify cyanide at spill situations; however, this is a strong oxidizer that may cause a violent reaction and should be avoided due to the potential for generation of HCN gas at the spill site.

One MSDS indicates that for small spills involving cyanide solutions, following adsorption of spilled material and removal of the cyanide-containing absorbent material, the spill area should be flushed away using water containing some alkaline material such as sodium carbonate. However, treated wastes should be contained, collected and disposed of appropriately. An alternative method involves adsorption of spilled material, followed by excavation and removal of a conservative amount of contaminated surface soil for treatment. The spill area and collected contaminated soil may be neutralized with an excess amount of dilute sodium hypochlorite or calcium hypochlorite.

Spills of sodium cyanide into natural waters are particularly difficult to remediate without further damaging the water body by, for example, adding oxidising agents. For such spills, an appropriate action may be to allow natural degradation, coupled with dilution and dispersal, to take its course. Preservation of sensitive fauna may be

possible by their collection and relocation, while netting and fencing may be used to prevent their entry to contaminated ponds. Pumping of contaminated water from natural waters into tankers for off-site treatment or holding ponds may also be possible to avert degradation of the environment. Remedial actions may potentially include blocking stream flow while in-situ treatment or pumping of contaminated water to tanks or containment areas, such as lined ponds. The choice of remediation option following spill incidents depends on public and worker safety, environmental, social and practical considerations.

Limited advice is provided in MSDS on spill incident management of sodium cyanide whether the incident occurs during rainfall or unfavourable weather conditions, or when associated with a fire and fire emergency services are required to extinguish the fire using water or other substances.

It is likely that these MSDSs will have been revised to address the revised MSDS Code. When such revisions occur it would be appropriate to ensure that advice provided which relates to the environment (spillage management, and ecological information if it is included) is consistent and correct.

11.5 Emissions management and monitoring

11.5.1 Pollution management

Each state and territory stipulates controls on discharges of contaminants to the environment through legislation, policies and guidance. Table 11.2 lists primary legislation pertaining to environment protection and pollution management.

Table 11.2. Primary environment protection legislation for pollution management

State/Territory	Relevant Legislation	Principal Authority
Australian Capital Territory	Environment Protection Act 1997 and regulations	Environment ACT
New South Wales	Protection of the Environment Operations Act 1997 and regulations; Marine Pollution Regulations (2001)	NSW DECC
Queensland	Environment Protection Act (1994) and regulations	Queensland EPA
Northern Territory	Waste Management and Pollution Control Act 1998 and regulations	Department of Infrastructure, Planning and Environment
Western Australia	Environmental Protection Act (1986) and regulations	WA Department of Environment and Conservation
South Australia	Environment Protection Act (1993) and regulations	EPA (SA)
Victoria	Environment Protection Act (1970)	Victorian EPA

State/Territory	Relevant Legislation	Principal Authority
Tasmania	Environmental Management and Pollution Control Act (1994) and regulations	Department of Tourism, Arts and the Environment

11.5.2 National Pollutant Inventory (NPI) Program

As discussed further in Section 5.1.3, emissions of 'cyanide (inorganic) substances' are included in the National Pollutant Inventory (NPI) program administered by the Department of the Environment, Water, Heritage and the Arts (DEWHA, 2009a; EPHC, 2007b). The NPI program was established in 1998 as a joint Australian Government, state and territory initiative, with each state/territory responsible for collecting emissions data from facilities and providing the collated data to DEWHA for publication on the NPI website. Individual facilities using or handling greater than 10 tonnes per annum of inorganic cyanides are required to report their emissions estimates to water, air and land.

11.6 Prevention of environmental contamination

11.6.1 General framework

Prevention of environmental contamination, as well as its assessment and management, is currently established through various state/territory regulations, policies and industry codes and guidance covering, for example, mine site operations (mill and heap leach), TSF management, contaminated sites assessment and management, environment protection, waste management and public and occupational health and safety.

At a national level, the Environment Protection and Heritage Council (EPHC) oversees the National Environment Protection Measures (NEPM) program. NEPMs are broad framework-setting statutory instruments defined in the *National Environment Protection Measures (Implementation) Act, 1998* (Cwlth). NEPMs outline agreed national objectives for protecting or managing particular aspects of the environment. The NEPM for the NPI (above) was the first NEPM to be made. The National Environment Protection (Assessment of Site Contamination) Measure (NEPC, 1999) establishes a nationally consistent approach for assessing site contamination through fourteen guidance documents, but does not provide guidance on how contaminated sites should be remediated.

For mining operations, action to remediate a site is usually addressed through mine rehabilitation plans to guide what sort of rehabilitation is required and when it is to be completed, and inspection and auditing processes to ensure this occurs. The use of environmental performance bonds or mining securities serve to protect a state from financial liability should a mineral tenement owner fail to comply with mine site rehabilitation requirements (WA DIR, 2006; NSW DPI, 2002; Qld EPA, 2004).

The publication Environment Australia (1999e) provides *Best practice environmental management in mining* guidance for mining agencies and industry on the avoidance of land contamination and contamination assessment and management in Australia.

11.6.2 Groundwater management

With respect to groundwater resources, the National Water Quality Management Strategy, ANZECC/ARMCANZ (1995) has developed guidelines for groundwater protection in Australia. This initiative stemmed from a review of the status of groundwater contamination and regulation in Australia by the Australian Water Resources Council (AWRC, 1990). The review found that for most states and territories, there was adequate legislation available to protect groundwater from contamination although it was fragmented across several areas of government in some states and territories. However, little protective action had eventuated. ANZECC/ARMCANZ (1995) provided the basis for a nationally consistent approach to the protection of groundwater from contamination in Australia. They distinguished between the terms 'contamination' and 'pollution' as pollution infers groundwater contamination '*has deteriorated to a point where the ability of the water to support or maintain the existing or potential identified beneficial uses is diminished'.* The framework enabled the states, territories and Commonwealth to develop policies and strategies, which are tailored to their specific legislative and resource management situations.

The ANZECC/ARMCANZ (1995) guidelines for groundwater protection rely on a framework in which there is the identification and classification of beneficial uses and environmental values for each groundwater resource. The goal of groundwater protection in Australia is to '*protect the groundwater resources of the nation so that these resources can support their identified beneficial uses and values in an economically, socially, and environmentally sustainable and acceptable manner'* (ANZECC/ARMCANZ, 1995). These classifications assist in determining the level of protection afforded to the groundwater resource. The choice of beneficial use classification for a groundwater body will depend on the quality of water present and the potential environmental values of the groundwater in the long term. The benefits of water use and non-use cover a range of exploitive benefits as well as environmental and conservation values. Environmental values are values or uses of the environment that are conducive to public benefit, welfare, safety or health and which require protection from the effects of pollution, waste discharge and deposits (ANZECC/ARMCANZ, 1995). Generally, the designated beneficial use of a groundwater body should aim to protect water quality to its greatest extent; however, there may be other factors to consider. A polluter pays principle is promoted. Once a beneficial use determination has been made, the developer of an industry or activity that has the potential to contaminate the groundwater body should bear the full cost of protection of the aquifer against any threats that the development may pose. On this basis, the developer would be required to show on a continuous basis that the activity did not pollute the groundwater body.

11.6.3 TSF management

General guidance

Internationally, the International Commission on Large dams (ICOLD), and the National Committees of its ~81 member countries, provides a forum for technical interaction amongst dam designers and constructors. ICOLD has published a range of technical guidance on dam design, construction and monitoring. The Australian National Committee on Large Dams (ANCOLD) is the Australian representative to ICOLD. ANCOLD is a learned society that has no regulatory powers, but has developed guidance on recommended practices on dam construction and operation

(http://www.ancold.org.au/). The *International cyanide management code for the manufacture, transport, and use of cyanide in the production of gold* (ICMI, 2006) provides additional guidance for management of mine wastes and environmental risks.

Guidance on the placement, siting, design, construction and safe management of TSFs and tailings, as well as environmental aspects (i.e. groundwater, wildlife) is available from various government and industry bodies in Australia and internationally. Most guidance on TSF and tailings management is relatively recent, developed largely since major TSF failures in Europe and Africa (Section 5.4.3). While recently developed guidance can be implemented at new facilities, some aspects (e.g. TSF siting studies, TSF type, liner and dam construction, operational processes) may not be capable of retrospective implementation at existing mine site operations and their TSFs. This may require the implementation of alternative strategies to manage risk issues.

Regulatory framework

The regulation of tailings and TSFs in Australia is principally a state and territory matter. The Commonwealth *Environment Protection and Biodiversity Conservation Act* (1999) has established a nationally consistent framework for environmental assessment of new projects and variations to existing projects, based on consultative agreement between the Commonwealth and state and territory governments. Tailings management is an important consideration in the assessment process for mining proposals at both the state and federal levels (MCMPR/MCA, 2003). Environmental planning/assessment and environmental impact assessment (EIA) procedures is established in Australia to allow analysis of significant developments/activities. The Cowal Gold Project, NSW provides a recent example of the EIA procedures established in Australia.

The regulation of tailings deposition and management (including rehabilitation and closure) in all states and territories has been the responsibility of mining regulatory agencies. In some states, environment protection agencies regulate pollution issues (MCMPR/MCA, 2003). More recently, responsibilities relating to environmental management of mines in Queensland were transferred from the Department of Natural Resources and Mines (Qld NR&M) to the Queensland Environment Protection Agency (Qld EPA - Section 11.10.2). Most states and territories do not currently regulate concentration limits for cyanide or products in tailings discharged to TSFs.

The regulation of TSF design, construction and ongoing integrity is more complex. In some jurisdictions, dam construction and operation is regulated by specific legislation (e.g. NSW's *Dams Safety Act 1978*) while in other states and territories, TSFs are principally regulated within the mining regulatory agency regulations. In some instances, regulation is based on the size of the dam, with large dams being formally regulated and smaller dams falling under general regulation (MCMPR/MCA, 2003).

The level of TSF management required to achieve environmental objectives is predetermined during the planning stage, being evaluated against site-specific risk-based factors such as the likely contaminants present and concentrations, potential effects on groundwater discharge areas and receiving environments, natural groundwater quality, groundwater level (e.g. potential watertable changes) and current and future beneficial uses of the groundwater. The risk of pollution of groundwater bodies can be evaluated by site-specific hydrogeological investigations, identification of beneficial uses and values, computer-based modelling and risk analysis, enabling risk management strategies to be developed into TSF design, construction, operational and post-closure requirements. This is typically initiated at the planning/development

phase and carried through operational and post-closure phases. States/territory regulatory agencies require detailed siting studies before approving the construction and operation of TSFs and other facilities using or containing cyanide solution. The National Water Quality Management Strategy for groundwater protection in Australia is applicable (ANZECC/ARMCANZ, 1995).

For example, the environmental impact statement for the Cowal Gold Project, NSW, included a TSF siting study in the approval process. Migration rates for cyanide (not including products such as cyanate and nitrogenous compounds) were simulated through computer modelling, which predicted minimal migration of contamination (i.e. probably not beyond the base of the TSF) and under worst-case conditions (i.e. continuous tailings impoundment, maximum permeability and low retardation and degradation) that cyanide would be unlikely to migrate more than 200 m, for which allowance was made in the final siting of the TSF (Train, 1999). In this instance, tailings cyanide concentration will be limited to 20 mg WAD CN/L (90^{th} percentile) and 30 mg WAD CN/L (maximum) at the point of discharge into the TSF. In addition, the operating license conditions require that the Cowal Gold Project TSF and contained water storage facilities have a basal barrier or impermeable liner with an equivalent permeability of $1X10^{-9}$ m/s over a thickness of 1 m. A holistic approach to tailings management and groundwater protection from cyanide is proposed. It should be noted that such stringent permeability requirements may not be appropriate in other

Regardless of the quality of the investigations undertaken during the design phase and the operational controls implemented to manage environmental risks from contaminants, uncertainties will remain regarding current and future potential risks. Monitoring provides an important means of validating planning assumptions and predictions about the expected behaviour of contaminants in the environment. State/territory agencies in Australia require groundwater monitoring around TSFs and other structures containing cyanide solutions in order to monitor groundwater quality and contamination.

The Western Australian Department of Water (WRC, 2000b) has published a series of guidance documents on water quality protection for mining and mineral processing, including guidance on TSFs, TSF impoundment liner requirements for tailings confinement, water quality monitoring and groundwater monitoring. Liners are used to restrict seepage of leachate from containment and storage areas. Their purpose is to prevent stored material from contaminating the environment (WRC, 2000b). In general, selection of a liner system depends on the hazard posed by the contained material, susceptibility of the liner material to attack by the contained material, time span of containment, local soil conditions and vulnerability of the environment. The mining and environment agencies in WA assess all proposals for TSF lining systems, and may seek advice from the Department of Water. Non-synthetic clay liners are commonly used at TSFs, and low permeability areas (e.g. 10^{-9} m/s) are favoured when selecting sites, but no matter what the permeability, seepage control and management will also be required.

A typical operating licence under Western Australia's *Environment Protection Act 1986* would require the licensee to manage the storage of all matter containing cyanide constituents within TSFs in a manner that prevents pollution. Migration of constituents of TSFs is required to be managed to prevent damage to vegetation and pollution of surface waters or underground water. Monitoring bores are required to be installed and data reported. A licence would typically also specify analytes and methods to be used to analyse groundwater samples. In Western Australia, relevant analytes typically

include free, WAD and total cyanide (a range of other analytes is also required to be monitored). Some licences have specified acceptable limits for WAD CN in groundwater (e.g. 0.5 mg/L or comparison to the background concentration range), but licence conditions may vary from site to site. Western Australian Department of Environment and Conservation advises that rather than specifying limit values, cyanide monitoring is required to track any plume and enable focused management response.

In NSW, Environment Protection Licence (EPL) conditions may require the monitoring of tailings cyanide concentrations. A standard EPL will identify sampling locations, sampling frequency, analytes and methods for analytical testing. Concentration discharge limits at strategic sampling locations are typically specified and licences typically refer to the relevant legislation (e.g. Section 120 of the *Protection of the Environment Operations Act 1997*). NSW does not set licence limits for groundwater contamination from a TSF. Licensees are required to undertake monitoring of groundwater to check whether contamination is spreading and the matter is considered in detail in the design/planning stage to ensure the TSF is well located and well designed.

Most state and territory agencies do not include potential cyanide products such as cyanate, thiocyanate or ammonia in the schedule of analytes required for groundwater monitoring programs.

In some states, the breach of a TSF liner and detection of contaminants in groundwater is not necessarily an automatic breach of compliance; however, where monitoring results indicate groundwater contamination has occurred above the specified acceptable limits or in contravention of planning criteria, risk management actions are typically required (e.g. installation of a groundwater recovery bore system, cessation of operations) with on-going monitoring until the issue is addressed.

Industry initiatives

The Mining Association of Canada has published guidance on the management of tailings facilities in collaboration with representatives of the Canadian mining industry (MAC, 1998). While there is no equivalent industry guideline for tailings management in Australia, the The Ministerial Council on Mineral and Petroleum Resources and the Minerals Council of Australia (MCMPR/MCA, 2003) indicates that industry's commitment to improved tailings management is evident through the development of mechanisms such as the Australian Minerals Industry Code for Environmental Management (2000) and through the adoption of environmental management system standards such as ISO14001. The Code for Environmental Management encourages self-regulation by the industry, with improved performance and enhanced community consultation as key components (MCMPR/MCA, 2003). Some key elements include:

- applying risk management techniques on a site-specific basis to achieve sound environmental outcomes over the life of a project;
- developing contingency plans to address residual risk;
- ensuring resources are adequate to implement the environmental plans during operations and closure;
- minimising waters through recycling, and by re-using process residues; and
- encouraging external involvement in monitoring, reviewing and verifying of environmental performance.

The Minerals Council of Australia recognises nine key principles of effective tailings management in its Tailings Management Policy adopted in April 2000. The key principles are:

- adopt a risk-based approach;
- minimise the production of tailings and maximize their safe re-use;
- ensure all tailings structures are operationally stable, able to be rehabilitated and retain their long-term integrity;
- consider economic, environmental and social aspects in all stages of tailings management to minimise short- and long-term impacts;
- contribute to focused and relevant research into strategic issues aimed at improved tailings management;
- share knowledge and expertise across industry on best practice approaches;
- recognise that effective stakeholder involvement is essential for successful planning, management and closure of TSFs;
- promote understanding of potential community health issues relating to tailings; and
- effectively monitor and report tailings management practice.

The Ministerial Council on Mineral and Petroleum Resources and the Minerals Council of Australia (MCMPR/MCA, 2003) provide a strategic framework for tailings management in Australia. The framework is designed to provide a broadly consistent framework for tailings management across the various Australian jurisdictions. The framework is not a detailed set of guidelines for tailings management, and a comprehensive list of codes, guidance and procedures is already available. The Strategic Framework provides a set of objectives and principles for tailings management grouped under five key areas: Stewardship, Stakeholder Engagement, Risk Management, Implementation and Closure. The framework has been developed to encourage consistency of purpose by regulatory agencies and industry in the effectiveness of tailings management.

11.7 Heap leach operation and management

Whereas there have been numerous heap leach operations in North America and elsewhere, this technique has had relatively little use in Australia (Section 4.4.2). No published guidance is available specifically on the management of heap leach operations in Australia, though a range of general guidance documents on cyanide management is available. Information for heap leach operations is available from various sources overseas.

Thiel and Smith (2003) identify a range of potential environmental risk issues associated with geotechnical aspects of heap leach operations (Table 11.3).

Table 11.3. Summary of key concerns of heap pads and heaps

Performance Area	Key Concerns
Slope stability	Global and deep-seated failures due to extreme heights and base pressures
	Sliding block stability along geomembrane interfaces
	Effects of active leaching, with elevated degrees of saturation
	Long-term chemical and biological degradation of ore
	First-lift stability affected by lift thickness (5 m to 50 m) and stacking direction
	Drain pipe failure
Liquefaction	Earthquake-induced failures
	Possible static liquefaction flow slides
Water management	Tropical installations can have large surplus water balances
	Designs include interim catch benches and temporary caps
	Phreatic levels range from 1 to 60 m over the base liner
Liner durability and leakage	Coarse rock 'overliner' systems and liner puncture
	Extreme pressures caused by weight of heap and equipment
	Durability against chemical attack – especially for 96% H_2SO_4 (for copper operations)
	Valley fill systems create very high solution levels

* Source: Thiel and Smith (2003).

11.8 Cyanide waste management

11.8.1 International requirements for cyanide waste management

International requirements for the management of cyanide-containing wastes are incorporated in various Conventions to which Australia is a signatory.

The Basel Convention aims to protect the environment and human health from the improper disposal of hazardous wastes (Department of Foreign Affairs and Trade, 1992). The Basel Convention has three key objectives:

- to minimise the generation of hazardous wastes;
- to ensure the availability of adequate disposal facilities for the environmentally sound management of hazardous wastes; and
- to reduce transboundary movements of hazardous wastes to a minimum consistent with their environmentally sound and efficient management.

Cyanide-containing wastes from heat treatment and tempering operations (Y7), inorganic cyanides (Y33) and organic cyanides (Y38) are classified as Hazardous Wastes (Annex 1) in the Basel Convention (Department of Foreign Affairs and Trade, 1992).

No organisations have been authorised to export cyanide-containing wastes from Australia.

Under Article 11 of the Basel Convention, Parties to the Convention may enter into bilateral, regional or multilateral agreements or arrangements with non-Parties provided these agreements or arrangements conform to the environmentally sound management of such wastes as required by the Convention. Australia is a signatory to two such multilateral agreements including:

- **Organisation for Economic Cooperation and Development Control System**. The OECD has special rules for shipments of waste for recovery purposes. The rules mean that waste can be shipped between OECD countries, even if they are not Parties to the Convention.
- **Waigani Convention.** A convention to ban the importation into forum island countries of hazardous and radioactive wastes and to control the transboundary movement and management of hazardous wastes within the South Pacific region (Department of Foreign Affairs and Trade, 2001).

The Basel Convention and associated Conventions are implemented in Australia through the *Hazardous Waste (Regulation of Exports and Imports) Act 1989* (Cwlth), administered by DEWHA.

11.8.2 Sea dumping of cyanide wastes

DEWHA administers the *Environment Protection (Sea Dumping) Act, (1981)*, which ratifies the International Protocol relevant to the Act - Protocol for the Convention on the Prevention of Marine Pollution Dumping of Wastes and Other Matter (London Convention) (Department of Foreign Affairs and Trade, 1985). The Act provides for the regulated disposal of wastes and other substances in waters off Australia and its External Territories. The International Maritime Organisation (IMO) has Secretariat responsibilities for the London Convention and Australia is a member of the IMO.

Australia is a signatory to the 1982 United Nations Convention on the Law of the Sea, which includes measures to prevent, reduce and control pollution of the marine environment by dumping of wastes (Department of Foreign Affairs and Trade, 1994).

More recently, Australia has implemented the 1996 Protocol to the Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter, 1972. The 1996 Protocol to the London Convention severely restricts the list of substances that may be disposed of at sea.

Australia is a signatory to the Protocol for the Prevention of Pollution of the South Pacific Region by Dumping (Department of Foreign Affairs and Trade, 1986), which provides that all appropriate measures are taken to prevent, reduce and control pollution in the Protocol Area by dumping of wastes at sea.

Examples of state legislation pertaining to sea dumping of wastes include the *Environment Protection (Sea Dumping) Act, 1984* (SA), the *Marine Pollution Act, 1987* (NSW), the *Marine (Sea Dumping) Regulations, 1982* (WA), and the *Transport Operations (Marine Pollution) Regulations, 1995* (Qld).

DEH/DoD (2003) provide a historical account of 39 recorded events involving the disposal of cyanide salts or cyanide-containing wastes in Australian oceanic waters occurring between 1979 and 1953. Waste types disposed at sea were described variously as sodium cyanide, cyanide residues, alkaline cyanide solution, neutralised electroplating vat waste, carbonate/cyanide, pots, cyanogen bromide, cyana-gas or heat treatment salts. Records indicate ~80 000 L was disposed of at sea, plus three disposal

events involving a total of ~26 tonnes of cyanide wastes (typically in drums) and 19 cyanide-impregnated vats. Wastes were disposed of offshore from New South Wales, South Australia, Queensland, Victoria and Tasmania. BRS (2002) also describe cyanide waste disposal in the 1970's into south east Australian marine waters (1500 m depth).

There have been no reported instances of sea dumping of cyanide-containing wastes in Australian waters since 1979 and since the inception of the *Environment Protection (Sea Dumping) Act, (1981),* which strictly prohibits the disposal of chemical wastes at sea.

11.8.3 Trans-national waste movement

Domestic movement of controlled waste, including cyanide-containing wastes between states and territories is managed through the National Environment Protection Measure (NEPM) *Movement of controlled waste between states and territories* (NEPC, 1998).

Cyanide wastes are controlled wastes under the NEPC (1998) NEPM. The NEPM provides a comprehensive, national system for monitoring and reporting all interstate movements of controlled waste. The system ensures that the controlled waste reaches the approved facilities for treatment, recycling, storage and/or disposal and thereby aims to minimise impacts to the environment and human health. Under the system, the waste producer is required to apply for a consignment authorisation number through the state or territory environment protection agency of the wastes destination. The producer is issued with a unique authorisation number for the type of controlled waste, their nominated licensed transporter and their nominated licensed waste facility.

A record is kept of each shipment of controlled waste by using a 5 docket Waste Transport Certificate available from the producer's state or territory environment protection agency. The waste producer, waste transporter, operator of the disposal facility and governments of the generating, receiving and any transit states or territories are informed about each shipment. The information gathered assists in dealing with emergency situations and in gaining a better overall understanding of the movement of controlled wastes between states and territories.

11.8.4 States and territories waste management

Each Australian state and territory provides statutory controls on waste generation and management (refer Table 11.4). Requirements are established for cyanide-containing substances that are classified as wastes to be handled and disposed of by licensed waste disposal or treatment contractors/facilities in accordance with state, territory and National legislation and policies. Due to their toxicity, cyanide-containing wastes are stringently regulated. In NSW, cyanide wastes are managed in accordance with the *Environmental guidelines: assessment, classification and management of liquid and non-liquid wastes* (NSW EPA, 1999). Such wastes are usually treated by means of chemical destruction (liquids) using sodium hypochlorite or chemical fixation (non-liquids) using cement or similar products. Electroplating sludges derived from plating facilities are stabilised as filter cake and/or solidified. Subject to passing leachate testing requirements, the waste is disposed of at a Solid Waste Class 2 Landfill with a currently operating leachate management system. Waste from heat treatment facilities can be in the form of sand and slag aggregate, which is usually treated prior to disposal.

The three major sodium cyanide manufacturing facilities in Australia produce gaseous, liquid and solid wastes containing the cyanide compounds. Product is recovered where practical within the processes and re-used and/or treated by various means to constituent by-products. Wastewater discharges and air emissions are monitored and environmental emissions typically only occur under license (e.g. trade waste agreements, permits) authorised by various state and territory environment protection agencies. The manufacturing facilities typically collect/recycle packaging materials, such as bulk bags, supplied to customers.

Mining wastes containing cyanide include tailings, which are emitted to land in TSFs. There, reactions occur leading to the volatilisation of much of the cyanide to the atmosphere, or other attenuation processes (e.g. complexation, biodegradation; refer Section 6.3). Cyanide destruction processes are implemented prior to the point of discharge at some mines. Recycling of cyanide solutions also occurs in order to minimise chemical costs and conserve water, which is typically associated with cyanide wastes. Containers used to store and transport sodium cyanide are generally returned to the manufacturer, and some packaging materials are disposed of in TSFs.

Table 11.4. Primary state and territory waste management legislation and guidance

State/Territory	Relevant Waste Management Legislation/Guidance	Principal Authority
Australian Capital Territory	Environment Protection Act 1997 and regulations; Environmental Standards: Assessment & Classification of Liquid and Non-liquid Wastes (Environment ACT, 2000)	Environment ACT
New South Wales	Protection of the Environment Operations Act 1997 and regulations; Environmental Guidelines: Assessment, Classification and Management of Liquid and Non-Liquid Wastes (NSW EPA, 1999); Environmentally Hazardous Chemicals Act (1985); Chemical Control Order in Relation to Aluminium Smelter Wastes Containing Fluoride and/or Cyanide; Trade waste guidance (Sydney Water, 2000).	NSW Environment Protection Authority; Sydney Water Corporation
Queensland	Environment Protection Act (1994) and regulations; Environment Protection (Waste Management) Policy (2000) and Environmental Protection (Waste Management) Regulation (2000)	Queensland Environment Protection Agency
Northern Territory	Waste Management and Pollution Control Act 1998 and regulations; Water Supply and Sewerage Services Act and associated guidance: Acceptance Guidelines for Trade Waste (PAWA, 2000) and Trade Waste Code (PAWA, 2001).	Department of Infrastructure, Planning and Environment; Power and Water Authority

State/Territory	Relevant Waste Management Legislation/Guidance	Principal Authority
Western Australia	Environmental Protection Act (1986) and regulations (e.g. Environmental Protection (Controlled Waste) Regulations 2004, Environment Protection Regulation 1998); Mine Safety Inspection Act (1994). Mining Act (1978)	Department of Environment and Conservation; Western Australian Environment Protection Authority; Department of Mineral and Energy
South Australia	Environment Protection Act (1993) and regulations; Sewer Act 1929	Department of Environment and Heritage, Environment Protection Agency
Victoria	Environment Protection Act (1970). Environment Protection (Prescribed Waste) regulations (1998); Industrial waste management policies	Victorian Environment Protection Authority
Tasmania	Environmental Management and Pollution Control Act (1994) and regulations; Plumbing Regulations (1994) (Trade Waste Standards)	Department of Primary Industries, Water and Environment

11.9 Environmental media quality guidelines for cyanide and products

Environmental media quality guidelines (e.g. water quality guidelines) provide a measure to assess environmental media for contamination and risk to the environment.

Currently, Australia has no nationally accepted or consistent sediment, soil or air quality guidelines for environmental protection for cyanide compounds. Surface water quality guidelines for the protection of aquatic ecosystems (freshwater and marine) for free cyanide, ammonia and nitrate are established in Australia (ANZECC/ARMCANZ, 2000a; refer below). However, currently Australia has no nationally accepted or consistent surface water quality guidelines for cyanide products such as cyanate and thiocyanate for the protection of aquatic ecosystems.

This section describes water quality guidelines for cyanide for the protection of aquatic ecosystems. Water quality guidelines for the protection of wildlife are described in Section 11.10.3.

11.9.1 Water quality guidelines for the protection of aquatic life

Australian water quality guidelines for the protection of aquatic ecosystems were published in 2000 (ANZECC/ARMCANZ, 2000a) and are described further in Section 9.8.2.

Table 11.5 provides a summary of Australian and international water quality guidelines for free and WAD cyanide species for the protection of aquatic ecosystems.

Table 11.5. Water quality guidelines for cyanide for aquatic ecosystem protection

Environment	Trigger Value	Jurisdiction	Reference
Freshwater	7 µg/L (protection of 95% of species)	Australia	ANZECC/ ARMCANZ (2000a)
	The one-hour average concentration should not exceed 22 µg/L more than once every 3 years on the average. The same value is listed by USEPA (2006b) as the 'Criteria Maximum Concentration' (CMC) for cyanide in freshwater. The CMC is described as 'an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect.' The four-day average concentration should not exceed 5.2 µg/L more than once every 3 years on the average. The same value is listed by USEPA (2006b) as the 'Criterion Continuous Concentration' (CCC) for cyanide in freshwater. The CCC is described as 'an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect'.	United States	USEPA (1985)
	5.0 µg/L	Canada	Environment Canada (2002); CCREM (1987)
	3 µg/L	Non-specific	Eisler et al. (1999)
	In a 30 day period the average concentration (based on a minimum of 5 weekly samples) of weak-acid dissociable cyanide (expressed as CN) in unfiltered samples should not exceed 5 µg/L. The maximum concentration should not exceed 10 µg/L at any time.	British Columbia	MWLAP (1986)
Marine and Estuarine	4 µg/L (protection of 95% of species)	Australia	ANZECC/ ARMCANZ (2000a)
	Acute: The one-hour average concentration of cyanide should not exceed 1.0 µg/L more than once every three years on the average. Listed by USEPA (2006b) as the Criteria Maximum Concentration (CMC) for cyanide in saltwater.	United States	USEPA (1985)
	Chronic: The one-hour average concentration of cyanide should not exceed 1.0 µg/L more than once every three years		USEPA (1985)

Environment	Trigger Value	Jurisdiction	Reference
	on the average.		
	Listed by USEPA (2006b) as the Criterion Continuous Concentration (CCC) for cyanide in saltwater.		
	Acute: The one-hour average concentration of cyanide should not exceed 9.2 µg/L more than once every three years on the average.	Puget Sound	Brix et al. (2000)
	Chronic: The one-hour average concentration of cyanide should not exceed 2.9 µg/L more than once every three years on the average.		Brix et al. (2000)
	The maximum concentration of weak-acid dissociable cyanide (expressed as CN) in unfiltered samples should not exceed 1 µg/L at any time	British Columbia	MWLAP (1986)

The *Implementation guidance for the international cyanide management code* (ICMI, 2006) stipulates that discharges to natural waters should not exceed 0.5 mg WAD CN/L nor result in concentrations of free cyanide in excess of 0.022 mg CN/L within the receiving surface water body, and downstream of any approved mixing zone. These values correspond to the target guideline for WAD cyanide discharges of 0.5 mg WAD CN/L and stipulated maximum concentration in the receiving water of 0.022 mg CN/L for mining projects by the World Bank Group (1995), which predate the development of the ICMC (see Section 11.12.4). At least the 0.022 mg CN/L value for free CN in receiving waters appears to have originated from US EPA National Recommended Water Quality Criteria (USEPA, 2006b), and the other World Bank guidelines may also relate originally to mining regulations in the United States.

The ICMC stipulated maximum concentration limit of 0.022 mg/L (22 µg/L) downstream of any established mixing zone and corresponding USEPA Criteria Maximum Concentration for freshwater are higher than the Australian water quality guideline trigger value of 7 µg CN/L for freshwater and 4 µg CN/L for saltwater for protection of 95% of species. However, as explained below, these guidelines are trigger values which enable further consideration of other site-specific factors.

Due to the range of possible forms of ecologically relevant cyanide in the environment (e.g. free and weakly complexed or rapidly dissociated under specific environmental conditions), site-specific ecotoxicological data may be required in order to derive accurate site-specific water quality guidelines for the protection of aquatic life. The Australian water quality guidelines for the protection of aquatic ecosystems (ANZECC/ARMCANZ, 2000a) are generic and widely applicable in Australia. However, they provide a hierarchical approach to water and sediment quality assessment that includes direct toxicity assessment (DTA) where investigation of site-specific ecotoxicological effects by testing site environmental media under laboratory or field conditions is one possible, more detailed, assessment option.

It is noted that WAD CN methods are generally recommended for measuring CN for National Pollutant Discharge Elimination System (NPDES) Permits which address these criteria in the USA (Section 11.9.3). The Australian water quality guidelines (ANZECC/ARMCANZ, 2000a) note that the toxicity of cyanide to aquatic organisms is related to the pH, with un-ionised HCN having greater toxicity than CN^- (Section

9.7.4). The guidelines qualify what types of cyanide measurements are appropriate as follows:

> For instance, if total cyanide is below the trigger value (TV) the risk is low and if above, users may proceed to 'weak-acid-dissociable' (WAD) cyanide measurement. Again, if WAD-CN is below the TV, the risk is low and if above, users may choose whether to accept this as exceeding the guideline and institute management action or to proceed to measurement of undissociated HCN for comparison with the TV. In waters of low ionic strength and low organic matter, total cyanide, WAD-CN and HCN will often be similar. However, in water with high content of complexing ions such as metals, it is likely that total cyanide > WAD-CN > HCN. Hence WAD-CN may overestimate the available cyanide concentration.

A further issue is the limit of detection of methods routinely used to measure WAD or free CN, which means that the above trigger values downstream of the discharge point are below concentrations which can be directly measured. Hence appropriate compliance limits at various measuring points need to be determined, allowing for subsequent dilution in the receiving waterbody.

11.9.2 Guidelines for WAD CN or metallocyanide complexes

As discussed above, the ANZECC/ARMCANZ (2000a) guidelines are expressed in terms of free cyanide and some caution is required if relating WAD CN values with the relevant guideline trigger value, as the undissociated HCN concentration is considered the most toxic form. The guidelines do not provide trigger values in terms of WAD CN or specific metal-cyanide complexes.

Literature reviews have been undertaken on the toxicity of total and iron-complexed cyanides (Mudder, 1995) and WAD cyanide (Mudder, 1997). Mudder (1997) indicates that criteria based on free cyanide are not appropriate due to the presence of other potentially toxic forms of cyanide and the lack of accurate analytical techniques for free cyanide, and the use of total cyanide is too conservative and is subject to a variety of analytical interferences. A concentration of 100 µg/L was used as the 'in-stream' site-specific aquatic life criterion for WAD forms of cyanide at the Golden Cross Mine, New Zealand (Mudder, 1997). In another instance, a site-specific final chronic value (FCV) for copper cyanide of ~80 µg/L was derived by multiplying a final acute value (FAV) of 290 µg/L by a corresponding acute to chronic ratio of 3.8 (Mudder, 1997). However, Mudder (1997) indicated that the FCV is conservative and not distinguishable analytically as there is inherent variability associated with the WAD cyanide analysis method. A method for the analysis of 'available cyanide' (USEPA, 1999) has been developed recently to improve the analysis of free and other forms of cyanide that may be dissociable and biologically available to wildlife.

The World Bank Group (1995) recommends target guidelines for free, WAD and total cyanide of 0.1, 1.0 and 5.0 mg/L for discharges below which there is expected to be no risk of significant adverse impact on aquatic biota. WBG (1995) indicates that in no case should the concentration in the receiving water outside of a designated mixing zone exceed 22 µg CN/L (the US water quality criterion for cyanide). No ecotoxicity data were provided in support of these recommended WAD or total cyanide concentrations.

11.9.3 Water quality monitoring

The Australian National Water Quality Management Strategy includes Australian Guidelines for Water Quality Monitoring and Reporting (ANZECC/ARMCANZ, 2000b). This provides guidance on appropriate sampling techniques.

Several state/territory agencies require water quality monitoring at sodium cyanide manufacturing facilities and mine sites that use sodium cyanide, and specify the types of sampling and analysis required.

The identification of diurnal changes to cyanide complexation and speciation in sunlight-exposed waters (Johnson et al., 2002) has implications for water quality monitoring programs. Factors such as sampling location (sunny, shaded), time of year (season) and weather patterns may influence the concentrations of free, WAD and iron-complexed cyanides obtained. For environmental monitoring, higher concentrations in surface water samples for free and WAD cyanide analysis may occur during daylight hours in solutions containing iron-cyanide complexes in sunlit locations due to photolysis (splitting) of the iron complexes to free cyanide.

Recent developments in the United States promote the monitoring of WAD cyanide species in surface waters rather than total or free cyanide, and the comparison of WAD cyanide concentrations to water quality criteria (trigger levels). Approximately 15 states in the United States adopt this approach, and approximately 345 National Pollutant Discharge Elimination System (NPDES) Permits use WAD cyanide for monitoring and/or discharge limits. The change to monitoring WAD cyanide species was instigated as total cyanide, which had previously been monitored, overestimates the amount of biologically available cyanide. Furthermore, analysis of WAD cyanide is considered a more accurate and reliable measurement of the free cyanide criteria and provides a scientifically rigorous basis for compliance and monitoring purposes while protecting aquatic life (Alaska Department of Environmental Conservation; ADEC, 2003). This approach has also been adopted in British Columbia (MWLAP, 1986).

Adequate precautions are needed to preserve samples, e.g. to avoid loss of HCN, or changes in total/WAD/free CN composition.

11.10 Wildlife protection and biodiversity conservation

11.10.1 Migratory waterbird conservation

Millions of migratory waterbirds make a long migration each year between the Arctic tundra of the northern hemisphere and the coastal beaches and mudflats of the southern hemisphere. These birds cross more than 20 countries along their migratory path known as the East Asian–Australasian Flyway. The migratory lifestyle of these birds poses great challenges for their conservation. It is important to protect the birds during all three phases of their annual life cycle: breeding, migration and non-breeding. Effective conservation of these birds relies on international action to protect the birds and their habitat in all the countries through which they move.

Australia is leading efforts to conserve migratory waterbirds, and shorebirds in particular, in the Asia Pacific region, through formal agreements with other governments, and through cooperative arrangements with governments, conservation organisations and local communities.

Migratory wildlife, including some species recorded at mine site TSFs (NTDME, 1998), are protected in Australia under the following international agreements.

International wildlife conventions

- Ramsar Convention: the Convention on Wetlands (Ramsar, Iran, 1971) is an international treaty that seeks to conserve, through wise use and management, wetland habitats. Australia and other parties to the Convention undertake to designate wetlands that meet specific criteria to the List of Wetlands of International Importance. Many sites of significance to migratory waterbirds are included on the list.

- Bonn Convention: the Convention on the Conservation of Migratory Species of Wild Animals (Department of Foreign Affairs and Trade, 1991) is an inter-government treaty that aims to conserve terrestrial, marine and avian migratory species and their habitats by providing strict protection for the endangered migratory species listed under Appendix I of the Convention, by concluding multilateral Agreements for the conservation and management of migratory species listed as threatened under Appendix II, and by undertaking co-operative research activities.

International wildlife treaties

- The China–Australia Migratory Bird Agreement (CAMBA; Department of Foreign Affairs and Trade, 1988b) and the Japan–Australia Migratory Bird Agreement (JAMBA; Department of Foreign Affairs and Trade, 1981) include a number of obligations including protection of migratory birds, preventing damage to migratory bird habitats, prohibiting the removal, sale, purchase or destruction of migratory birds, and reporting on progress towards protection.

Other agreements and policies

- World Summit on Sustainable Development: in September 2002, the Governments of Australia and Japan announced a partnership to strengthen the protection of migratory waterbirds in the Asia Pacific region. The partnership is guided by the Asia Pacific Migratory Waterbird Conservation Strategy, and aims to conserve a network of internationally important sites for migratory waterbirds across the region.

- Asia–Pacific Migratory Waterbird Conservation Strategy: at an international meeting at Kushiro, Japan, in 1994, it was agreed that greater multilateral cooperation was necessary to promote the conservation of migratory waterbirds in the Asia–Pacific region. This prompted the creation of the Asia–Pacific Migratory Waterbird Conservation Strategy: 1996–2000 and 2001–2005. Implementation of the Strategy is dependent on the capacity and ability of governments, conventions, nongovernment organisations, technical experts and local communities to work cooperatively to implement actions to achieve the conservation of migratory waterbirds and their habitats. The Strategy sets out objectives relating to habitat management, training, information exchange, establishment of networks of significant wetland sites, and development of action plans for priority species groups (the Anatidae (ducks, swans, geese), cranes and shorebirds).

- Shorebird action plan: the Action Plan for the Conservation of Migratory Shorebirds in the East Asian–Australasian Flyway: 2001–2005 identifies the key priority actions needed to ensure the long–term conservation of migratory

shorebirds and their habitats in the Asia Pacific region. Actions have been identified under three themes:

- development of the East Asian–Australasian Shorebird Site Network,
- appropriate management of Network sites, and
- increasing the information base on migratory shorebirds.

Australia strongly supports the Shorebird Action Plan, as approximately 2 million migratory shorebirds in the Asia Pacific region spend their non–breeding season in Australia.

11.10.2 Australian wildlife protection legislation and policies

Wildlife conservation legislation

Most Australian native fauna, unless classed as vermin, are protected under legislation administered by wildlife conservation agencies, as follows:

- Commonwealth*: Environment Protection and Biodiversity Conservation Act 1999*
- Australian Capital Territory: *Nature Conservation Act 1980*
- New South Wales: *National Parks and Wildlife Act 1974*, *Threatened Species Conservation Act 1995*
- Queensland: *Nature Conservation Act 1992*
- Northern Territory: *Territory Parks and Wildlife Conservation Act 1998*
- Western Australia: *Wildlife Conservation Act 1950*, *Conservation and Land Management Act 1984*
- South Australia: *National Parks and Wildlife Act 1972*
- Victoria: *Flora and Fauna Guarantee Act 1988*
- Tasmania: *National Parks and Wildlife Act 1970*, *Threatened Species Protection Act 1995*.

Under these legislative statutes, permits are usually required in order to take, harm or kill protected native wildlife, such as may potentially occur during developments or activities. Various laws have some avenues where discretion can be applied (e.g. motor vehicle collision with wildlife) such that a permit is not required. Additional policy and legislative measures protect rare or other special-status species and their habitats. Biodiversity conservation policies are established at all levels of government throughout Australia.

At a national level, the *Environment Protection and Biodiversity Act 1999* (EPBC Act) provides for protection of migratory waterbirds as a matter of national environmental significance, e.g. to address potential impacts of developments proposed near Ramsar wetland sites (Ramsar Convention on wetlands, Ramsar, Iran, 1971). A number of projects funded from the Natural Heritage Trust encourage the conservation of migratory waterbirds. They include the Shorebird Conservation Project, being undertaken by a consortium of non-government conservation groups across Australia, which is engaging communities in conservation activities at priority sites for migratory shorebirds.

Strategies, policies and regulations for the protection of wildlife from cyanide

Internationally and in Australia, management practices used to minimise the risk of exposure of wildlife to process solutions containing cyanide at mine sites has historically involved one or more wildlife management strategies including:

- deterrence (hazing techniques);
- habitat alteration; (e.g. TSF shape and size, tailings thickening);
- limiting the cyanide concentration; and/or
- restricting wildlife access to process solutions containing cyanide.

Various wildlife hazing techniques are implemented on a case-by-case basis at mine sites in Australia and internationally (Donato, 1999; Donato et al, 2007; AngloGold Ashanti, 2004, 2005). The objective of these methods is to deter wildlife from inhabiting facilities such as TSFs. However, the general consensus (e.g. Hallock, 1990; Clark, 1991; Henny et al., 1994; Eisler et al., 1999; NSW EPA, 2002; ICMI, 2006) indicates that hazing techniques (e.g. noises, flashing lights, decoys, fireworks, music, aircraft, helicopters, hovercraft, shotguns, flagging, etc) are ineffective in the long term at deterring wildlife from exposure to cyanide at TSFs and other cyanide-containing facilities. In addition, modifications to TSF designs (types, shape, sizes, depth, wildlife accessibility) are being suggested as methods for minimising the habitat value of these areas to wildlife; however, this is at the research stage. Detoxifying cyanide in tailings to acceptable concentrations for wildlife and/or total exclusion methods (e.g. fencing, overhead netting, floating balls) are preferred strategies to minimise the risks to wildlife from exposure to process solutions containing cyanide.

Although risk management strategies involving concentration reduction below threshold levels may minimise risks to wildlife, wildlife incidents may occur due to the unpredictability of wildlife. It is therefore important that contingency mechanisms are in place to identify the cause of such wildlife incidents and to reduce further impact by discouraging wildlife from the tailings while remedial measures are implemented, stressing the need for remedial strategies to be readily available.

During this assessment, a survey of wildlife protection agencies in Australian states and the Northern Territory was undertaken to ascertain the current regulations and policies for wildlife protection and their management requirements at facilities that contain cyanide solutions (refer below).

New South Wales (NSW)

Significant policy development has occurred in NSW to protect wildlife from process solutions containing cyanide, primarily due to the national public concern raised by the Northparkes wildlife mortality incident in 1995 (Section 9.9; OSS, 1995) and the Cowal Gold Project (NSR Consultants, 1995; North Limited, 1998; Simpson and Cleland, 1996; Train, 1999).

The NSW Department of Environment and Climate Change (NSW DECC) has indicated that the appropriate goal for wildlife protection at TSFs, irrespective of fauna pressure, is zero native fauna deaths from cyanide toxicity (NSW EPA, 2002, 2003, Simpson and Cleland, 1996). While the policy goal emphasises the prevention of wildlife mortality, risk reduction controls and wildlife monitoring requirements at gold mines using sodium cyanide in NSW are precautionary and intended to minimise acute and chronic adverse impacts on fauna.

The NSW DECC has reviewed its overall approach to limits (Standards) where cyanide-rich process water is discharged to tailings dams with high likelihood of fauna access. The approach considered toxicity literature, industry experience, site sensitivity and the application of the precautionary principle.

The NSW DECC (NSW EPA, 2002) indicates that a precautionary approach is required in developing risk management objectives for limiting the cyanide concentration at the point of discharge to TSFs and other facilities to achieve the stringent NSW DECC goal for wildlife protection from cyanide in TSFs and similar structures accessible to wildlife due to:

- the range of fauna that may inhabit or use these facilities including sensitive, highly exposed, rare or migratory species;
- general agreement that techniques for fauna (and particularly bird) exclusion or hazing techniques have not been consistently effective or reliable;
- the absence of toxicity data for the majority of Australian native and migratory species that inhabit these facilities, as well as information on faunal drinking behaviour;
- difficulties in predicting the levels of exposure to wildlife where environmental conditions are dynamic; and
- the potential for exposure to mixtures of free and other cyanide compounds, for which toxicity data are limited.

The reduction of cyanide concentration in tailings is widely regarded as the most effective means to prevent fauna deaths, but the limitations of toxicity data and fauna exposure data require a precautionary approach to setting the required concentration limits.

The NSW DECC review determined that for less sensitive sites (presumably sites with a low probability of wildlife habitation or exposure to process solutions containing cyanide), the limits for discharge to the tailings dam of 30 mg WAD CN/L (90th percentile of time) and 50 mg WAD CN/L (not to be exceeded) provide an appropriate level of confidence of achieving the goal of zero fauna deaths. For example, the 30/50 mg WAD CN/L discharge limits are currently established for discharges to the TSF at the Mineral Hill Mine, Condobolin.

For the Cowal Gold Mine, West Wyalong (NSW) located adjoining an ecologically important wetland (Lake Cowal), the concentration limits at the discharge point to the TSF are: 20 mg WAD CN/L (90^{th} percentile of time) and 30 mg WAD CN/L (not to be exceeded). These limits are set to achieve the NSW DECC goal of zero fauna deaths from cyanide toxicity, using a precautionary approach and these concentration limits are for more sensitive sites in NSW (e.g. ecological areas inhabited by fauna with the potential to access process solutions containing cyanide).

The application of the tailings discharge limits to existing mines in NSW is currently being considered on a site-by-site basis, in the context of the risk of fauna access. Not all mines operating in NSW are required to meet the proposed discharge limits at this stage. Where limits are established by NSW DECC they will continue to be subject to a stringent monitoring regime of both cyanide levels and fauna deaths, as well as investigation of the cause of any deaths. Monitoring and reporting of fauna deaths or injury (including bogging or miring) associated with TSFs and process water dams is generally required under NSW Environment Protection Licensing conditions. Review of wildlife incidents provides a means for control of future incidents. Should fauna deaths caused by cyanide occur, the tailings cyanide discharge limits will be reviewed and potentially lowered by NSW DECC.

Western Australia (WA)

Under licences issued by the WA Department of Environment and Conservation under the *Environmental Protection Act 1986*, mine sites in WA need to meet a range of conditions to minimise environmental contamination and protect wildlife. These may include conditions such as:

- frequent (e.g. at least twice daily) visual inspection of tailings delivery lines, return water lines, tailings deposition areas, ponding on the surfaces of TSFs, internal embankment freeboard and external walls of TSFs, with the results of visual inspections recorded in a log book;
- burial or bunding of pipelines containing cyanide, with catch pits at appropriate low points to contain spills;
- logging and reporting of all spills >5000 L outside bunded facilities;
- quarterly surface water monitoring of free, WAD and total cyanide, as well as pH, electrical conductivity (EC), total dissolved solids (TDS) and major anions and cations in nominated surface water sites;
- a limitation of 0.5 mg/L to the WAD CN concentration (and other limitations on pH and TDS) in surface water discharges from the project operations and monitoring bores, other than those to the tailings storage facility and decant ponds; and
- in some situations, e.g. where threatened species are present, there may be additional reporting requirements, such as reporting of all wildlife incidents (ranging from animals killed by vehicles to deaths of wildlife from cyanide).

Cyanide concentration limits for tailings discharges to TSFs have not been regulated in WA. According to information provided by the DoIR (prior to introduction of the ICMC), in the past most mines have discharged tailings with cyanide concentrations typically in the range of 50-100 mg WAD CN/L based on process considerations.

Northern Territory

Based on the research by Donato (1999), the Northern Territory Department of Minerals and Energy (NTDME, 1998) has developed *Best practice guidelines for reducing impacts of tailings storage facilities on avian wildlife in the Northern Territory of Australia*. The value of 50 mg WAD CN/L has been recommended for the protection of wildlife exposed to process solutions containing cyanide.

Adoption of the guideline Australia-wide is voluntary and currently inconsistent between mine operators with many discharging tailings with cyanide concentrations above this level.

Queensland

In Queensland, the environmental aspects of mining activity, including activities leading to the development of a mine (e.g. prospecting), operation of a mine and rehabilitation and remediation of sites impacted by mining are covered by the *Environmental Protection Act 1994* (EP Act). The object of the EP Act is to 'Protect Queensland's environment while allowing for development that improves the total quality of life, both now and in the future, in a way that maintains the ecological processes on which life depends ('ecologically sustainable development')'. Under this Act, activities with an inherent potential to cause environmental harm or nuisance are designated 'environmentally relevant activities' and are regulated by the granting of 'environmental authorities' (licences).

Under the Environmental Protection and Other Legislation Amendment Act 2000, provisions in the *Mineral Resources Act 1989* relating to environmental management of mines were transferred, with amendments, to the EP Act, with subsequent amendments in 2004 (Qld EPA, 2005). The Qld NR&M now has a limited role in environmental management decision making except for activities on prospecting permits and mining claims.

Under the EP Act a proponent is required to prepare an EIS if the EPA or the Minister decides an EIS is appropriate for the mining project. If the project is determined to be of state or national significance then the proponent may be required to prepare an EIS under either the *State Development and Public Works Organisation Act 1971* (SDPWO Act) or the *Environment Protection and Biodiversity Conservation Act 1999* (Commonwealth) (EPBC Act). Under the EP Act, a mining project is either a level 2 (low risk of serious environmental harm) or a level 1 (medium to high risk of serious environmental harm) environmentally relevant activity, depending on whether it does or does not comply with criteria in the Environmental Protection Regulation 1998 (EP Reg). An applicant for an environmental authority (mining activities) for a level 1 mining project (as could be anticipated for a gold mining operation using sodium cyanide) is required to submit an environmental management plan during the assessment process. A plan of operations must also be submitted prior to carrying out any activities on a mining lease, describing the actions and programs to achieve compliance with the conditions of an environmental authority (mining lease), including actions and programs to achieve or implement the relevant environmental monitoring plan.

The EPA will refer to these plans and other requirements in setting the site-specific conditions for environmental authorities for level 1 mining projects, including how to address management of TSFs to avoid impacts on wildlife.

Victoria

DSE (2006) explains the approvals process for mining to proceed in Victoria. Once a Mining License is granted conferring mineral rights from the Crown to the licence holder, a planning process is undertaken before a Work Plan can be approved and a Work Authority is granted by the Minerals and Petroleum Regulation (MPR) Branch of the Victorian Department of Primary Industries. Depending on the situation, the planning process may proceed through consideration of a Draft Work Plan by the

Department of Primary Industries, or through an Environment Effects Statement (EES) process undertaken under the *Environment Effects Act 1978* by the Department of Sustainability and Environment.

While there is no specific policy for wildlife protection at mines, there are standard conditions associated with the licence issued by the Department of Primary Industries (DPI) which address issues relating to the use of cyanide in mines. If required, special conditions can be added. The actual work plan submitted may also address issues relating to wildlife, and reference to wildlife is also made in the Management of Tailings Storage Facilities document prepared by the Minerals and Petroleum Division of the Victorian Department of Primary Industries (MPD, 2004).

Section 16.3 of the MPD (2004) document indicates that work plans of all large mining and extractive sites are required to incorporate a monitoring program to address key environmental issues and a process for reporting outcomes to the community, and that such monitoring may also be required for TSFs at small sites (<5 ha). The purpose of the monitoring is to assist the operator to run the operation and TSF efficiently and with minimum impact on the environment and to demonstrate that performance to the community based on standard conditions. Environmental impacts that may require monitoring include impacts on surface water, groundwater quality and level, vegetation, fauna (birds in particular), dust, noise and odour, and spray drift of sprays used to reduce evaporation or dust. Remedial action is expected if conditions are found to be outside the design or predicted parameters. A separate document provides advice on procedures for monitoring and sampling for cyanide, and a specific 14 page form has been prepared to assist auditing reporting.

Sections 16.4 and 16.5 of the MPD (2004) document refer to monitoring of the volumes and chemical characteristics of transfers to the TSF, and to requirements for regular third party auditing and reporting on the systems and procedures used, including actual performance of the TSF against design parameters, expectations or assumptions. The document also describes requirements for other aspects, such as TSF design and decommissioning and revegetating the site.

All mines are licensed under the *Mineral Resources Development Act 1990* (MRDA). The Work Plan and associated conditions would incorporate site specific controls for cyanide and any other hazards. A chain mesh security fence would normally be specified in the work plan or further enforced through the conditions. Any OH&S or environmental incident relating to the operation of the mine is required to be reported, but wildlife is not specifically mentioned in this context.

Tasmania

The Environment Division of the Tasmanian Department of Tourism, Arts and the Environment (formerly under the Department of Primary Industries, Water and Environment) has no direct policy in relation to wildlife protection from harm or mortality due to cyanide solution use. However, this is achieved by application of the requirements of the *Environmental Management and Pollution Control Act 1994* (EMPCA) (Tasmania DPIPWE, 2007) and by requiring all mining operations regulated by the Division to follow best practice environmental management in relation to the prevention of environmental harm from the use/disposal of controlled substances/wastes, such as sodium cyanide. Specific permit conditions related to the detoxification of cyanide in tailings liquors and cyanide concentration in TSFs are applied in Tasmania. Historically, the Division has also imposed requirements for fencing around TSFs where sodium cyanide is used in mine processing activities, but

this has been relaxed in one situation where the company adequately demonstrated that it consistently destroyed cyanide concentrations in the tailings stream to environmentally safe levels and showed a record of no animal fatalities associated with the TSF.

Under the EMPCA, all mining operations which produce ≥ 1000 tonnes of minerals per annum are classified as a level 2 activity and are therefore regulated (environmentally) by the Environment Division. Mineral activities under this threshold are regulated by the local planning authority (i.e. Council). In addition to the land use permit, all mining activities need a mining lease (registered by Mineral Resources Tasmania) and also have to comply with Workplace Standards Tasmania requirements for occupational health and safety requirements.

Regarding environmental permit condition requirements related to sodium cyanide usage, there are currently no heap leach processing activities in Tasmania. Specific permit conditions applied regarding cyanide usage/monitoring and reporting include:

- provision of a Cyanide Management Plan for approval prior to commissioning of the ore processing plant;
- monitoring requirements that tailings slurry/storage be monitored continuously for total and WAD cyanide and reported quarterly, discharge to the receiving environment be monitored monthly and reported annually, and groundwater be monitored and reported annually (wildlife monitoring is not a requirement, but as a requirement of the permit, a company is obliged to immediately advise the Director of any incidents where activities may cause environmental harm (including harm to wildlife) due to pollution);
- requirements for detoxification of cyanide processing liquor prior to disposal: criteria applied are for the leach residue to be considered detoxified are an annual mean WAD CN < 1 mg/L and maximum discharge limit of 2 mg/L, and discharge to the receiving environment of <0.05 mg/L. No limits are currently imposed in permits for thiocyanate or cyanate, but there are discharge limits of <10 mg/L for nitrogen as nitrate or nitrite, and <0.5 mg/L for ammonia. Review of current discharge limits has been underway under the state Policy on Water Quality Management 1997 and ANZECC revised trigger levels, with a proposed maximum discharge limit for a goldmine discharging to an estuary of ~0.005 mg/L as free CN.

Generally mines monitor at or close to the decant, and/or prior to discharge to the receiving environment, seepage and ambient receiving environment. The majority of mines undertake groundwater monitoring of WAD and total CN, with annual reporting. The principal instrument applied for groundwater management in Tasmania is the state Policy on Water Quality Management 1997, the purpose of which is to protect the sustainable management of Tasmania's surface and groundwater resources by protecting or enhancing their qualities while allowing for sustainable development.

Advice by way of guidance for new TSF proposals is provided in Development Proposal and Environmental Management Plan guidelines, but this advice relates largely to the approval process for dam works.

South Australia

South Australia has had very few mines using sodium cyanide in recent years, though there have been several sites which used sodium cyanide with heap leaching to re-treat

waste dumps in the past. Sites currently using sodium cyanide use the International Cyanide Management Code (ICMC) and are also encouraged to use the Best Practice booklet for hazardous materials management (Environment Australia, 1997). The Mining Lease conditions and/or Mining and Rehabilitation Program (MARP) also set out site specific details to protect wildlife. Licensing requirements for sodium cyanide use are regulated by the Department of Administrative and Information Services, under the *Dangerous Substances Act 1979*.

Requirements such as monitoring of cyanide concentrations in TSFs are outlined in the site MARP or Environmental monitoring and Management Program (EMMP). Monitoring of concentrations is only undertaken on the active sites, and not those using heap leaching. Concentrations of cyanide products found in TSFs are reported in the Annual Environment Reports for the mine, as are environmental incidents such as spillages.

Guidance for managing TSF operations has been drawn from WA's *Mining environmental management guidelines: safe design and operations standards for tailings storage* and the WA Department of Minerals and Energy *Cyanide management guideline 1992*. In the past (pre 1994), an internal Code of Practice created by the Department of Mines and Energy SA entitled *Code of practice for the use of cyanide on gold mining leases* was used. Guidance for heap leach operations is set out in the MARP and lease conditions individually. For groundwater, companies provide seepage modelling and data such as salinity levels before mining commences. If monitoring results in values markedly different from the preliminary data, further investigation is required. Groundwater quality is based on NEPM and ANZECC guidelines.

If wildlife impacts are identified as a problem, scaring devices are implemented. Bird netting has been used in the past, but scare guns were perceived to be more effective. Wildlife incidents would be reported in the company's Annual Environment Report and there are regular site inspections.

Overall comments

In summary, the review of state/territory Government agencies on policies and strategies implemented to protect wildlife from process solutions from cyanide has found that:

- All mining regulatory agencies promote the protection of the environment, including wildlife;
- Few state agencies have established policies or regulatory requirements specific to the protection of wildlife from process or other solutions containing cyanide;
- Few states specify concentration limits for WAD cyanide in tailings discharged to TSFs in licence conditions. Emphasis is on TSFs and tailings;
- No agencies require monitoring of potential cyanide products in tailings (e.g. cyanate, thiocyanate or nitrogenous compounds) to which wildlife may also be exposed;
- Most agencies that recommend guidance values (e.g. ≤50 mg WAD CN/L in tailings) or specify cyanide concentration limits in licence conditions, aim to prevent or minimise wildlife mortalities from exposure to process solutions containing cyanide;

- Some states require that frequent wildlife monitoring be undertaken at mine site facilities in licence conditions; and
- Most state/territory agencies require wildlife incidents involving mortality due to cyanide poisoning to be investigated, documented and reported on request.

11.10.3Water quality guideline levels to protect wildlife

Australian wildlife protection initiatives

As indicated above, to meet policy requirements several state/territory and industry organisation either recommend or require concentration limits of ≤50 mg WAD CN/L in tailings discharged to TSFs where wildlife may be exposed to the solutions. The NSW DECC WAD CN targets of 20 or 30 mg WAD CN/L discussed above were evidently based on a consideration of available evidence, including anecdotal reports that only incidental bird deaths occur at concentrations <~50 mg WAD CN/L, reports that current policy in the southern USA was moving toward a target of 25 mg/L where ponds were not netted, a value of 20 mg/L derived from reports of the *Fletcher (1986, 1987) studies with an AF of 10 to allow for interspecies variation, and on interpretation of the biochemical studies (recovery between 2-24 h from test concentrations of ~40 mg/L in the 10 mL dose given). The NSW targets are at the point of discharge, which is considered to be more protective than measuring in the decant water as it provides control on the worst case concentration. Some mines elsewhere have already adopted a target of 30 mg/L in decant water.

International wildlife protection initiatives

In the United States, migratory birds are protected, in terms of their death from cyanide toxicity during their migration by the Migratory Bird Treaty Act. However, the US Migratory Bird Treaty Act does not stipulate an acceptable concentration of WAD CN in TSFs and other water bodies that are accessible to wildlife, but provides an overall requirement that the concentration cannot be acutely lethal to migratory birds. Based on field observations, a concentration limit of 50 mg WAD CN/L for surface waters accessible to migratory wildlife has historically been adopted to meet this Treaty objective for the protection of migratory species from mortality due to cyanide at mine sites (Kay, 1990).

The World Bank Group (1995) recommends that measures should be implemented to prevent access by wildlife and livestock for all open waters (e.g. tailings impoundments and pregnant leach ponds) where cyanide concentrations exceed 50 mg WAD CN/L. No ecotoxicological data or calculations are provided in support of this cyanide concentration. Furthermore, whether this operating limit is suggested to protect only against wildlife mortality or sublethal effects of cyanide is not described.

In the ICMC (ICMI, 2006), the International Cyanide Management Institute (Section 11.12.4) recommends that measures should be implemented to prevent access by wildlife and livestock for all open waters (e.g. tailings impoundments and pregnant leach ponds) where cyanide concentrations exceed 50 mg WAD CN/L. However, no ecotoxicological data for birds or wildlife risk model are provided in support of this cyanide concentration. The ICMC indicates a threshold of 50 mg WAD CN/L as a risk management guideline to protect wildlife and livestock other than aquatic organisms from adverse effects of cyanide process solutions. However, this concentration is not viewed as a toxicity threshold or “safe level”, and is recommended with emphasis on the mitigation of wildlife mortality rather than sublethal effects. Where operations are

discharging WAD cyanide at concentrations greater than 50 mg/L and do not have significant mortalities attributable to cyanide, the Code allows for an operation to demonstrate, via scientific peer review, that protective measures are in place at that specific operation, as has been shown for hypersaline sites (see Sections 7.3.2, 9.9.2, 10.2.3). The Code further requires demonstration of code compliance, including protection of wildlife, as part of the third-party re-certification process every 3 years.

As indicated above, international measures implemented to protect wildlife from process solutions containing cyanide emphasise the protection against mortality due to cyanide and not necessarily protection against sublethal effects of cyanide, and in each case a limit of 50 mg WAD CN/L in cyanide solutions accessible to wildlife is recommended to meet this wildlife protection goal.

11.11 Chemical manufacturing industry initiatives

11.11.1 Manufacturing facility programs

Each sodium cyanide manufacturing facility operates under legal constraints and obligations from a variety of local, state and Commonwealth government legislation and the chemical industry. These include the Responsible Care® program (refer below) and various Codes of Practice for chemical storage, handling, transport (e.g. ADG Code, IMDG Code). In addition, each manufacturing facility has established Environmental Management Systems (EMS; or equivalent environmental safety systems), and a Quality Management System (e.g. ISO9001, ISO14000).

The manufacturing industry operates with a 'cradle to grave' approach to sodium cyanide products, which means that responsibility for sodium cyanide product is broadened beyond the manufacturing facility operations to cover use and appropriate waste management.

Other manufacturing industry initiatives include:

- Safety Management Systems, emergency procedures, and guidance documents for the safe handling of sodium cyanide products (e.g. Ticor, 2000);
- Transport Management Plans for sodium cyanide;
- Controlled document systems for operational and administrative systems and procedures; and
- Safety Data Sheets and emergency procedure guidance.

11.11.2 Responsible Care® program

The Responsible Care® program is an initiative of the international chemical industry to improve the health, safety and environmental performance of its operations and to increase community involvement and awareness of the industry. It was introduced in September 1989. Australia was the third country to join, and approximately 46 countries currently participate in the Responsible Care® program (PACIA, 2002).

Adherence to Responsible Care® is a condition of membership of the Australian industry's peak body, the Plastics and Chemicals Industries Association, Inc. (PACIA), for companies manufacturing, importing and distributing chemicals in Australia. Each of the major sodium cyanide manufacturers in Australia is a member of PACIA.

The Responsible Care® program operates under guiding principles that include operational safety, product stewardship, resource sustainability, community involvement, industry collaboration, and co-operation with government. Six Codes of Practice define the performance practices required for PACIA member company operations and products. These Codes of Practice complement existing legal requirements and require co-operative action with the community.

Codes of Practice include:

- Product Stewardship: Product Stewardship is the responsible and ethical design and management of products throughout the entire product life cycle, in order to ensure health and safety and protect the environment. It is a demonstrable process that places an ongoing responsibility on a company to identify, monitor, manage and continually improve the health, safety and environment performance of its products and packaging. The purpose of product stewardship and of the associated Code of Practice is for a company to actively engage in the identification and management of the risks associated with its products, to the extent consistent with its degree of influence at each stage of the product life cycle. It covers member company actions necessary to fulfil the Guiding Principles of Responsible Care®.

- Community Right to Know: This Code governs member company action regarding Community Right to Know, particularly in order to fulfil the Guiding Principle of Responsible Care®. This Code is intended to result in member companies responding to community concerns about their activities by providing mechanisms for community consultation on processes and products and by providing extensive information in a simplified, readily accessible way. The level of effort will be proportionate to the inherent risk and the degree of community concern.

- Environment Protection: This Code governs member company actions regarding management of the environmental aspects of their activities, conservation of resources and reduction of waste in order to fulfil the Guiding Principles of Responsible Care®. In general, implementation of this Code will reduce the burden of member company activities on the environment and contribute towards industry sustainability.

- Manufacturing Process Safety: This Code governs member company actions regarding safety of chemical manufacturing processes. This Code provides guidance as well as a means to measure continual improvement in the management of process safety in manufacturing.

- Employee Health and Safety: This Code governs member company action regarding health and safety of people involved in operational activities, particularly in order to fulfil the Guiding Principle of Responsible Care®. It is recognised that education / training of employees and prevention of incidents is fundamental to the achievement of the purpose of this Code. Prevention only occurs when there is a conscious systematic effort to make it happen.

- Storage and Transport Safety: This Code governs member company actions regarding storage and transport consistent with the Guiding Principles of the Responsible Care®. In general, the implementation of this Code involves setting management plans and objectives, carrying out hazard evaluations, implementing risk reduction programs, prompt and effective emergency response and supporting a community awareness program. With these in place, the member companies and PACIA will be able to quantitatively measure performance on safety associated

with storage and transport activities. PACIA provide an accreditation scheme for carriers of dangerous goods in Australia. Chemical and transport industry representatives developed the PACIA Carrier Accreditation Scheme. This industry-regulated scheme aims to measurably improve the safety performance of transport carriers for the chemical industry by introducing an integrated, national standard of performance auditing. This will have the effect of streamlining the implementation of the audit requirements of the Responsible Care® Transportation Code of Practice, whilst minimising duplication and audit costs.

PACIA notes that many companies have tailored quality, environment and safety systems such as ISO 9001 and ISO 14001 and that implementing equivalent elements from those systems would meet the requirements of the PACIA Codes of Practice.

In response to international environmental incidents involving cyanide, the major Australian sodium cyanide manufacturers undertook a review of the Australian situation. This led to the development of a working party of the major manufacturers as a Responsible Care® program initiative (PACIA, 2000).

11.12 Mining, metal extraction and cyanide management

11.12.1 General comments

Industry has implemented a number of initiatives that are aimed at safety and environmental management. The mining and metal extraction industries operate within government and self-regulating initiatives and Codes of Practice for safety and environment protection.

Primary mining industry representative organisations include the Minerals Council of Australia (MCA), its state Chambers and the International Commission in Mining and Metals (ICMM). Each organisation has stated that it is committed to sustainable development. International mining industry initiatives include the Global Mining Initiative (GMI), the declaration by the International Council on Mining and Metals (ICMM, 2002) and the associated Mining, Minerals and Sustainable Development (MMSD) project (IIED, 2002).

Signatories to the Australian Mineral Industry Code for Environmental Management, published by MCA (2000) commit to obligations including:

- Integration of environmental, social and economic considerations into decision-making and management, consistent with the objectives of sustainable development.
- Openness, transparency and improved accountability through public environmental reporting and engagement with the community.
- Compliance with all statutory requirements, as a minimum.
- A continually improving standard of environmental performance and, through leadership, the pursuit of environmental excellence throughout the Australian minerals industry.

The Australian Minerals Industry Code for Environmental Management was formally retired on 1 January 2005 and replaced by Enduring Value - the Australian Minerals Industry Framework for Sustainable Development. The MCA website (MCA, 2006) indicates that Enduring Value:

- aligns with global industry initiatives, and in particular provides critical guidance on the International Council on Mining and Metals (ICMM) Sustainable Development Framework Principles and their application at the operational level;
- builds on the Australian Minerals Industry Code for Environmental Management - the platform for industry's continual improvement in managing environmental issues since its introduction in 1996;
- provides a vehicle for industry differentiation and leadership, building reputational capital with the community, government and the finance and insurance sectors; and
- assists the industry to operate in a manner which is attuned to the expectations of the community, and which seeks to maximise the long-term benefits to society that can be achieved through the effective management of Australia's natural resources. (http://www.minerals.org.au/enduringvalue/enduring_value/index.html)

Various Australian and International Codes of Practice and guidance documents regarding the management of cyanide in mining are available. This includes guidance documents described below available from the DRET website (Environment Australia, 1998, 1999e, 2002; EPA 1995a,b), NTDME (1998) and other material produced by Australian states and territories, guidance published by the Minerals Council of Australia (e.g. MCA, 1997), the International Cyanide Management Code for the Manufacture, Transport and Use of Cyanide in the Production of Gold (ICMI, 2006), and publications by the US EPA and other overseas agencies.

11.12.2Sustainable development program for the mining industry

The Australian Government Department of Resources, Energy and Tourism's (DRET) Best Practice Environmental Management in the Mining Industry (Sustainable Minerals) series originally produced by DEWHA (Environment Australia, 1998, 1999e, 2002; EPA 1995a,b) provided a range of best practice guidance on environmental management in mining. This included a booklet on Cyanide Management (Environment Australia, 1998), which provides guidance for:

- establishing a cyanide management strategy as part of environmental management;
- implementing initial and refresher cyanide management training for managers, workers and contractors;
- establishing well-defined responsibilities for individuals with clear chains of command and effective lines of communication within the mine workforce;
- instituting safe procedures for cyanide handling, governing transport, storage, containment, use and disposal;
- integrating a mine's cyanide and water management plans;
- identifying and implementing appropriate options for reusing, recycling and disposing of residual cyanide from plant operations;
- conducting regular cyanide audits and revising cyanide management procedures;
- developing a cyanide occupational and natural environment monitoring program, and supporting this with a sound sampling, analysis and reporting protocol; and
- establishing carefully considered and regularly practiced emergency procedures.

This series is being replaced over time by DRET under the Leading Practice Sustainable Development Program for the Mining Industry, and the Cyanide Management document has been published recently (DRET, 2008) – see also DITR (2006, 2007).

11.12.3Wildlife management at mining operations

Following bird deaths at the TSF at the Northparkes mine in 1995 due to cyanide poisoning (Sinclair et al., 1997), and a Senate referral of a preliminary inquiry relating to 'the need for governments to work together with industry to avoid the death of wildlife, risk to groundwater and destruction of native vegetation caused by the toxic tailings dams in the gold mining industry' (Hansard, 1995), the Northern Territory Department of Mines and Energy (NTDME) published the *Best practice guidelines for reducing impacts of tailings storage facilities on avian wildlife in the Northern Territory of Australia* (NTDME, 1998), following a detailed investigation of bird utilisation of TSFs in the Northern Territory (Donato, 1999).

Internationally, cyanide management and cyanide-related wildlife incidents have also received considerable attention in recent years. The ICMC and associated guidance (ICMI, 2006) are international mining initiatives that provide guidance on protecting wildlife from exposure to cyanide at mine sites. The ICMC proposes to include a system of auditing of individual participating mine sites that use cyanide, which will incorporate wildlife protection monitoring.

11.12.4International Cyanide Management Code (ICMC)

The *International cyanide management code for the manufacture, transport, and use of cyanide in the production of gold* (ICMI, 2006) was developed by a multi-stakeholder Steering Committee under the guidance of the United Nations Environmental Program (UNEP) and the International Council on Metals and the Environment (ICME). The main impetus for the original workshop to discuss developing this Code was the incident at Baia Mare, Romania on January 30, 2000 (Balkau, 2000; Section 5.4.3). Other parties to the ICMC included the Gold Institute, the International Finance Corporation (IFC) and the Worldwide Fund (WWF) for Nature. Information about the scope and nature of the Code from the ICMC website (http://www.cyanidecode.org/about_code.php) includes the following:

> The Code is a voluntary initiative for the gold mining industry and the producers and transporters of the cyanide used in gold mining. It is intended to complement an operation's existing regulatory requirements. Compliance with the rules, regulations and laws of the applicable political jurisdiction is necessary; this Code is not intended to contravene such laws.
>
> The Code focuses exclusively on the safe management of cyanide that is produced, transported and used for the recovery of gold, and on cyanidation mill tailings and leach solutions. The Code originally was developed for gold mining operations, and addresses production, transport, storage, and use of cyanide and the decommissioning of cyanide facilities. It also includes requirements related to financial assurance, accident prevention, emergency response, training, public reporting, stakeholder involvement and verification procedures. Cyanide producers and transporters are subject to the applicable portions of the Code identified in their respective Verification Protocols.

It does not address all safety or environmental activities that may be present at gold mining operations such as the design and construction of tailings impoundments or long-term closure and rehabilitation of mining operations.

As it applies to gold mining operations, the Code is comprised of two major elements. The Principles broadly state commitments that signatories make to manage cyanide in a responsible manner. Standards of Practice follow each Principle, identifying the performance goals and objectives that must be met to comply with the Principle. The Principles and Practices applicable to cyanide production and transportation operations are included in their respective Verification Protocols. Operations are certified as being in compliance with the Code upon an independent third-party audit verifying that they meet the Standards of Practice, Production Practice or Transport Practice.

The programs and procedures identified by the Code's Principles and Standards of Practice and in the Cyanide Production and Transportation Verification Protocols for the management of cyanide can be developed separately from other programs, or they can be integrated into a site's overall safety, health and environmental management programs. Since operations typically do not have direct control over all phases of cyanide production, transport or handling, gold mines that are undergoing Verification Audits for certification under the Code will need to require that other entities involved in these activities and that are not themselves Code signatories commit to and demonstrate that they adhere to the Code's Principles and meet its Standards of Practice for these activities.

Thus the primary objective of the ICMC is to improve the management of cyanide used in gold mining world wide and assist in the protection of human health and the reduction of environmental impacts. As the gold mining industry is the predominant user of sodium cyanide in Australia, the ICMC is of particular relevance to the sodium cyanide industry in Australia. The ICMC is a voluntary program for the industry. While not all gold mining operations will attain or seek full code compliance, the code establishes current industry best practice. It is an excellent initiative to lift international standards and demonstrate the environmental commitment of an operator, complementing state/territory legislative requirements.

Mining companies that adopt the ICMC nominate the operations that use cyanide to recover gold that they wish to have certified. These must be audited by an independent third party to determine the status of Code implementation. Those operations that meet the ICMC requirements can be certified. A unique trademark symbol can then be utilised by the certified operation, which is intended to demonstrate environmental responsibility. Audit reports are made public to inform stakeholders of the status of cyanide management practices at the certified operation. Current signatories to the code and audit reports on certified operations are listed on the ICMC website (http://www.cyanidecode.org/signatorycompanies.php). Mines, transport operations and production facilities in Australia have been among the earliest formal adopters of the ICMC worldwide.

The MCA advises that about 65% of the gold produced in Australia is now produced by mines engaged in the Code process. In Australia, a total of 14 gold operation sites (five companies) are listed as signatories and 11 sites had been fully certified as of 27 November 2009, plus both manufacturers and one transporter (MCA, 2009 – updated via the ICMC website). Comparison with the total number of gold mines operating in Australia (Section 4.4.2) suggests that while large producers are evidently involved,

many mines are not yet engaged formally in this voluntary ICMC process. Progress in adoption of the ICMC is occurring, and the ICMC provides valuable guidance and a formal means of evaluating the adequacy of environmental protection measures at individual sites.

However, existing voluntary measures are not adequate to ensure environmental safety for all mines where sodium cyanide is used in Australia. Therefore, additional measures are warranted.

11.13 Practical measures to protect wildlife at gold mines

11.13.1 Limiting access and the use of hazing techniques

Various strategies can be used to minimise exposure of wildlife to tailings and other process and waste solutions in TSFs and associated infrastructure as a means of reducing risks to wildlife health from cyanide in those solutions. However, there are various considerations in determining appropriate measures at a particular site, and there are difficulties with some approaches which may limit their usefulness or practicability, as discussed below.

Most TSFs in Australia are not fenced or netted off to exclude wildlife. Netting an entire TSF would generally be impracticable because of their large size (Section 4.4.2), but netting of decant ponds is done in some cases (e.g. where WAD CN levels are known to be high), and netting of other limited areas may be practicable (e.g. a netting structure is used to protect the supernatant area on the TSF at Gidji Roaster in WA: Environment Australia, 1998; KCGM, 2005). Similarly, the strategies of covering ponds or floating a dense bed of plastic, hollow balls on the surface to reduce access by birds may not be feasible for large areas, or where high evaporation rates are desirable (Read, 1999).

Read (1999) also observed that because many long-distance waterfowl movements occurred at night, any non-illuminated structures, such as cables or netting, are unlikely to be efficient deterrents and may in fact themselves cause injuries. Hence these additional measures may also be needed (e.g. additional flagging tape and a strobe light have been installed to deter birds from landing on the bird netting at night at Gidji Roaster: KCGM, 2005).

Most wildlife hazing techniques practiced at mine sites (e.g. loud noises from propane gas guns, shotguns, bird whalers, and music, movement from coloured streamers, flags, flying kites, flagging tape, fishing line) are ineffective at deterring wildlife in the long term or are impractical, and are also ineffective once wildlife are exposed to the toxic solutions (Donato, 2002; USFWS, 2000; Eisler et al., 1999; Ramirez, 1999; Read, 1999; Donato, 1999; Donato et al., 2007). A major difficulty is the sheer size of the area that needs to be protected. While these techniques may have some value for small areas such as a decant dam, their impact is much too localised for them to work on a TSF that may be equivalent to several football fields or more in size (Donato, pers. comm., 2006).

Donato (pers. comm., 2006) explains that many of the hazing techniques described, although intended as preventative measures, have traditionally been implemented as contingencies in much of the industry. Thus, an increase in hazing effort is usually triggered by incidences. Subsequent studies suggest that some hazing techniques may have increased effectiveness as a proactive measure when combined with a reduction

in suitable habitat area, thereby reducing the spatial scale over which hazing needs to be effective.

Species differences in bird behaviour

Read (1999) noted that in the acid liquid evaporation ponds at Olympic Dam, the very low pH (< 1.5) meant that waterfowl or other wildlife did not drink from the ponds, but waterfowl were still attracted to them and they accounted for the majority of wildlife deaths. Research reported in this paper provides some interesting insights into the difficulties likely to be encountered in deterring waterfowl from gold processing facility TSFs, where the situation may be even more difficult because a wider range of species may be present, as except possibly when the water used is saline/hypersaline, birds are not averse to drinking TSF water.

Ducks, coots and grebes habitually retreat to water when threatened by predators (e.g. wedge-tailed and little eagles and peregrine falcon, which had been observed taking waterfowl disturbed from the Olympic Dam ponds during the day), hence even if the waterfowl were coerced to leave a toxic waterbody during the day, they would often retreat to the safety of the water after a short flight. Read (1999) therefore proposed that a deterrent to waterfowl should operate at night. Tests with various sound and light deterrents at night indicated that a bright, focused searchlight beam held close to the water was most effective at scaring the majority of waterbirds from the ponds. It was considered that this light should be intermittent, as continuous light may attract birds, or insects which may themselves attract birds, and to avoid habituation. A floating, solar-powered, rotating beacon was found to reduce total waterfowl abundance by more than 90% during trials, but with some interspecific differences, such as grebes, which dived under the water when the searchlight was activated, or masked lapwings, black-fronted dotterels and red-necked avocets, which were neither attracted nor deterred. These differences illustrate the need for multiple measures to deter all species. For example, Read (1999) suggested that an underwater sonic alarm could be added to deter grebes.

11.13.2 Reducing the attractiveness of facilities to wildlife

The above and various other measures are described in publications or papers such as Adams et al.. (2008b), Donato (1999, 2002, 2005), Donato et al. (2004, 2007), Donato and Smith (2007), Smith and Donato (2007); NTDME (1998), and Read (1999). They need to be considered on a site specific basis and for some measures, with a knowledge of the species present. Read (1999) indicated the need for a multifaceted site-specific management approach to deter or prevent birds from accessing areas containing cyanide residues and listed the following additional measures which can be considered together with those discussed above:

- protecting or even enhancing alternative waterbodies to attract waterfowl away from toxic ponds (but not to the extent that numbers at the TSF/pond site are exacerbated);
- keeping toxic dams small, as smaller dams attract fewer birds than larger storages;
- increasing human activity and noise levels near ponds to discourage waterfowl (but Read et al. (2000) comment that species differ in the extent to which human activity discourages them);

- rendering toxic dams less attractive to waterfowl than decoy waterbodies, such as engineering steep, lined banks to discourage roosting.

Adams et al.. (2008b), Donato (1999, 2002, 2005), Donato et al. (2004, 2007), Donato and Smith (2007), Smith and Donato (2007); and NTDME (1998) elaborate on such strategies and make various other suggestions on managing and designing TSFs so they are not attractive as refuges or for nesting or settling to feed or drink. These include avoiding the formation of islands (favoured roosting sites) and pools against the walls (habitat for waders and drinking access for granivorous birds), placing decant ponds near mining infrastructure, lining dam or pond walls with black plastic, using steep sides (so birds feel unsafe because their sightlines are impaired), removing vegetation so that no nearby roosting trees are available, and removing dead animals promptly so they do not attract predators. The area and duration of ponding of water to which birds might be attracted and/or exposed can be minimised by strategies such as the use of thickened slurry or paste discharge to minimise the volume of water discharged with tailings, actively decanting supernatant water to netted or screened ponds, use of a Central Tailings Discharge design, using multiple cells and limiting cell size in paddock facilities, and managing discharge from multiple spigots (see Section 4.4.2). It is clear that measures which may be practicable and effective at one site may not be at another, and measures need to be compatible with modern large scale operations.

There are aspects peculiar to certain situations that may also be relevant, e.g. it has been thoroughly demonstrated that a higher concentration of WAD CN in hypersaline tailings water can be tolerated because birds do not drink it, together with other aspects of hypersaline sites that minimise food availability and make the habitat unattractive (Section 9.9.2). Salinity may provide partial protection, but cannot be considered reliable. Clearly, if hypersalinity/salinity is relied upon as a means of minimising exposure, it is important to monitor waters for salinity levels to ensure they remain hypersaline. Tailings pH and Cu levels affect the rate of volatilisation of HCN (Section 6.6.4). Adams et al.. (2008b) made specific recommendations (below) for monitoring and managing the sites examined in their study which would need to be adapted as necessary to suit other sites:

1. A toxicity threshold will exist for every system, but no such threshold was determined at any of the sites studied, because no wildlife deaths were recorded. It is therefore considered that these sites are benign to wildlife at the operating parameters experienced during the course of this study. Critical operating parameters were specifically determined for each site for WAD cyanide at spigot and supernatant; soluble copper at spigot and supernatant; salinity; and pH value.

2. Structured monitoring regimes should be in place for each site for the above chemical parameters and wildlife.

3. Minimise infrastructure in the vicinity of cyanide-bearing habitats.

4. Suppress all vegetation growth and subsequent regrowth within the TSF.

5. Cover open seepage trenches with gravel to limit food availability within the TSF.

Eisler et al. (1999) indicated that some chemical repellents when added to dump leachate pond water showed promise at reducing consumption of leachate water when tested on European starlings (citing *Clark and Shah 1993). However, this approach appears not to have been taken up, possibly because it is not successful with other species and/or because of the costs of maintaining an adequate concentration of the repellent.

11.13.3 Using a combined approach of controlling CN concentrations and minimising exposure

As discussed above as well as Sections 7.3.1 and 10.2.2, control of the concentration of WAD CN present in tailings waters is not the only means available for mitigating the risk presented by TSFs and associated facilities. Other measures which could be taken include hazing techniques to actively deter wildlife, reducing or preventing access by birds and mammals to the contaminated water, and designing and operating facilities in such a way that they do not attract wildlife. The latter is particularly relevant to flying species (birds and bats), though some of the measures listed below would also reduce attractiveness to terrestrial animals. For terrestrial animals, fencing to prevent access is likely to be a practicable and effective option that also reduces the risk of animals being harmed by becoming bogged.

Wildlife deterrent or hazing techniques such as loud noises from scare guns, lights and flagging are ineffective and/or impractical at deterring wildlife in the long term because of habituation, species differences in response, the sheer size of the areas that may need protection, as well as difficulties gaining access close to critical areas in a large TSF. However, hazing techniques may have increased effectiveness as a proactive measure when combined with other measures, such as a reduction in suitable habitat area. Hazing techniques may also be of value as short term reactive techniques in response to monitoring. The use of chemical repellents has been considered, but has evidently been found insufficiently effective and/or impracticable.

Measures to inhibit or prevent access include fencing to keep out emus, livestock and marsupials, netting ponded areas or covering them with floating balls or other means to reduce access or exclude birds and bats, and minimising or avoiding pond formation in the first place. Practical considerations and the scale of the area needing protection determine what may be effective and affordable, e.g. netting of decant ponds may be practicable, whereas netting of an entire 50 ha or larger TSF would not, and reduced evaporation may be a problem if ponds are covered or enclosed.

Strategies in managing and designing TSFs so they are not attractive to wildlife (specifically birds) as refuges, for nesting or for settling to feed or drink include:

- minimising the area and duration of ponding of water to which animals might be attracted or exposed;
- avoiding the formation of islands (favoured roosting sites) and pools against the walls (habitat for waders and drinking access for granivorous birds);
- placing decant ponds near mining infrastructure;
- lining dam or pond walls with black plastic;
- using steep sides (so birds feel unsafe because their sightlines are impaired);
- removing vegetation so that no nearby roosting trees or refuges are available; and

- removing dead animals promptly so they do not attract predators.

The use of thickened slurry or paste discharge minimises the volume of water discharged with tailings so that less ponding or flowing water occurs on the TSF. Appropriate design and operation (e.g. a Central Tailings Discharge, or multiple cells and controlled discharge from multiple spigots in paddock facilities) can enable the area of surface water forming to be restricted and controlled, and/or water to be directed to smaller, deeper ponds where it can be netted or screened. A complementary measure to reducing the attractiveness of areas where cyanide presents a risk to wildlife is to provide alternative safe areas to attract birds away from toxic ponds, but care may be needed so numbers attracted to the overall area are not exacerbated.

Concentration control is not a feasible option for heap leach facilities, as the solutions applied must contain effective levels to recover the gold. For tank leach facilities (the predominant situation in Australia), various processes to detoxify or recover cyanide in tailings streams are available (Section 0). These enable mines to reduce WAD CN concentrations to levels comparable to those specified by the ICMC (50 mg WAD CN/L) or lower levels currently specified at some sites (e.g. 20-30 mg WAD CN/L at Lake Cowal in NSW). Some of these techniques also enable concentrations to be reduced to very low levels to protect downstream aquatic environments, e.g. ~1 mg WAD CN/L in Tasmania. However, a requirement to achieve this level of CN destruction in tailings discharge to protect birds and mammals appears unlikely to be generally practicable at present. Field observations indicate that few mortalities are likely to occur provided the WAD CN concentration remains satisfactorily below 50 mg/L, but some lethal and sublethal impacts may still be expected based on studies conducted with birds exposed to water containing cyanide in a fashion reasonably representative of field exposure (Section 10.2.3). The environmental implications presented by the volumes of various reagents that would be required to drive WAD CN concentrations to low levels and the relatively high concentrations of cyanide degradation products (e.g. thiocyanate) and reagent products that could be produced may also need to be considered if such extensive treatment were required. Depending on the ore characteristics and method used, destroying remaining WAD CN may also become more difficult with decreasing concentration (Schulz, pers. comm. 2006).

For these reasons, concentration control is not likely to be a practicable mitigation measure at the concentrations that would be needed to assure safety to wildlife if it were the only measure used. This has been recognised by the industry in development of the ICMC, and suitable guidance information has been prepared, as discussed in Section 7.3.1 and above. From evaluation of the available information, it is concluded that a combination of site specific exposure limitation measures, including access limitation, habitat modification and the use of deterrents should be applied, together with a practicable concentration-based approach to help minimise the risk to wildlife where exposure does occur. As part of such an approach, suitable monitoring and response programs are essential, including monitoring of cyanide concentrations in water accessible to wildlife, monitoring to ensure netting or other exclusion methods remain sound, monitoring for the presence of wildlife and impacts on wildlife, and monitoring to look for the development of habitat attractive to wildlife (the emphasis being on habitats attractive to birds) on or near TSFs. Active measures could then be applied, including hazing to deter birds while a hazard is present, and correction of conditions creating higher concentrations of cyanide. This risk control framework and supporting information is discussed in much greater depth in the recommendations from this assessment.

11.14 Summary of current risk management

Nationally and internationally, there is a large body of information and risk management legislation and guidance documentation in existence that comprehensively covers the lifecycle of sodium cyanide from manufacture, storage, transportation, packaging, labelling, procurement, emergency response and use, including cyanide management at mining operations (e.g. Best Practice guidance now provided by the Australian Government Department of Industry, Tourism and Resources). The National Pollutant Inventory manages a database of information on cyanide emissions to the Australian environment. Manufacturing and mining industry programs have been established to promote the safe use of sodium cyanide, including the Responsible Care® program.

Each state and territory has legislation pertaining to the protection of the environment, waste management, contaminated land, and wildlife protection, supported by Commonwealth legislation, international treaties, and policies.

Environmental media quality assessment guidelines (trigger values) have been published for cyanide in surface waters for the protection of aquatic ecosystems. There is uncertainty regarding the acceptable concentration of cyanide in solutions that are accessible to wildlife. At least one state (NSW) has implemented concentration limits for WAD cyanide to minimise wildlife deaths due to cyanide at mine sites.

Australia does not have sediment or soil quality guidelines for cyanide for the protection of sediment-dwelling or soil-dwelling organisms, respectively.

Recent environment protection initiatives by the mining sector and government include the ICMC (ICMI, 2006), and various best practice guidelines for cyanide management and wildlife protection (NTDME, 1998; Environment Australia, 1998). These are expected to have a major influence on sodium cyanide management and environmental protection by the mining sector in Australia.

It is concluded that existing legislative and voluntary control measures for the manufacture and storage of NaCN are adequate to protect the environment, but that the adequacy of measures to protect the environment during transport should be monitored by the relevant state and territory authorities, particularly when transport incidents involving cyanide occur. The Northern Territory Government initiated a review of the regulatory regime for dangerous goods transport in the Northern Territory as a result of concerns arising from a transport accident in 2007 involving a spill of NaCN. The review report is not yet a public document, but NT WorkSafe advise that the key recommendations from that review were being actioned, including the adoption of the 7th Edition of the Australian Dangerous Goods Code (ADG7) and improvements to coordination across Government agencies, both for compliance monitoring arrangements and for emergency response procedures. NT WorkSafe also indicate that the principal transporters of sodium cyanide in Australia no longer use triple road-trains for the transport of solid sodium cyanide in containers and that configurations now used would be considered lower risk than the configuration used at the time of the 2007 accident.

As noted in Section 10, potential risks to the environment resulting from use of sodium cyanide in gold mining are high, particularly in relation to birds and terrestrial mammals which may imbibe contaminated water. It is concluded that existing legislation and voluntary measures are adequate to protect groundwater and surface water from planned or unplanned releases, and that the risk to the environment from release of HCN to the atmosphere at these facilities is acceptable. However, it is concluded that existing legislation and voluntary measures for the protection of wildlife at gold mines and associated facilities using NaCN are inadequate, particularly as engagement in the ICMC is voluntary. It is proposed that risks could be mitigated by a combination of concentration controls and exposure minimisation measures, as discussed in Section 11.13 and recommended in guidance for the ICMC. The proposed risk control framework is discussed in much greater depth in the recommendations. The recommendations also address wildlife protection at heap leach operations, where concentration controls are not appropriate, and the need for suitable habitat, wildlife and cyanide concentration monitoring, response and reporting programs at both tank leach and heap leach operations. If WAD CN concentration exceeds 10 mg/L, similar standards should apply to wildlife protection at tailings storage facilities at base metal mines using NaCN for flotation.

It is concluded that existing legislative and voluntary control measures for other uses of sodium cyanide are adequate to protect the environment.

12. Conclusions

12.1 Use in Australia

Australia is a significant producer, user and exporter of sodium cyanide, with annual production of approximately 100 000 tonnes, compared to around 500 000 tonnes worldwide. As is the case worldwide, sodium cyanide is primarily used in Australia by the gold mining industry, where it is used in the cyanidation process to extract gold from ore. Consequently, greatest use has been in Western Australia (WA), where annual gold production is greater than all the other states and territories. A lesser amount of sodium cyanide is used in Australia for ore flotation and in the electroplating, metal cleaning and metal hardening industries.

As well as a difference in the scale of use, use in mining presents the greatest risk of environmental exposure through transfer of waste to tailings storage facilities or through heap leach operations. In contrast, electroplating and metallurgical processes using cyanide are generally closed systems, where residues in waste can be contained and treated prior to disposal. Release is then to the sewer or to landfills, where further biodegradation of the low level remaining is expected. This risk assessment has therefore focused on gold mining use, as existing management procedures minimise exposure with industrial uses.

12.2 Environmental exposure

Cyanide releases from sodium cyanide manufacturing facilities are unlikely to pose a significant adverse risk to the environment because the volume of HCN released in manufacture is minimised by recovery and by treating effluent so that any cyanide residues are destroyed.

Large amounts of sodium cyanide are transported from the manufacturing sites to mines by rail and road transport. It may be argued that transportation of bulk liquefied sodium cyanide by road and rail poses a significantly greater risk to the environment and human health than the solid form due to the potential for spillage and release in the event of a transportation incident. The liquefied form would be more mobile and difficult to contain before impacts occur, and there are likely to be greater difficulties for emergency response organisations undertaking clean-up procedures. However, there are also advantages in using the liquid form, particularly in Western Australia, due to the proximity of many mines to the Kwinana factory, and difficulties where hypersaline groundwater is used. In Western Australia, extensive community consultation has been undertaken in planning transport of sodium cyanide by rail and road, together with preparation and training with emergency response agencies along transport routes. Relatively little liquid transport occurs from the Gladstone factory in Queensland.

Available data on incidents where unplanned release of material containing cyanide has occurred are often lacking in detail, and reports are not necessarily reliable. Consideration of such data for incidents that have occurred in Australia and around the world indicates the nature of incidents that can occur, the potential for serious impacts on downstream aquatic areas or other wildlife, and the necessity for measures to

prevent them occurring. These include spillage or leaks during transport, or leaks, spills, seepage, overflows and failure of storage structures and associated facilities.

Information on the relatively few transport incidents with NaCN which have occurred during transport of the substance in Australia indicate that where solid NaCN has been spilt, it has been recovered and/or contaminated soil and water collected and disposed of appropriately. Intensive clean-up operations have been required for two accidents, both of which involved transport in CIBCs. Rehabilitation of the site was conducted at the recent Northern Territory (NT) truck accident site, where material spilt into a pond and contaminated soil and water were removed. Release of NaCN in solution occurred in an incident in the Tanami Desert in the NT, but this involved release of liquid remaining in the StoL container used on the return trip after delivery, and was not as a result of overturn or fracture of the StoL container used. Information for occasions where isotainers containing NaCN in solution have been involved in accidents indicates that the vessels have retained their integrity, e.g. with only a minor amount of release occurring through a pressure release valve when a truck overturned. Thus the existing legislative and voluntary control measures in Australia have generally assisted in preventing significant adverse effects on the environment from transport incidents. Additional measures have been taken to reduce the risk of an incident such as that which occurred in the Tanami Desert from recurring.

However, concerns arising from a NaCN spill resulting from a truck accident in Northern Territory in 2007 led to the Nothern Territory Government initiating a review of the regulatory regime applying to dangerous goods transport in the Northern Territory. Key recommendations from that review included the adoption of the 7th Edition of the Australian Dangerous Goods Code (ADG7) and improvements to coordination across Government agencies, both for compliance monitoring arrangements and for emergency response procedures. All jurisdictions, including the NT, have either legislated already or aim to legislate by the end of 2009 for the adoption of ADG7. Improvements in the transport configurations used by the principal transporters of sodium cyanide in Australia have also been made. However, the incident indicates a need for the relevant authorities to monitor the adequacy of legislation and voluntary measures used in the transport of sodium cyanide.

12.3 Environmental risk assessment

Cyanide has very high acute toxicity to aquatic and terrestrial animals and is also toxic to plants and certain micro-organisms. It is toxic by various routes of exposure and may also have harmful sublethal or chronic toxicity effects. For this risk assessment, exposure via drinking water was considered to be the predominant route for birds and animals at TSFs, with the contribution to toxicity from dermal absorption and inhalation of HCN considered to be relatively minor.

However, for birds, the available drinking water studies were not considered to be of an acceptable standard for determining endpoints to be used in risk assessment, and suitable dietary studies with birds were also lacking. For this reason, Toxicity Reference Values (TRVs) for assessment of the risk to birds were based on acute toxicity studies. Endpoints (LD50s) for seven bird species were available and that for the most sensitive species was used (mallard ducks, 1.4 mg CN/kg bodyweight), with an assessment factor of 10. There is some support for this value in studies of sublethal toxicity and effects on biochemistry in birds. The resulting TRV of 0.14 was related to allometric drinking water consumption estimates for a range of bird bodyweights, at a

range of possible WAD CN concentrations in TSF discharge. This risk assessment indicated that to assure protection of sensitive avian species from acute mortality and from potentially harmful sublethal effects that might lead to delayed mortality (such as greater susceptibility to predators or reduced flying ability of migratory birds), the concentration of WAD CN in water available to birds would need to be ≤1 mg/L.

This assessment is highly conservative, as it is based on the assumption that birds consume all their day's water in a single dose. However, differences in drinking behaviour between species make it difficult to extrapolate toxicity results from one species to another. Thus, while waterbirds take several drinks per day and may be able to detoxify a dose of cyanide they have taken in before their next drink, birds with different drinking behaviour may consume a toxic dose within a short period. This may also be the case for bats.

Information on wildlife impacts confirms that major events involving large numbers of bird deaths in a short period - or significant numbers of ongoing deaths - have occurred at heap leach and tailings storage facilities in the USA, as well as at tailing storage facilities in Australia. Information from these reports and from very comprehensive and detailed observations of bird visitation, behaviour and impacts at Australian TSFs gives a good indication of the species of birds and other animals that visit, the types of habitat that are attractive, possible measures to minimise exposure through minimising water areas or making them inaccessible, and shows the relative inadequacies and benefits of active deterrent measures such as scare guns and flashing lights. The Australian evaluations also indicated the difficulties involved in monitoring for wildlife impacts and inadequacies in wildlife monitoring procedures which were common practice, and guidance has been developed to enable more reliable monitoring in the future.

It is concluded from field observation data from a range of sources including comprehensive scientific observations in TSFs in the Northern Territory and Western Australia that significant wildlife mortalities are likely if wildlife are exposed to WAD CN concentrations exceeding 50 mg/L, with the exception of sites where water is hypersaline and animals do not consume the cyanide-containing waters, but that significant wildlife mortalities are unlikely to occur at WAD CN concentrations below 50 mg/L. At concentrations below 50 mg WD CN/L laboratory data indicate that some mortalities may still occur, but few deaths conclusively due to cyanide have been observed at <50 mg WAD CN/L in field studies. Laboratory studies also indicate that sublethal effects may develop, potentially leading to mortality due to other causes (e.g. greater predator susceptibility), but there are no data to confirm this in the field.

Consideration of these possibilities is greatly complicated by differences in bird behaviour, site differences and the actual toxic effects exhibited. Observations indicate that birds do not become averse to drinking cyanide-contaminated mine waste water and may take further drinks even after awakening from cyanide stupefaction. It has also been proven that aversion to drinking hypersaline water does help protect birds from exposure to toxic cyanide concentrations.

The 1 mg WAD CN/L target based on a risk quotient approach is much lower than the protective level of 50 mg WAD CN/L used by the ICMC and is unlikely to be considered generally practicable with present technology, or justified based on other available evidence and the difficulty of extrapolating from the acute toxicity studies. Available field data does indicate that above 50 mg WAD CN/L significant wildlife mortalities are likely to be observed if animals (in particular birds and bats) are

exposed. While available data indicate that few mortalities are likely if concentrations remain below 50 mg WAD CN/L, it cannot be concluded that this level is totally safe.

However, reduction of cyanide residues to relatively low levels may be required in some situations to protect downstream aquatic areas. The use of existing technology to recover cyanide for re-use may also be feasible in some situations. However, because of the uncertainties regarding what level of WAD CN is safe and the impracticability of a general 1 mg WAD CN/L limit, it is concluded that a benchmark concentration approach for mitigating the risk to birds is not satisfactory unless supported by other measures. A risk management framework combining concentration controls with measures to minimise exposure and ongoing monitoring and response programs is therefore proposed for the protection of wildlife at TSFs. This is outlined in detail in the recommendations section.

A similar conclusion can be reached for protecting mammals, where again the TRV was based on acute toxicity data. However, it is also noted that a high percentage of reported mammal deaths at TSFs were thought due to the animal becoming bogged in the dam, rather than cyanosis. Hence while a combination of measures is again thought appropriate, measures such as fencing to prevent access are likely to be preferable. Prevention of access to birds or mammals is essential at heap leach operations, where reduction of concentrations is not a feasible approach.

While TSFs, decant ponds, and associated infrastructure containing cyanide solutions do not constitute natural waters, risk assessment confirms the potential for cyanide-contaminated water to harm aquatic life if waste were released into downstream waters. Existing standards and controls on TSF design and operation are considered adequate to minimise the risk of such aquatic exposure occurring, with managed release into receiving waters based on the ANZECC/ARMCANZ (2000a) guidelines.

Impacts on surrounding vegetation due to cyanide contamination are possible, but other factors are also likely to contribute to impacts arising through seepage and rising groundwater (e.g. salinity). Site rehabilitation plans ultimately address the restoration of vegetation on and near TSFs or other structures.

12.4 Current risk management

As noted above, most of the sodium cyanide used in Australia is used in tank leach facilities at gold mine sites, with cyanide compounds and products then disposed of with tailings into TSFs managed by mine operators. TSFs are mostly designed to be permanent tailings confinement structures. Heap leach operations also use cyanide solutions, and treated ore heaps and associated infrastructure also provide potential sources of seepage and groundwater contamination. The cyanide deposited in tailings and ore piles may remain for a period of time, probably beyond the lifespan of the mine. There it may undergo a range of reactions to form stable metal-cyanide complexes, less stable simple cyanide compounds, and degradation products such as cyanate, thiocyanate and nitrogenous compounds (e.g. ammonia, nitrite, nitrate). A proportion of cyanide will also volatilise to the atmosphere as HCN. It is established that TSFs and treated ore heaps will remain a waste repository requiring rehabilitation/revegetation and long term management. Guidance documents on mine site rehabilitation and long term management are available for this purpose.

Seepage of water containing cyanide products to groundwater may potentially occur, particularly below TSFs, heap leach pads and associated facilities that are unlined,

have poorly designed and constructed liners or where liner integrity is violated. In general, the presence of engineering controls (e.g. liner, under-drainage, groundwater recovery system) will reduce the risk of migration of contaminants in seepage. The National Water Quality Management Strategy (NWQMS) indicates that site-specific factors, local groundwater conditions and factors other than environmental considerations determine the level of protection and consequently the level of risk management (e.g. engineering controls) required to protect these beneficial uses and ecological values. Available data show that actively managed monitoring and recovery programs are crucial to effective risk management, enabling on-going evaluation of the effectiveness of existing risk management strategies or the potential requirement to establish additional risk management measures.

Groundwater monitoring of selected analytes is a requirement of most state and territory agencies, with cyanide and related substances only a part of these requirements. In addition to free CN and WAD CN, monitoring of total CN may be appropriate to detect movement of iron cyanides. Breakdown or reaction products such as thiocyanate should also be monitored where conditions may lead to significant concentrations developing. The location of monitoring should be selected carefully to ensure that movement in various directions (not necessarily only down gradients) is detected promptly.

Limited information available on use for ore flotation suggests that in Australia the quantities used at individual sites are low, and that in contrast to gold beneficiation, the cyanide used is consumed in the process, without the large excess of free cyanide required for gold ore beneficiation. Information suggests that the forms of cyanide present in tailings are likely to be low in solubility and bioavailability, and significant release of HCN to the atmosphere may occur where process streams become acidic after the point sodium cyanide is used. However, similar standards should apply to base metal mine TSFs if cyanide is present.

A literature source (Korte et al., 2000) has proposed that the formation of open ponds should be avoided with the gold cyanidation process because of the large amount of HCN evaporating yearly from their surfaces, which they considered could accumulate in the atmosphere and may add to the contribution of greenhouse gases, such as CO_2 and methane. However, HCN is not currently listed among other gases in the atmosphere which are considered to have significant Global Warming Potential, and is not a significant source of other gases which are considered to be greenhouse gases. HCN is also not considered likely to act significantly either directly or indirectly as an ozone depletor. Modelling of the behaviour of HCN in the atmosphere based on measured concentrations and other information also indicates that the contribution of gold mine sources to global release is minor compared to the major source, biomass burning. In addition, modelling indicates that longterm accumulation is limited by its atmospheric lifetime of ~5 months. For these reasons, measures to reduce HCN release are not warranted.

Due to the hazard of cyanide to human health and the environment, relatively stringent regulations and management strategies for sodium cyanide are established in Australia. The manufacturing, procurement, industrial use, storage, handling, transportation and discharge of sodium cyanide or its residues to the environment are controlled by state and territory regulations pertaining to major hazard facilities, dangerous goods, safety and emergency procedures, emissions, waste management and protection of the environment that are enforced by means of a system of conditional permits, licenses and warrants. In addition, the major industry groups, such as sodium cyanide chemical

manufacturers and mining companies, have established self-regulating programs for safety and environmental protection. These include environmental management systems (EMS), quality assurance/quality control (QA/QC) systems, safety and environmental management (SEM) systems, and Standards and Codes of Practice (e.g. Responsible Care® Program, International Cyanide Management Code). There is a general philosophy of continuous improvement within these industries. Furthermore, Australia has water quality guidelines for the protection of aquatic ecosystems for use in evaluating risks to aquatic ecosystems from aquatic releases. Thus there are various strategies and programs in existence to manage the risks to the environment from sodium cyanide.

Despite current strategies and programs for sodium cyanide, risks to wildlife are still unacceptable in some circumstances. Additional risk mitigation measures to minimise these risks are proposed (see Recommendations).

Appendix 1 -
Methods for analysing cyanide

Table A1-1 Summary of analytical methods for cyanide.

Analyte	Methods of Analysis	Comments
Free Cyanide	Silver nitrate ($AgNO_3$) titration (typically with rhodanine indicator)	Measures cyanide ion (CN^-) and weakly bound metal complexes (e.g. complexes of Zn and some of Cu). In most process solutions, this method will not measure the HCN species (Staunton et al., 2003). Used for process solutions primarily >1 mg/L. Lowest quantitation limit (LQL) of 1 mg/L.
	Ion selective electrode. APHA 4500-CN F (APHA, 1998). USEPA Method 9213 (USEPA, 1996c)	Close to free cyanide.
	ASTM Method D4282 (ASTM, 2002). Micro diffusion of HCN from static sample into NaOH trap. The cyanide concentration is determined colorimetrically using a spectrophotometer.	Close to free cyanide. In this method, free cyanide refers to CN^- and HCN and/or readily dissociable metal-cyanide complexes that yield, at pH 6 and room temperature, HCN.
Weakly Dissociable Inorganic Cyanide Forms	Weak Acid Dissociable (WAD) Cyanide: Manual distillation (pH 4.5-6.0) and potentiometric or colorimetric finish. ISO Method 6703/2 (ISO, 1984a) DIN 38405/13 (DIN, 1988); APHA 4500-CN I (APHA, 1998); ASTM D2036-98C (ASTM, 1998). APHA (1998) propose an additional method for analysis of WAD cyanide (APHA 4500-CN O).	WAD-CN. Measures free cyanide, $Zn(CN)_x$, $Cd(CN)_x$, $Cu(CN)_x$, $Ni(CN)_x$ and $Ag(CN)_x$. The WAD-CN method is less prone to interferences than the CATC method. There is also an automated version of APHA 4500 (Automated Weak Acid Dissociable Cyanide by Thin Film Distillation; WAD-TFD).

Analyte	Methods of Analysis	Comments
	Cyanide Amenable to Chlorination (CATC) (CN total minus non-chlorinatable part). USEPA Method 335.1 (CATC, titrimetric, spectrophotometric). ASTM D2036-B (CATC by difference) or ASTM D2036-C (CATC without distillation (ASTM, 1998); USEPA 9010C (USEPA, 2002) APHA 4500-CN G (distillation) or APHA 4500-CN H (without distillation).	Measures free cyanide, $Zn(CN)_x$, $Cd(CN)_x$, $Cu(CN)_x$, $Ni(CN)_x$ and $Ag(CN)_x$ (i.e. total cyanide except for iron-cyanide complexes; Kjeldsen, 1999).
	FIA in-line micro distillation pH 4.5 with colorimetric finish. ASTM Method D4374 (ASTM, 2000).	Measures free cyanide, $Zn(CN)_x$, $Cd(CN)_x$, $Cu(CN)_x$, $Ni(CN)_x$ and $Ag(CN)_x$
	Available Cyanide. FIA In-line ligand exchange and amperometric measurement of the cyanide ion. USEPA OIA-1677 (USEPA, 1999).	Measures free cyanide and the cyano-complexes of zinc ($Zn(CN)_4^{2-}$), copper ($Cu(CN)_4^{2-}$), cadmium ($Cd(CN)_4^{2-}$), mercury ($Hg(CN)_4^{2-}$ and $Hg(CN)_2$), nickel ($Ni(CN)_4^{2-}$) and silver ($Ag(CN)_4^{3-}$). Iron-cyanide complexes are not included, and none or only traces of complexes of gold ($Au(CN)_2^-$) and cobalt ($Co(CN)_6^{3-}$) are included (USEPA, 1999).
	Picric acid, colorimetric determination.	Measures free cyanide, $Zn(CN)_x$, $Cd(CN)_x$, $Cu(CN)_x$, $Ni(CN)_x$ and $Ag(CN)_x$

Analyte	Methods of Analysis	Comments
Total Inorganic Cyanide	Strong acid (heated, sulphuric acid) digestion followed by manual batch distillation (APHA 4500-CN C; USEPA 9010C (USEPA, 2002); USEPA 9013 of SW-846 (USEPA, 1992a); ISO/DIS 6703/1 (ISO, 1984b; German Standard Methods); DIN 38405/14; DIN, 1988); ASTM D2036A (ASTM, 1998): With determination either by: - titration (4500-CN D; USEPA 9014 (USEPA, 1996b); USEPA 335.2); - colorimetry (4500-CN E; USEPA 9012A (USEPA, 1996a) or 9014 (USEPA, 1996b); USEPA 335.3); or - potentiometry (APHA 4500-CN F). APHA (1998) also propose an additional methods analysis of total cyanide (APHA 4500-CN N and O).	LQL: 0.10 mg/L. Measures free cyanide, and cyano-metal complexes (e.g. $Zn(CN)_x$, $Cd(CN)_x$, $Cu(CN)_x$, $Ni(CN)_x$ and $Ag(CN)_x$, parts of $Au(CN)_x$, $Co(CN)_x$, $Pt(CN)_x$ and $Pd(CN)_x$). Does not include cyanate, thiocyanate, and certain nitriles (Kjeldsen, 1999).
	FIA, in-line UV Digestion, micro-distillation and colorimetric measurement. ASTM Method D 4374 (ASTM, 2000).	Measures free cyanide, and cyano-complexes (e.g. $Zn(CN)_x$, $Cd(CN)_x$, $Cu(CN)_x$, $Ni(CN)_x$, $Fe(CN)_x$ and $Ag(CN)_x$, parts of $Au(CN)_x$, $Co(CN)_x$, $Pt(CN)_x$, and $Pd(CN)_x$). There is an automated version of this analysis: Automated Total Cyanide by UV Digestion and Thin Film Distillation, ASTM D 4374-93.
	Draft Method OIA-1678 USEPA (1998b), Online UV digestion with acid, amperometric monitoring and segmented flow injection analysis	Free cyanide and cyano-metal complexes (e.g. $Zn(CN)_x$, $Cd(CN)_x$, $Cu(CN)_x$, $Ni(CN)_x$, $Hg(CN)_x$, $Fe(CN)_x$ and $Ag(CN)_x$)

Sources: Adapted from Schulz (2002) and Zheng et al. (2003).

Appendix 2 - Effect of Tailing Storage Facilities on Bird Species

Table A2-1 Distribution, migration and seasonal movement of some bird species recorded by Donato (1999) experiencing mortality at tailings storage facilities

Species	Habitat Used – Activity	Utilisation Period*	Observed Effects & Comments
Black Swan *Cygnus atratus*	Supernatant – Roosting	Vagrant. Responding to drought conditions in usual range	Some mortalities observed at CNT. Observed to weaken then get bogged in slurry.
Pacific Black Duck *Anas superciliosa* (S)	Supernatant-roosting & feeding	CNT: all year TE: May-Oct	Some mortalities.
Grey Teal *Anas gracilis* (S)	Supernatant-roosting & feeding	CNT: all year TE: May-Oct	Suffers significant mortalities. Disperses after rain, returning to TSFs in dry conditions. Large flocks travel by night.
Pink-eared Duck (S) *Malacorhynchus membranaceus*	Supernatant-roosting	CNT: all year TE: May-Oct	Few mortalities, although likely to be attracted to TSFs, depending on environmental conditions. Known to form large flocks if conditions suitable at CNT. Travels by night.
Hardhead *Aythya australis* (S)	Supernatant-roosting	CNT: all year TE: May-Oct	Significant mortalities recorded. Low silhouette in water, frequently diving, so exposed to toxicity. Can form large flocks; attracted to deep supernatant. Can travel at night.
Australian/Hoary-headed Grebe *Tachybaptus novaehollandiae* /*Poliocephalus poliocephalus*	Supernatant-roosting & feeding	CNT: all year TE: all year	Overlooked and mortalities grossly underestimated. Low silhouette and frequently diving. Carcasses removed by raptors and buried by slurry.
Australian Pelican *Pelecanus conspicillatus*	Supernatant-roosting	CNT: Vagrant? TE: May-Oct	Some mortalities. Requires large expanses of water.
White-faced Heron *Ardea novaehollandiae*	Supernatant & slurry-Feeding	CNT: all year TE: May-Oct	Regular mortalities observed. Attracted to TSFs. Solitary or in pairs.
White-necked Heron *Ardea pacifica*	Supernatant & slurry-Feeding	CNT: all year TE: May-Oct	Fewer mortalities than White-faced Heron, perhaps due to lower visitation rate.
Great Egret *Ardea alba*	Supernatant & slurry-Feeding	CNT: all year TE: May-Oct	The most common egret visiting TSFs during the surveys. Fewer mortalities than abundances would indicate, possibly due to feeding habitat
Nankeen night Heron *Nycticorax*	Supernatant & slurry-	CNT: all year	Very few mortalities. Nocturnal and common in vegetated areas around

Species	Habitat Used – Activity	Utilisation Period*	Observed Effects & Comments
caledonicus	Feeding	TE: May-Oct	TSFs.
Brahminy Kite *Haliastur indus*	Carrion-feeding, Ponding-drinking	TE: Dec-Apr	Drinks from ponding at sprinkler heads on heap leach pads. Generally rare visitor to mining leases in this study.
Brown Goshawk/Collared Sparrowhawk *Accipiter fasciatus*/*A. cirrhoceophalus*	Carrion-feeding?	CNT: all year TE: all year	Not known to take carrion, mortalities have been recorded. Possibly mis-identified (for Brown Falcon?). Not expected to be attracted to TSFs.
Wedge-tailed Eagle *Aquila audax*	Carrion-feeding	CNT: all year TE: all year	Possibly susceptible when feeding on large carrion on site.
Australian Bustard *Arteotis australis*	Supernatant-drinking	CNT: all year TE: May-Oct	Dead on TSF wall (possibly drinking)
Marsh Sandpiper *Tringa stagnatalis* (S,J,C)	Supernatant & slurry-feeding	CNT: Sept-May TE: Sept-Nov, Mar-May	Feeds in wet slurry. Possibly overlooked during passage migration. More thorough observations required.
Common Greenshank *Tringa nebularia* (S,J,C)	Supernatant & slurry-feeding	CNT: Sept-May TE: Sept-Nov, Mar-May	Feeds in wet slurry. Possibly overlooked during passage migration. More thorough observations required.
Black Kite *Milvus nigrans* (S)	Carrion-Feeding. Bare ground-roosting. Supernatant-drinking. Thermals – soaring	CNT: all year TE: May-Oct	Continually patrolling TSFs for bird carcasses (& other wildlife), and large insects embedded in slurry. Small prey items eaten on the wing or removed from slurry. Suffers significant mortalities when eating large prey items on site when exposed to toxic tailings, fumes and possibly flesh. Drinks from seepage on the outside of TSFs where mortalities have been recorded. On heap leach pads, drinks (dry season) from small ponds around irrigation heads.
Whistling Kite *Haliastur sphenurus* (S)	As for Black Kite (refer above)	CNT: all year TE: May – Oct (all year?)	As for Black Kite (refer above)
Red-necked Stint *Calidris ruficollis* (S,J,C)	Supernatant & slurry – feeding	CNT: Sept-May TE: Sept-Nov, Mar-	Feeds in wet slurry. Possibly overlooked during passage migration because of small size. More thorough observations required.

Species	Habitat Used – Activity	Utilisation Period*	Observed Effects & Comments
		May	
Sharp-tailed sandpiper *Calidris acuminata* (S,J,C)	Supernatant & slurry – feeding	CNT: Sept-May TE: Sept-Nov, Mar-May	Feeds in wet slurry. Possibly overlooked during passage migration. Because of small size and coloration. More thorough observations required.
Black-winged Stilt *Himantopus himantopus* (S)	Supernatant & slurry – feeding	CNT: all year TE: May-Oct	Feeds in wet slurry. Attracted to TSFs, where almost continual mortalities recorded. Mostly found in shallow supernatant.
Red-necked Avocet *Recurvirostra novaehollandiae*	Supernatant & slurry – feeding	CNT: all year TE: May-Oct	Feeds in wet slurry. Less frequently observed on TSFs compared with Black-winged Stilt, consequently suffers fewer mortalities.
Masked Lapwing *Vanellus miles*	Bare ground – feeding	CNT: all year TE: all year	Common around TSFs but its feeding preference on short grassland generally does not expose it to tailings
Oriental Pratincole *Glareola maldivarum* (S,J,C)	Bare ground-feeding, Supernatant-drinking, Thermals – feeding	CNT: Nov-Feb TE: Oct-Nov	Passage migrant (one way in Top End). Drinks from TSFs' supernatant and ponding around sprinkler heads on heap leach pads
Australian Pratincole *Stiltia isabella* (S)	Bare ground-feeding, Supernatant-drinking, Thermals – feeding	CNT: all year TE: May-Oct	Drinks from TSFs' supernatant and ponding around sprinkler heads on heap leach pads
Silver Gull *Larus novaehollandiae*	Supernatant – feeding	CNT: all year	Usually associated with garbage dumps on mining sites. In one case a mortality identified as Silver Gull could have been a Tern species.
Gull-billed Tern *Sterna nilotica* (S)	Supernatant & slurry-feeding,	CNT: all year? TE: all year?	Suffers significant mortalities. Disperses away from TSFs/dams after rain.
Caspian Tern *Sterna caspia* (S)	Supernatant & slurry – feeding	CNT: all year? TE: all year?	Not common on tailings, although some mortalities recorded. More coastal in Top End.
Whiskered Tern *Chlidonias hybridus* (S)	Supernatant & slurry – feeding	CNT: Sept-Apr TE: Apr – Dec	Suffers significant mortalities. Appears to prefer TSFs to natural waterholes, because of stranded or dead insects, etc. TSFs raised above the surrounding terrain apparently attracts this species, probably anti-predator behaviour.

Species	Habitat Used – Activity	Utilisation Period*	Observed Effects & Comments
Cockatiel *Nymphicus hollandicus* (S)	Supernatant – drinking	CNT: all year TE: May – Oct	In CNT, will drink from open water bodies, such as TSFs. Occurs in large flocks after good seasons, thus susceptible to significant mortalities. In the Top End, usually travels in small flocks preferring waterholes. No mortalities recorded during this study although unquantified anecdotal information suggests that considerable mortalities may occur under some environmental conditions.
Budgerigar *Melopsittacus undulatus* (S)	Supernatant-drinking and feeding	CNT: all year TE: May-Oct	In CNT, will drink from open water bodies, such as TSFs. Occurs in large flocks after good seasons, thus susceptible to significant mortalities. In the Top End, usually travels in small flocks preferring waterholes. No mortalities recorded during this study although unquantified anecdotal information suggests that considerable mortalities may occur under some environmental conditions.

Source: Donato (1999) & cited in Donato (2002). CNT = Central Northern Territory (dry arid climate). TE = Top End of Northern Territory in wet/dry tropical climate. J = Japan-Australia Migratory Bird Agreement. C = China-Australia Migratory Bird Agreement. S = susceptible species as nominated by Donato (2002).

Appendix 3 - Classification under the Globally Harmonized System

Classifications under the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) (UNECE, 2005) will come into force when the GHS is adopted by the Australian Government and promulgated into Commonwealth legislation. GHS background information and documentation are available at:

http://www.unece.org/trans/danger/publi/ghs/ghs_welcome_e.html

The environmental hazard classification of sodium cyanide using the GHS classification system is presented in Table A3-1. As yet, in regard to toxicity in the environment GHS only addresses acute and chronic aquatic toxicity. As sodium cyanide dissolves readily in water to form free cyanide (i.e. cyanide present as molecular HCN and ionic CN^- - Sections 3.3.1 and 6.3.1), the aquatic toxicity of sodium cyanide has been based on data for free cyanide.

Based on the data presented for free cyanide toxicity in Section 9.7, sodium cyanide is very highly toxic to various species of fish, aquatic invertebrates and algae (EC/LC50 < 1mg CN/L). Some tests show lower toxicity, which is likely to be due to differences in water conditions and the way the tests were conducted, as well as species differences (Section 9.7.4). From available data, cyanide appears to be much less toxic to aquatic macrophytes (EC50 > 10 mg CN/L).

At present, GHS classifications for chronic aquatic toxicity are based on the acute toxicity of a substance together with consideration of its environmental persistence and bioaccumulation behaviour, rather than on actual chronic toxicity data (NOECs). The high water solubility of sodium cyanide and low Log P_{ow} value < 4 (Section 3.2.2) mean that cyanide is unlikely to partition to fat and bioaccumulate, studies with animals show that it is metabolised to thiocyanate and eliminated (Sections 8.3-8.4), and it has not been found to biomagnify in food webs or cycle extensively in ecosystems, probably because of its rapid breakdown (Eisler et al., 1999). The rate of degradation or loss by volatilisation as HCN depends on conditions (Section 6), but in natural environments it is likely that the free cyanide would be removed or transformed by biotic or abiotic processes (volatilisation, conversion to cyanate etc) at a faster rate than that indicated as meeting the description 'rapidly degradable' in the GHS guidance document (Part 4, Environmental Hazards: Section 4.1.2.10). Under the current GHS classification for chronic toxicity, free cyanide would then be categorised as 'Not classified'.

However, the GHS guidance document notes that it is the intention that the scheme should be further developed to accommodate actual chronic toxicity data. Chronic toxicity tests with fish (Section 9.7.3) show that it may have high chronic toxicity (NOEC in the range 10-100 µg CN/L for most measured effects in freshwater fish, but ≤ 10 µg CN/L for spawning and egg production). While chronic effects are unlikely to arise from a single exposure event, such effects could arise if there were continuous or repeated release at concentrations below acutely toxic levels. Hence this classification

is likely to be different once actual chronic toxicity data are considered in the GHS classification system.

Table A3-1. GHS classification for environmental hazards of sodium cyanide.

Hazard	Classification	Hazard communication
Environmental hazard		
Acute toxicity		
Aquatic organisms (fish, aquatic invertebrates and algae)	Category 1	**Symbol:** Environment  **Signal word:** Warning **Hazard statement:** Very toxic to aquatic life (Code H400)
Chronic toxicity		
Aquatic organisms	Not classified	**Symbol:** No symbol is used **Signal word:** No signal word is used **Hazard statement:** No chronic hazard statement is used

Appendix 4 - Response Measures for Sodium Cyanide Release

SPILL RESPONSE AND DISPOSAL

This appendix provides a general consensus of measures to be taken in the event of an accidental environmental release of sodium cyanide. It does not replace or override specific advice provided by manufacturers and suppliers.

Immediate Action:

- Immediate action is required following a spill incident. Initiate emergency spill response procedures immediately. Cyanide spills should be cleaned up as soon as safe to do so.

Communication:

- Notify emergency services (Police and/or Fire Brigade), appropriate personnel, government safety, health and environment protection authorities of spill incident.
- Contact manufacturer for advice on spill management (include emergency contact phone number in MSDS)

Evacuation/Access Restriction:

- Evacuate spill area of all unprotected personnel. Move away, upwind and upgradient.
- Restrict access to spill site until clean-up is completed and validated. Vacate area completely if spill is in a confined space. Ensure spill area is well ventilated to minimise gas accumulation.

Training:

- Ensure that only adequately trained personnel are involved in spill management, cleanup and validation.

Personal Protective Equipment:

- Avoid all contact (skin, eye) and inhalation. Full protective clothing should be worn by personnel working in contaminated areas to prevent skin and eye contamination and inhalation of dusts, gases (e.g. hydrogen cyanide) and mists.
- PPE – refer to MSDS or seek manufacturer's advice. After use, wash all PPE prior to storing or reusing, or dispose of appropriately.

Spill Source Control:

- Stop or reduce leaks only if safe to do so. Wear PPE.

Containment:

- Contain spills within a bund and avoid run-off to drains, waterways, and sewers. Do not wash off or allow this chemical to enter drains, waterways, or sewers.
- Use absorbent materials (e.g. sandbags, soil, sand, kitty litter or other inert material) to contain spill. Do not use sawdust, which is acidic and may lead to HCN gas generation, or other reactive materials.
- Cover spill (e.g. with tarp) in wet weather. Ensure adequate ventilation to avoid HCN gas accumulation.

Cleanup Procedures:

- For Small Spills of Solid Material to Soil:
  - Recover (shovel/sweep) all visible material and seal in clean, dry, properly labelled drums. Keep spilt material dry. Do not wash to drain. Avoid generating dusts or mists. Reclaim and re-use product as much as possible.
  - Spill area residues and collected contaminated material can be treated with an appropriate neutralising reagent. Contact manufacturer for advice on suitable neutralising reagents and methods. Treatment of spill area residues may include excess of dilute sodium hypochlorite, calcium hypochlorite, or ferrous sulphate after the addition of soda ash or lime to raise the pH to greater than 10.5.
  - Sodium hypochlorite and calcium hypochlorite should not be used in or near sensitive aquatic environments. Do not flush treated residues to waterways or sewer.
  - Contact manufacturer and government waste disposal authority for advice on appropriate spill management strategy for cleanup residues.
  - Store and transport collected residues appropriately (refer to MSDS).
- For Large Spills of Solid Material to Soil:
  - Contact emergency services and supplier for spill management advice. Liaise with appropriate personnel, government safety, health and environment protection authorities. In general, manage as for small spills of solid material (refer above). Do not attempt to neutralise in bulk without expert assistance.
- For Small Spills of Liquid Solution to Soil:
  - Soak up spill with suitable absorbent material that does not react with spilt material. Remove a conservative amount of soil. Collect all contaminated soil and seal in clean, dry, properly labelled drums.
  - Treat residue at spill area and in collected contaminated soil with neutralising reagent on advice of manufacturer. Contact manufacturer and government waste disposal authority for advice on appropriate spill management strategy for cleanup residues.
  - Store and transport collected residues appropriately (refer to MSDS).
- For Large Spills of Liquid Solution to Soil:

- Contact emergency services and supplier for spill management advice. Liaise with appropriate personnel, government safety, health and environment protection authorities.
- Remove top layers of contaminated soil for treatment in-situ or ex-situ (e.g. lined ponds, wastewater treatment plants, salvage containers). Do not attempt to neutralise in bulk without expert assistance. Contact manufacturer for advice on suitable neutralising reagents and methods.
- Store and transport collected residues appropriately (refer to MSDS).

- For Spills (solids/liquids) to Waterways and Sewers:
  - Notify emergency services immediately. Liaise with appropriate personnel, government safety, health and environment protection authorities. Do not attempt to neutralise in bulk without expert assistance.
  - Spills to waterways may not require treatment due to natural attenuation. Spills to waterways can potentially be detoxified, but expert advice is required for this treatment (contact manufacturer).
  - Neutralisation and Detoxification:
  - Contaminated media may be detoxified with appropriate treatment reactants as advised by the manufacturer. Avoid contact with detoxification substances/solutions, which are corrosive.
  - Treatment chemicals may potentially include sodium hypochlorite, calcium hypochlorite and ferrous sulphate. Do not use water (alone), acids or strong oxidizing reagents.
  - Do not use sodium hypochlorite and calcium hypochlorite in or near sensitive aquatic environments. Hypochlorites are toxic to aquatic organisms. Use only where immediate run-off water can be contained and treated.
  - Neutralising reagents may have narrow pH limits within which they react effectively.
  - Neutralising reagents must never be used without the full knowledge of their limitations. If used in bulk, they can initiate hazardous reactions or generate excessive heat and toxic byproducts. With heat, HCN and ammonia gases may evolve. Contact with water (alone) may cause HCN gas to be released.
  - If sodium hypochlorite or calcium hypochlorite is used, allow adequate time (approximately 1 to 24 hours, but contact manufacturer for specific advice) for chemical reaction and complete decomposition to occur. The detoxification procedure converts the cyanide ion to the cyanate ion that on continued reaction breaks down to carbon dioxide and nitrogen.
  - Reaction with ferrous sulphate produces a relatively stable ferrocyanide compound. HCN may evolve if exposure to sunlight occurs. Ferrous sulphate increases the generation of HCN gas, and produces a residue that is potentially toxic to animals (e.g. cattle, wildlife) if consumed.

Cleanup Validation:

- Validation of spill site cleanup may include visual assessment, surface soil sampling and analysis, and air monitoring for hydrogen cyanide (HCN) using specific, calibrated gas detection equipment. Contact relevant environment protection authority for advice.

Disposal/Recycling:

- Contact manufacturer for advice on appropriate spill management strategy for cleanup residues. Liaise with government waste management authority. Treatment, storage, transportation, and disposal of waste must be in accordance with applicable Federal, state/territory and Local Government regulatory requirements.

AUSTRALIAN STANDARD AS1678

Australian Standard AS1678.6.0.009 provides the following spill response recommendations:

- Immediately contact Police or Fire Brigade.
- Spill or leak area should be isolated immediately for at least 25 m in all directions.
- Keep unauthorised personnel away. Keep upwind and on higher ground.
- Ventilate enclosed spaces before entering.
- Shut off electrical equipment and leave off.
- Send message to Police and Fire Brigade. Tell them location, material, UN Number, quantity and emergency contact (name and phone number) as well as condition of vehicle and damage observed.
- For Large Spills: Consider initial downward evacuation for at least 250 m.
- Do not touch or walk through spilled material.
- Do not touch damaged containers unless wearing appropriate protective clothing.
- Stop leak if safe to do so.
- Prevent entry into waterways, drains or confined areas.
- Cover with plastic sheet to prevent spreading.
- Absorb with earth, sand or other non-combustible material and transfer to container.
- Do not get water inside containers.
- Seek expert advice on handling and disposal.

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