

Hydrofluoric Acid (HF)

Priority Existing Chemical Assessment Report No. 19



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ISBN 0 642 70986 6

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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 (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 Environment Australia and the Therapeutic Goods Administration, which carry out the environmental and public health assessments, respectively.

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 (Chemicals Notification and Assessment) 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*.

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 may be inspected by the public at the library of the National Occupational Health and Safety Commission (NOHSC). Summary Reports are published in the *Commonwealth Chemical Gazette*, which are also available to the public at the NOHSC library.

Copies of this and other Priority Existing Chemical reports are available from NICNAS either by using the prescribed application form at the back of this report, or directly from the following address:

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

- NICNAS Service Charter;
- information sheets on NICNAS Company Registration;
- information sheets on PEC and New Chemical assessment programs;
- safety information sheets on chemicals that have been assessed as Priority Existing Chemicals;
- subscription details for the NICNAS Handbook for Notifiers; and
- subscription details for the Commonwealth Chemical Gazette.

More information on NICNAS can be found on the NICNAS Web site:

http://www.nicnas.gov.au/

Other information on the management of workplace chemicals can be found at the website of the National Occupational Health and Safety Commission (NOHSC):

http://www.nohsc.gov.au/

Overview

The chemical hydrofluoric acid (hydrogen fluoride, HF, CAS No. 7664-39-3) was declared a priority existing chemical (PEC) for preliminary assessment on 7 April 1998 because of concern about the chemical's high toxicity and general availability. The focus of the assessment was on use and exposure in Australia.

Total imports of HF are about 700 tonnes yearly, with about half consisting of anhydrous (100%) material and half aqueous solutions ranging from 35% to 70% in concentration. HF is not manufactured in Australia but additional aqueous HF is formed in solution from bifluoride salts or acidified fluoride salts through *in situ* manufacture.

Most anhydrous HF is used as an alkylation catalyst at five petroleum refining sites in Australia. Other uses are for surface fluorination of plastic articles, in research and in gas mixtures for excimer lasers.

Aqueous HF is commonly formulated into lower concentration products. The major use of aqueous HF is in varied metal treatment and cleaning processes. Other important uses include laboratory analysis, floor and wall cleaning and etching, fabric rust removal, etching silicon in semiconductor manufacture, glass etching and cleaning and manufacture of inorganic fluoride compounds. Other niche uses occur. Most is used occupationally but some aqueous HF products are available to the public through retail sale, trade outlets, factory-door sales and craft suppliers.

HF is also produced incidentally in other processes e.g. aluminium smelting, ceramic production, and phosphate fertiliser manufacture. HF may also occur as an impurity in other chemicals, can be produced through the reaction of other chemicals, and can occur naturally.

Environmental exposure to HF can occur from releases to water or air. Release to the atmosphere as a result of incidentally produced HF is much greater than through deliberate use of the chemical. HF is slightly to very slightly toxic to fish, aquatic invertebrates, algae and aquatic plants, with soft water tending to show higher toxicity than hard water. However, terrestrial plants can be sensitive to fluoride at very low levels in the atmosphere, with conifers, fruit, berries and grasses being the most sensitive.

The assessment identified potential for impact on the environment through incidentally produced HF. Air concentrations could be expected to be higher near sites where HF is produced incidentally such as coal burning power stations and aluminium smelters. Susceptible plants in these areas will be adversely affected. Fluorides also accumulate primarily in the skeletal tissues of terrestrial animals that consume fluoride-containing foliage and the possibility of biomagnification is unclear. Normal use of HF is not expected to have environmental impact.

Workers can be exposed to HF through inhalation or skin contact. In Australia there is potential for exposure at various stages of handling, including transport, formulation, use and disposal. Exposure to incidentally produced HF can also occur. Public exposure is most likely to occur from skin contact with consumer products containing HF. Acute exposure in humans would be a result of accidental spillage or release. Chronic exposure may occur where low levels of HF are inhaled over a long period, and possibly where there is long-term skin contact with low concentrations.

HF is both corrosive and toxic to humans, with higher concentrations causing greater harm. Acute exposure results in burns and respiratory damage, and in systemic effects that can be fatal. Acute exposure through either inhalation or skin contact has led to deaths in humans.

Skin contact with HF can cause painful second and third degree burns that heal very slowly, and injury through delayed burns can be caused by even dilute solutions (0.1%) if not treated promptly. Inhalation of low concentrations can cause upper airway and eye/skin irritation, and high concentrations can cause serious injury.

Chronic exposure to HF may cause skeletal fluorosis. HF is not believed to be genotoxic, carcinogenic or a sensitiser. Some studies have found reproductive effects.

The high chemical reactivity of HF requires care in choosing packaging materials and controlling corrosion in processing equipment. Contact with metals can lead to the formation of hydrogen gas which forms explosive mixtures in air, and can build up pressure in closed containers. If released, anhydrous HF can form a mobile cloud under some conditions. Concentrated aqueous solutions can fume in air and heat is produced on dilution.

In Australia transport and occupational use of HF is controlled through a number of national standards and codes and corresponding State and Territory legislation. Appropriate workplace controls must also be implemented if the chemical is to be used safely. Consumer use is controlled through the provisions of the *Standard for the Uniform Scheduling of Drugs and Poisons*.

For occupational use of HF this assessment found that there is reason for concern about acute accidental exposure through inhalation or skin contact, and that chronic exposure could be of concern in some workplace scenarios. There is poor compliance with regulatory controls in some areas. Users need to improve workplace controls on exposure, including considering whether HF needs to be used at all, or whether a lower concentration could be used.

Despite public health controls, incidents and injury to the public are occurring, and existing public health controls are not uniformly applied.

A detailed risk assessment by NICNAS is not recommended at this time, as considerable information on human exposure is available and this assessment has identified many actions that industry can take to improve safety. However, a full assessment and associated risk reduction recommendations may be required in the future, should appropriate action not be taken to effectively control HF. Additional information would be required to assess environmental impact from incidentally produced HF.

A major recommendation of the assessment is that industry take steps to comply with all existing regulatory controls and implement extra voluntary controls, in order to improve the safety in use of HF. State and Territory occupational health and safety authorities are asked to assist by checking compliance of material safety data sheets (MSDS) and labels and by encouraging voluntary initiatives.

Other recommendations for industry relevant to occupational use of HF focus on hazard communication, emergency procedures, atmospheric monitoring and health surveillance. Updating of the occupational hazard classification and injury coding and full take up of the *Standard for the Uniform Scheduling of Drugs and Poisons* requirements for licensing of users of high concentration HF have also been recommended.

It is recommended that environmental monitoring be carried out around sites known to produce HF incidentally.

In order to protect the public it is recommended that all required packaging and labelling instructions on HF products be strictly adhered to. Further labelling and scheduling matters have been referred to the National Drugs and Poisons Scheduling Committee for their consideration.

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Acronyms and Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
ACT	Australian Capital Territory
ADG Code	Australian Dangerous Goods Code
ANZECC	Australian and New Zealand Environment and Conservation Council
BAT	Biologischer Arbeitsstoff-Tolreanz-Wert (biological tolerance value for occupational exposure)
BCF	bioconcentration factor
BEI	Biological Exposure Index
b.p.	boiling point
BSA	body surface area
С	centigrade
CaCO ₃	calcium carbonate
CaF ₂	calcium fluoride
CAS	Chemical Abstracts Service
CFCs	chlorofluorocarbons
CTEF	Comité Technique Européen du Fluor
EA	Environment Australia
EASE	Estimation and Assessment of Substance Exposure
EC	European Commission
EC50	median effective concentration
EINECS	European Inventory of Existing Commercial Chemical Substances
EU	European Union
F	fluoride
g	gram
h	hour
HCFC	hydrochlorofluorocarbon
HF	hydrofluoric acid
HF ₂ -	bifluoride ion
HFC	hydrofluorocarbon
hPa	hectopascal
IARC	International Agency for Research on Cancer
IUCLID	International Uniform Chemical Information Database
IUPAC	International Union of Pure and Applied Chemistry
kg	kilogram
kPa	kilopascal
L	litre
LC ₅₀	median lethal concentration

LEV	local exhaust ventilation
LOAEL	lowest-observed-adverse-effect level
m	metre
μg	microgram
mg	milligram
mL	millilitre
ML	megalitre
MSDS	Material Safety Data Sheet
MT	megatonne
NaF	sodium fluoride
NDPSC	National Drugs and Poisons Schedule Committee
ng	nanogram
NICNAS	National Industrial Chemicals Notification and Assessment Scheme
NIOSH	National Institute for Occupational Safety and Health (USA)
NOEC	no-observed-effect concentration
NOAEL	no-observed-adverse-effect level
NOHSC	National Occupational Health and Safety Commission
NPI	National Pollutant Inventory
NSW	New South Wales
OECD	Organisation for Economic Cooperation and Development
OHS	occupational health and safety
PACIA	Plastics and Chemicals Industries Association
PEC	predicted environmental concentration
PEC	Priority Existing Chemical
PNEC	predicted-no-effect concentration
ppb	parts per billion
PPE	personal protective equipment
ppm	parts per million
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
RTECS	Registry of Toxic Effects of Chemical Substances
SA	South Australia
SCID	Stored Chemicals Information Database (maintained by WorkCover NSW)
SIAR	SIDS Initial Assessment Report
SIDS	Screening Information Data Set
SiF ₄	silicon tetrafluoride
STP	sewage treatment plant
SUSDP	Standard for the Uniform Scheduling of Drugs and Poisons
t	metric tonne
TAFE	Technical and Further Education
TGA	Therapeutic Goods Administration

TGD	Technical Guidance Document
TSCA	Toxic Substances Control Act (US)
TWA	time-weighted average
UK HSE	United Kingdom Health and Safety Executive
UN	United Nations
US EPA	United States Environmental Protection Agency
VIC	Victoria
W	weight
WA	Western Australia
WWTP	waste water treatment plant
Y	year

1. Introduction

1.1 Declaration

The chemical hydrofluoric acid (hydrogen fluoride, HF, CAS No 7664-39-3), was declared a priority existing chemical (PEC) under the *Industrial Chemicals* (*Notification and Assessment*) Act 1989 (Cwlth) (the Act) by the Minister for Employment, Workplace Relations and Small Business by notice in the *Chemical Gazette* of 7 April 1998. The reason for declaration was concern over the chemical's high toxicity and general availability. The death of a worker in Western Australia in 1994 from skin contact following an accidental spillage had highlighted these concerns.

1.2 Scope of the assessment

The assessment is a preliminary one, focussing on use patterns and the potential for occupational, public and environmental exposure to the chemical in Australia. Summary information on health and environmental effects is included. The Act prescribes that risk assessment and risk management are not covered in preliminary assessments. However, as an outcome of a preliminary assessment, the Act requires NICNAS to determine the significance of the assessment findings for risk. If the findings indicate that there may be a significant risk of adverse health, safety or environmental effects, then a full (risk) assessment may be recommended.

The assessment covers the use in Australia of both anhydrous (100%) HF and aqueous solutions of HF. In this report the generic term HF is used to describe both forms. Where the forms are referred to separately in the report, the term anhydrous HF is used for 100% strength material, and aqueous mixtures are referred to as hydrofluoric acid or aqueous HF. The assessment also covers potential exposure to HF via incidental and *in situ* production.

1.3 Objectives

The objectives of the assessment are:

- to review the properties of HF;
- to determine the likely uses of HF in Australia;
- to review the literature and summarise any adverse health or environmental effects of HF;
- to determine the extent of occupational, public and environmental exposure to HF in Australia;
- to determine the significance of the assessment findings for risk of adverse health or environmental effects, and if necessary, recommend a full (risk) assessment.

1.4 Sources of information

Information for the assessment was obtained from a number of sources:

Industry sources

Applicants and notifiers to the assessment supplied information on:

- volumes imported;
- imported or formulated mixtures containing hydrofluoric acid;
- known uses and potential uses;
- methods of transport, handling, storage and disposal; and
- health and environmental effects.

Applicants were also requested to supply information on incidental manufacture of HF, and on chemicals used to produce HF *in situ*, such as fluorosilicic acid. One aluminium producer and one phosphate fertiliser manufacturer provided information on incidental manufacture. Information was also received on grades of fluorosilicic acid containing varying quantities of HF, and on *in situ* production of HF from soluble fluoride salts.

Most of the applicants were not themselves users or formulators, but supplied contact details for their customers. NICNAS conducted a questionnaire survey of industry (HF survey). The survey allowed information to be gathered about the method of use and the distribution chain for hydrofluoric acid and hydrofluoric acid products. Survey forms were sent to purchasers of HF, who were themselves asked to nominate purchasers of their products if resold. The areas covered by the survey included formulation details, workplace handling and disposal methods (Appendix 5).

A total of 405 questionnaires were sent to companies and organisations handling HF. Of these, 186 responses (46%) were received, including those who no longer used the chemical or could not confirm their use of it, and those who completed only part of the questionnaire.

Import data

Information on imports of HF for 1996 to 1999 was also obtained from the Australian Customs Service, and for 1994 to 1999 from the Australian Bureau of Statistics.

Literature review

One of the major sources of information on the toxicology of hydrofluoric acid was a risk assessment carried out by the Organisation for Economic Cooperation and Development (OECD) under its Screening Information Data Set (SIDS) program. The report was prepared by the Netherlands. The summary of health effects (Section 8) is based on the OECD report.

Other relevant data for the assessment was obtained from literature searches of publically available databases, other bibliographic sources, discussion list archives and internet sites. Current Australian guidance material on HF includes the NOHSC publication "Hydrogen Fluoride" and the Plastics and Chemicals Industries Association (PACIA) "Hydrofluoric Acid Code of Practice".

Site visits

A number of site visits were made during the assessment to assess modes of use of and potential exposure to HF. The visits included an oil refinery using anhydrous HF, a manufacturer of semiconductors, several car detailers, several dry cleaners, two formulators of chemical products and one repacker of glass etching paste.

Other sources

Other sources of information for the assessment included Commonwealth, State and Territory governments, Austin and Repatriation Medical Centre (Melbourne), Auburn Hospital (Sydney), National and State Poisons Information Centres and several individuals with specialised interest in hydrofluoric acid who provided information in their areas of expertise.

1.5 Peer review

During all stages of preparation, the report has been subject to internal peer review by NICNAS, Environment Australia (EA) and the Therapeutic Goods Administration (TGA). Associate Professor James Beattie of the School of Chemistry, University of Sydney, reviewed sections of the report related to *in situ* production of HF.

2. Background

2.1 International perspective

Hydrogen fluoride was first obtained at the end of the eighteenth century and known then as a product capable of attacking glass (Gerhartz et al., 1988). Even earlier, the etching of glass by acid-treated fluorspar (calcium fluoride) was reported in 1670 (Kroschwitz & Howe-Grant, 1994). A pure and highly concentrated aqueous solution of HF was first prepared in 1809 (Simons, 1950). Early production was as aqueous solutions for uses such as glass etching, foundry scale removal and manufacture of inorganic fluorides. Its uses became diversified from 1930 onwards, for fluorocarbon production, production of aluminium fluoride and synthetic cryolite for the aluminium industry and pickling of stainless steel. During World War II HF was used in alkylation catalysis to produce aviation gasoline and in the manufacture of fluorine to produce UF₆ for isotopic enrichment of uranium (Kroschwitz & Howe-Grant, 1994). Many fluorinated organic compounds including polymers have been developed since then.

Hydrogen fluoride is produced by the reaction of calcium fluoride (CaF₂) and sulfuric acid in a reaction furnace at 200 °C. The main source of calcium fluoride for the manufacture of hydrogen fluoride is the mineral fluorspar. The volatile HF formed is condensed and purified by distillation (Kroschwitz & Howe-Grant, 1994). On an industrial basis HF is the starting material for the production of most organic and inorganic chemicals containing the fluorine atom, as well as fluorine gas and is the most important manufactured fluorine compound (Kroschwitz & Howe-Grant, 1994; Lewis, 1997). The industrial applications of anhydrous and aqueous HF tend to be different, but can overlap.

HF is acknowledged as a highly hazardous chemical due to its toxic, corrosive and reactive properties. It can be used in the anhydrous (100%) form or in aqueous solutions commonly known as hydrofluoric acid. The latter range in concentration from < 1% to 70%. The degree of hazard decreases with decreasing concentration, which also reduces the likelihood of inhalational exposure.

Under certain accidental release conditions HF can travel significant distances downwind as a dense vapour and aerosol.

Global production of HF in 1992 was estimated at 875 000 tonnes with a further 204 000 tonnes captive production, with the greatest manufacturing capacity in Europe and North America. Captive production is usually a feedstock for aluminium fluoride compounds used in aluminium smelting (Kroschwitz & Howe-Grant, 1994).

In the past, production of chlorofluorocarbons (CFCs) was one of the major uses of HF. The phasing out of CFCs during the 1990's because of their ozone depleting potential resulted in a drop in demand for hydrogen fluoride (Government of Canada, 1993; ATSDR, 1993; Roskill Consulting Group, 2000). However HF is also used in the manufacture of alternatives such as hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs), and often in higher proportions than in CFCs, and this market is currently leading a growth in demand for HF (Anon, 1999a).

The broad uses of HF reported in Europe and North America are shown in Table 1.

Uses in Europe (OECD, 1999)		Uses in North America (Anon, 1999a)	
Synthesis of organofluor compounds	60%	fluorocarbons	60%
Synthesis of inorganic fluorides,	30%	chemical derivatives	18%
Pickling agent of metal surfaces	4%	aluminium manufacturing	6%
Glass etching	3%	stainless steel pickling	5%
Petroleum alkylation catalyst	2%	petroleum alkylation catalysts	4%
Other	1%	uranium chemicals production miscellaneous (includes glass etcl berbicides and rare metals)	3% hing, 4%
			170

Table 1 - Uses of HF in Europe and North America

Various legislative controls applicable to HF in both the EU and USA are noted in Section 10.

In the United States, HF is included in a proposed testing program under the Toxic Substances Control Act (TSCA), focussing on inhalation exposure. It is one of 21 hazardous air pollutants (HAP) chosen for testing (Anon, 1998). The areas to be covered by the testing are currently under negotiation between industry and the US EPA.

2.2 Australian perspective

Australia differs from some other countries using HF in not manufacturing the chemical domestically. Two former production facilities have closed and at present all material is imported. The pattern of use in Australia also differs from that in Europe and North America, primarily because fluorine-based chemicals that are a large part of their industry are not manufactured here. It would also be expected that a higher percentage of the material used in Australia would be as aqueous solutions.

As in other countries, Australia has a framework of regulations and standards applicable to HF, aimed at protecting workers, the public and the environment. The chemical is listed in the *Standard for the Uniform Scheduling of Drugs and Poisons* (SUSDP) (Australian Health Ministers' Advisory Council, 1997), the *Australian Code for the Transport of Dangerous Goods by Road and Rail* (FORS, 1998), the National Occupational Health and Safety Commission's (NOHSC) *List of Designated Hazardous Substances* (NOHSC, 1999), the NOHSC *Adopted National Exposure Standards for Atmospheric Contaminants in the Occupational Environment* (NOHSC, 1995) and the NOHSC *National Standard for the Control of Major Hazard Facilities* (NOHSC, 1996a).

2.3 Assessments by other overseas bodies

HF has been assessed by several other national or international bodies. The most recent is the OECD SIDS risk assessment sponsored by the Netherlands, used as the major source of toxicological data in this report. Some reviews have covered the general topic of fluorides, including hydrogen fluoride. Reviews in 1993 (US) and 1995 (UK) focussed on hazard potential and accidental releases. Assessments include:

- "A review of the manufacture, uses, incidents and hazard models for hydrogen fluoride", HSE (UK) Contract Research Report, 1995 (Lines, 1995).
- "Hydrogen Fluoride Study: Report to Congress, Section 112(N)(6), Clean Air Act as Amended: Final Report", US Environmental Protection Agency, 1993 (US EPA, 1993).
- "Inorganic Fluorides: Priority Substances List Assessment Report", Government of Canada, 1993 (Government of Canada, 1993).
- "Fluorides, Hydrogen Fluoride, and Fluorine (F)", Agency for Toxic Substances and Disease Registry, U.S. Public Health Service, 1993 (ATSDR, 1993).
- "Fluorine and Fluorides: Environmental Health Criteria 36", World Health Organization, Geneva 1984 (World Health Organization, 1984).

The OECD SIDS Initial Assessment Report, which has been agreed by Australia as an OECD Member country, concluded that there is a need for further information and further consideration of of exposure and risk assessment for the environment and human health.

HF has been agreed in the European Union Risk assessment program under Regulation EEC/793/93. The EU risk assessment concluded that there are need for specific measures to limit the risks for workers and consumers and for exposure via the environment for some sites.

3. Applicants

Following the declaration of hydrofluoric acid as a PEC, 35 organisations importing hydrofluoric acid into Australia, manufacturing *in situ* or with other interest in the chemical applied for assessment of the chemical. The applicants supplied information on the properties, import quantities and uses of the chemical. In accordance with the *Industrial Chemicals (Notification and Assessment) Act 1989*, NICNAS provided the applicants with a draft copy of the report for comments during the corrections/variation phase of the assessment. Data for the assessment were also provided by other companies, including those who took part in the NICNAS HF survey.

The applicants were, as follows:

Agfa-Gevaert Limited

372-394 Whitehorse Rd Nunawading VIC 3131

Alpha Chemicals (Australia) Pty Ltd 18 Inman Rd Dee Why West NSW 2099

Amtrade International Pty Ltd 2/570 St Kilda Rd Melbourne 3004

Asia Pacific Specialty Chemicals Limited 15 Park Rd Seven Hills NSW 2147

Australian Council of Trade Unions 393 Swanston St Melbourne VIC 3000

Barrier-Pak Pty Ltd

152 Magowar Rd Girraween NSW 2145

B.J. Services Company

19-21 Sorbonne Cr Canning Vale WA 6155 **Allcrafts Wholesale** 6 Devlan St Mansfield QLD 4122

Alphabond Dental Pty Ltd 202 Sydney St Willoughby NSW 2068

Applied Chemicals Pty Ltd Australia 121 Lewis Rd Wantirna South VIC 3152

Australian Chemicals and Coatings 2 Lanyon St Dandenong VIC 3175

Australian Manufacturing Workers Union 3/440 Elizabeth St Melbourne VIC 3000

Bio-Scientific Pty Ltd 28 Monro Ave **Kirrawee NSW 2232**

BOC Gases Australia Ltd 428 Victoria St Wetherill Park NSW 2164 **Fernz Specialty Chemicals** 70 Marple Ave Villawood NSW 2163

Halliburton Australia Pty Ltd 306 St Vincent Street Port Adelaide SA 5015

ICN Biomedicals Australasia 12/167 Prospect Highway Seven Hills NSW 2147

Kendon Chemical & Manufacturing Co Pty Ltd 71 McClure St Thornbury VIC 3071

Merck Pty Ltd 207 Colchester Rd Kilsyth VIC 3137

Palloys Pty Ltd 74-84 Foveaux St Surry Hills NSW 2010

Redox Chemicals Pty Ltd Locked Bag 60 Wetherill Park NSW 2164

Semal Pty Ltd T/A Consolidated Chemical Co 52-62 Waterview Close Hampton Park VIC 3976

Sigma-Aldrich Pty Ltd 2/14 Anella Ave Castle Hill NSW 2154

Tomago Aluminium Company Pty Ltd Tomago Rd Tomago NSW 2322

Wesfarmers CSBP Ltd PO Box 345 Kwinana WA 6167 Halas Dental Ltd Unit 1/44 O'Dea Ave Waterloo NSW 2017

Henkel Australia Pty Ltd 135-141 Canterbury Rd Kilsyth VIC 3137

Incitec Ltd – Industrial Chemicals PO Box 31 Chester Hill NSW 2162

Kirby Refrigeration 284-286 Horsley Rd Milperra NSW 2214

Orica Australia Pty Ltd 1 Nicholson St Melbourne VIC 3000

Pisani Australia Pty Ltd 15/2-12 Beauchamp Rd Matraville NSW 2036

Selby-Biolab 2 Clayton Rd Clayton VIC 3168

Shell Refining (Australia) Pty Ltd PO Box 26 Granville NSW 2142

Specialty Trading Pty Ltd 2 Lanyon St Dandenong VIC 3175

Valvoline (Australia) Pty Ltd 30 Davis Rd Wetherill Park NSW 2164

Wingate's Laboratory 6th Floor, 19 North Terrace Hackney SA 5069

4. Chemical Identity and Composition

4.1 Chemical identity

Chemical name (IUPAC)	Hydrogen fluoride	
Other names	Hydrofluoric acid Fluoric acid	
CAS Number	7664-39-3	
EINECS Number	231-634-8	
RTECS Number	MW 7875000	
Empirical formula	HF	
Structural formula	H - F	
Molecular weight	20.01	

4.2 Impurities

Impurities reported in commercial grades of HF include sulfuric acid and fluorosilicic acid. High purity grades are available for special uses.

5. Physical and Chemical Properties

5.1 Physical state

Anhydrous (100%) HF may be found in both liquid and gaseous states, depending on temperature. Aqueous mixtures (hydrofluoric acid) are liquid.

5.2 Physical properties

Table 2 - Physico-chemical properties of HF

Property	Value	Reference and comments	
Boiling point (anhydrous):	19.5 °C at 1013 hPa	(OECD, 1999)	
Melting point:	- 83 °C	(OECD, 1999)	
Relative density:	1.016 g/cm ³ at 0 °C (liquid) 0.901 g/cm ³ at 22 °C (liquid)	(OECD, 1999)	
Vapour pressure:	1033 hPa at 20°C	(OECD, 1999)	
Partial vapour pressure of aqueous solutions:	70% 120 mm Hg 35% 2.5 mm Hg 8 –10% 0.16 mm Hg	(Dupont, 1984) Values estimated from graphs.	
Water solubility:	Miscible in all proportions	(OECD, 1999)	
Henry's Law Constant:	2.07 Pa.m ³ /mol at 20 ⁰ C	Calculated value.	
Partition coefficient (Log Kow):	- 1.4	(OECD, 1999)	
Flammability:	Non-flammable	(OECD, 1999)	
Explosive properties:	Non-explosive	(OECD, 1999)	
Oxidising properties:	Not oxidising	(OECD, 1999)	
Odour threshold:	30 μg/m ³	(OECD, 1999) (This is not a reliable warning sign if levels are increased gradually.)	
Conversion factors:	1 mg/m ³ = 1.22 ppm (101 kPa, 25°C)	(OECD, 1999)	
	1 ppm = 0.82 mg/m ³ (101 kPa, 25°C)		

5.3 Chemical reactivity

HF itself is not flammable, explosive or oxidising but is a highly reactive chemical and the materials for its storage and handling must take this into account.

Contact with many metals can lead to the formation of hydrogen gas, which forms explosive mixtures in air at concentrations between 4% and 75% (CTEF, 1993). The reaction occurs at concentrations of aqueous HF less than 65% approximately (OECD, 1999) but over time can also occur at higher concentrations and with anhydrous HF. In closed containers, hydrogen formation can cause dangerously high pressures. Hydrogen embrittlement of metals has been observed (CTEF, 1993).

As the reaction of hydrogen fluoride or concentrated hydrofluoric acid with water is exothermic, it may react violently on mixing. Therefore in the deliberate dilution of hydrofluoric acid, the acid should be added to water, and this should be done with stirring. This property also has implications for the handling of spills. The heat of dilution during preparation of solutions will raise the temperature of mixtures and increase vapour pressure.

Fumes of high concentration solutions of HF react with moisture in the atmosphere to form a white smoggy cloud (CTEF, 1993).

HF has a significant corrosive action on silica and silicates (e.g. glass, fibreglass, ceramics, asbestos, cement) (AEC, 1995, Dupont, 1984); and leather and natural rubber (Davletshina & Cheremisinoff, 1998). It is extremely reactive in contact with most organic substances and metal carbonates, oxides and hydroxides (CTEF, 1993, Dupont, 1984).

6. Use, Manufacture, Importation and Occurrence

6.1 Manufacture

HF is not currently manufactured in Australia. Until 1995 it was produced at Camellia in Sydney, and earlier also at Kooragang Island in Newcastle. It is reported that a HF manufacturing facility is planned in WA, to make HF as a precursor to aluminium fluoride flux for aluminium refining.

6.1.1 In situ manufacture

HF may be produced in solution from other chemicals without purchasing HF. This may be known as *in situ* or insidious production and occurs in the following ways:

Acidified fluoride salts

Solutions of HF can be formed if fluoride salts are acidified with other acids in solutions. Hydrogen fluoride in water is not completely ionised as it is a weak acid. Its conjugate base, the fluoride ion F⁻, can re-associate to form HF at acid (low) pH. In the presence of solutions of strong acids, the pH of the fluoride-containing mixture will be low and the free F⁻ formed from the ionisation of the fluoride salt in aqueous solution will be present quantitatively as HF. Therefore soluble fluoride salts in solution with acids stronger than HF should be treated as a solution of HF. Further details are in Appendix 1. Examples of such manufacture in Australia are:

- 1.5% to 3% solutions of HF *in situ* from hydrochloric acid and ammonium bifluoride (or ammonium bifluoride solutions), for use in acidising oil wells. Up to 27 000 L of the solution is produced annually.
- A range of cleaning products using ammonium bifluoride and either sulphuric or phosphoric acid. The equivalent HF concentrations in these products ranged from 1.7 to 5.9% w/w.
- Ammonium bifluoride / sulphuric acid used to top up a metal treatment dip tank.
- Mixing HF, ammonium bifluoride and nitric acid to produce a stainless steel cleaner for resale. The ammonium bifluoride in this product contributes the equivalent of an extra 1.6% HF, above the amount added as HF itself.
- Recirculating acid/fluoride solutions to clean high silica scale from boiler tubes was reported.

Insoluble fluoride salts such as calcium fluoride in aqueous solution are a poorer source of HF, as they are limited by the solubility of the salt. However, in aqueous suspensions that are acidified, solubility will be increased by the presence of the acid, and a significant quantity of HF can be formed.

Solutions of bifluoride salts

Bifluoride salts (ammonium, potassium and sodium bifluoride) are a special subset of soluble fluoride salts because they form HF in solution when dissolved in water. The bifluoride ion dissociates in solution to HF and fluoride ions (F^-). The pH of the solution drops because the HF that is formed partially ionises. The equilibrium between the fluoride ion (F^-), the bifluoride ion (HF_2^-) and HF is complex, varying with concentration and pH (Appendix 1).

In Australia, glass etching and glass washing are two applications that use these chemicals in aqueous solution without the addition of other acids. The following uses were reported during the assessment:

- Imported glass-etching paste repacked for sale to primarily retail craft outlets. The same product is used by contractors to etch identifying information via stencil onto vehicle windows (trucks, cars, boats, trains).
- Another glass-etching paste supplied primarily to industry for decorative work on mirrors and glass. Some may also be sold through retail outlets.
- Five per cent ammonium bifluoride solution to clean glass bottles prior to decoration.
- A small dip bath based on ammonium bifluoride is used in a home studio by an artist to polish lead crystal. The preparation called "sugar acid" is also used to frost glass for art purposes.

It is likely that all areas of use were not identified as bifluoride users were not specifically targeted in the HF survey. It is not clear if some imported glass etching products contain bifluoride alone or whether an acid is also present.

6.1.2 Incidental production

HF may be formed incidentally during other manufacturing processes. These processes are outlined below.

Production of phosphate fertilisers

HF is a by-product of the commercial production of phosphate fertilisers. In the process insoluble phosphate is converted to the soluble form through reaction with sulfuric acid. During the acidulation of naturally occurring phosphate rock, HF and SiF4 (silicon tetrafluoride) gases are evolved. In the production plants of one Australian single superphosphate manufacturer, these gases are drawn into a series of scrubbers and dissolved in water to form an aqueous solution of fluorosilicic acid. The fluorosilicic acid solution formed is used for water fluoridation or neutralised with lime and stockpiled.

It is not known if double and triple superphosphate are manufactured in Australia.

Aluminium smelting

HF is a by-product of aluminium smelting in the Herr-Heroult electrolysis process, which is carried out at several sites in Australia. One Australian smelter reported total fluoride emissions to atmosphere (both gaseous and particulate) of approximately 214 tonnes in 1997. This is based on a production volume of 396 000 tonnes and average emission of 0.54 kg fluoride per tonne of aluminium produced.

Thermal degradation

HF is formed during thermal degradation of fluorine-containing compounds.

The emission of HF has been recorded in fires where fluorine-containing extinguishants are used, and where the heat of the fire has decomposed and released refrigerant gases.

Fluoride emissions can occur during metal welding, originating from the electrodes or coatings (South Australia. Department of Labour, 1990, Parmeggiani, 1983).

Articles made of fluorine-containing polymers e.g. polytetrafluoroethylene (PTFE) can decompose if burnt or overheated, producing a mixture of toxic by-products including HF. Such decomposition may result from fires or from high-temperature processing such as thermoplastic welding.

It is reported that HF is also formed as a by-product in steel production, in the ceramic industry such as brick/tile plants (OECD, 1999), and from the combustion of coal for power (Thiessen, 1988).

Impurities in other chemicals

HF can be present in commercial grades of chemicals such as fluorosilicic acid and in hexafluorotitanic acid (Kroschwitz & Howe-Grant, 1994). Fluorosilicic acid used in Australia contains an average of 1% HF with the concentration ranging from 0.5% to 2% in various products.

One survey respondent reported using fluoroboric acid which contains traces of HF.

Reactions of other chemicals

Fluorosilicic acid exists only in aqueous solution (Gerhartz et al., 1988) and HF is formed on the surface of evaporating solutions (Chemtech Industries, 1990). HF fumes may be emitted on leakage, spillage or heating of fluorosilicic acid solutions or by concentrated solutions (Henkel Dusseldorf, 1993). HF is also produced when fluorosilicic acid is highly acidified with sulfuric acid (Gerhartz et al., 1988) or anhydrous hydrochloric acid (Simons, 1950).

Metal fluorosilicates also disintegrate on treatment with concentrated sulphuric acid and may liberate HF (Simons, 1950).

Hydrolysis of fluorine (Harbison, 1998), silicon tetrafluoride, boron trifluoride and other fluorides may also yield HF (HSDB, 2000, Segal, 1998, Gerhartz et al., 1988).

6.2 Natural occurrence

The major natural sources of airborne HF and other airborne fluorides are volcanic emissions, spray from oceans and weathering of rocks (Thiessen, 1988). The gas emissions measured from a volcano in Italy in 1989 included 0.04 to 0.66% HF (Baxter et al., 1990).

6.3 Importation

Anhydrous (100%) HF and aqueous solutions of 35 to 70% strength are imported into Australia, as are some products containing HF.

Approximately 350 tonnes per annum of anhydrous material is imported. Most is supplied in 15 to 20 tonne capacity isotainers, designed to contain the low-boiling liquid. Smaller quantities are imported in 45 kg, 11 kg, 4 kg and 230 g cylinders.

A similar quantity, approximately 350 tonnes per annum, of aqueous solutions is imported, packed in drums or bottles, with pack sizes ranging from 100 g to 200 kg. It is estimated that imports of aqueous solutions are divided as follows:

Solution concentration	Proportion of imports
70%	44%
40-60%	17%
35%	39%

Import quantities of HF obtained from the Australian Bureau of Statistics are shown in Table 3 below.

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Year	1994	1995	1996	1997	1998	1999
Tonnes imported	198	392	740	872	655	699

 Table 3 - Yearly total imports of HF (aqueous and anhydrous)

A number of imported products were also identified and in general were in pack sizes of < 10 L, one as low as 12.5 mL. The total quantity of imported products containing HF cannot be easily estimated, as they are likely to cover niche markets and be imported under different customs tariff classifications. In the imported products identified the concentration of HF ranged from 2% to 15%.

6.4 Repacking, reselling and formulation of products in Australia

Anhydrous HF in Australia is either used by the importer or supplied directly to the end-user. A similar pattern exists for imported products based on aqueous HF.

For aqueous HF imported in bulk, formulations and dilutions of various strengths are produced to make the correct product for the intended use. Therefore the distribution chain within Australia is generally longer. Sometimes the HF is simply diluted to a suitable concentration for the use. More complex formulations include ingredients such as other acids and surfactants. Acids reported as part of formulated products include sulfuric, nitric and chromic. Formulation may also be carried out in more than one stage e.g. dilution of imported material to facilitate safe handling and later formulation by another company for their own use or resale. Repacking and re-labelling of formulations also occurs for commercial reasons.

Fifty data providers resold the HF/HF product in the same package and 5 repackaged it. Sixty-two respondents reported that they carried out a formulation process with HF, including simple dilution. Of these, 31 were formulating for resale, and 31 for their own use. Table 4 sets out the use patterns reported during the assessment.

Import	Resell (without repacking)	Repack and then sell	Formulate for sale	Formulate for own use (includes simple dilution)	Use as is	Number of companies with this use pattern
					\checkmark	85
			\checkmark			27
	\checkmark					26
				\checkmark		24
\checkmark	\checkmark					20
\checkmark					\checkmark	5
				\checkmark	\checkmark	4
\checkmark				\checkmark		2
		\checkmark				1
		\checkmark			\checkmark	1
			\checkmark	\checkmark		1
		\checkmark	\checkmark			1
	\checkmark	\checkmark				1
						1
						1
						1
	\checkmark					1

 Table 4 - Patterns of use for HF and HF product

A variety of methods of distribution of HF and HF products were identified during the assessment. Examples of different chains of supply found during the assessment are listed below.

Short distribution chains for HF

Example 1: Cleaner/etchant for preparation of aluminium for powder coating

Company 1 - imports 55% HF in bulk for resale.

Company 2 - buys 55% HF and uses to formulate a product for resale.

Company 3 - (metal processor) purchases and uses product for own use.

Example 2: Laboratory reagent.

Company 1 - imports 50% HF packed in 500 mL or 2.5 L bottles for resale. *Company 2* - buys packed product for resale.

Company 3 - (laboratory) purchases and uses product for own use.

Long distribution chains for HF

Example 1: Rust remover for drycleaning industry:

Company 1 - imports 70% HF and dilutes to 10%

Company 2 - buys 10% HF in 200 L drums, adds extra ingredients to formulate, then packs into 500mL bottles and labels product, of brand name A.

Company 3 - buys bottles of product A and relabels as product B for resale.

Company 4 - buys product B for resale.

Company 5 - (drycleaner) buys product B for own use

Example 2: Mag wheel cleaner for car detailing

Company 1 -	imports 70% HF for resale.
Company 2 -	buys 70% HF and formulates 4% HF mag wheel cleaner for
	resale in 200 L drums
Company 3 -	purchases, repacks and labels mag wheel cleaner into 5 L and
	20 L drums for resale.

Company 4 - purchases these packs for resale.

Company 5 - (car detailer) purchases for own use.

Unusual methods of supply of HF

Example 1 Supply for use on ships

Company 1- imports 35% HF for resale.

- Company 2 formulates a metal treatment product with 10% HF and packs into 25 L drums for resale.
- *Company 3* purchases product for supply to ships, but does not take delivery of it, directing Company 2 to deliver to Company 4.
- *Company 4* takes delivery of product and forwards to ships, but is not aware of details of the product, as they are not the purchaser.

NICNAS was unable to contact the final user of the product.

Example 2: Supply via contract or tender to large institutional users.

Company 1 - imports 35% HF for resale.
 Company 2 - purchases 35% HF to formulate a stainless steel passivator and weld burn cleaner containing 3% HF, and packs this product into 20 L plastic drums for resale.

Company 3 - purchases the product for delivery to several of its many branches throughout Australia, for resale. Sales of the product are not recorded through the normal system, because they are part of contracts for bulk provisions. Organisations which may use this method of purchasing include the armed forces, airlines, mining sites and isolated communities.

In this example NICNAS was unable to contact any of the final users of the product.

Availability to the public

Example 1: Spray packs for cleaning mag wheels

Company 1 - imports wheel cleaner already packed and labelled in 500 mL trigger spray bottles for resale.

Company 2 - which may be a retail chain or independent spare parts supplier, purchases bottles for resale.

Retail customer - purchases product for own use.

(In some cases the product may be sold through a wholesaler, which would introduce one extra step into the chain.)

Example 2: Supply through trade showroom:

Company I imports refrigeration coil cleaner already packed for resale in 4 L containers. Strength is 8-15% HF. Product is stocked by many of the company's branches in Australia, where it is primarily purchased by the refrigeration trade. However, the public can also purchase at these outlets.

Example 3: Supply through factory door sales.

Company 1 formulates several metal cleaning products containing HF, which are packed in 20 L drums. While the bulk of their sales is through formal ordering, product can also be purchased in small quantities, and no records are kept of these purchasers.

Unauthorised Use

During the course of the assessment, NICNAS became aware of one instance of informal supply of HF. A tradesman had carried out a once-off job requiring pickling solution. He was unable to purchase > 10% HF without a licence in his state, and planned instead to obtain some from a colleague.

A hospital reported that some of the HF burns they had treated were a result of workers taking home small quantities to clean metal buttons etc. The burns resulted when inappropriate containers leaked.

6.5 Uses

It is believed that the information collected during the assessment reflects the profile of use of anhydrous HF in Australia with reasonable accuracy. The NICNAS survey covered only a proportion of formulators and users of aqueous HF from a wide range of industry sectors. Therefore the profile of users disclosed by the survey may not be representative, and has been supplemented by information on use from other industry sources.

The survey attempted to reach users of HF through the distribution chain. For some industry sectors using aqueous HF where there can be several steps in the distribution chain, the end-user may not have been reached by the survey.

6.5.1 Anhydrous (100%) HF

In Australia the majority of anhydrous HF is used as an alkylation catalyst. Other uses for anhydrous HF are surface fluorination of plastic articles and in research. It has also been reported recently that gas mixtures for excimer laser systems contain a small (1 to 2%) proportion of HF.

Chemical catalyst in petrol refineries

Anhydrous HF is used as a catalyst in alkylation in five oil refineries in Australia. Alkylation is the process of combining two gases such as butylene and isobutane to form high-octane gasoline. The approximate annual amount of anhydrous HF used for this purpose is > 300 tonnes. Some other refineries in Australia carry out alkylation using sulphuric acid as catalyst (Australian Institute of Petroleum Ltd, 1995).

Fluoro-Seal treatment process

Anhydrous HF is imported in 45 kg containers for surface fluorination of plastic containers and other articles that have been moulded or formed from plastics, usually polyolefins. The process creates a fluorinated hydrocarbon surface layer that provides a barrier against the absorption and permeation of non-polar materials into or through plastic containers. The annual quantity used for this purpose is < 5 tonne.

Research

Anhydrous HF is imported in small (250 g to 10 kg) containers for laboratory/research use. Use of anhydrous HF to carry out peptide cleavage in a closed apparatus was reported. Mixtures of hydrogen fluoride and pyridine are also marketed for research applications.

6.5.2 Aqueous solutions of HF

The survey identified varied uses of aqueous HF in Australia. Table 5 shows the uses identified by survey respondents who were end-users of aqueous HF, or of formulations containing aqueous HF with other chemicals. It was noted that while formulations may be directed at a particular market, they can be and sometimes are used for other purposes. Some endusers used HF for more than one application.

End Use	No. of End User Respondents	
Metal surface treatment and cleaning	61	
Laboratory processes*	24	
Rust removal in dry cleaning, laundering and carpet cleaning	9	
Cleaning exterior walls	6	
Polishing/removing images from printing plates	4	
Dental uses:		
a) Ceramic etching in dental laboratories	2	
b) Polishing metal castings	1	
Anti-slip floor treatments	1	
Oil and gas well use (acidified fluoride)	2	
Etching or cleaning of glass	2	
Chemical synthesis	3	
Etching of semiconductors	2	

Table 5 - Uses of aqueous HF

*Laboratory processes may overlap with other categories listed here e.g. metal surface treatment.

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Industries in which the above end-users operated included:

Aircraft manufacture	Gold prospecting	
Automotive – (car detailing & repairs)	Hospitality	
Boat building/repair & fishing	Jewellery Manufacture	
Bulk transport	Metal Processing	
Cement Manufacture	Mineral Analysis	
Chemical manufacture	Mining	
Cleaning	Oil/gas well servicing	
Dental/Medical	Optical lens processing	
Detergent manufacture	Powder coating	
Dry cleaning / laundry	Printing	
Food Manufacture	Research and development	
Glass Manufacture	Shipping and commercial fishing	
	Solar energy	

Further information on uses from formulators of HF products is presented in Table 6. The quantities reported would not represent the total market.
Target market of formulation	Number of formulated products	% HF	Approx total amount of HF formulation sold annually
Metal surface treatment (various types)	71	<1 – 35%	> 500 tonnes
Cleaning/etching of brick/stone/ceramic	5	2.4 – 26%	40 tonnes
Rust removal in dry cleaning, laundering or carpet cleaning	2	9.8 – 10%	4 tonnes
Paint stripping	2	2 %	9 tonnes
Therapeutic dental products	4	0.003 – 0.346	Not reported

Table	6 -	Products	formulated	for resale	using	aqueous	HF
Lanc	v	Troutes	Ioimulateu	Ior resarc	using	aqueous	***

Metal surface treatment

Metal surface treatment is clearly the largest use of HF formulations in Australia. However, the applications within this area are varied, covering a range of concentrations, small and large users, and processes intrinsic to manufacture as well as after-market activities such as cleaning. In this section, use of HF in the metal processing industry is described separately to other metal treatment. The niche uses in cleaning gold nuggets and in the printing industry are also described separately.

Metal processing industry

In the metal processing industry hydrofluoric acid products are used to clean, brighten and/or etch aluminium and stainless steel and some other metals such as titanium. These activities usually form part of larger processes designed to produce finishes that will protect against corrosion and abrasion and/or provide decoration. Cleaning removes contaminants such as dirt, oils and oxides such as scale deposited on the articles from treatments such as welding. Brightening and etching provide a uniform surface that can improve the effectiveness of subsequent processes such as conversion coating (anodising, phosphating, chromating), electroplating and powder coating. Etching can also be used to bring components to the correct dimensions. In addition to these uses large quantities of HF formulations are used for automotive steel coating and in pickling/passivating products for stainless steel.

Typically, the formulations will contain hydrofluoric acid with sulphuric acid or nitric acid and are used in dipping tanks. Nitric acid-HF combinations are mainly used with stainless steel. HF is also an ingredient in some conversion coating solutions.

Some of these processes are likely to be carried out at a relatively small number of sites in Australia e.g. during high speed production of aluminium cans or during large-scale production of aluminium coil. However, they can also be used in smaller operations and it is estimated that HF in powder coating may be used at > 200 sites and pickling products for stainless steel at > 1000 sites in Australia.

Smaller uses of HF in the metal treatment industry are:

- etching aluminium aircraft parts prior to fluorescent penetrant non-destructive testing;
- removal of ceramic cast from platinum in jewellery manufacture;
- electrolytic etching (electropolishing) of alloys prior to electroplating; and,
- cleaning new aluminium cylinders before they are put into service.

The concentration of HF in the metal processing products ranges from 0.1% to 35%. Many of them are diluted further before use, or used to "make-up" solutions in dip baths. Typical products formulated for use on stainless steel after welding contain initially 2 to 6% HF and those for brightening aluminium 2 to 15% HF. The lowest percentage products ($\leq 1\%$) reflect the use of HF in coating formulations.

It is not possible to accurately distinguish products used for metal processing from those used for other metal cleaning applications. However, it is estimated that > 500 tonnes of product containing HF is sold annually for metal processing. (This quantity is larger than the amount imported, because it reflects a diluted product).

Cleaning gold nuggets

This is a specialist metal-cleaning application of HF for removing other minerals from the gold. It is reported to be the standard method for preparing small gold nuggets for sale. Concentrations used for cleaning gold nuggets ranged from 50 to 70%, although in some cases this is diluted for use.

Cleaning printing plates

HF has a specialist use in the printing industry for the removal of scratches or unwanted images from metal printing plates. HF is applied from a deletion pen (felt-tipped), or a solution is sponged on. The range of concentrations in the pens varies from 4.8% to 10.2% with one solution reported to contain < 0.05%.

Deletion pens are used by platemakers, printers and typesetters. Amounts used at a site varied from 20 pens and 2 bottles (100 mL) of solution a year to approximately 48 L of < 0.05% solution per year.

Other metal treatment

Apart from the specific categories above, there are many areas in which primarily metal surfaces are cleaned or brightened with products containing HF. For some applications HF brightens by removing oxides, in others it may dissolve adherent silica-containing dirt or protein residues, or may degrease surfaces. The majority of these products are formulated locally.

Reported applications include:

- treatment of aluminium bicycle rims;
- cleaning dirt from vehicles e.g. red dust from personnel carriers used on mine sites;
- removing rust from stainless steel rails on boats, cleaning stainless steel during boat re-fits and repairs and other equipment on a ship;

- cleaning engine bays of vehicles, cement tankers, bulk transport tankers, caravans, carburettors prior to repair and mag or alloy wheels. Some of these products are used in spray packs;
- cleaning refrigeration coils as part of maintenance program;
- degreasing prawn processing equipment;
- cleaning/descaling commercial dishwashing machines;
- cleaning stainless steel ion source in pathology laboratory;
- etching medical instruments to reduce shine;
- pickling stainless steel electrodes to remove machine oil and oxidation; and,
- contained in an imported kit for repairing gas analyser.

Recommendations for the following additional uses were made on labels, MSDS or product guidance sheets:

- removal of rust from cast iron, steel, copper and brass;
- internal cleaning of shipping containers;
- cleaning of stainless steel urinals, railroad equipment, aluminium siding, aluminium window frames and louvres and rust from car bodies;
- removal of stains, dirt and grease from aluminium truck trays, walls, boats and utensils;
- as a concentrated toilet and bath house cleaner;
- as a one-off treatment to clean and brighten the stainless steel sinks in a large motel/apartment complex;
- cleaning and deoxidising fuel tanks, bull bars, steps and other aluminium or stainless steel components; and
- removal of water scale, detergent stain, rust spots and general grime from most metals.

Concentration ranges of products for this category are similar to those for metal processing, and some products would be used for both applications.

It is estimated that > 100 tonnes of product containing HF would be sold annually for general metal cleaning applications, excluding the amount used in metal processing. The formulations are often labelled as being suitable for general metal treatment rather than a specific use, but mag wheel cleaning is a specific target of several formulations. Recommendations for use in marine applications are also common.

It is not possible to estimate the number of sites at which HF and HF products are used for metal cleaning in Australia. The use in vehicle detailing and in some general cleaning applications suggests that the number of sites would be high.

Laboratory use

The most important laboratory use of HF is as a reagent in analytical chemistry for acid digestion, particularly where dissolution of silica is required. Specific examples of this use mentioned by respondents to the HF survey included:

- silica analysis;
- silicon determination in metals;

- removal of silicate minerals from rock and soil;
- dissolution of quartz to liberate diamond indicator minerals;
- digestion of marine sediment for elemental analysis; and,
- analysis of mineral samples;
- determination of phosphorus by bomb digestion; and,
- preparation of pollen samples.

Other laboratory uses of HF include:

- as a reagent solvent in the preparation of samples for atomic absorption spectrophotometric analysis;
- in standards for instrumental analysis;
- etching of metal for inspection.
- etching evaporated titanium thin film;
- cleaning probes;
- dissolving glass slag in materials research;
- removal of protein from glass and plastic ware, prior to critical analyses; and,
- occasional cleaning of laboratory equipment to remove build-up.

Laboratory uses also overlap those of other categories, sometimes reflecting smallscale operations occurring in a manufacturing environment (cleaning of coatings from lenses) or research work (development of semiconductors).

Twenty four respondents to the survey used HF in laboratory processes. Over one third of users were from the metal, mineral or petroleum mining sectors, including exploration and analysis. Other industries included iron and steel production, research and development, aircraft manufacturing, analytical chemistry, and detergent manufacture.

The concentration of HF in the products ranged from 10% (1/24) to 70% (2/24), with the most common concentration being between 40 to 50% (21/24). Quantities used varied from less than 1 kg/y to 350 kg/y, with the larger quantities being used for acid digestions. The total amount reported by end-users in the survey is approximately 1.5 tonnes per year.

HF for laboratory use is imported in finished packs. No formulations for resale were reported for this use category, reflecting the fact that most lab applications require high concentrations of the pure chemical. The metallurgy reagents Kellers Etch, Tucker's Reagent and Kroll's Reagent contain HF and may be formulated by users.

It is estimated that HF use may be occurring at > 200 laboratory sites in Australia.

Rust stain removal in dry cleaning /laundry /carpet cleaning

Eight respondents to the survey used HF-containing products for removal of rust stains in commercial dry cleaning and laundry processes and one used it in carpet cleaning. HF can also be used to finish off removal of other stains, if there is residual metal in the stain. Concentration of HF in products ranged from 1 to 10 %, with most using a product containing 9% to 10% HF.

Monthly consumption figures varied from < 10 mL to 500 mL, and the total amount of product used annually by the survey respondents was calculated to be approximately 33 L.

From the information on products formulated for resale for this use, > 2500 L was formulated for commercial use and > 1500 L for retail sale, at strengths from 9.8% to 10%.

There are approximately 1200 drycleaning enterprises in Australia (Drycleaning Institute of Australia, 2000) and it is estimated that most would carry out rust spotting with an HF product.

Treatment of building surfaces

This category consists primarily of products that will clean or etch ceramic based building materials such as brick, tiles or stone. It includes some graffiti removers which partially dissolve the substrate and anti-slip floor formulations which etch and roughen the surface. Some spray cleaning formulations for buildings may overlap with formulations designed to clean vehicles.

Cleaning

Six respondents to the survey used HF products for cleaning external walls of buildings. Specific cleaning purposes included removal of bore stains and rust stains, removal of dye or shadow left on brickwork after paint removal, graffiti removal, stripping off paint prior to painting and removal of dirt and pollution. Four of the respondents were companies primarily dedicated to building cleaning, one was a metropolitan railway and one was a government graffiti removal program.

The strength of HF in the products used by these companies ranged from 2% to 7%, and annual usage > 1 tonne.

From the information on products formulated for resale, 40 tonnes approximately was formulated for use on a wide range of masonry surfaces, at strengths from 2.4% to 26%. Specific recommended uses include graffiti removal, cleaning calcium silicate from bricks, cleaning terracotta tiles, sandstone, concrete, and removing darkening of masonry caused by pollution or fire. In some areas of Australia it is reported that bricks become stained with a green vanadium compound, which can be removed by HF.

One product was recommended for removing stains, dirt and wax build-ups from automatic car washes.

Paint stripping

One of the two products specifically formulated for paint stripping contains methylene chloride as well as HF and is recommended for treatment of difficult-to-remove organic finishes.

Anti-slip treatments

HF can be used to give an anti-slip finish through etching of surfaces. One respondent to the survey used approximately 90 kg annually of products containing 2%, 4% or 6% HF and floors treated are typically outside near an entrance and

composed of granite, marble, terrazzo or terracotta. The products are occasionally diluted further before use. Another product is specifically designed for tile etching. One anti-slip product identified recently is recommended for the treatment of a range of floor surfaces, tubs and shower floors. After the anti-slip treatment, all future routine cleaning of the surface is carried out with a more dilute solution of the etching product.

It is difficult to distinguish anti-slip uses from general cleaning from formulation data and it is expected that other anti-slip formulations are in use.

Dental use

Three different applications of hydrofluoric acid in the area of dental health were identified during the assessment. These include etching dental ceramics, polishing metal castings, and use in fluoride mouth rinses and topical gels to increase uptake of topical fluoride by dental enamel.

Etching ceramics

HF is used by dental technicians and dentists in etching ceramic dental prosthetic objects, inlays, onlays, veneers and crowns. Etching strengthens the adhesion of adhesive agents to the ceramic surface. Three imported etching products are in use in Australia, containing < 5% and 9.5% HF. Pack sizes range from 6 to 12.5 mL. The products are used in quantities of < 100 mL/y.

Production of metal castings

HF is used in dental laboratories in the production of precious metal castings. A product containing 14 % HF is used for polishing titanium castings and a 40% HF product is used to pickle gold castings. An imported product containing < 5% HF is used to etch metal which is the base of crowns and partial dentures. HF has also been used to dissolve ceramic inserts used in the casting of metal frameworks.

Therapeutic products containing fluoride

HF is an ingredient of five topical fluoride mouth rinses and gels. The HF in these products assists uptake by dental enamel of the topical fluoride. Some of the products are intended to provide the necessary daily systemic fluoride intake in areas of low fluoridation of the water supply, by swallowing of the solution after rinsing. The products are also intended to supplement fluoride intake in areas where the water supply may be fluoridated, through rinsing and spitting out, or brushing on gel and rinsing. The products are for professional use in the dental surgery, and to be taken for use in the home by patients. The concentration of HF in these products ranges from approximately 0.003% to 0.346%.

Use in oil and gas wells

HF is produced on site from a bifluoride salt and acid and pumped into oil or gas wells to react with clays and rock. Percentage range of HF in the solutions varies from 1.5% to 3%. The approximate amount used yearly is a total of 2 tonnes. The process is not a routine one and is only carried out when necessary to stimulate production of the well.

Etching / cleaning of glass or glazes

Etching

Etching glass is the traditional use of HF, but the survey did not indicate a large use for this purpose in Australia. HF is used to etch codes and logos onto glass moulds and in the production of decorated glass. One company dilutes HF to a concentration of 5% to 10%, producing 200 L annually of a glass and ceramic etchant. A glass artist uses 50% HF to etch flash glass.

More commonly, bifluoride paste formulations are used to etch glass, both in the craft market and industrially. These are imported in bulk and repackaged or imported in small bottles for retail sale. Formulations are used by contractors to etch logos on windows of cars, trucks, buses and ferries. The use of bifluoride pastes in etching vehicle identification numbers onto car windows, as an anti-theft measure, has been reported.

HF can be used to etch or strip porcelain or glaze, before further processing in bathtub resurfacing. Although not reported in the survey, it is believed that 15 to 35% HF, diluted before use, is used for this application.

Cleaning

A liquid product containing 7% HF is diluted before use to clean bore stains from windows. Another product, also containing 7%, is recommended to remove built up scale and wax deposits from glass. A bifluoride formulation is used for polishing crystal in a craft application, and another is used to clean glass bottles.

Semiconductor manufacture

Etching silicon wafers is a large use of HF overseas as part of the production process for computer chips and solar cells. In Australia, 40% to 50% HF is purchased for etching silicon wafers. The material is diluted before use in dip tanks. It is expected that the number of sites carrying out this process in Australia would be small, but more than 5 tonnes is used annually.

Similar processes are carried out on a smaller scale for research.

Chemical synthesis

HF is used in Australia as a raw material for the manufacture of inorganic salts such as nickel, zinc, calcium, barium and other fluorides. It is also used in the manufacture of fluorosilicates and fluoroborates. Quantities were not reported.

6.6 Export

The Department of Defence reported that HF in concentrations of > 25% has been exported over the last few years for metal treatment and laboratory use. Exports were primarily to the Asia-Pacific region. Some information received via customer lists confirms this data.

6.7 Other uses

Some major overseas uses of HF do not occur in Australia. These are:

- as a starting material for organic fluorides such as propellants and fluoropolymers. The former were manufactured in Australia until 1995.
- manufacture of uranium hexafluoride in the nuclear power industry;
- manufacture of synthetic cryolite or aluminium fluoride for aluminium smelting. These chemicals are currently imported.
- frosting of light globes; and
- large-scale use of HF in mining. It was previously used in the diamond and mineral sands sectors.

Other reported overseas uses of HF which were not confirmed during the assessment were in removing sand from metal castings, cleaning windows in semiconductor manufacturing, repair of porcelain, ingredient in automatic carwash formulations, cleaning wood, cleaning glasshouses and as part of asbestos test kits.

Recently a new method of on-site treatment of fireproofing materials containing asbestos has been proposed (Block, 2000). HF is formed *in situ* at a controlled rate through the reaction of phosphoric acid and a fluoride salt that hydrolyses very slowly under acidic conditions. Field trials have been carried out in the US, but it is not known if the method has been commercialised.

7. Exposure

7.1 Environmental exposure

7.1.1 Release

The quantities of HF used deliberately need to be put in perspective compared to the quantities of HF produced naturally or incidentally through other industry activities such as aluminium smelting, fertiliser (superphosphate) production and within the brick, ceramics and clay products industry.

Natural occurrence

HF may enter the environment from natural sources such as volcanoes, weathering of minerals and marine aerosols. The greatest total amount of natural fluoride is contributed by volcanoes, and this is primarily in the form of hydrogen fluoride. Passive degassing of volcanoes has been estimated to contribute up to 6.7 million tonnes per annum. Weathering of fluoride containing rocks and minerals also contributes to atmospheric fluoride. The marine aerosol is potentially a major source of tropospheric HF, although this will be confined to the air over oceans (ATSDR, 1993). Natural releases in Australia would be expected to come more from weathering of minerals though atmospheric concentrations will contain fluoride released elsewhere due to rapid mixing of continental air masses.

HF incidental production

Aluminium industry

It is difficult to quantify the volumes of HF incidentally produced during these activities. During aluminium production, the majority of HF appears to be released during alumina reduction. The National Pollutant Inventory (NPI) lists emission of HF being 2.5 kg/tonne aluminium produced, with another 0.26 kg/tonne during anode baking, giving a total of 2.76 kg/tonne (NPI, 1999a). Based on actual figures provided by one applicant, where measured total fluorides emitted averaged out at around 0.54 kg total fluorides per tonne aluminium produced, this would appear to be a significant overestimate. However, without data from all companies involved in aluminium smelting, and to assume a worst case, the emission factors provided from the NPI will be used.

Statistics from the aluminium industry show that in 1998, aluminium production was over 1.6 million tonnes, with production steadily increasing since 1974. With a maximum emission of 2.76 kg/tonne, it could be expected that over 4,400 tonnes of HF will be produced incidentally through aluminium smelting within Australia per annum.

Phosphate manufacturing industry

The Australian market for superphosphate is in the order of 4 million tonnes per annum, for which some 75% (3 million tonnes) is supplied by locally manufactured superphosphate.

The NPI has provided emission factors for fluorides emitted during the production of superphosphate. As a worst case, assuming the process is uncontrolled, an emission factor of 1.9 kg fluorides per tonne of superphosphate produced is given (NPI, 1999b). Assuming 3 million tonnes of superphosphate produced per annum, and all fluorides are emitted as HF, then up to 5,700 tonnes HF may be emitted through the production of superphosphates. With control technology, this figure may be as low as 60 tonnes.

Bricks, clay and ceramics industry

HF is also produced incidentally within the bricks, ceramics and clay products industry. The NPI has provided an emission factor of 0.23 kg HF per tonne of ceramic product produced and an emission factor of 0.295 kg total fluorides where no control measures are in place per tonne of bricks manufactured (NPI, 1999c). These emissions are reduced significantly when pollution controls are in place. For example, with a dry scrubber, the emission factor during brick manufacture is 0.014 kg total fluorides per tonne produced, and with a high efficiency packed bed scrubber, the emission factor is 0.00065 kg total fluorides per tonne.

Again, it is difficult to quantify the amount of HF produced through this industry. Advice received from the Clay Brick and Paver Association is that in the 1998/99 year, 1.95 billion clay brick and pavers were produced (up from 1.85 billion the previous year, and 1.76 billion in 1996/97). At around 3 kg per unit, this is almost 6 billion kilograms of product, which could result in between 4 and 1770 tonnes HF produced incidentally depending on pollution control measures. This does not consider any production from ceramics and other clay products.

Fossil fuel combustion for power generation

Fluoride compounds including HF may be emitted during the combustion of coal. The Australian Greenhouse Office has provided forecasted figures for 1998/99 of 60.7 MT black coal and 65.8 MT brown coal being consumed in Australia. The NPI has provided emission factors for fluoride compounds (expressed as hydrogen fluoride) of 0.08 kg/tonne of black coal combusted and 0.075 kg/tonne of brown coal combusted (NPI 1999d).

These figures indicate up to 9800 tonnes of HF may be emitted to the atmosphere through combustion of coal in power generators.

Industry end use

Table 7 demonstrates a very crude break up of the use of HF in Australia. While the level of detail received on the use of this chemical in Australia is far more complex than this, for the purposes of this preliminary assessment, this simplified breakdown will be satisfactory for estimating releases. The main uses are described below with release estimates in Tables 8 and 9.

Assuming aqueous solutions of HF imported have the maximum concentration of HF reported in a range, the estimated breakdown of use of HF into categories is as per Table 7:

Table 7 - Estimation of	f quantities HF per annu	m for end uses
End use of HF		Approx. total (kg)*

Alkylation catalyst.	580 000
Metal cleaning/brightening; pickling; etching	180 000
Boat/truck etc. aluminium cleaning	5600
Raw material for manufacture of inorganic salts	5100
Fluoro seal treatment process	3000
Masonry cleaning	1800
Laboratory	1000

* Not accurate, figures used only for estimating releases

These quantities per end use are largely speculative as the information received was not of sufficiently high quality to be more accurate. They will be acceptable for this preliminary assessment. Because processes for metal cleaning, pickling and etching (also of glass and ceramics) is expected to be largely similar, these end uses have been grouped together.

Alkylation process

Hydrofluoric acid is delivered to refinery sites in dedicated tankers. The method of transferring the chemical from the tanker to storage vessels is closed with limited scope for release to the environment except in the case of faulty lines.

Similarly, the alkylation process is conducted in a closed system, so scope for release to the environment is limited. The system is completely sealed, and acid addition is done by pressuring it into the system from the storage vessel.

During the alkylation process, acid is recycled where appropriate. When the acid is no longer usable, it is neutralised with eg lime. Neutralisation will be carried out on site, with the waste stream expected to be held in pits or enter on site waste water treatment plants (WWTP) directly. If shutdown and entry to vessels are required, chemical cleaning takes place and wastes are likely to be disposed of by a licensed contractor. Likewise, cleaning of equipment involves neutralisation with the waste stream sent to on site pits or a WWTP. Contamination of water (e.g. cooling towers) can occur through ruptured lines. This could lead to release during blowdown operations, where acid contaminated water would be sent to the WWTP.

Companies involved in alkylation operations have estimated release to the atmosphere and water as minimal, with no release anticipated to soil. For the purposes of this assessment (based on company estimations), release to the atmosphere will be assumed to be 0.1%, with release to water assumed to be 0.01% after neutralisation. These figures compare well to the emission factors assumed within the EC Technical Guidance Document (TGD) (European Commission, 1996). For production processes using isolated intermediates stored on-site (in this case, HF used as a catalyst), it is estimated that chemicals with the solubility and vapour pressure of HF will result in 0.1% being released to air, and 2% released to

water. Because of the neutralisation of HF prior to release, the amount going to water could be expected to be significantly less than this.

Releases to water will be assumed to initially go to an on site WWTP prior to discharge to sewer.

Metal cleaning (pickling), glass etching etc.

Metal cleaning/brightening/pickling involves running the metal being treated through a series of baths including acid and rinsing baths, and possibly a drier. Information provided regarding releases during these processes is varied. Generally, release to both air and water can be expected. Atmospheric release will vary depending on the workshop practices. It is expected many will keep baths covered when not in use. However, the widespread nature of operations suggests non-optimal practices will also occur and significant environmental release may be expected from some sites due to volatilisation from uncovered baths. For the purposes of this assessment, it will be assumed that releases from glass, metal and ceramic etching will be the same as for metal cleaning and pickling.

For wide dispersive uses such as for metal cleaning, the TGD indicates that for a chemical with the vapour pressure of HF, 25% will be emitted to air. Assuming 180 tonnes per annum is used in these industries, a maximum release to air of 45 tonnes per annum can be expected, or 150 kg per day around the country (assuming use on 300 days per annum).

The TGD indicates that for a chemical with the solubility of HF, 65% will partition to waste water (European Commission, 1996). In the case of HF, it is highly unlikely to be this high because the practice is to neutralise liquid waste prior to discharge. When the pickling bath is neutralised (e.g. with calcium hydroxide), the resulting metal hydroxides and calcium fluoride form a sludge that can be disposed of to landfill without further treatment. The assumption of 0.01% release to water after neutralisation used above is not considered appropriate for these end uses because HF is largely used in an open system allowing more release through spillage and splashing. It will be assumed that after neutralisation of liquid waste, 1% HF is released to water through the sewer system. This equates to approximately 1.8 tonnes per annum, or 6 kg per day assuming 300 days per annum of operation.

Cleaning of aluminium on boats/trucks etc., and masonry cleaning.

These uses are estimated to account for 7400 kg HF per annum. With cleaning on boats, the expected practice is to use acid cleaners while the boat is dry docked. This type of cleaning involves applying dilute solutions of HF to aluminium surfaces and washing off with water. While measures may be in place to collect liquid waste and treat, this can not be assumed as these products may be used by the public. For the purposes of this assessment, it will be assumed that all chemical used in cleaning aluminium on boats, trucks etc. is released to receiving waters. Based on Table 7, this suggests 5600 kg per annum through this use (28 kg per day assuming use over 200 days of the year).

Masonry cleaning also involves application of dilute HF solutions to stone/brick work, with water used to wash the surface before it dries. Release of HF through this use is expected to be split between all three environmental compartments, but for this assessment, it will be assumed that all release is to stormwater drains. 1800 kg per annum is expected to be released to receiving waters through this activity (9 kg per day assuming use over 200 days of the year).

Laboratory use

Concentrated hydrofluoric acid solutions (30 to 71%) are used for mineral assay and other analyses and also for research purposes. Details on use patterns for HF in the laboratory are not sufficient to accurately predict losses. It will be assumed that any liquid releases will be neutralised prior to disposal, and disposal will be to on site waste water treatment plants prior to discharge to the sewer. With neutralisation, actual HF expected to be released to water will be relatively low.

The HF survey indicates that 780 kg per annum are used in the laboratory. For release estimates, 1 tonne per annum is assumed. The nature of laboratory work suggests the system will be largely an open one, and releases to air and water will be assumed to be the same for those with metal cleaning and pickling, ie, 25% to air, and 1% to water (following neutralisation). This indicates releases of 250 kg to air and 10 kg to water annually, or 5 kg to air per day, and 0.2 kg to water per day assuming 50 days per annum of laboratory use.

Production of fluorine compounds

HF is used in Australia as a raw material for the manufacture of inorganic salts such as nickel, zinc, calcium, barium and other fluorides. It is also used in the manufacture of fluorosilicates and fluoroborates. Release during this end use is expected to be minimal as the chemical should be largely consumed during its use. Release will be assumed to be the same as that when used as a catalyst in alkylation reactions (above), ie, 2% to air, and 0.01% to water. Based on an expected 5100 kg per annum used for this activity, annual release to air and water will be in the order of 100 kg and 0.5 kg respectively. Assuming 100 days manufacture per annum, this equates to 1 kg per day to air, and a negligible amount to water.

Expected daily releases can be summarised in the following tables. It is anticipated all incidentally produced HF will be released to the atmosphere.

Table 8 demonstrates that atmospheric releases from HF used in industry is insignificant when compared to that released through incidental production, even though these figures are worst case, and likely to be a significant overestimation.

Activity	Annual Release	Days per year	Daily release
Alkylation process	11 600	300	39
Metal cleaning (pickling), etching etc.	45 000	300	150
Cleaning of boats, trucks etc. and masonry	-	-	-
Laboratory use	250	50	5
Production of fluorine compounds	100	100	1
Fluoro-seal treatment process	negligible	-	-
Total expected release through HF industry:	56 950		195
Incidental Releases			
Aluminium Industry	4 400 000	300	15 000
Superphosphate manufacturing	5 700 000	300	19 000
Bricks, clay and ceramics industry	1 770 000	300	5900
Coal burning for power generation.	9 800 000	365	27 000
Total expected release through incidental production:			66 900

Table 8 - Estimated release of HF to the atmosphere (kilograms)

Table 9 - Estimated release of HF to water (kilograms).

Activity	Annual Release	Days per year	Daily release
Alkylation process	58	300	0.2
Metal cleaning (pickling), etching etc.	1800	300	6
Cleaning of boats, trucks etc. and masonry	7400	200	37 ^a
Laboratory use		50	0.2
Production of fluorine compounds	0.5	100	<0.01
Fluoro-seal treatment process			
Total expected release:	9268		43.4

a) This release is assumed to go direct to receiving waters.

7.1.2 Fate

The level 1 fugacity model predicts that at equilibrium, approximately 70% of the chemical will partition to water with 30% to air. Only negligible amounts are expected in soil, aerosols, sediment or biota.

The following discussion on fate is paraphrased from the OECD report (OECD, 1999) and the US Public Health Services report (ATSDR, 1993) and the Henry's law constant has been calculated.

Once released to the environment, HF is expected to be transformed to a variety of other F-compounds relatively quickly.

Aquatic fate

In water, HF is ionised at neutral pH and does not degrade. The presence of calcium will immobilise the fluoride ions.

In freshwater, where the pH is above 5 the free ion is the main fluoride species. As pH lowers, the proportion of fluoride ion decreases, while HF_{2} and non-dissociated HF increases. In the presence of phosphate, insoluble fluorapatite is formed, a large part of which is transferred to the bottom sediments. The calculated Henry's Law constant of 2.07 Pa.m³/mol at 20^oC indicates hydrogen fluoride will be highly volatile from water.

In seawater, fluoride belongs to the macrocomponents. Total fluoride content is divided in 51% F^- , 47% MgF⁺, 2% CaF⁺, and traces of HF and HF₂⁻.

Precipitation by calcium carbonate dominates the removal of dissolved fluoride from sea water with the next most important removal mechanism being incorporation into calcium phosphates. Undissolved fluoride is generally removed by sedimentation. The residence time of fluoride in ocean sediments has been computed at 2 to 3 million years.

Atmospheric fate

Fluorides are emitted to the atmosphere either in gaseous form or as solids in the form of aerosols. It is estimated from the OECD report that emissions in gaseous or solid form is split 75% and 25% respectively. Gaseous fluorides in the atmosphere are predominantly HF (and SiF₄). HF is removed relatively rapidly from the atmosphere by both wet and dry deposition.

Gaseous fluoride is eliminated from the atmosphere by both dry and wet deposition with estimated half lives of 14 and 12 h respectively. Fluoride aerosol is eliminated more slowly, predominantly by wet deposition, with an estimated half life of 50 hours. Dry deposited fluoride aerosols have an estimated half life of 12 days.

Terrestrial fate

Anthropogenic sources of fluoride may enter the terrestrial environment via atmospheric deposition, fluoride containing sludge or phosphate fertilisers. It is expected that HF being released to soil would largely be removed through volatilisation.

In soils (pH < 6) fluoride is predominantly found in bound form in fluoride containing minerals such as fluorspar, cryolite and apatite, and clay minerals. In these forms, it is immobile in soils, but some leaching is possible in soils with a low clay content. A direct consequence of the strong complex forming properties of fluoride is that with increasing F⁻ concentrations in pore water and groundwater, the aluminium and iron concentrations also increase. In addition, a positive correlation has been found between the concentration of fluoride and that of organic carbon in the soil solution, which may indicate that fluoride also forms complexes with carbon. At a pH above 6, the fluoride ion is the dominant species.

Biodegradation and bioaccumulation

Due to its nature the term biodegradability is not appropriate for HF. In water around neutral pH, HF ionises readily. While this is not considered degradation, the free fluoride ions will precipitate out of solution upon reaction with calcium carbonate. Calcium is commonly found in Australian surface waters suggesting HF will be removed from the system relatively quickly.

Aquatic bioaccumulation

The OECD report provides the following discussion on bioaccumulation in aquatic species.

In freshwater aquatic organisms, fluoride accumulates primarily in the exoskeleton of crustacea and in the bones of fish. No fluoride accumulation was reported in edible tissues. In fish, bioconcentration factor (BCF) values of 53 to 58 (dry weight) and < 2 (wet weight) were found. In crustacea, BCF-values based on whole body fluoride content were found to be <1 based on dry weight. The highest reported BCF-values for mollusca and aquatic macrophyta were 3.2 and 7.5 (wet weight) respectively.

In marine organisms, fluoride was found to accumulate in fish, crustaceans and plants. The highest value, 149, was found in fish. BCF-values for crustacea ranged from 27 to 62. Fluoride concentrations up to 30 mg F/kg were found in "consumption" fish.

The IUCLID* data sheet provides a further result for the grass carp *Ctenopharyngodon idellus* exposed to 15 ppm fluoride. Bone fluoride contents were up to 300 times higher than those found in controls. It is assumed that this test is invalid as it is not reported in the OECD document. Nonetheless, it may provide further guidance to the bioaccumulation of HF.

It is stated in the IUCLID data sheet that, on the basis of available data, it appears that fluoride has a low potential for biomagnification in aquatic systems.

Terrestrial bioaccumulation

The following results are reported in the OECD report, and in part, the IUCLID data sheet.

Earthworms collected from polluted sites around a fluoride chemicals factory reflected contamination. At the highest polluted sites the fluoride content in worms reached values of up to 135 mg/kg without gut, where as worms from unpolluted sites showed contents of 6 to 14 mg/kg. The fluoride content in the whole worm from unpolluted sites was found to be much higher and reached values up to 150 mg/kg due to the fluoride content of soil contained in the gut.

Woodlice from different sites in the vicinity of a fluoride producing plant showed 10 to 1800 mg/kg F concentration dry weight in *Oniscus asellus* and 240-1360 mg/kg F concentration dry weight in *Porcellio scaber*. This compared to levels of 35 and 180 mg/kg respectively from animals in the control site.

^{*} The IUCLID data sheet is taken from the International Uniform Chemical Information Database. Results from this datasheet are non-confidential data supplied to the European Commission by European industry. They have not undergone any evaluation or validation by the European Commission.

Fluorides accumulate primarily in the skeletal tissues of terrestrial animals that consume fluoride containing foliage. Symptoms of "fluorosis" are seen at bone fluoride levels of about 100 times those in animals collected from unpolluted areas. The IUCLID data sheet states that, on the basis of available data, it appears that fluoride has a low potential for biomagnification in terrestrial systems. However, the OECD report states that data on a variety of invertebrates collected from fluoride-polluted sites showed that the lowest fluoride levels were found in feeders and herbivores, followed by omnivores, and were the highest in predators, scavengers and pollinators, indicating possible biomagnification.

Fluoride uptake by plants from soil may occur, but the bioavailability of fluoride in soil is usually low. The application of fluoride containing sludge or phosphate fertilisers may lead to considerable increase of fluoride contents in plants dependent on soil characteristics and pH.

The most important exposure route of F for plants is uptake from the atmosphere. Grass species have in comparison to other plant species a relatively high uptake rate. The equilibrium between the concentration in the atmosphere and in the grass is generally reached within 24 hours. In a period without rainfall, the half-life of fluoride in grass is approximately 4 days in the summer and 12 days in the winter.

One test outlined in IUCLID indicates plants only appear to accumulate fluoride significantly above background levels at elevated water fluoride levels of at least 10 to 50 ppm.

Summary of environmental fate

The environmental fate of hydrogen fluoride has been summarised from three main sources, the report written under the OECD SIDS programme (OECD, 1999), a US Department of Health and Human Services report (ATSDR, 1993), and from information within the IUCLID data sheet. The majority of release from use is expected to go to air, specifically from from metal cleaning, pickling, etching etc, where HF may volatilise from uncovered baths. The major release to water is expected to come from end uses in the public domain such as cleaning aluminium on boats and trucks, and masonary cleaning. Incidental release of HF is expected to be significantly higher than releases from HF using industry, and comes from ceramic such industries as aluminium smelting, brick/clay/ production, superphosphate production, and coal burning.

At equilibrium, HF is expected to partition predominantly to the aquatic compartment (70%), with a significant proportion partitioning to the atmosphere (30%). Negligible amounts are expected to partition to soil/sediments, aerosols or biota.

In water, the chemical will dissociate at pH above 5 where the fluoride ion is expected to precipitate out of solution through reaction with calcium carbonate relatively quickly. Additionally, volatilisation is expected to be an important process involved in partitioning of fluorides between surface waters and the atmosphere. In seawater, fluoride is a macrocomponent.

In the atmosphere, fluorides are emitted predominantly in gaseous form, with a significant quantity being emitted in solid form (aerosols). HF is removed relatively rapidly from the atmosphere through both wet and dry deposition with an expected half life around 13 hours. Fluoride aerosols are eliminated more slowly (half life 2-12 days), and generally by wet deposition.

Negligible amounts are expected to partition to the soil at equilibrium as it would be expected to largely be removed through volatilisation. Where pH is less than 6, fluoride is predominantly bound where it is largely immobile. At a pH above 6, the fluoride ion is the dominant species.

In non acidic solutions, the chemical will readily ionise and the F⁻ ion will complex with calcium carbonate and precipitate out of solution.

Fluoride accumulates primarily in the exoskeleton of crustacea and in the bones of fish and is not expected to biomagnify in aquatic systems. Marine organisms seem to show higher BCF values than freshwater species. Fluorides accumulate primarily in the skeletal tissues of terrestrial animals. Symptoms of "fluorosis" are seen at bone fluoride levels of about 100 times those in animals collected from unpolluted areas. The potential for biomagnification is uncertain, although it appears possible.

While fluoride uptake by plants from soil may occur, its most important route is uptake from the atmosphere, with grasses shown to have a comparatively higher rate of uptake than other plant species.

7.1.3 Predicted environmental concentrations

Aquatic

A worst case local predicted environmental concentration (PEC) can be calculated based on the following assumptions:

1. 10% of all releases to water will go through a single sewage treatment plant (STP) with a daily output of 250 ML.

2. 47% will be removed through volatilisation to the atmosphere while in the STP (based on the SIMPLETREAT model outlined in the EU Technical Guidance Document, 1996 (European Commission, 1996).

3. No degradation of HF will occur in the STP, so 53% will be discharged to receiving waters, where it will be diluted by a factor of 10:1.

Based on these assumptions, 4.34 kg per day will be released to the STP, with 20.4 kg volatilising to the atmosphere. This leaves 2.3 kg in the STP at a concentration of 9.2 μ g/L (ppb). After dilution in receiving waters, the local PEC can be calculated as 0.92 ppb.

This is worst case in that it is unlikely that 10% release will occur to a single STP. Also, HF would be expected to be in the ionic form in the STP, and the fluoride ion will be subject to precipitation out of solution through reaction with calcium carbonate. This would lead to far lower concentrations being discharged.

Comparison with background and measured values

The OECD report provides ambient (being defined as with anthropogenic influences but not close to local sources) and natural (without anthropogenic influences) background concentrations of fluoride in natural waters. This depends on the geological, physical and chemical characteristics at the location. In surface waters not influenced by fluorine containing rock formations, the natural F⁻ concentration is between 0.01 and 0.3 mg/L (ppm). Where fluoride containing rock formations are present, the concentration is considerably higher with water of small rivers in the German highlands containing up to 4.7 ppm. High fluoride levels (>20 ppm) are also reported in natural waters from other European countries. In seawater, F⁻ concentrations are higher than in freshwater with an average of 1.4 ppm.

The local PEC determined above is several orders of magnitude lower that these background levels.

Atmosphere

Table 8 indicates that 195 kg hydrofluoric acid will be released to air per day due to various end use activities. The major contributor (excluding activities where HF is produced incidentally) is expected to come from metal cleaning, pickling, etching etc, where HF may volatilise from uncovered baths. This use has been estimated to release 150 kg per day to the atmosphere around the country. From the HF survey, at least 60 respondents were noted to be involved in this type of activity. Using a total of 60 sites, the average release per site will be 2.5 kg per day.

A PEC_{local} for air via point source emissions from processing raw hydrofluoric acid can be calculated, again using the methodology from the Technical Guidance Document. As a worst case, it will be assumed that 2.5 kg per day is released from a single point source.

C_{air} = Emission.Cstd_{air}

where:

C _{air}	=	concentration in air at 100 m from a point source (kg/m ³)
Emission	=	emission rate to air (kg/s)
Cstd _{air}	=	Standard concentration in air at source strength of 1 kg/s
		= 24 x 10 ⁻⁶ kg/m ³ .

A daily release of 20 kg per day to the atmosphere equates to 2.9×10^{-5} kg/s. This gives a concentration of hydrofluoric acid at 100 m from the point source of 0.7 μ g/m³. Based on the conversion factor of 1 mg.m⁻³ = 1.22 ppm, the PEC in atmosphere is 0.85 ppb.

Comparison with background and measured values

The OECD report provides the natural occurring background concentration of fluoride in air as 0.5 ng/L, which is three orders of magnitude lower than that calculated above. Further, it is claimed that accounting for anthropogenic

emissions, the worldwide background concentration is estimated at 3 ng/L, which is still two orders of magnitude lower than that calculated above.

However, the calculated PEC represents a concentration expected near a point source, which would be considerably higher than for the wider atmosphere. Urban air samples in the USA showed a maximum fluoride concentration of 1.89 μ g/m³. This maximum was found during a study of over 9000 urban air samples, 88% of which did not detect fluoride. Only 18 measurements exceeded 1μ g/m³ (ATSDR, 1993).

These figures suggest the above calculation is an overestimate, but may be used as a worst case.

7.2 Occupational exposure

7.2.1 Routes of exposure

An evaluation of available information on Australian use scenarios, obtained from suppliers, users and from site visits, indicates that workers are potentially exposed to anhydrous and aqueous HF by both inhalation and skin contact. Ingestion is unlikely to be a route of exposure in the occupational environment.

Exposure to HF may occur through inhalation of vapour, especially with anhydrous HF or concentrated aqueous solutions. At 100% strength (anhydrous), HF is either a gas or a low-boiling (b.p. 19.5°C) liquid. Volatility of aqueous solutions increases with increasing strength, with visible fuming apparent at higher concentrations, up to the maximum commercial concentration of 70%. Heating or agitation of HF may also lead to an increased generation of vapour. Inhalation of aerosol droplets, from accidental release or from spraying or brushing applications of HF solutions, is also a possible route of exposure.

Dermal exposure may occur from spills or splashes of HF and exposure of the skin to aerosol droplets. No information was available on the potential dermal absorption of HF vapours.

7.2.2 Methodology for estimating exposure

In the assessment of occupational exposure to HF, exposure estimates must take into account inhalational uptake of vapours and aerosols and dermal absorption of liquid, vapour and aerosol form. Insufficient data were available to estimate dermal exposure to vapour/liquid HF and no data were available for skin absorption kinetics.

Acute exposure to HF is particularly relevant because of the corrosive nature of the chemical. Routine full shift atmospheric monitoring data is not applicable to such exposures. The potential for accidental exposures may be estimated through consideration of factors such as the method of use, potential for leakage or spills, and the controls in place.

For estimation of routine occupational exposure via inhalation, Australian workplace monitoring data is preferable. Where available, actual monitoring data for HF has been used for exposure estimations, however monitoring is not carried out at most workplaces using aqueous HF in Australia. Overseas data gathered for

the OECD assessment (OECD, 1999) and other published literature have been used where possible to supplement Australian data.

Where monitoring data were unavailable, the EASE (Estimation and Assessment of Substance Exposure) model, developed by UK Health and Safety Executive (European Commission, 1996) was used to predict inhalation and/or dermal exposure to anhydrous and aqueous HF. Ease for Windows, Version 2 (August 1997) was used for the estimations. EASE predicts exposures as ranges in the form of conventional 8 hour time weighted average (TWA) concentrations. It is generally accepted that the EASE model takes a conservative approach and is likely to overestimate actual exposure.

The EASE model has been used to predict inhalation exposure to anhydrous and aqueous HF for three typical uses – alkylation, formulation and metal treatment/cleaning. Dermal exposure was not considered at high concentrations as HF is highly corrosive and causes severe burns and dermal contact should only occur through accidental contact. HF even at low concentrations can cause delayed burns and is considered an irritant at concentrations as low as 0.1%. Exposure is not likely to occur as a daily event resulting in chronic exposure but some workplace scenarios may involved repeated exposure to dilute solutions. Calculations for dermal exposure to 1% HF have been carried out and combined inhalational / dermal intake estimated on the basis of dermal exposure to 1% HF. Estimates of exposure are in Table 10 below and calculations are detailed in Appendix 2. The modelled values for some scenarios are high in relation to the NOAEL determined in the OECD report (0.72 mg/m³ or 0.88 ppm).

The following sections provide details of potential occupational exposures identified for Australian workplace scenarios. Where monitoring data was available it has been included. Where exposure data was lacking this has been supplemented with data from EASE. EASE estimations were not carried out for scenarios involving incidentally produced HF, as some atmospheric and biological monitoring data were available for aluminium smelting and phosphate fertiliser manufacture, which are major sources of incidentally produced HF in Australia.

Table 10 - Es	stimat	es of potent	ial occupati	onal dermal	and inhalati	on exposure	to HF	for different o	ccupational (exposure scen	arios	
Process		Conc. of HF	Vapour pressure	EASE use p	oarameters			EASE exposu estimates	Ð	Available air	Estimated	Total estimated
(scenario no. i	Ē	solutions	kPa	Use	Pattern of	Contact	LEV	Dermal	Inhalation	monitorina	(inhal*)	intake
brackets)		(w/w)		nattern	control	laval	Ì	(malem ² /d)	(nnm)	data		linc
						(skin)			(inidal)	500		dermal**)
						,				(mqq)	(mg/kg/d)	
												(mg/kg/d)
Alkylation	(E)	100%	103.3	Closed	FC	NR	1	NR	0-0.1		0.012	0.012
	(2)			Closed,	SEG	NR	٥N	NR	200 - 500	0.2 and	24 - 61	24 - 61
				with						below		
				system						(Brown, 1005)		
				breaching						(COR)		
Formulation	Ð	20%	15.96		LEV		Yes	5-15	20-50	An one of the second	2.4 - 6.1	3.6 - 7.3
				NDN		Extensive				IN		
	(2)				SEG		No	5-15	70-100		8.5 – 12	9.6 - 13.2
	(3)	35%	0.33		LEV		Yes	5 -15	0.5-1		0.06 - 0.12	1.26 1.32
	(4)				SEG		۶	5-15	3-5		0.36 - 0.6	1.56 – 1.8
Motol	11	100 t 0	0.12		1 61/							1 00
		e 01-0	-0.010		L L	L	62	<u></u>	0.1-0.0		0.UD - U. IZ	76.1 - 07.1
treatment &	į		0.021			Extensive	:			0.17 – 3.3		
cleaning	(2)				DH, DV		۶	5-15	10 - 20	(Sheehy &	1.2 – 2.4	2.4 – 3.6
	(C)			NDU	DH, DV		Ŷ	5-15	100 - 140	Jones, 1985,	12 - 16.8	13.2 – 18
	(4)			NDU or	DH, DV,		Ŷ	5-15	500 - 1000	Cited in	60 - 122	61 - 123
				WDU	with					UECU 1889)		
					aerosol							
* using EASE esti	imates	of inhalational e	exposure (i.e., n	ot actual monitor	ring data)							5
** dermal intake b	o pased o	n exposures to	1.0% soln HF (i	i.e. lower concer	ntration, because	of corrosive eff	ects of hic	ther concentrations				
WDU = wide disp	ersive i	nse										
DH = direct nandi	ling											
EC = full containn	nent											
NDU = Non-dispe	srsive u	se										
NR = not conside	red rele	svant due to irrit	tant/corrosive po	otential at HF co	nc present.							
SEG = segregatic	ñ											

7.2.3 Exposure during importation, transportation and storage of HF

Anhydrous HF

Most anhydrous HF imported into Australia is used for petroleum alkylation and is packed in steel tanks of approximately 15 tonne capacity, also called isotainers. Most imports arrive at Port Botany (NSW), with a minority going to Fremantle (WA) or Port Melbourne (VIC). The isotainers are transported from the ports either directly to oil refineries for use, or to the storage site of the importer. Both road and rail transport is used for final delivery. Some isotainers are also stored on refinery sites before use. Used (empty) isotainers are returned to the supplier. Empty containers may contain sufficient HF to be hazardous, and are a potential source of exposure during subsequent storage and transport.

A small proportion (< 1%) of anhydrous HF is imported in smaller containers. For fluorination of plastic, 45 kg steel cylinders with manual control valves are transported in racks of 9 cylinders which can be handled by forklift. They are unpacked from a mixed shipping container at a freight forwarding depot, before being transported by road to the site of use. The cylinder valves are protected from impact by a screw on cap, and the racking provides further protection. Onsite storage is in an external Dangerous Goods store.

Anhydrous HF is also available in small cylinders of varying capacity suitable for users such as universities and research facilities. HF in containers of 230 g to 11 kg capacity is imported into Australia. These are stored and transported in accordance with the Dangerous Goods requirements. No information was obtained on the conditions of storage at the site of use.

As isotainers and smaller cylinders of anhydrous HF are transferred unopened to the sites of use, the major source of potential exposure to HF during transport and storage is leakage. Workers potentially exposed from accidental release include dock workers, road transport drivers, employees at the storage or petroleum refinery sites, and emergency workers. The high vapour pressure of anhydrous liquid HF and its potential to form a mobile vapour cloud under certain conditions mean that larger releases could affect workers some distance from the point of release.

HF is a highly reactive chemical, and can form hydrogen gas as a product of corrosion, particularly where stored for long periods. The formation of this gas in closed containers or pipework may cause a build up of pressure leading to loss of containment (Young, 1997; Anon, 1997) and a fire hazard (Department of Energy, 1995).

Aqueous HF

Aqueous solutions of 35 to 70% HF are imported in sealed containers in a variety of pack sizes. Solutions of 70% strength are commonly imported in 200 L PVC-lined steel drums. Other containers used include 200 L PVC drums and 60 L, 20 L, 5 L, 2.5 L, 1 L, 500 mL and 100 g plastic containers. Containers are usually transported from wharfs by road to warehouses and to customers. Some importers use external storage and distribution companies for pick up, warehousing and/or delivery to customers. Similar containers are used to pack and transport HF products that are formulated in Australia. At least one formulator transports a

product in 1000 L rigid plastic intermediate bulk containers (IBCs) with supporting cage.

Information on a specific situation of potential dermal exposure during unpacking of containers imported by air freight was provided by one importer. The company imports 500 mL and 2.5 L containers made of high density polyethylene. Containers are packed in a plastic bag, surrounded by vermiculite and contained in a steel tin inside a cardboard box. HF molecules migrating through the plastic containers which would normally evaporate may dissolve in water vapour present in the plastic bag, producing small droplets of HF acid. For this reason, upon receipt the containers are unpacked from the steel tins and visually inspected for the presence of liquid. Bags containing more than a drop of liquid are handed to laboratory staff. Otherwise, the bags are removed, and the containers allowed to sit overnight to breathe. They are then stored as individual bottles, open to the atmosphere to allow breathing.

Generally, importation, transportation and storage of aqueous HF should not pose a potential for exposure except in the case of spills or leaks through faulty containers or accidents resulting in damage to containers. Four respondents to the HF survey were aware of at least one incident in transport. Where details were provided these have been included in Appendix 3. Six respondents to the HF survey had at some stage received HF in damaged packaging, but this appeared to be usually a one-off occurrence. However, faulty packaging had influenced one company to use a contractor rather than formulating the product themselves.

The distribution pattern for aqueous HF is more complex than for anhydrous HF. It is imported by both air and sea, in a range of container sizes and transported to a larger number of sites. It is widely formulated into products that are themselves transported and stored. Workers that may be exposed to aqueous HF in transport and storage include transport depot staff, goods receiving and despatch staff, warehouse staff, forklift drivers, a range of road transport drivers and emergency services workers.

As with anhydrous HF, larger accidental releases (e.g. full drum quantities) have the potential to cause exposure to a larger number of workers, not just those in the immediate vicinity of the release.

7.2.4 Exposure during in situ manufacture of HF

Many uses of aqueous HF can also be carried out using HF produced *in situ* i.e., produced from other chemicals rather than direct use of HF solution. (See Section 6.1.1 and Appendix 1).

Acidified fluoride salts

Solutions of HF can be formed if fluoride salts are acidified with other acids in solution (e.g. hydrochloric acid). Generally the solubility of the fluoride salt in water acts as the limiting factor on the upper concentration of HF formed. Once formed, potential exposure to HF will be similar to that from aqueous HF of the same concentration obtained from other sources. It may not be recognised that HF is being formed, because the process is analogous to blending or formulation. When *in situ* HF is produced using fluoride salts, there is also a potential for exposure to dusts of the salts. However, handling of concentrated HF for dilution is avoided.

In situ production of HF from fluoride salts was identified during the assessment for metal treatment and cleaning, fabric rust removal, cleaning automatic car washes and for acidizing oil wells and could be used for the range of uses of aqueous HF.

Solutions of bifluoride salts

Solutions containing HF can also be formed by dissolving bifluoride salts in water. The equilibrium between HF, the fluoride ion (F^{-}) and the bifluoride ion ($HF_{2^{-}}$) means that high concentrations of HF are not formed in these solutions. Potential exposures to HF from use of bifluorides identified in this assessment were during glass etching, rust removal from carpets, bottle washing and polishing of lead crystal.

Bifluorides are claimed to be safer alternatives to HF. This may be based on the lower concentrations formed in solution and to the use of a solid (bifluoride salt) rather than liquid HF. Some etching agents are in paste form, which reduces the potential for accidental spillage. However, exposure to the dust of bifluoride salts can also be hazardous.

If bifluoride salts are acidified in solution, rather than just dissolved in water, their characteristics will be those of acidified fluorides, described above.

7.2.5 Exposure due to incidental production of HF

Manufacture of phosphate fertilisers

Potential for exposure

HF is a byproduct of phosphate fertiliser manufacture. Particulate fluoride is also present, and it is estimated (Perry et al., 1994) that 60 to 80% of airborne fluoride in the processing of rock phosphate may be present as dust. However, an Australian manufacturer stated that particulates are not considered to be a problem in their operation.

During manufacture of single superphosphate fertiliser, phosphate rock is crushed and mixed with sulfuric acid, in a closed process. In this process, HF and silicon tetrafluoride gases are evolved, which are drawn into a series of scrubbers and dissolved in water to form fluorosilicic acid solutions. This solution is recirculated into the process as far as possible or is eventually removed and used for water fluoridation. Small amounts of HF remain in the fluorosilicic acid solution. The material from some sites is not sold, but neutralised and stored on site.

Production may be carried out via batch or continuous processes.

The phosphate fertiliser is granulated and screened to separate the different particle sizes. The fresh granular superphosphate is conveyed to a storage shed where it is allowed to cure (mature) for several weeks before being distributed to the market.

One company manufacturing fertiliser at several sites estimated that approximately 50 of their workers would be potentially exposed. Possible workers exposed to HF would include those handling the uncured fertiliser, as well as those working with the acid by-products of the process.

Monitoring data

Air monitoring and biological monitoring data were provided for several sites manufacturing single superphosphate fertiliser by both batch and continuous processes.

A total of 135 air samples from 1993-1998 were analysed for total gaseous fluoride. These analyses did not distinguish between HF and silicon tetrafluoride, which is also produced during fertiliser manufacture. Most monitoring samples were taken over a number of hours and did not measure short term exposure. In 4 of the 5 plants all results were below the Australian exposure standard for fluoride of 2.5 mg/m³. In the fifth plant, a number of readings exceeded this value.

In order to account for 12 h working shifts, the company used an exposure standard of 1.25 mg/m^3 , adjusted by the Brief and Scala model to one half the standard value (2.5 mg/m³). The Brief and Scala model is a conservative model, based on the number of hours worked per 24 h day and the period of time between exposures (Tieman & Ban Zanten, 2000). Using this lower exposure standard, only 1 of 5 plants had all readings below the standard.

The company reported that the highest levels monitored occurred in two areas near the mixers (kneaders) where the acid is first added to the ground rock and in the den (oven) where the reacting material is spread out.

Sampling had not been carried out in the granulation area, or where the fertiliser is stored for curing (maturation), as these areas were not considered to be of concern.

The results of biological monitoring of urinary fluoride from 1995 to 1998 were provided but were not identified as pre-shift or post-shift sampling. Of 573 samples, 2.3% were higher than 7 mg/g creatinine. Recommended limits for urinary fluoride vary and are listed in Section 10.3.2. It was stated that some high readings may be due to contamination of the sample with particulate fluoride. Contributors to urinary fluoride levels would include exposure to HF, silicon tetrafluoride and particulate fluorides.

There are a small number of overseas reports on exposure to fluoride compounds via phosphate fertiliser manufacture. Short-term measurements of < 1 to 10 mg/m³ have been reported (Hodge & Smith, 1970, as cited in OECD 1999). Gaseous fluoride emissions from various processes at a plant manufacturing phosphate fertiliser in Jordan were measured in 1993 (AbuDhaise & AbuOmar, 1998). The measured levels varied widely from 0.1 to 30 ppm (0.09 to 26 mg/m³), with twenty percent of samples being > 1 ppm.

Aluminium smelting

Potential for exposure

Exposure to gaseous and particulate fluorides can occur during the smelting of alumina to produce aluminium metal. Although emissions are complex it is believed that the gaseous fluoride component is predominantly HF (Frank et al., 1999).

In the Herr-Heroult electrolysis process used for aluminium production in Australia, smelting is carried out by electrolytic reduction of alumina (aluminium oxide) in baths (pots) which use molten cryolite (sodium aluminium fluoride) as the solvent. The pots are large, shallow, steel shells lined with a carbon cathode with 20 to 30 carbon anodes suspended in each pot. The alumina dissolves in cryolite and is electrolysed to aluminium and oxygen, allowing the molten aluminium to be periodically siphoned off from the bottom of the pot. The carbon anodes are gradually consumed, and are replaced every few weeks. The molten aluminium is transferred to holding furnaces where impurities are removed and alloying elements added, before being cast in various forms for transport to semi-fabricating plants.

Due to the high temperatures (over 900°C) some gaseous fluoride evaporates from the surface of the cryolite pot. Emissions are reduced by a solid semi-permeable layer on top of the pot, but can still occur, especially if this crust is broken as in changing electrodes, when alumina or cryolite are added or when aluminium is tapped. Hoods fitted to each pot also help to capture emissions and direct them to scrubbers. The anode baking process is also a source of fluoride, because spent anodes that have been in contact with the fluoride ingredients are recycled. (Australian Aluminium Council, 2000). Other areas such as casting may experience high peak emissions (Table 13).

Recycling of spent potlinings (Ausmelt Ltd, 1996) and dross (NSW Land and Environment Court, 1995) are also possible sources of HF exposure.

Monitoring data

Information on air and biological monitoring was supplied by one Australian smelter. For 12 h working shifts, the Australian occupational exposure standard for airborne contaminants (8 h, TWA), used for reference was adjusted by the Brief and Scala model to one half the standard value. Thus an exposure standard for total fluoride of 1.25 mg/m^3 was used.

Personal air sampling for total fluoride, which does not distinguish between particulate and gaseous, was carried out for workers in different sections of the plant in 1996-97 as part of a regular program (Table 11).

Area of plant	No. of samples	TWA (mg/m ³)
Casthouse	19	0.01 - 0.08
Engineering Services	2	0.01 - 0.03
Potline 1	21	0.02 - 2.16
Potline 2	21	< 0.01 - 1.19
Potline 3	19	0.04 - 0.64
Potline Services	14	0.01 - 0.26

Table 11 - Personal air monitoring data for total fluoride in various areas ofan aluminium refinery (1996-97)

In a separate project for the Australian Aluminium Council Health Panel, personal monitoring was carried out in 1996 by the same company to assess pot-room exposure to both gaseous and particulate fluoride. Samples were collected over the 12 h shift and the gaseous and particulate fluorides separated out. Analysis was carried out using an acid leach technique and ion selective electrode analysis. For groups of workers carrying out anode changes and pot tending in 12 h shifts, the geometric mean of exposure was as shown in Table 12. Approximately one third of total fluoride exposure was due to gaseous fluoride.

Table 12 - Personal air monitoring data (mg/m³ TWA) for gaseous and particulate fluoride in pot-room

Particulate fluoride	0.24 (GSD* 0.17)
Gaseous fluoride	0.11 (GSD* 0.05)
Total fluoride	0.37 (GSD* 0.19)

* Geometric standard deviation

Static air monitoring for gaseous fluoride in the working environment of the casthouse was carried out in 1992 to follow up complaints of respiratory irritation. Real-time monitoring was carried out in order to capture peak emission levels using a modified Tess-Com source HF monitor. Varying numbers of samples and protocols were used to characterise the factors influencing emissions. The results are shown in Table 13 and indicate that very high peak readings can occur.

Biological monitoring of urinary fluoride levels was carried out by the same company in 1996-7 as part of a regular monitoring program. Out of nearly 500 samples, all except 2 (from electrode rodding and electrolysis potline workers) were below the biological limit value of 7 mg fluoride/L (internal company standard).

Urinary fluoride monitoring of pot-room workers was also carried out in 1996 for the Australian Aluminium Council Health Panel. Pre-shift samples were collected at the beginning of the shift after a 4-day break, and post-shift samples at the end of the 12 h shift. For this project results were expressed as mg/g creatinine, and can be compared to the ACGIH Biological Exposure Index (BEI). The average preshift and postshift results of 1.06 mg/g creatinine and 2.09 mg/g creatinine respectively were well below the BEI of 3 mg/g and 10 mg/ g creatinine respectively.

	Daily TWA in mg/m ³	Peak emissions measured in mg/m ³	Comments
Casthouse roof			
Position 1	0.34 - 0.45	0.97 - 1.58	Very high peaks occurred when full and
Position 2	0.49 - 0.73	1.13 - 3.39	empty ladies were under sampling point.
Position 3	1.05 - 2.91	7.65 - 20.81	
Over ladles			
Position 1		2.07 - 5.46	Samples were collected around the edge
Position 2		3.00 - 27.30	and sample durations of 3-23 minutes
Position 3		0.16 - 21.75	were used. The presence of dross, which contains fluoride and will evolve HE at
Position 4		7.25 (1 reading)	high temperatures, was considered one factor in the high peak emissions.
Service catwalk	0.03	0.03 - 0.04	Readings were low and consistent in this area
Atop furnaces	-	0.07 – 34.65	Sampling duration varied from 10 to 20 minutes. Results varied with the condition of the furnace.
Ground level			
Various positions tested	0.03 - 0.14	< 0.03 - 5.01	Peak of 5.01 mg/m ³ occurred for approximately 30 minutes.
Between furnaces			
Position 1			
Position 2	0.04 -0.06	0.11 - 0.18	
	-	0.05 and 0.16	

 Table 13 - Casthouse atmospheric static monitoring data for gaseous fluoride

 (1992)

Impurities in other chemicals

HF may be present in small quantities as an impurity in other chemicals.

Fluorosilicic acid solutions were reported during the assessment to contain small quantities of HF. Fluorosilicic acid solutions are both imported into Australia, and manufactured as a byproduct of the phosphate fertiliser industry. A 40% strength grade imported for metal surface treatment contains < 0.05% HF. Fluorosilicic acid at 22% concentration sold for water fluoridation contains an average of 1% HF, ranging from 0.5 to 2.0%.

The MSDS for one grade of hydrochloric acid warned that it may contain low levels of HF. This could occur if there were any fluoride impurities in this grade of acid.

No information was received on other chemicals containing HF as an impurity.

Thermal degradation

HF can be formed on heating or burning of fluorine-containing materials. Possible sources of exposure are halogenated chemicals used as fire extinguishers/flame retardants, refrigerants that may be released in a fire, welding processes that use fluoride-coated electrodes and decomposition of fluoropolymers.

Data on this topic is primarily based on literature and occurrences overseas, but is expected to be relevant to Australian conditions.

- High levels of HF were reported to be generated when large scale hydrocarbon pool fires were extinguished with Halon 1301 (bromotrifluoromethane) by total flooding (Sheinson et al., 1981, as cited in Lines, 1995) and during trials of maritime fixed fire extinguishant systems that used both Halon 1301 and its alternatives (Beck et al., 1997, Mever, 1999). The levels recorded were variable and in some cases > 6000 ppm, with the alternatives producing 5 to 10 times higher levels than Halon. It is reported (Meyer, 1999, Young, 1996) that many new fire extinguishing agents produce more decomposition products than the older ones (e.g. Halon 1301) that are being phased out because of their ozone-depleting potential. The level of HF formed during decomposition would tend to be higher when large fires are extinguished in confined spaces (Meyer, 1999) and when the extinguishant is highly fluorinated. The levels of decomposition products formed can affect the safety of re-entry to an area after a fire. Fixed flooding extinguishant systems are likely to be installed in a variety of areas where there may be flammable liquids or gases, wood and paper or energised electrical equipment e.g. engine compartments and switchgear rooms.
- Refrigerant chemicals containing fluorine atoms can also generate HF on combustion. In one incident reported in the USA (Walker, 1997) firefighters experienced respiratory distress while cleaning up after a small grocery fire that had occurred in a display cooler. It was determined that the refrigerant had decomposed in the heat and leaked from the sealed system into the air.
- Gaseous and particulate fluorides, including HF, can be released during welding (Perry et al., 1994) as fluoride can be present in some electrodes or their coatings and in flux (South Australia. Department of Labour, 1990). An increase in urinary fluoride was found in electric arc welders using basic electrodes (Sjorgren, 1984).
- Fluorocarbon polymers and elastomers are specialty materials which are resistant to chemical change and to temperatures up to 287°C (Lewis, 1997). However these materials will break down when overheated, forming HF and other chemicals (Zenz, 1988). Polytetrafluoroethylene (PTFE, known as TeflonTM) is the largest fluoropolymer in commerce (Ring, 1998). Others include polyvinylidene fluoride (PVDF), fluorinated ethylene-propylene (FEP) and a copolymer of vinylidene fluoride and hexafluoropropylene.

In the USA, workers were exposed to HF when TeflonTM grommets in airconditioning heater rods degassed at high temperatures (Lawrence et al., 1986). A researcher testing fluoroelastomers to destruction sustained a serious injury through contact with the degraded material (Friar, 1992). Testing was done in a sealed, acid resistant chamber preventing vaporisation of any HF formed. The source of the injury, HF or heat, has however been debated (Fire, 1992).

Fluoroelastomers are used in small automotive components such as engine gaskets, seals and fuel lines (Anon, 1995). It is possible that HF may contaminate surfaces or cavities in burnt-out cars. However, the total amount of fluoroelastomer in a car is small (estimates range from 40 g to 250 g) and injury has not been reported from this situation. Friar (1992) notes that there have been exaggerated media reports on this subject and concludes that in practice there are unlikely to be significant quantities of HF associated with burnt-out vehicles, although small quantities may be trapped and only released during dismantling.

Processing of fluoride-containing plastics with heat, e.g. cutting or welding, may also produce HF. An Australian injection moulder of a fluoro terpolymer at 230°C monitored for HF using Drager tubes, but none was detected.

- Other organic and inorganic fluorine-containing chemicals may break down on heating to form HF. Inorganic fluorides used as coatings for sand moulds in metal casting vaporise in contact with the hot metal, and partially decompose to HF and other compounds (Perry et al., 1994). Similar reactions occur in fires.
- The use of high-energy HF or deuterium fluoride chemical lasers can cause atmospheric discharges of several fluorinated and non-fluorinated compounds, including HF (DeFrank et al., 2000). Excimer laser systems may also cause discharges.
- It is not known whether the reported emission of HF in steel manufacture, brick and other ceramic plants, and coal-fired power plants leads to occupational exposure.

Chemical reactivity

The potential for other chemicals containing fluorine atoms to form HF is a source of possible occupational exposure. A number of these chemicals have been identified during the assessment such as fluorosilicic acid, metal fluorosilicates, silicon tetrafluoride and boron trifluoride. However this list is only indicative and other compounds may also be reactive in the same way.

7.2.6 Exposure during use of anhydrous HF

Petroleum alkylation

The major use of anhydrous HF in Australia is as a catalyst in petroleum alkylation. Information on exposure was obtained for five refinery sites.

Alkylation is one of several processes used in the refining of crude oil to produce a range of petroleum products. The process combines two gases, such as butylene (butene) and isobutane to form high-octane gasoline. As a catalyst, HF is not consumed in the reaction, but has to be replenished periodically because small amounts are unintentionally removed by the process, for example with the acid soluble oil (ASO) that is removed from the acid during the regeneration step. As part of the continuous process of refining, the alkylation plant is completely enclosed. Various sections of the subsequent product stream may also contain HF in a dilute form. This is eventually removed by various processes and neutralised.

The greatest potential for exposure in HF alkylation occurs (OSHA, 1993):

- during receipt and unloading of HF;
- during process stream sampling;
- due to process leaks (fugitive emissions);
- due to equipment failures; and
- during equipment maintenance.

The process of "tri-cocking", or opening a series of valves to determine the level of acid, also involves some release of HF to the atmosphere (Brown, 1985).

At the refinery sites, exposure could occur to HF via the raw material (anhydrous HF), alkylate, acid soluble oil or unneutralised acid wash water.

Refinery workers with potential for contact with HF include:

- process technician;
- maintenance technician;
- fitter;
- tradesman assistant;
- instrument/electrical mechanic;
- sampling and testing staff; and
- contractors involved in maintenance or shut-down procedures.

During any accidental loss of HF or product stream containing it, those workers in the alkylation section of the refinery would be at most risk of exposure, particularly those closest to the leak. In addition, those transporting or testing process stream samples could be exposed while carrying out this work. In any larger loss of containment, additional workers could be exposed if the release was volatile.

The reported number of workers directly involved with alkylation varied between refineries, depending on rotation of duties, ranging from 10 to 50 at each site. A typical summary of the duties required was as follows:

- Receipt and unloading of product from isotainers, usually 4 to 5 h on each occasion.
- Inspection and maintenance of pipe systems and valves on HF unit and sampling, estimate 2 to 3 h/day, 330 days/year.
- Major maintenance work during plant shutdown, every 2 to 3 years, 5 to 8 operators, 8 to 10 h/day over 14 days.

It was estimated that about 25% of the time spent on the above tasks would involve operations where potential HF exposure exists.

In addition to direct exposure to HF from an accidental release, there is the everpresent possibility of contact with HF or material contaminated with HF from equipment or personal protective equipment.

Neither personal monitoring nor biological monitoring for HF is carried out at any of the sites. Atmospheric (static) monitors were installed at one plant.

Air and biological monitoring of petroleum alkylation workers for HF at an Australian plant was reported in 1985 (Brown, 1985). Personal air monitoring of 23 plant operators and maintenance men was carried out for 5 h of a shift. The highest TWA recorded was 0.18 mg/m³, for a maintenance worker who had been subject to a definite vapour exposure on the day of testing. The remaining results were considerably lower, and 10 were below the limit of detection of 0.005 mg/m³.

Pre-shift urinary fluoride levels were 0.4 to 2.0 mg/L, with a mean of 0.89 mg/L and a standard deviation of 0.42. Post-shift levels were 0.5 to 2.4 mg/L, with a mean of 1.16 mg/L and standard deviation of 0.49.

The exposure level during alkylation predicted by the EASE model varies from 0 to 0.1 ppm for a fully enclosed system and 200 to 500 ppm for a breached system. Based on the EASE predictions the total daily intake was estimated at 0 to 0.012 mg/kg/day and 12 to 24 mg/kg/day respectively (Table 10 and Appendix 2). Breaching of the system is likely to occur only during sampling, which is a one-off procedure, and the predicted intake levels for the second scenario are likely to be an overestimation. The scenario assumes substantial breaching and estimates inhalational exposure of 200-500 ppm. This level is high enough to cause acute effects, and thus is not relevant to normal usage.

Fluorination of plastic

A specialty use of anhydrous HF, carried out at one site in Australia, is the surface fluorination of plastic containers and other items moulded or formed from plastics.

In this process, HF is electrolysed to form fluorine as an intermediate, which reacts with the surface molecules of the plastic. HF is also a byproduct of the reaction and is removed by a stripper column from the waste air. Plastic containers are treated in a batch process in an autoclave at less than atmospheric pressure.

Full cylinders of HF are connected to the electrolysis cell feed line and remain until the cylinder is empty and has to be changed. After the plastic containers are reacted with the fluorine gas in the process chamber, the chamber is evacuated and purged.

The reaction system is a closed one, so that significant exposure could occur only through accidental release of HF or failure of the purging, evacuation or stripping systems. Exposure to smaller quantities of HF may occur during cylinder changeover, contact with treated containers or the processing chamber, or from fugitive emissions.

A possible source of exposure is the complicated system of handling cylinders when they are close to being empty. The procedure involves changing back and forth between two cylinders, tilting the low cylinder in order to test its contents (weight of cylinder is 30 kg), and there is potential for errors to occur.

Entry to the fluorination cell for maintenance activities may involve exposure to HF and fluorine gas, and requires full personal protective equipment.

The workers involved in fluorination at this plant are:

- One fork-lift operator accepts deliveries and takes to store.
- Two plant operators transfer, connect and disconnect HF cylinders to processing plant and operate plant on a routine basis, transfer plastic containers

in and out of processing chamber and assist technical management group in maintenance.

- Three packers unpack and repack plastic containers before and after treatment, in a different part of the plant.
- Three members of technical management check and supervise operations, adjust settings, carry out maintenance and troubleshooting.

No personal or biological monitoring of worker exposure is carried out, but detection sensors in the plant monitor for any accidental leakage of either HF or fluorine gas.

Research uses

Little information on this category of use was provided.

Use of anhydrous HF to carry out peptide cleavage in a closed apparatus was reported. The greatest potential for exposure would be from leaks and during connection and disconnection of the cylinder.

No information was obtained on use of HF in gas mixtures for excimer laser systems.

7.2.7 Exposure during formulation of aqueous HF products

Information for this section was provided by formulators and from site visits conducted by NICNAS staff. Fumes and accidental spills and splashes on to the skin or eyes are potential sources of HF exposure.

Types of formulation activities identified include simple dilution of solutions of hydrofluoric acid with water or blending with other chemicals, for resale. Many end-users of HF products may also dilute HF products, or mix them with other ingredients before use. More specific information on potential exposure to end-users from dilution or mixing of HF products before use is contained in Section 7.2.8.

Formulators making products for resale commonly handle HF in concentrations \geq 35%. Of those formulators who responded to this section of the HF survey, more than half (18/29) used 35% HF, 4/29 used HF in concentrations from 48 to 55% and 7/29 used 70% HF. Formulated end products can contain from <1% HF, therefore occupational exposure to aqueous HF during formulation can be from solutions ranging from <1% to 70%.

Formulation processes are generally very simple as the ingredients to be blended and the final product are usually low viscosity liquids. Processes common to most formulators are the transfer of HF from drums or smaller containers to a mixing vessel, blending of ingredients in the mixing vessel and filling of containers from the mixing vessel. Cleaning and maintenance procedures vary but usually include the rinsing of mixing vessels and other equipment, including pumps, drums and transfer containers. Rinse water is sometimes added to the next batch, or collected in waste tanks, neutralised and discharged to sewer. At some workplaces, samples of the product mix are taken for the purposes of analysis and quality control.

Formulation of thickened pastes for metal treatment was also reported but no details of the method were provided.

Information from the HF survey indicate a variety of methods of transfer (Table 14). Where HF is supplied in 200 L drums, a smaller container may be filled from a tap in the drum, or by syphoning from the drum, and transferred into the mixing vessel. Alternatively pumps are used to transfer directly from the drum into the mixing vessel. Transfer of HF from smaller containers is usually handled manually.

At one site the transfer of HF is avoided by obtaining HF of the correct concentration in 200 L drums. An extra ingredient is added to each drum and the drums are shaken on purpose-built cradles to mix the solution.

Methods of blending include agitation by circulating with a pump, stirring with a paddle and physical shaking of the mixing container. When HF is added to a blend, it is often the last chemical added, and is added slowly due to the possibility of an exothermic reaction. Similarly, in the case of simple dilution, HF is usually added slowly to water, although one workplace described a dilution process where water was added to acid (Table 14).

Methods used for filling product into containers were: taps, syphons, gravity hoses, pumps, a transfer wand and hose. Size of filling containers varied from 500 mL containers to 1000 L intermediate bulk containers.

Mixing vessels were closed in at least 7 of the 29 workplaces and open topped in at least 2. Most worksites where formulation was carried out had exhaust ventilation.

Formulation of HF products is usually a batch process, conducted intermittently, on less than 20 days a year. However there were some companies (4/29) that formulated products on a continuous or very regular basis, with the process taking between 2 to 8 h a day, for 190 to 276 days a year. It is usual for only one or two workers to be employed at the task. From the survey, a total of at least 71 workers at 29 worksites are potentially exposed to HF through formulation (this includes one workplace where 28 employees worked on HF product formulation). Descriptions of formulation processes at some of the worksites are provided in Table 14. It is expected that there are more worksites in Australia where formulation occurs.

Potential sources of exposure identified in the formulation of products containing HF include:

- Transfer of HF drums from storage site to mixing site;
- Transfer of HF from original containers into mixing vessels;
- Sampling and transfer from the mixing vessels for quality control analysis;
- Filling containers from mixing vessels; and
- Rinsing/cleaning of tanks and other equipment.

Workers involved in these stages of formulation are potentially exposed to HF. In addition, maintenance workers and chemical analysts may also be potentially exposed. Workers involved in transferring HF to mixing vessels are particularly vulnerable to exposure to high concentrations of HF.

The potential for dermal exposure through accidental spills and splashes and exposure through inhalation of vapour is likely to be higher for workers where:

• transfer is a manual process;

- there is an intermediate step of filling a smaller container from a larger one, especially if it is open-topped;
- the mixing vessel is open-topped;
- the blending process causes agitation;
- during manual stirring where the worker is close to the mix;
- the mix is heated (there were no reports of this happening);
- water is added to acid rather than vice versa; and
- higher concentrations of acid are used.

Where pumps are used, uncapping drums and attachment and detachment of pumps pose potential for exposure from drips, splashes and fumes. Leaks from hoses or piping also pose a risk of exposure, as does overfilling containers. A risk of exposure from splashes or sprayed droplets may exist when hosing down and rinsing equipment. In addition a catastrophic failure of a pump connection or hose during transfer could result in spillage over a wider area than would occur when manual handling is used.

No atmospheric or biological monitoring data were supplied by formulators, but one reported that biological monitoring for fluoride was carried out yearly.

EASE estimates for exposure during formulation were carried out for use of both 70% and 35% HF in a non-dispersive system (Table 10 and Appendix 2). Air concentrations of 20 to 100 ppm in air and inhalational intake of 2.4 to 12 mg/kg/day were estimated for 70% HF. For 35% HF, air concentrations were estimated at 0.5 to 5 ppm and inhalational intake at 0.06 to 6 mg/kg/day. Dermal exposures to 1% HF were included in the calculations for the purpose of demonstration but may not be realistic contributors to exposure because of the corrosive effect of HF.
		cond turner		and a manage of a second with some of the second of the se					
Work site	% HF used	% HF in final product	Activity	Work Process	No. work- ers	Dura- tion	Frequ- ency (days per year)	ЪРЕ	Engineering Controls
-	70%	10 - 35%	Formulation of metal cleaning products and simple dilutions of HF with water.	27 kg containers of HF are added one by one to the mixing vessel by a worker lifting to shoulder height and resting them on the edge of tank and pouring into tank. Each drum is then rinsed with a hose, including the bung area, and the dregs added. A removable metal propeller stirs the mixture, a wooden paddle is used for higher strengths. Filling is done by pumping from the top of the vessel using an air pump and syphon. A sample is taken for lab analysis prior to filling.	÷	5 h/day	190	Gloves, glasses, rubber apron, gumboots, armlets, filter mask or full face filter combo.	Natural ventilation and exhaust ventilation
р	70%	3.5 - 5%	Formulation of pickling solution for stainless steel	HF is transferred from 200 L drums into a 1000 L closed mixing vessel using closed lines and an air driven pump. The mixture is agitated by a circulation pump. Filling into 1 kg and 2.5 kg containers is done via a tap, filling of 200 L drums is done via a syphon.	N	4 h/day	S	Safety glasses with side shields or chemical goggles or full face shield; elbow length PVC gloves; steel capped safety shoes or wellington boots; overalls and PVC apron / HDPE protective suit.	Natural ventilation; bocal exhaust ventilation at opening at top of vessel
m	35%	10%	Formulation of rust remover	HF is decanted from a 200 L drum into a 20 L pail dedicated for measuring HF. It is then poured through a funnel into a separate 200 L drum dedicated for mixing. Water is added to dilute HF to 10% and vessel is sealed. Vessel is shaken to blend ingredients. 500 mL bottles filled by hand from tap in drum.	-	5 h/day	ñ	Full face mask with filter; PVC multipurpose gloves; splash apron or full suit	Exhaust ventilation
4	35%	1-21%	Formulation of products for metal cleaning and coating	HF is decanted from 6 kg. 22 kg and 220 kg drums into 2000 L and 5000 L tanks. The operator gains access to the tank via a mezzanine floor level with the top of the tank. A drum pump is used when decanting from 220 kg drum, smaller containers are emptied manually. After use, drum pumps are hosed down on the floor (floor slopes to a drain to collect waste water). Whole containers are emptied into the tank at a time. Filling is done by gravity feed, on to a loadcell.	10	1 h/day loading mixers; 4 h/day filling	200	PVC gloves, face shield, respirator ½ mask acid/organic vapours; rubber boots; pvc apron	Exhaust ventilation; gravity feed onto loadcells

Table 14 - Examples of formulation of aqueous products and solutions, with control measures

7.2.8 Exposure during use of aqueous HF and products containing aqueous HF

Metal surface treatments

The processes described in this section are quite diverse, varying in scale, concentration of acid used, methods of handling and use and industries involved. Metal processing and cleaning cannot be clearly distinguished, as a preparatory cleaning step with HF is part of some metal processing protocols. Both semiclosed and open processes may be used, and these two scenarios are the basis of EASE modelling carried out for chronic inhalational exposure. Details of some work processes in metal treatment are in Table 15.

Common potential sources of exposure in metal processing activities are transfer from storage site to activity site, transfer of HF solutions from their original containers into acid bath tanks, immersion of products into dipping and rinse tanks, unloading product and handling of HF wastes.

No Australian monitoring data was provided for the assessment. Four overseas full shift measurements at the edge of acid baths at a plating facility were 0.14 to 0.19 mg/m³. The concentration of HF was not known (Sheehy & Jones, 1985, cited in OECD 1999). The authors reported another full shift measurement of 2.7 mg/m³ at the edge of a bath containing 13% HF.

EASE estimations were carried out for different scenarios of metal treatment and cleaning with a product containing 8 to 10% HF (Table 10 and Appendix 2). For a non-dispersive use with local exhaust ventilation, air concentrations of 0.5 to 1 ppm and inhalational intake of 0.06 to 0.12 mg/kg/day were predicted. These values are similar to the measured overseas data near dip tanks.

Significantly higher values were estimated if engineering controls were reduced, if the use was a wide dispersive one, or if aerosols were formed. For a wide dispersive use, direct handling and dilution ventilation, air concentrations of 100 to 140 ppm and inhalation intake of 12 to 16.8 mg/kg/day were predicted. Dermal exposure calculations for 1% HF were included, but may not be relevant to normal use because of the corrosive properties of HF.

Metal processing

Workers in the metal processing industry may be exposed to hydrofluoric acid through the use of products used to clean, brighten and etch aluminium, stainless steel and other metals. HF products are often a pretreatment to further processing such as conversion coating, electroplating and powdercoating, or used to remove oxidation formed during processing. Some conversion coating solutions also contain HF and workers may be exposed during the coating process. The removal of metal from components in order to meet predetermined dimensions (chemical milling) is also carried out.

Metal finishing typically involves several steps, one or more of which may involve the use of solutions containing HF. Anodising may involve precleaning, alkaline etching, desmutting, anodising, coloring or dyeing, and sealing, with water rinses in between each step. Chromating with chromium salts can involve the steps of alkaline cleaning, acid deoxidisation, and chromate conversion coating, with water rinses in between. Phosphating may involve degreasing and cleaning, pickling, activation with hot water, phosphating, with water rinses in between steps and a final after-rinse with deionising or passivating chemicals. (Kroschwitz & Howe-Grant, 1994]

Out of 111 enduser respondents to this section of the HF survey, 30 used it in metal finishing processes. Concentrations of HF in the purchased product and final strength varied widely and other acids were often part of the formulation used.

Dipping was the method of application at almost all the workplaces. However two examples were reported where stainless steel pickling was carried out by brushing or mopping the product onto the article to be treated and rinsing in a tank or washing off by hose. In one of these cases, dipping was not done because of the large size of the components being treated. A large quantity of stainless steel pickling products is sold in small pack sizes, suggesting that this use would often be carried out by manual application rather than dipping.

Methods used in preparation of dipping baths were similar to those used in formulation. Processes were generally described as open or partially closed, but two respondents used large enclosed tanks. One respondent reported heating a pickling tank with steam, however most processing is believed to be done at ambient temperature.

A typical work scenario would be loading items into a basket or tray, lowering them by overhead hoist or forklift crane into an acid tank for 5 to 10 minutes, lifting and then lowering into a rinse tank, lifting allowing to drain, and then unloading the basket.

At a little more than half (16) of the workplaces, use of HF product was a regular activity, taking place on at least 200 days per year for periods that ranged from 0.5 h to full shifts of 8 to 10 h a day. At 8 of the workplaces the activity was more intermittent, from between 30 to 150 days of the year, for periods ranging from 0.25 h to a full shift. While one workplace had 9 employees involved in the activity, the more usual pattern was for 1 or 2 people to be involved.

Information obtained from formulators and resellers of products indicate that a large amount (> 69 tonnes) of HF product is also used in aluminium can lines and in automotive zinc phosphating lines. No information was provided on work methods for these uses.

Spraying was another method of applying metal cleaning solutions and was recommended on some of the labels supplied. No information was provided on work activities that involved spraying.

Automotive and boat detailing

Sixteen of the 111 enduser respondents to the HF survey (14%) carried out car, truck and boat detailing. The following workers are potentially exposed to hydrofluoric acid during this use:

- boat builders and repairers;
- fishermen;
- deckhands;
- seamen;
- automotive mechanics and detailers; and

• traders in cars, trucks, caravans and trailers and boats.

HF products are used to clean and remove rust from decks and railings of boats, by brushing or wiping on and then hosing off. One reported usage was to clean rusted deck plates in the confines of poorly ventilated and hot engine rooms (Table 15), with the applied product being hosed down into the bilge. The use of HF product in this particular situation ceased after investigation into bilge plate corrosion revealed the work practice and it was deemed unsafe.

In the automotive industry, the best-known use of HF is in cleaning mag wheels of cars. Other uses include washing down the exteriors of various types of road vehicles, including tankers, trucks, caravans and personnel carriers. A common method of application for the latter group of users included brooming or spraying the product onto the exterior of the tanker and hosing off. Cleaning of other vehicle components and trim such as bumper bars, bullbars, fuel tanks, steps, window frames, trailers and skirts were reported in the survey or in product literature.

All respondents to the HF survey using products for this purpose described their work processes as "open". Product concentrations were 10% and below, with further dilution often recommended.

The potential for inhalational exposure to vapour increases if the product is applied to hot surfaces. One respondent reported that HF solution was sometimes sprayed onto mag wheels that were hot.

At most workplaces engaged in car or boat detailing, 1 to 2 people were employed on the cleaning task, although in the case of two worksites, 7 and 10 people respectively were employed washing down tankers.

Site visits were made to 4 car detailing workplaces using HF mag wheel cleaners. Control measures were considered to be poor; the product used at 3 of the 4 sites did not state the concentration of HF on the label, gloves and other personal protective equipment were not routinely worn, dilutions were not labelled and only 1 of 4 workers had an MSDS. At one site the workers had been assured by the supplier that the product was not dangerous. The comments of workers indicated that some exposure to the product was occurring – spray drift made legs itchy, stinging occurred if there was a cut on the hand or if product went under fingernails and hands became red and painful after use.

Cleaning gold nuggets

The following workers may be exposed to hydrofluoric acid through its use in cleaning gold nuggets:

- jewellers;
- gold refinery workers;
- gold prospectors; and
- traders in gold nuggets.

Concentrations of HF solutions of 50 to 65% were reported to be used for this purpose by 4 respondents to the HF survey. The HF was packaged in 500 mL plastic containers in all cases. Work processes were described as 'open' by all respondents except one, where transfer of the solution to plastic beakers for

immersion of nuggets was conducted in a fume cabinet. At least one of the other three respondents poured the solution directly into an open container, while one used a funnel to transfer to a container. The cleaning operation generally takes one hour, and is done infrequently.

Cleaning printing plates

The following workers are potentially exposed to hydrofluoric acid as a result of its use in deletion pens and fluids designed to remove unwanted images such as scratches from metal printing plates:

- newspaper employees,
- platemakers, and
- printers and typesetters.

Small amounts of a mixture containing 4.8 to 10.2% HF are contained in the imported pens. It is believed deletion fluids are also supplied in 100 mL and 1 L bottles, containing < 1% and < 10% HF respectively. The pen product is applied by rubbing the felt tipped pen against the image and the fluid is applied by dabbing on with a sponge. The plate is then wiped with a sponge dipped in water, or rinsed under running water.

One importer of deletion pens estimated that approximately 25 workers in Australia are likely to be using their pens. From responses to the HF survey an average of 4 to 5 people use the products regularly, for 0.5 to 5 h, 240 to 250 days a year. One company employed 20 people who used the products for 8 h a day, 5 days of the year.

Potential sources of exposure in the printing industry include:

- accidental or deliberate misuse of pens by pulling them apart or not recapping them;
- pouring fluid onto sponge from bottle containers;
- applying pens and sponges to printing plates; and
- rinsing the printing plates.

Miscellaneous metal cleaning

HF has wide application in the cleaning of metals, particularly aluminium and stainless steel, and use in a number of industry areas may be occurring other than those mentioned above. General or niche uses reported via the HF survey or through other industry sources are as follows:

- Soaking carburettors prior to overhaul;
- Cleaning automotive radiator coils
- HF products had previously been used to clean the internal aluminium walls of shipping containers. While no details were provided on method of use, the potential for inhalational exposure in this location would be high.
- Cleaning the inside of dishwashers, by running a HF product through the wash and rinse cycle.
- A product containing phosphoric acid and 5 to 10% HF was recommended for cleaning all stainless steel sinks in a motel/apartment complex.

Work site	%HF used	%HF in final moduct	Activity	Work Process	No. warkers	Duration	Frequ- ency	PPE	Engineering Controls
Metai	orocessing	product							
Ģ	35%	<5%	Pickle stainless steel containers	HF delivered to tank from 200 L drum via a pump. Tank contains nitric acid and water. Tank is heated by steam.			1-2 days/ fortnight	Air supplied hoods, aprons, shoulder length gloves, steel inner gloves, steel capped boots	Air extraction to tank, restricted area
~	- 10%	<0.4%	Etching metal in dip tank	Concentrate is added to water in a 15 L plastic container then poured into the holding tank. Aluminium is placed in steel cage/basket, winched up and dipped, then rinsed in water tank, then pre-treated in the chromate tank, then rinsed in water tank, allowed to drain, lowered for unloading.	N	1 h/day	250 days/year	Elbow length acid resistant rubber gloves, face shield, twin respirator, coat/hood, rubber boots.	Bunding, large industrial vents, winch system controls situated to alto alto verseeing of job while at safe distance
ω	10%	1.5 g/L	Prepare aluminium sheet surface for lacquer coating	Combine HF with deionised water, chromic and phosphoric acid in tank. HF delivered to enclosed tank from 1000 L drum automatically via pump and pipework. Drum changoever: operator disconnects and raises syphon spear cap assembly and replaces top screwing by hand and not overtightening, washes down top of HF drum without entering enclosure, winds out drum using winch, Joads onto forklift with anclosed perspec- cabin, reverses into storage shed, deposits empty container with "empty" label on it. Loads new container, drives forward into HF enclosure, wind drum in via winch. Removes drum cap, inserts syphon assembly, screws down by hand to avoid overligtening.	ω	0.25 h/day	Drum changeov er done once per week (50 days/year)	Hetmet and visor with nape cloth, venttess goggles, gloves, acid proof jacket.	Fully enclosed and automated mixing process, exhaust ventilation
თ	10%	1.7%	Remove oil film from aluminium products prior to powdercoating	HF is pumped from a 200 L drum via a peristaltic pump affixed to a wall which delivers 25 L at a time to a dip tank approx. 6m long, 3 m wide and 1 m high. Parts are lowered in a tray or basket by overhead crane by remote control, aided by manual guidance of the load. Parts are then rinsed in a tank of similar size containing water.	-	8 h/day	233 days/year	Face shield, rubber gauntlet gloves, rubber boots.	Well ventilated area with overhead fan. Drain in floor between tanks, isolated
10	8%	8%	Etch titanium jet engine turbine blades	HF is pumped from 1000 L containers through a sealed manifold system and PVC piping with solenoid operated valves into an enclosed tank. Parts are placed in the solution in a PVC basket using an overhead monorail crane.	No data	8 h/day	215 days/year	Polypropylene rubber gloves, face shield and gas masks and rubber annors	Wet scrubber fume extraction system on tank
ב	2.6%	2.6%	Passivation of small stainless steel articles	A 20 L container is manually poured into a 50 L container to fill or top up. Parts are soaked for 5-20 minutes, then moved to a 50 L rinse bath.	~	irregular	30 days/year	PVC and neoprene gloves, gpgg;es, PVC apron	Dipping done outside of factory

Table 15 - Metal processing and cleaning with control measures

ith control measures (continued)	Process No. Duration Frequ- PPE Engineering workers ency Controls		solution from a 20 L container into an open tank. Immerse 3 1-3 h/day 100 Rubber gloves, Tank closed or one minute then rinse. when not in use use	ict poured into an open bucket from a 20 L drum, parts 2 12 261 'brickie's gloves', Well ventilated d, then removed and hosed down, then blow dried. area long sleeves	entrate poured from 20 L plastic drum into another and 3 8 h/day 280 Goggles, rubber Well ventilated 1. 500 mL spray bottle filled from the container. Sprayed days/yea gloves area els, wheels scrubbed with nyion brush, then hosed off.	HF solution from 25 L container into 10 L bucket, add 8 1 1 h/day 250 Sunglasses, hat - water to 1 part HF product. Broom on then hose off, repeat ssary.	ited into a 10 L container, applied with a brush and rinsed 4 1 h/day 180 Gloves, safety Open to h water.	ct splashed undiluted from 20 L containers or in 1:5 2-3 >0.5 h irregular Overalls, steel Nil – n with water from plastic buckets onto deck plates, spread broom, left to effervesce for at least half an hour, then into the bilge tank.		x 10-20 mL HF tipped from 500 mL bottle into a small 1 - 1 day/year Full length heavy Restricted
	No. workers		erse 3	N	d 3 ed Sff.	8 1 epeat	4 4	2-3 rread n		
ning with control measures (continued)	Work Process		Pour solution from a 20 L container into an open tank. Imrr rims for one minute then rinse.	Product poured into an open bucket from a 20 L drum, par soaked, then removed and hosed down, then blow dried.	Concentrate poured from 20 L plastic drum into another an diluted. 500 mL spray bottle filled from the container. Spray on wheels, wheels scrubbed with nyion brush, then hosed	Pour HF solution from 25 L container into 10 L bucket, add parts water to 1 part HF product. Broom on then hose off, r if necessary.	Decanted into a 10 L container, applied with a brush and ri off with water.	Product splashed undiluted from 20 L containers or in 1:5 dilution with water from plastic buckets onto deck plates, st with a broom, left to effervesce for at least half an hour, the hosed into the bilge tank.		Approx 10-20 mL HF tipped from 500 mL bottle into a smal
cessing and clear	Activity		Cleaning bicycle rims	Clean carburettors	Clean mag wheels	Wash caravans	Clean prawn processing equipment and decks of vessels	Cleaning rusted deck plates in engine room of patrol boats and landing craft		Clean rock from
Metal pro	%HF in final product		10%	8%	Diluted 6:1	Diluted 8:1	~5%	0.74 - 3.7%	uggets	50%
ole 15 - I	%HF used	cleaning	10%	%8	5-10%	6%	-5%	3.7%	ng gold n	50%
Tat	Work site	Metal	12	13	14.	15	16	17	Cleani	IJ.

cleaning with Table 15 - Metal pro

Rust removal from textiles

Workers potentially exposed to hydrofluoric acid due to its use in the professional spot removal of rust stains from garments, carpets and other textiles include dry cleaners, laundry workers and carpet cleaners.

Approximately two workers are exposed per drycleaning business (dry cleaner and spotter), three workers at laundries (plant chemist, foreman and spotter) and one person per carpet cleaning business (usually single operator businesses).

A product containing 10% HF used in Australia is supplied in 20 L, 5 L and 500 mL containers. The 500 mL container comes supplied with an extra dispensing cap, designed to control emission of the fluid to a few drops at a time. A similar product packed in a 50 mL container with a screw top and restricted flow nozzle is primarily marketed through retail outlets. It may have limited occupational use.

Decanting via a funnel from 5 L containers to 250 mL or 500 mL containers prior to use was common (4/8 respondents). The product was either dripped directly from the bottle, dabbed on with an applicator, or applied with an eyedropper or wet towelling. Application time was from a few seconds to 10 minutes, followed by rinsing or flushing with water. One person was employed at the task in 7/8 worksites, 1/8 employed two people.

Potential sources of exposure in these work scenarios include:

- decanting from larger containers into smaller containers, with the possibility of accidental splashing of skin or eyes;
- application of the product to the textile; and
- contact with rinse water or wet towelling used to apply the product.

The products mentioned above are those which are formulated, packed and labelled specifically for use on textiles. In addition several formulated products are recommended for rust removal on both metal and textiles. These tend to be packed in larger containers without the dispensing aids that would allow small quantities to be easily transferred.

Cleaning of brickwork, tiles and walls

Workers potentially exposed as a result of its use in cleaning masonry and tiles include:

- cleaning contractors, including graffiti cleaners, and specialist brick and tile cleaners;
- other cleaners carrying out maintenance; and
- building restoration workers and supervisors.

At least 31 tonnes of solution containing from 2 to 26% HF is used per year in masonry cleaning. It is believed that bifluoride products are also formulated for this use. Uses and surfaces cleaned may be quite varied, ranging from cleaning of shower blocks to removing stains from sandstone to graffiti removal.

Cleaning of masonry with HF products generally involves brushing, swabbing, or spraying the product onto the surface, and then hosing it off with copious amounts of water. The product is sometimes applied with a garden spray. Decanting and dilution of the product prior to use is common. Methods reported include adding

product to a bucket containing water or adding water to a bucket containing some of the product. At one workplace a 70% mixture was diluted down to 10% by pouring from one 20 L drum to another drum containing 50% water and pouring from this drum into another one again etc, diluting by 50% each time, until the desired dilution is reached.

Information from five respondents suggests that exposure is intermittent, with tasks taking from 0.5 to 2 h, carried out from 5 to 52 days a year. A HF/methylene chloride gel product was used for graffiti removal 1 to 2 h per day for 200 days/year.

Potential sources of exposure during masonry cleaning include:

- skin contact with liquid and inhalation of fumes during decanting and diluting product prior to use and during application;
- contact with waste water used to hose down the wall; and
- contact with cleaning tools and containers that have been cross contaminated with HF due to handling with gloves used to apply the product.

Overseas full shift stationary monitoring values of 0.6 to 1.3 mg/m^3 were reported during cleaning/protection of brick and tile surfaces (INRS, 1995, as cited in OECD, 1999).

Bathtub resurfacing

Ceramic and porcelain finishes such as bathtub surfaces must be etched before refinishing. This use was not reported during the HF survey but is believed to occur in Australia. HF of 15 to 35% is used and the acid is brushed or wiped onto the surface to be etched. After the surface has softened it is neutralised and rinsed for further processing. If bathtub refinishing is done without adequate controls, inhalational exposure could be a major concern.

Anti-slip treatments for floors

One company using an imported HF product in an anti-slip treatment for tiles was contacted and a site visit made. A description of that work process is in Table 16. Information has been received on another anti-slip product containing HF, which is applied in a similar manner, but also requires that a very dilute HF solution be used for cleaning and maintenance of the treated surface.

Glass etching

Workers potentially exposed in this application would include:

- glass artists;
- other workers in glass industry; and
- lens manufacturers.

HF of 50% concentration is used for etching flash glass, a process that requires deep etching. Lower concentrations (1 to 2%) and bifluoride pastes are marketed and used for other types of glass etching.

One glass artist reported that HF is used to strip coloured layers from flashed glass (a traditional hand blown glass where one or more colours are layered onto a base glass) to produce multicoloured effects. The technique is mostly used in church

restoration work and it is believed that there would be a number of glass workers using HF in Australia.

Potential for exposure during etching of flash glass include the inhalation of fumes from containers and etching baths containing concentrated HF and accidental dermal exposure. Spills, splashes and drips are likely during transfer of HF acid into etch bath or during brushing or other agitation of of the glass in the etch bath, when removing glass from the bath and when disposing of rinse water. In addition the small open plastic containers used for etching could overturn, spilling the contents. Faulty gloves could also lead to exposure.

An imported bifluoride glass etching paste is repacked from 25 L plastic drums into 90 mL and 170 mL bottles through the tap of the drum. This product is used occupationally and sold as a craft product through retail outlets. The paste contains 20% ammonium bifluoride at a pH of 5.2. At this pH only a small proportion of the fluorine atom would be present as HF (Appendix 1). It was stated by one user that no injury occurred after skin contact with the paste, if it is removed promply. Irritation was experienced if unnoticed paste was left on the skin, or if it went under the fingernails.

There is potential for exposure during application, in scraping back the product into the bottle for re-use and in washing the treated object. Because of the characteristics of bifluorides, the physical (paste) form and the relatively high pH, this product poses less potential for injury from acute exposure than many HFbased products but the potential for chronic absorption of fluoride is still present. Although use of gloves is recommended on the label, the promotional literature showed it being used without gloves.

Details of different scenarios in glass etching are in Table 16.

No atmospheric monitoring data is available in Australia. Overseas monitoring in the etching department of a glass company included personal and static sampling. Personal breathing zone air levels ranged from 0.34 to 3 mg/m³. TWA general air levels ranged from not detectable to 1.7 mg/m³ TWA (NIOSH, 1990).

Glass cleaning

At least three products containing 6 to 7% HF for cleaning scale, bore water stains and buildup from glass are formulated in Australia. The product is used in a diluted form to clean bore water stains from windows. Directions for use for another product instruct that it be applied with a brush or spray, left in contact for several minutes, agitated with a brush and washed off. The MSDS states it is for wax/scale removal in car washes. Dilution before use is recommended for another product.

Workers potentially exposed include general cleaners, window cleaners and car wash workers.

Laboratory uses

There is a potential for dermal exposure to the high concentrations of HF commonly used in laboratories, through drips, spills or splashes onto skin or eyes while transferring HF to and from beakers, and through contact with wastewater used to wash instruments. There is also potential for inhalational exposure to fumes during transfer of acid and during heating of HF solution, which occurs in

acid digestion. The effectiveness of the fume cabinet in extracting fumes from the fume cabinet will influence the potential for exposure. Also, considering the degree of manual handling that laboratory processes involving HF can entail, the ergonomic design of the laboratory and fume cabinet, combined with work procedures and training, are important factors influencing the potential for exposure through accidental splashes and spills.

Industries which reported use of HF in laboratory processes include:

- mining and exploration;
- iron and steel production;
- research and development;
- aircraft manufacturing;
- analytical chemistry;
- medical laboratories; and
- detergent manufacture.

Types of workers potentially exposed to HF through its use in laboratories include chemists, metallurgists, geologists, technical officers and laboratory technicians and assistants.

One laboratory use scenario for HF is detailed in Table 16.

Acid digestion of mineral samples

Hydrofluoric acid is the only common aqueous acid that can dissolve silica (Patterson, 1997) and is frequently used in mineral analyses for this purpose. Out of the 26 respondents to the HF survey who used it in the laboratory, 16 used it in the acid digestion of mineral samples. A similar process was reported by one respondent, for the measurement of silicate in detergents for the purpose of quality control.

Concentrations used varied from 40 to 70%, with the majority of workplaces using 40 to 50% concentration. Amounts used per year varied from < 1 kg to 480 kg. Transfer of HF to beakers was from 500 mL or 2.5 L containers. Methods of transfer included the use of metering bottle top dispensers, pipettes, mechanical dispensers and more commonly manual pouring from the container into a measuring cylinder and then into the beaker. It was unclear whether transfer always took place within fume cupboards. The acid digestion took place in fume cupboards. Some processes common to acid digestion are heating of solutions in open vessels on hotplates within fume cupboards; transfer of solutions from test tubes; centrifuging of test tubes and pouring out solutions from test tubes, beakers and rinsing vessels.

The duration of the laboratory processes involving HF ranged from ¹/₄ h per day up to 7.5 h per day. Frequency of the laboratory processes ranged from 1 day a year to 356 days a year. In 10/16 workplaces, the process was a regular activity, for > 200 days per year (6/16) or between 100 - < 200 days a year (4/16). Numbers of workers in each laboratory ranged from 1 to 12, with 2 to 6 being most common.

One respondent who had observed the use of HF for sedimental analysis in a university laboratory commented that the procedure was often performed by people with insufficient training and skills, and that the laboratory was open to hallways, potentially exposing members of the public.

Metallurgy testing

Five respondents to the HF survey used it for the etching of metal samples for microscopic examination. Concentrations of HF used vary between 40 to 50%, from which etching solutions containing between 0.1 to 5% of HF are made. Samples are usually immersed for a few seconds or up to several minutes, or sometimes the solution is swabbed on. Fume cabinets are used.

Between 4 to 15 technicians were involved in this process at each workplace, usually for < 1 h to 2 h per day, < 30 days/year, although at one workplace the activity took place for > 50 days a year.

Miscellaneous

The use of HF solutions in the following laboratory applications was also reported:

- Occasional cleaning of stainless steel ion sources in a pathology laboratory. The sources are soaked and sonicated in a 1.5% solution prepared from 48% HF and then rinsed. In a similar use, the metal probes for silicate in an analytical titrator are washed 4 times a year under a fume hood.
- As a reagent solvent in the preparation of samples for atomic absorption spectrophotometric analysis. Forty percent HF is dispensed directly into samples. This task takes one person 10 min a day and is carried out for 200 days a year.
- Used in combination with other concentrated acids to clean certain types of glassware 2 or 3 times a year.

Stripping coatings from optical lens

HF is used in Australia to strip metallic anti-reflective coatings from plastic and glass optical lens. Stripping is done either because the coating is defective, or because a customer has specifically requested a non-coated lens. Stripping at three plants was reported via the HF survey, but other sites may carry out the same process. Workers potentially exposed include laboratory technicians and assistants, process workers and supervisors.

Coatings are removed by dipping in acid baths. HF acid in concentrations of 48% or 50% are used to charge dip baths in the three workplaces known to perform this task. Final concentrations of HF in the baths range from 2.4% to 10.8%. Amounts of concentrated HF used per year for stripping in the three workplaces was 1 L, approximately 6 L, and < 42.5 L respectively.

A detailed description of the work processes for one workplace is in Table 16. At the other two workplaces, the dip bath comprised an open plastic container and a glass tank. HF is charged to the tank by manually pouring into a measuring container which is then emptied into the tank. Stripping lens is a batch task performed regularly. At one workplace, one worker performed the task up to 6 times per shift, with an exposure time estimated by the company of 30 seconds maximum each time. At another workplace, 4 people performed the task for 15 min per day, for 200 days a year. No details were available from the second workplace.

Potential for exposure through inhalation of fumes or splashes onto skin or eyes could occur in the following processes:

- transfer of HF from containers into the bath;
- stirring the bath;
- loading and unloading rack of lens;
- rinsing instruments;
- disposal of the acid solution;
- scraping lens with gloved hands immersed in bath; and
- neutralising and emptying bath.

The practice of manually scraping lens with gloved hands immersed in acid solution poses a potential high risk of dermal exposure through faulty or insufficient personal protective equipment.

Semiconductor manufacture

HF is used by at least one company in Australia for etching silicon wafers used in the manufacture of semiconductors in the electronics industry and is also used for solar cell manufacture. HF is used for an initial cleaning of the wafer, with dry etching techniques used to etch the patterns (Table 16).

The rigorous standardisation of work procedures that is an intrinsic part of work in a cleanroom of this class in many ways assists in reducing the potential for exposure to HF in this type of work scenario. Workers are trained to avoid cross contamination of baths and contamination of the room by the workers themselves. Steps in the manufacturing process are tightly controlled and vigilance is given to anything that may contaminate the processes such as spills or drips. The situation of highest potential exposure in this type of scenario is considered the transfer of the HF from its original containers into measuring cylinders and hence into the baths. In any work scenario of this type, the design of the wet benches and methods employed for emptying and neutralising baths will also be important in determining the risk of exposure.

HF is used for etching silicon wafers and thin films for use in solar cell manufacure by at least two companies and one research and development group. At least 6 tonnes per year is used for this purpose.

Oil and gas well stimulation

At least two companies in Australia use HF in solutions that are pumped down oil and gas wells (on land or at sea) in order to react with sandstone formations and increase well production. The companies carry out the process under contract to the well operators.

The HF acid is generated inside semi-closed mixing tanks through the reaction of hydrochloric acid and ammonium bifluoride and water. The mixture is agitated

after HF is formed and the end solution containing between 1 to 3% HF acid is used immediately or stored at the well sites until needed.

Mixing the solution and pumping it down the wells is done as a batch process, on an occasional rather than a regular basis. At one contracting company 5 workers are involved (acidising supervisor, operations engineer, equipment operators) for 12 h a day, 5 days a year.

No information was provided on the method of pumping.

Exposure is possible during the following processes:

- *in situ* preparation of HF;
- pressure testing prior to pumpout;
- pumping of solution into well;
- attachment/detachment of pump; and
- neutralisation and disposal of waste left in container.

Dental uses

HF is an aid to the manufacture of dental appliances and restorations through its action on both the ceramic and metal components. Quantities used are small and specialty products of 5% to 15% strength were reported. It is believed that more concentrated HF has also been sold for this purpose. There is potential exposure to dentists, dentists' assistants and dental laboratory technicians in the processing of dental prostheses. HF is also a minor ingredient in therapeutic fluoride topical treatments.

Etching prosthetics

Information was obtained on the use of products sold for etching dental ceramics, such as crowns, veneers and ceramic moulds.

One gel product containing < 5% HF is part of a proprietary computer assisted system for the production of inlays, onlays and veneers. It is reported that use of this system is increasing due to improved technology. There are at least 100 of these units in Australia, used by dentists and dental technicians, and training in the units is provided by the manufacturers. The products are applied directly to the ceramic surface either from a 6 mL dropper bottle or by painting on with a small disposable brush or a plastic disposable application needle. The ceramic is then rinsed under sprayed water or in an ultrasonic bath and immediately inserted and bonded to tooth.

Two other imported products containing 7.5% and 9.5% HF were identified for stripping, repair or bonding of porcelain prostheses. Both products are packed in small bottles and one is in gel form. HF is also used in dental laboratories when a precious metal is cast with a ceramic insert to produce a cylindrical hole that will take a pin. HF is later used to dissolve the ceramic insert to the casting.

Exposure to these products could occur from accidental drops onto skin or splashes from rinse water. However the small size of the prosthetics and corresponding small amounts of product and the relatively small amount of time reported to be spent on this task (1 minute/day) reduces the likelihood of exposure. The likelihood of exposure is further reduced by the colouring of at least one of these products red to make it more visible.

Polishing metal castings

A product containing 14% HF is used to polish metal castings in the dental industry. It is dispensed from a 500 mL bottle into a plastic dish, castings are immersed for 1 minute and then flushed and rinsed with running water.

Topical fluoride rinses and gels

Therapeutic fluoride products for teeth are applied by dentists. Exposure could occur from accidental spillage of product when transferring to a cup, or from contact with rinse water, however the concentration of HF in these products is low.

Synthesis of other chemicals

Information was obtained from three companies on the use of aqueous HF to manufacture other inorganic fluoride chemicals, using methods analogous to formulation. Seventy percent HF is used to make an aqueous solution of fluoroboric acid for resale. Some of this material is further reacted to form solutions of metal fluoroborate salts such as lead and stannous fluoroborate. Heat is generated by the reaction and would increase the potential for inhalational exposure. Seventy percent HF is also used to produce inorganic fluoride salts such as nickel, zinc, calcium and barium. Thirty five percent HF is diluted and reacted with sodium silicate solution to produce sodium silicofluoride solution, which is resold as a concrete hardener.

Work	%HF	%HF in 8555	Activity	Work Process	No.	Duration	Frequ-	PPE	Engineering
slle	nsea	product			workers		ency		Controis
Rust	emoval f	rom textile					200 - 100 100		
21	%6	%6	Spotting of carpet & upholstery	Decant using plastic funnel from 5 L to 500 mL bottle in outdoor area . Container and area is washed or wiped down with damp towelling. Apply approx 5 mL with wet toweling or eyedropper, then flushed using vacuum water extraction machine	÷	<5 minutes/ day	Every working day	Gloves	•
ı	10%	10%	Rust removal in drycleaning	Typical stain-spotting work process as described by drycleaners: A small amount of product is dispensed onto stained area from tapered nozzle of bottle before main machine drycleaning process. If stain still present after cleaning process, product is reapplied and stain is "blown away" with steam gun.	5	< 5 minutes/ day	Not often used. 500 mL bottle lasts > I year.	None	None
Labor	atory wo	li i i i i i i i i i i i i i i i i i i					ani		
<u>0</u>	50%	<50%	Mineral assay	Measure 10 mL HF from 500mL bottle into plastic measuring cylinder by slowly titting bottle, pour into beaker, touching lip of cylinder on side of beaker, rinse plasticware and replace. Cover beaker with tefton watchglass and boil 30 minutes, swirl every 10 minutes, releasing steam by tilting Id slightly before swirling. Remove from hotplate and place in furme hood to cool for 10 minutes, rinse lid and sides of the tefton beaker with DI water. After adding another chemical and swirling, filter under vacuum, rinsing 3 times. Rinse filter paper, remove filter paper, rinse filter funnel before and after removal from flask. Add another chemical to filtrate and indicator tablet. Rinse down the sides of the flask and titrate. Neutralise solution prior to disposal.	2	0. 6	242 days/year	Glasses, butyl or rubber gloves.	Fume cupboards
Glass	etching	1991 1991					3. 11월 - 12일 3. 11월 - 12일		NATION
0 	20	≤ 50%	Stripping coloured layers back from flash glass in church restoration work	A small amount of HF (approx. 100 mL) is poured from a 500 mL screw top container into a small marked plastic container similar in size to a food takeaway container. The acid resist (a type of tape) is placed onto the glass and the glass is placed not the plant in the glass. The bath can take up to 2 h, during which time it is periodically checked. The bath is sometimes used to spread the acid over the glass. The bath can take up to 2 h, during which time it is periodically checked. The bath is sometimes made stronger by addition of acid through pouring it down a stick so that it trickles into the bath. or made weeker by the addition of water in a similar way. Different methods are used to take the glass to the glass up, or the glass is removed with gloved hands. Glass and paint brush are placed in a 10-20 L container of water for rinsing and resist is removed. Rinse water is emptied onto lawn.	~~	≤2 h	Infrequent (once or twice a year)	Gloves and mask	

• HF with control ć microllon Tahle 16 - Some

Table 1	l6 - Some n	iiscellaneous use sce	marios for aqueous HF with control measures (cont	inued)				
Work % site us	HF %HF ir ed final produc	n Activity	Work Process	No. workers	Duration	Frequ- ency	PPE	Engineering Controls
Glass etch	ing (continued	6						
8 9 8 8 8	% <1% Is ste	Etching logo into glass moulds	The etch solution is prepared in bulk by measuring out a portion of 50% HF solution from a 2.5 L container stored in a bunded area close to the fume cabinet, adding it to distilled water at a temperature of $21-23^{\circ}$ C and agilating the solution to mix it. The final etch solution contains <1% HF. For etching a prepared mould is placed within a fume cabinet and HF is poured onto the mould so as to pool over the area to be etched. An etching cream is also dabbed onto the mould with cotton buds. After 2 min the HF acid and etching cream are rinsed off under running water in the sink of the fume cabinet.	1-2 for etching	Several times in a shift for etching.	Frequently	Safety glasses, face shield, rubber gloves, acid apron.	Fume extraction
čc	2	Etabling Jose is	Channel is should be acceled as a subset of the second second second second second second second second second		1111			
Bif	ya Iuori	etcrirrig logo iri window glass	Stencil is applied to surface of glass. Faste is prushed onto stencil in an even laver 1-2 mm thick After 5 min the evcess is	known	known	NOT KNOWN	IZ	N
Ge (removed by brush and returned to the container for re-use. The					
pa	ste		paste remaining is removed with a damp cloth. The stencil is peeled off and discarded, and hands are washed.					
Stripping c	oating from o	ptical lens						
		reflective coating from plastic optical lens Disposing of acid bath solution	emptied slowly into a 9 L bath of delonised water, producing a concentration of 10.8% HF. The bath is stirred with a rod for 30 seconds. The used bottle is rinsed 2-3 times within fume cabinet, capped, and discarded in rubbish bin. The rod is rinsed. The bath is kept stored in the furme cabinet. Lens are loaded into a stripping sonic rack. Lid is removed from acid bath and rack lowered into solution. If level is low it is topped up with delonised water using beaker. Lid on bath is replaced and back and placed from bath, rack removed and placed in sink of water. Lid is put back on bath. Any spills on bench top are wiped up with damp sponge, acid rinsed from gloves. Taps are wiped on with damp sponge, acid rinsed from gloves. Taps are wiped on with damp sponge, acid rinsed from gloves. Taps are wiped on with damp sponge, acid rinsed from gloves. Taps are wiped on a flore in spray wash if necessary. Rack is placed in sink for band head lens removed. Lens are clean with a fint free cloth and actorne.		max each time	per shift,	gloves, lab safety glasses,	in exhaust vented treatment room
			repeated for fermander or acid bath solution, bath is rinsed, taps and bench and lid of bath wiped down.					

	Wet bench, exhaust ventilation of baths		1
	Faceshield , gloves, apron over cleanroom garments		Wrist length gloves; overalls; length apron
	100 days/year		5-30 days/year
	12 h/day		1-2 h/day
	ω		ې ۲
	Cassette loads of wafers are dipped into a 3 L bath inside a wet bench. The load is then moved to a dump rinse bath located in the same wet bench, using a handle grip. The HF bath is changed every 1-2 weeks. It is emptied using an aspirator that dilutes the waste water 10:1 with water as it empties. The new bath is made up by decanting from a 2.5 L container into a measuring cup and adding to the bath. Baths contain HF diluted either 10:1 or 50:1 with water.		The tiles are first tested to ascertain what strength product is needed by the operator pouring some of the solution into a bucket, dipping a rag into it and rubbing on the tiles. The appropriate strength product is then measured from the labelled container into a measuring cup, which is held inside the bucket, and then emplication (it is reported to splash less than the normal mop used for application (it is reported to splash less than the normal mop used for the cleaning process). When the HF solution has been applied to the whole floor surface, and left for the few minutes it needs to come to the correct degree of slip, neutralising solution is applied fiberally to the whole area with the ordinary mop. Then the area is rinsed by pouring over a couple of buckets of water, which is allowed to run away along the ground. The mopheads and sponges, after soaking in the neutralising solution, are squeezed out and put away in the neutralising solution, are squeezed out and put away in the crates (tubs). The waste neutralising solution is disposed to ground or grass or drain.
	Etching silicon wafers		Applying anti-slip treatment to tiles in outside area.
nductor wafe	3.7%	art.	Diluted with small quantitie s of water
g semicol	20%	ip treatm	2% 6%
Etchin	52	Anti-si	73

Table 16 - Some miscellaneous use scenarios for aqueous HF with control measures (continued)

7.2.9 Exposure from used containers

Varied methods are used to handle empty containers of aqueous solutions of HF or HF product. The following methods were used by a significant proportion of the survey respondents:

- rinse and re-use;
- return to supplier;
- sell to drum recycler; and
- send to landfill.

Several respondents used more than one of the above methods and several rinsed containers before disposal. Additional methods were neutralisation, burning, disposal with contaminated medical waste, disposal via garbage bin and storage on site. Extra precautions used were damaging container so that it could not be re-used and wrapping in plastic before disposal.

Isotainers and cylinders of anhydrous HF used in Australia are reported to be returned to the supplier when empty. However, it is noted from technical literature that at least one international supplier of anhydrous HF supplies small quantities in non-returnable lecture bottles, which are small cylinders.

Each of the disposal processes used in Australia could lead to additional occupational exposure, inside or outside the site of use.

7.2.10 Incidents reported during occupational use of HF

Where potential exposure to a chemical may occur routinely during use, exposure can be monitored or estimated through modelling. For HF, a significant additional source of potential exposure is through accidental releases or accidental contact. Information on these occurrences may highlight hazardous steps in handling, likely types of incidents, or the range of situations in which they may occur.

Overseas reviews of HF have included incidents occurring in the USA (US EPA, 1993) and the European Union (Lines, 1995). More recently, accidents in US formulation plants using hydrofluoric acid in October 1999 and May 2000 resulted in the deaths of workers (Segal, 2000, US Chemical Safety and Hazard Investigation Board, 2000).

Appendix 3 contains information on workplace incidents occurring in recent years in Australia. The workplace incidents listed include incidents with and without injury as well as one fatality in Western Australia which occurred in 1994. The data was collected from various sources during the course of the assessment, and some incidents are reported in more detail than others. The injuries reported cover a range of severity. NOHSC data on serious lost-time injuries could not be used because the coding does not distinguish HF from other acids.

Details of the sources and the methodology used to collect the data are below. The incidents reported would be a subset of the total that have occurred, and may not be representative of the total.

Sources of incident data

<u>Source</u>	Comments
Industry	Approximately 10% of respondents to the HF survey listed one or more incidents. Applicants and notifiers provided additional information.
State/Territory government sources	Various State and Territory authorities were contacted for information, but a comprehensive survey was not carried out. Sources included OHS authorities, health departments and emergency services.
MHIDAS database	Two Australian incidents recorded on MHIDAS, a Major Hazard Incident Data Service developed on behalf of the Major Hazards Assessment Unit of the United Kingdom Health and Safety Executive. This database records details of those incidents involving hazardous materials that resulted in, or had the potential to produce, a significant impact on the public at large. (MHIDAS, 2000)
Other sources	One case was reported by a hospital and one in a journal article. Three anecdotal incidents were reported in an unpublished OHS thesis

7.3 Public exposure

7.3.1 Consumer exposure

A small number of HF products are distributed primarily through retail outlets e.g. fabric rust remover, car wheel cleaner. HF and products containing HF are also supplied to several smaller distributors for supply wholesale to professional tradesmen (e.g. rust stain removers to professional dry cleaners, stainless steel and aluminium cleaners to truck drivers and car care industries, gold cleaners to prospectors with permits, refrigerator coil cleaners to electricians, radiator coil cleaners to car mechanics), however the general public may also have access to some of the same products through wholesale or retail outlets, or factory-door sales. Products which are available to the general public and which were identified through the HF survey include rust remover for clothes, stainless steel and aluminium cleaners (e.g. mag wheel cleaner, rust remover for boats), tile and brick cleaners, glass etching solutions, refrigerator and car radiator coil cleaners, and dental cleaners.

The concentration of HF in these products varies according to the intended use, and ranges from < 1% for over-the-counter and prescription dental care (anti-caries fluoride toothpastes and mouthwashes) products where the hazard to public health is considered low, up to 10% for stainless steel and aluminium cleaners where the public health hazard is considered high, and are covered by an entry in Schedule 6 of the SUSDP for concentrations between 0.5 and 10% of HF.

In two instances identified by the HF survey, concentrations of HF included in Schedule 7 (greater than 10%) were apparently available to the public. These were a rust remover for boats supplied over-the-counter to the general public at a

concentration of 10 to 30% HF (Queensland), and a refrigerator coil cleaner available through trade showrooms to the general public at a concentration of 8 to 15% HF (NSW). The exact concentration of the latter product was not known to the importer. In both circumstances, there was no indication that licensing of users was occurring. Concentrations of HF (greater than 10%) are covered under Schedule 7 of the SUSDP with an entry in Appendix J regarding the Conditions for Availability and Use of Schedule 7 Poisons. In the case of HF, the condition is "not to be available except to authorised or licensed persons".

Accidental exposure from the use of consumer products containing HF is not uncommon. Available data from the National and State Poisons Information centres (Table 17) indicate that NSW (including national after-hours calls) receives about 60 calls per year; Victoria 15 to 20, WA and Qld 20 each. Most exposures are dermal (71%) or inhalational (17%), while accidental ingestion (9%) and ocular exposure (3%) are less common. Almost all calls to poisons centres relating to HF exposure require referral to hospital for assessment and treatment. In a recent incident reported to a State health authority (Tasmania. Department of Health and Human Services, 2000) burns from a household rust remover required surgery on the fingers and thumb.

Secondary exposure to HF can occur, for example, where clothes treated with a rust removal treatment are not adequately washed prior to wearing. Secondary exposure following the use of HF as a concrete or glass etching compound can also occur, where the product is not completely removed after the treatment. The use of HF products in domestic situation by tradespeople (ie for bathtub refinishing, wall cleaning and floor etching) may also result in secondary exposure of the public.

7.3.2 Transport and spills

Public exposure to HF could occur as a result of accidental spills or release during transport, storage or industrial use. An HF spill or leak can be a combination of vapour and liquid. In warmer weather, the liquid will vaporise rapidly due to its low boiling point.

HF is classified as a dangerous good and must be transported by licensed professional carriers under appropriate Commonwealth, State and Territory regulatory controls. In the event of a transport accident or spill, the contaminated area is required to be restricted to authorised personnel only, wearing suitable protective clothing and self-contained breathing apparatus.

In the event of a large spill in a populated area, care must be taken to avoid public exposure. The appropriate emergency services would decide on the need for evacuation or other management strategies to minimise the potential for exposure of the public to HF vapour or liquid. Appropriate techniques are needed to limit the release of HF to the environment during the process of cleaning up the spill. Where industrial use of HF takes place in or near public areas, smaller spills may also have the potential for public exposure.

7.3.3 Exposure via the environment

HF may enter the environment from both natural (volcanoes, weathering of minerals and marine aerosols) and anthropogenic sources. The latter includes production of HF itself (not relevant in Australia), but HF is also formed as a by-product during other industrial processes (e.g. aluminium production). Once

released to the environment HF is unlikely to remain in its original form for very long. In air, water and soil HF is transformed to a variety of other F^- compounds. Release to the aquatic, terrestrial and atmospheric compartments and emissions from industry are strictly controlled and monitored by EPA guidelines.

	. ,		
Age (if child)	Product type or HF concentration (if known)	Route of exposure	Comments
Adult	Rust remover	Dermal	Severe burn
Adult	Aluminium brightener	Dermal	Hand and under nails very sore
14	Rust remover	Dermal	Child had burns and blistering on both feet
Adult	Rust remover	Dermal	Severe pain and swelling of finger
Adult	Alloy wheel cleaner	Dermal	Pain
Adult	HF, unknown %	Dermal	Burn
Adult	HF, unknown %	Dermal	Painful hand
Adult	HF, unknown %	Dermal	Leaking gloves - forearms burnt
Adult	Aluminium brightener	Dermal	
Adult	Rust remover	ingestion	Intentional ingestion 100 mL
Adult	Aluminium brightener	Dermal	Possible acid burns to hands and under nails
Adult	HF, unknown %	Dermal	
Adult	Alloy cleaner	Dermal	
Adult	HF, unknown %	Dermal	Finger swollen and painful
Adult	Rust remover	Dermal	Stinging around nails
Adult	HF/bleach	Inhalation/nasal	Pain in nose
Adult	HF, unknown %	Ingestion	
Adult	Aluminium brightener	Ocular	
adult	Rust remover	dermal	Asymptomatic
8	Rust remover	Dermal	Child wore stocking all day which had been treated with rust remover and not washed
Adult	Mag wheel cleaner	Dermal	Severe pain
Adult	Cleaner	Inhalation/nasal	Shallow breathing
Adult	Rust remover	Inhalation/nasal	Asymptomatic
Adult	Rust remover	Dermal	
Adult	HF dilute	Dermal	
Adult	Rust remover	Dermal	
Adult	Rust remover	Dermal	Leaked into overall pocket, mild burn on leg
Adult	HF, unknown %	Dermal	

Table 17 - Hydrofluoric acid exposures reported to Poisons InformationCentres in NSW (1996) and Victoria (Jan 99 – Jul 2000)*

Age (if child)	Product type or HF concentration (if known)	Route of exposure	Comments
Adult	HF, unknown %	Dermal	
Adult	Aluminium cleaner	Dermal	
Adult	HF, unknown %	Dermal	
Adult	HF, unknown %	Dermal	
Adult	HF 2%	Ingestion	Blood stained vomitus
Adult	HF, unknown %	Dermal	Asymptomatic
Adult	HF, unknown %	Dermal	Burns on large areas of body
18mo.	Rust remover	Ingestion	Only drop or two but vomited milk
Adult	HF, unknown %	Inhalation/nasal	Asymptomatic
Adult	HF, unknown %	Dermal	Also exposed to sulphuric acid, skin blistered, patient in hospital
Adult	HF, unknown %	Dermal	Patient in hospital
Adult	HF, unknown %	Dermal	Patient at GP
2	Car cleaning fluid, HF 1.7%, H2PO4 14.9%	Ingested (swig)	Patient in hospital
2	Mag wheel cleaner containing HF	Ingested (couple of mouthfuls)	Referred to hospital
Adult	HF 9.8%	Dermal	Excruciating pain, fingers went black, referred to hospital.
Adult	HF 9.8%	Dermal	Referred to hospital
Adult	HF 9.8%	inhaled	Referred to hospital
Adult	Mag wheel cleaner	Dermal	Referred to hospital
Adult	Mag wheel cleaner, HF 5.4%	Inhaled	Referred to GP
Adult	HF, unknown %	Dermal	Also exposed to HCI, referred to hospital
Adult	HF, unknown %	Inhaled	Patient at GP
Adult	HF, unknown %	ocular	Patient in hospital

Table 17	· Hydrofluoric aci	d exposures reported	to Poisons Inform	ation Centres
	in NSW (1996) an	nd Victoria (Jan 99 –	- Jul 2000)* (cont.)	

* Occupational exposures have been excluded where known; however, the list above may also include some occupational exposures, particularly where the concentration of HF is unknown.

8. Health Effects

8.1 Overview from published reports

The major source of information for this summary has been the OECD SIAR (SIDS Initial Assessment Report) for Hydrogen Fluoride (OECD, 1999), prepared by the Netherlands Organization for Applied Scientific Research and National Institute of Public Health and the Environment. Other sources of information consulted for this summary are referenced in the text.

8.1.1 Toxicokinetics

Inhaled HF is almost completely absorbed in the upper respiratory tract, before reaching the lungs, and distribution to the blood is rapid (ATSDR, 1993).

Hydrofluoric acid is absorbed through the skin in humans. The degree of absorption is not known, and is expected to be influenced by concentration, duration of exposure, and corrosive effects on the skin (ATSDR, 1993).

After uptake fluoride distributes through all soft tissues. It may also cross the placenta during pregnancy. About half of the absorbed fluoride is sequestered in bone and teeth.

8.1.2 Effects in experimental animals and *in vitro* data

 LC_{50} values for inhalation exposure to HF after exposure for one hour are about 280 mg/m³ in mice, from 792 to 1909 mg/m³ in rats, and 1470 mg/m³ for rhesus monkeys. No data are available for acute oral and dermal studies.

In rats a dermal HF burn of only 1.7% of the skin surface may result in fluoride poisoning and disturbances of calcium and other electrolyte homeostasis. Appendix 4 sets out animal and human data on the effects of acute dermal exposure to anhydrous HF, and aqueous HF of varying concentrations. Systemic as well as corrosive effects were observed in some cases.

No sensitisation studies are available in animals with HF.

In a 91 day inhalation study rats were exposed to 0.098, 0.72 and 7.52 mg/m³ of HF. Death was reported at 7.52 mg/m³ in addition to tissue irritation, dental malformations, haematological and biological changes, and changes in organ weight. Small decreases in serum albumin/globulin ratio and lymphocytes were reported at 0.72 mg/m³. These decreases were not considered to be biologically significant by the OECD and 0.72 mg/m³ was determined to be the no observed adverse effect level (NOAEL).

A limited number of *in vitro* and *in vivo* tests with HF were complemented by data from other tests on inorganic fluorides such as sodium fluoride, as toxicokinetics should be similar. Using this data, the OECD review concluded that fluoride from any inorganic source does not induce chromosomal damage *in vivo*.

Studies investigating the carcinogenicity of HF are not available. Because of the similar properties of HF and fluoride salts once they are absorbed into the body,

tests on the latter may be relevant, especially for systemic tumours. Studies have been conducted in rats and mice with sodium fluoride administered via drinking water and diet. The OECD report concluded the available data is sufficient to suggest that fluoride is not carcinogenic in animals.

Reproductive data on HF itself has not been reported, but data on sodium fluoride was considered an appropriate substitute, as reproductive effects are systemic. Although conclusive results are not available, some animal studies indicate that oral exposure to fluoride may damage testicular tissue and reduce male fertility. Embryotoxicity was observed in currently available studies. A two-generation study not yet fully reported gives indications that fluoride does not affect male or female fertility.

8.1.3 Human data

Acute toxicity is a major hazard of HF relevant to accidental exposure. Fatalities from accidental exposure to HF have occurred through inhalation, and also the dermal route (Muriale et al, 1996; Tepperman, 1980). High blood fluoride levels with severe dermal lesions and damage to the respiratory tract and lungs are reported. Systemic fluoride results in disturbances in calcium and other electrolyte homeostasis and in cardiac arrhythmias.

Human dermal contact with HF causes second and third degree skin burns. Severe pain is experienced shortly after exposure, and the burns tend to heal very slowly. Five grams of anhydrous HF caused second and third degree burns to approximately 2.5% of the body surface. Burns from dilute solutions are reported to cause delayed pain if not recognised and treated (Perry et al., 1994).

When human volunteers were exposed to constant concentrations of HF via inhalation, increased upper airway symptoms (itching, soreness) were observed after one hour at 2.5 mg/m³ and above. In a separate study, some irritation of eyes, skin and nasal mucosa were found at average HF concentration as low as 1.16 mg/m³. A recent study in human volunteers (Lund et al., 1999) used bronchoalveolar lavage to assess the effects of 1 h exposure to inhaled HF. There were indications of inflammation at the intermediate (0.7 to 2.4 mg/m³) and high (2.5 to 5.2 mg/m³) levels tested, but not the lowest level (≤ 0.6 mg/m³).

No human data on sensitisation was available for HF.

In humans, skeletal fluorosis is a known effect of prolonged intake of fluoride, by both oral and inhalation routes. This effect has been reported in some but not all studies of workers in aluminium plants, where exposure occurs to both particulate fluoride and to gaseous fluoride. Benke et al (1998) reported that this risk has been virtually eliminated in aluminium smelting through improved technology and the introduction of PPE.

Fluoride is one of several agents suspected in the etiology of respiratory disease in smelter workers. The health of workers in the alumina and primary aluminium industry is currently under investigation in Australia through the Healthwise project. The project involves Alcoa smelters, Monash University and the University of Western Australia. The different areas of the study include a prospective cohort study commenced in 1996 and a retrospective mortality study focussing on the incidence of lung and bladder cancer.

Human data on reproductive toxicity of fluoride are inconclusive.

Dermal exposure to 5 g of anhydrous HF has caused severe hypocalcemia (Burke et al., 1973). It has been estimated that wounds as small as 2.5% of the body surface area (BSA) from concentrated aqueous acid can produce lethal hypocalcemia within 2 to 3 hours (Greco et al., 1988). This area is the size of a hand (WorkSafe Western Australia, 1998a). The same author estimates that the risk of hypocalcemia exists after contact of 1% BSA with HF of 50% or greater concentration or 5% BSA with HF of any concentration.

8.2 Classification

HF is classified by NOHSC and the European Union (EU) as corrosive and very toxic. Risk phrases are:

R26/27/28 Very toxic by inhalation, in contact with skin and if swallowed.

R35 Causes severe burns.

The International Agency for Research on Cancer (IARC) has classified inorganic fluorides as Category 3 (Unclassifiable as to carcinogenicity to humans).

9. Effects on Organisms in the Environment

No ecotoxicity tests have been provided by Australian industry. Tests from the IUCLID data sheet have been provided by industry to the European Union, and have not been validated. However, where tests below are referenced from the OECD SIDS report (OECD, 1999), it is believed these have been validated by the Dutch authorities for use in the draft SIDS report.

HF exists in water primarily as the fluoride ion. The tests provided below where referenced to the IUCLID datasheet have generally described the test substance as "F ions".

The OECD report has also provided many test results. These were performed with NaF as it is stated this can act as a surrogate for the evaluation of HF effects in aquatic organisms. All test results from this report have been corrected for the fluoride ion. Very few experimental details have been provided.

It is further stated that there is a clear relation between toxicity and water hardness. Tests performed in soft water ($<50 \text{ mg CaCO}_3/L$) showed a higher toxicity than those performed in hard water ($>50 \text{ mg CaCO}_3/L$), due to the precipitation of fluoride as CaF₂.

	Species	Test Duration	Hardness mg CaCO ₃ /L	Result (mg/L)
Acute (1)	Leuciscus idus melanotus	48 h	25	LC ₅₀ = 255
(2)	Oncorhynchus mykiss	96 h	17	LC ₅₀ = 51
(3)	Oncorhynchus mykiss	96 h	22	LC ₅₀ = 108
(4)	Salmo trutta	96 h	21	LC ₅₀ = 165
(5)	Gasterosteus aculeatus	96 h	78	LC ₅₀ = 340
Chronic	Oncorhynchus mykiss	21 day	12	LC5 = 4

9.1 Toxicity to fish

Table 18 – Toxicity to fish as reported in OECD report

The values of tests 1, 3 and 5 (acute) are based on nominal concentrations, while the remaining two tests were measured concentrations. The chronic 21 day test result for rainbow trout was reported using a measured concentration. This value is considered to be equivalent to the NOEC for mortality. The test was conducted in very soft natural water with daily renewal of the test water, ie, expect maximum toxicity, but still indicates at worst slight toxcity.

	Species	Test Duration	Result (mg/L)
Acute	<i>Leuciscus idus</i> (freshwater)	48 h	LC ₅₀ = 660
	Goldfish	96 h	LC₅₀ not provided. Described as lethal at 120 ppm.
	Mosquito fish	96 h	LC ₅₀ = 925
	Mugil cephalus (mullet)	96 h	LC ₀ = 100
	Rainbow trout	Not given	LC ₅₀ = 2.3-7.3
	Trout	Not given	LC ₅₀ = 5.9-7.5
	Trout	240 h	$LC_{50} = 64$
	Brown trout	96 h	LC ₅₀ = 164.5
	Rainbow trout	96 h	LC ₅₀ = 107.5
Chronic	Mugil Cephalus (mullet)	72 day	Increased mortality and physical deterioration reported at 52 ppm

Table 19 – Toxicity to fish as reported in IUCLID (European Chemicals
Bureau, 1996)

The above results are largely in agreement with those reported in Table 18. Two outlying results appear where LC_{50} values are reported to be <10 ppm. These results can not be relied on as not enough information is available. HF can be described as slightly to very slightly toxic to fish.

An LC_{50} of 1.5 ppm is reported for fish eggs with hatching being the end point. No data is provided on exposure period and duration.

9.2 Toxicity to aquatic invertebrates

	Species	Test Duration	Result (mg/L)	Hardness mg CaCO₃/L	Ref:
Acute	<i>Daphnia</i> sp.	48 h	EC ₅₀ = 270	204	(European Chemicals Bureau, 1996)
	Daphnia magna	48 h	EC50 = 97	250	(OECD, 1999)
	Daphnia	48 h	EC50 = 153	173	(OECD, 1999)
	Penalus indicus and Peneus monodan (prawns)	96 h	NOEC = 100	Marine	(European Chemicals Bureau, 1996)
	Lobster	Not given	NOEC = 4.5	Marine	(European Chemicals Bureau, 1996)
	Perna perna (brown mussel)	120 h	EC ₅₀ = 39	Marine	(OECD, 1999)
	Perna perna (brown mussel)	120 h	EC ₅₀ = 20	Marine	(OECD, 1999)
	Mysidopsis bahia	96 h	EC50 = 10.5	Marine	(OECD, 1999)
Chronic	Crab	72 day	Physical deterioration reported at 52 ppm Effect on reproduction reported at 52 ppm		(European Chemicals Bureau, 1996)
	Palaemon pacificius (sand shrimp)	72 day			(European Chemicals Bureau, 1996)
	Daphnia magna	21 day	NOEC = 3.7	250	(OECD, 1999)
	Daphnia magna	21 day	NOEC = 14.1	250	(OECD, 1999)

Table 20 - Toxicity to aquatic invertebrates

Acute and chronic results for freshwater and marine invertebrates indicate HF can be considered slightly to very slightly toxic to these species. Based on the limited number of studies, the marine species (brown mussel and mysid shrimp) appeared more susceptible than their freshwater counterparts.

A number of freshwater benthic macroinvertebrates are reported as tested over 96 h. The following results are given, and while it is not apparent from the IUCLID datasheet what the endpoint is, the OECD report states them as an EC₅₀. The tests were performed in relatively soft water, with CaCO₃ reported as ranging from 12-19 mg/L and the results are provided in Table 21 below. Again, slight toxicity is indicated.

Species	Result (mg/L)
Hydropsyche bulbifera	26.3
Hydropsyche exocellata	26.5
Hydropsyche pellucidula	38.5
Hydropsyche lobata	48.2
Chimarra marginata	44.9

Table 21 - Toxicity to benthic insect larvae

9.3 Toxicity to algae and aquatic plants

Species	Test Duration	Result	Hardness	Reference:
		(mg/L)	mg CaCO₃/L	
Scenedesmus quadricauda	8 days	NOEC = 249	Unknown	(OECD, 1999)
Scenedesmus sp.	48 h	EC ₅₀ = 95	Unknown	(European Chemicals Bureau, 1996)
Scenedesmus sp.	96 h	EC50 = 43	Unknown	(OECD, 1999)
Selenastrum capricornutum	96 h	EC50 = 122	Unknown	(OECD, 1999)
Skeletonema costatum	96 h	EC50 = 81	Unknown	(OECD, 1999)

Table 22 - Toxicity to algae and aquatic plants

Data on test conditions are not available. *S. costatum* is a marine algae, and these limited results suggest there is no real difference in sensitivities between freshwater and marine species.

The OECD report provides NOEC values of 50 mg/L for a further 6 freshwater algae species where exposure was over a 7 day period. These results are all indicative of slight to very slight toxicity.

The OECD report also provides chronic toxicity data for a number of marine algae as follows:

Species	Test Duration (days)	NOEC, biomass	
		(mg/L)	
Ampidinium carteri	14-21	50-100	
Chaetoceros gracilis	14-21	200	
Dunaliella tertiolecta	14-21	200	
Pavlova lutheri	14-21	50	

Table 23 - Chronic toxicity to marine algae

No test conditions are available, but the results are suggestive of very slight toxicity.

9.4 Toxicity to micro-organisms

Two studies are summarised in the IUCLID datasheet (European Chemicals Bureau, 1996). 96 hour exposure of the bacteria *Escherichia coli* resulted in a toxicity threshold of 180 mg/L while 16 hour exposure of the bacteria *Pseudomonas putida* gave a toxicity threshold of 231 mg/L.

Further test results have been provided in the OECD document as follows:

Species	Test Duration	Hardness	NOEC
		mg CaCO₃/L	(mg/L)
Activated sludge	3 h	Unknown	510
Chilomonas paramaecium	48 h	42.3	83
Entosiphon sulcatum	72 h	35.3	101
Uronema parduzci	20 h	35.3	7.1
Microegma heterostoma	28 h	204	226

Table 24 – Toxicity to micro-organisms as reported in OECD report

9.5 Toxicity to terrestrial plants

Table 25 - Toxicity to plants (IUCLID datasheet) (European Chemicals Bureau, 1996)

Species	Exposure period	Concentration	Comments
Rice	1 day	10 mg/m ³	leaves surface destroyed; sugar content of leaves reduced
Corn	32 day	0.5 ng F/m ³	chloritic lesion on leaves; fluoride accumulation in leaves
Wheat	96 day	0.95 ng F/m ³	Reduced yield, leaves not damaged
Scotland pines	2 days @ 6 hrs per day	0.021 mg/m ³	Carbonic exchange rhythm modified. Photosynthesis modified.

These results are only a sample of results outlined in the IUCLID data sheet. Many other results cannot be used as levels are in unfamiliar units and may be the result of translation errors. These results show terrestrial plants may be quite susceptible to fluoride poisoning. It is further stated in the IUCLID data sheet that most vegetables and broad-leaf trees are quite resistant. The most sensitive species to fluorides are conifers, fruit, berries and grasses which are injured at concentrations ranging from 0.5 to 1.2 ppb (0.42-1 μ g/m³) when duration exposure lasts for several days (5-10 fluoride ppb are usually accumulated by most of the plants in the absence of an atmospheric source). The most visible fluoride effect on vegetation is necrosis or burn at the end of the leaves. Decrease in reproduction capacity may be caused by fluoride exposure.

Further information is obtained from the OECD report where a table of NOEC-values for HF (in $\mu g/m^3$) for plants of differing sensitivities is provided.

	Exposure			
	1 day	1 month	7 months	
Highly sensitive species	1.0	0.3	0.2	
Sensitive species	2.0	0.6	0.4	
Slightly sensitive species	7.5	2.5	1.2	

Table 26 – NOEC Values for HF (in µg/m³) for plants (OECD, 1999)

These outcomes are based on a large number of fumigation experiments with such plants as ornamental crops, fruit crops and conifers exposed to HF and indicate plant species can be highly sensitive to the chemical.

9.6 Summary of environmental effects

A large range of results on the toxicity of HF and fluoride to organisms in the environment is available. Two main sources have been used for this report, namely the IUCLID data sheet and the OECD report.

Tests performed in soft water tended to show higher toxicity than those performed in hard water due to precipitation of fluoride with calcium carbonate in hard water.

Following the guidelines of Mensink *et al* (Mensink et al., 1995), HF can be considered slightly to very slightly toxic to fish from validated test results obtained from the OECD report. However, additional tests believed to be unvalidated show moderate toxicity to rainbow trout and a second trout species, although the test duration's are not provided. Other unvalidated test results support a conclusion of slight to very slight toxicity to fish.

Similarly for invertebrates, all test results are indicative of slight to very slight toxicity. Fluoride showed slight toxicity to benthic macroinvertebrates. Chronic results for invertebrates are suggestive of very slight toxicity with NOECs all reported to be >1 ppm.

The toxicity of fluoride to algae and aquatic plants can be described as slight to very slight. However, terrestrial plants can be sensitive to fluoride at very low levels in the atmosphere with effects including chlorotic and necrotic leaves, lowering of yield and reproductive effects. The most sensitive species to fluorides are conifers, fruit, berries and grasses.

10. Current Controls

The key elements in the management of health and safety risks from exposure to hazardous substances include:

- control measures;
- hazard communication;
- atmospheric monitoring;
- regulatory controls; and
- emergency procedures.

An assessment of the measures currently employed to reduce occupational health risks associated with the use of HF and products containing it is included in this chapter. Basic information concerning the MSDS and labels supplied by the importers and formulators is also included.

10.1 Occupational control measures

According to the NOHSC National Model Regulations for the Control of Workplace Hazardous Substance (Model Regs) (NOHSC, 1994a), exposure to hazardous substances should be prevented, or where that is not practicable, controlled to minimise risks to health. NOHSC's National Code of Practice for the Control of Workplace Hazardous Substances (NOHSC, 1994b) lists the hierarchy of control measures, in priority order, that should be implemented to eliminate or minimise exposure to hazardous substances. These are:

- elimination;
- substitution;
- isolation;
- engineering controls;
- safe work practices; and
- personal protective equipment.

10.1.1 Elimination and substitution

Elimination is the removal of a chemical from a process and should be the first option considered when minimising risks to health. In situations where it is not feasible or practical to eliminate the use of a chemical, substitution should be considered. Substitution includes replacing with a less hazardous substance or the same substance in a less hazardous form.

An importer reported that there is a general trend away from the use of aqueous HF. Some users of HF also reported that they had ceased their use of it, or planned to do so due to the ever-present possibility of a burn occurring and the need to take calcium gluconate gel home in case of a delayed burn. Elimination of the use of aqueous HF because of its hazards was reported in the following cases:

- cleaning of cement tankers;
- cleaning ceramic coatings from badges before re-use;

- all use of HF at a multi-site mining operation. Uses include cleaning and laboratory analysis, part of the latter being out-sourced. It is reported that two other mining operations with large use of HF have ceased to use it in the last two years;
- use by a gold recycler;
- purchased for trial synthesis reaction, but returned when toxicity of material was realised from safety literature; and
- removal of HF from all products of one company by mid 2000.

Substitutes for aqueous HF have been found in some processes:

- an alternative method was devised for testing of cement in a laboratory;
- a different acid combination used on difficult-to-clean glassware in a laboratory;
- in Australia, production of "pearl" light globes by etching glass with HF/bifluorides has been replaced by an electrostatic powder coating process;
- an alternative 2-step chemical treatment used to remove matrix from industrial diamonds, prior to recycling;
- a formulation using alkali and hot water is being trialed for graffiti removal;
- alkali solution for the cleaning of some shipping containers;
- nitric-acid based alternative, which works more slowly, instead of a HF-based aluminium cleaner;
- phosphoric acid to remove rust from boats;
- surfactant-based formulation in automated cleaning of trucks, although this is likely to be less effective;
- regular cleaning schedule of food-processing machine, to avoid buildup that would require HF to remove;
- use of HF in cleaning reduced by restricting to certain types of vehicle; and
- blast cleaning techniques are reported to have replaced chemical etching of glass in many cases. Carbon dioxide (dry ice) blasting technique has been reported as an alternative in the removal of graffiti. In general mechanical cleaning processes instead of chemical ones may be suitable for some metal-cleaning operations e.g. maintenance of equipment.

In general, lower concentrations of HF pose lower risks, following dermal or inhalation exposure, than higher concentrations. Fuming of HF is absent below 40% (Gerhartz et al., 1988) and in practice lowering the concentration reduces the hazard from inhalational exposure. A formulator advised that in addition to aiming for complete elimination of HF from products they were working with overseas affiliates to reduce the concentrations in their products. A substantial proportion of the aqueous HF imported into Australia is lower than 70% in concentration, the maximum commercial concentration for aqueous solutions. This would improve safety, for applications where the most concentrated material is not needed.

Bifluoride salts have been described as safer alternatives to HF in glass etching. Unlike HF, the sodium, potassium and ammonium bifluorides are solids and may be handled more safely than liquids However bifluorides in aqueous solution, or in contact with moisture in the air or on skin or mucous membranes, produce HF by dissociation of the bifluoride molecule. Aqueous solutions of bifluorides do not produce high concentrations of HF, as this is limited by solubility and the equilibrium between HF, F^- and HF_{2^-} . (See Appendix 1)

Acidified fluoride or bifluoride salts are also used as substitutes. However, substitution of HF by acidified fluoride salts or acidified bifluoride salts does not substantially reduce hazard as these combinations are able to generate quite concentrated solutions of HF. A major drawback of both bifluoride and acidified fluoride substitutions is the likelihood that users will not know that HF is present. From information received during the assessment, it is clear that bifluorides or acidified fluorides are used as substitutes for HF in several industry sectors.

When considering a substitute for HF, users need to consider the health and environmental hazards of the alternative material or process.

Oxalic acid is reported to have rust-removing properties and, may be a substitute for HF in some formulations (Klauder et al., 1955). However, oxalic acid is itself toxic and a comparison of the two chemicals is outside the scope of this assessment.

Substitutes for anhydrous HF are being considered overseas for petroleum alkylation, which is the major use of this form of HF in Australia. Sulphuric acid is used instead of HF for petroleum alkylation in some petroleum refineries. A US government review of HF (US EPA, 1993) considered that the safety of these two catalysts could not be easily compared, because of the larger quantities of sulphuric acid required, and the consequent increase in hazardous transport loads.

Substitution of alkylation catalysts remains an active question overseas because of the possibility that large-scale accidental releases of HF could threaten nearby communities. Other substitutes suggested are HF modified to reduce its ability to form a gas cloud and solid acid catalysts (Lewis & Lapkin, 1998). It has recently been reported (Anon, 1999b) that one alternative, the Reduced Volatility Alkylation Process (ReVAP), can be used in existing HF alkylation units, and makes it possible to reduce airborne HF by as much as 60 to 90% in the event of an accidental release. The first licence for this technology was granted overseas in 1998.

HF is probably infrequently used if alternatives of equal technical efficacy are available, and in some cases replacement may involve sacrifices in product performance. Despite this, a number of previous users have discontinued its use because they believe the monetary or non-monetary costs of handling it are too high. For example, the WA Dept of Minerals and Energy reported that its enforcement of safety regulations in the use of HF in mines, such as provision of showers and proper procedures, has reduced the number of people using it. Among informed users, the safety incentives for elimination of HF are strong.

10.1.2 Isolation

Isolation as a control measure aims to separate employees, as far as practicable, from the chemical hazard. This can be achieved by distance or enclosure.

In many uses of HF it is not practicable to separate it from workers. However, isolation may ensure that nobody is unnecessarily in the vicinity of HF. Examples of strategies used are:
- all parts of the process where the product stream may contain HF fenced off and access strictly controlled;
- remote control operations at alkylation plants;
- formulating area is roped off when the area is in use;
- work area located away from busy sections in a laboratory. Similarly, a metal dip tank operation was isolated in one corner of a factory area, away from forklift paths and other processes to improve safety. Several formulators mix products containing HF in an area separate to the main plant;
- fume cupboard pull-up screens provided a barrier in a laboratory;
- separation of the formulation area from the packing area by barrier screens; and,
- barriers or markers used to restrict entry during use in public areas, during graffiti removal and anti-slip floor treatment.

10.1.3 Engineering controls

Engineering controls are plant or processes which minimise the generation of hazardous substances, suppress or contain hazardous substances, or which limit the area of contamination in the event of spills or leaks.

The need for engineering controls differs because the uses, quantities and concentrations used for HF are so variable. Anhydrous (100%) HF is handled in closed systems in all alkylation plants, in surface treatment of plastics and in the one laboratory use reported. Almost all users of aqueous HF use open or partially closed processes.

Varied engineering controls were reported for anhydrous HF in alkylation, as part of the complex overall control systems used in the petroleum refining process. These measures include flushing provisions to remove all HF from piping, special sampling vessels, isolation equipment, some of which is controlled remotely, special weighing and pumping equipment, HF-detecting paint, spray water systems and visual and audible alarm systems.

Recent updating of one Australian alkylation plant improved engineering controls relevant to safety (Anon, 2000). If accidental release occurs, a rapid acid-transfer system will quickly dump all acid and hydrocarbons that are in the reactor/settler into a storage tank. As this process occurs via gravity feed, it will operate without power or pumps.

For road transport of containers of aqueous HF to customers, one importer reported that pallets are shrinkwrapped to minimise movement during transport. Smaller containers have been reported to be packed in boxes or overpack drums with shock insulation before transportation.

Most engineering controls reported by users or formulators of aqueous HF were aimed at reducing exposure to acid fumes. Of 112 replies on engineering controls, the following methods were mentioned, with more than one measure used in several cases:

• exhaust ventilation (40);

- fume cupboard or hood, usually in laboratories (26);
- natural ventilation, including roof vents (24);
- processes carried out outside (13);
- air curtain (1); and,
- fan (1).

In two cases exhaust ventilation was available but not considered necessary for the particular process.

Other engineering controls mentioned in conjunction with the use of aqueous HF were:

- mechanical hoists for moving components in and out of dip tanks;
- remote operation for hoists;
- gravity feed to load cells in filling process, to reduce risk of overfilling;
- dip tank located at foot level, to avoid spills onto operator;
- covers for tanks;
- automatic dosing of product to tank;
- mechanical dispenser for laboratory dosing;
- overfill drain on tank;
- use of industry standard wet bench for semi-conductor processing;
- bunding of areas to limit the spread of spills On small scale fume cupboard operations, a similar effect was obtained by the use of deep trays inside the cupboard; and,
- mechanical pumps to transfer HF from containers to mixing tanks.

A number of respondents, including formulators and users, indicated that engineering controls were not applicable to their operations. Others did not complete the section at all, suggesting that they also had no engineering controls to report.

10.1.4 Safe work practices

Safe work practices may aid in the control of risks from hazardous substances. For HF these may be quite varied, as it is handled in both anhydrous and aqueous forms, at concentrations ranging from 100% to < 1%, in both large and small quantities and is used in a wide range of industry sectors and applications.

Some specific safe working practices adopted for HF were:

- use of whole drum quantities during formulation;
- special warning signs or labels in work area or at entrance to area, specifying that HF is in use. Some suppliers provide special labels;
- use of bottles with internal lip in neck to avoid airlocks, so that liquid will pour out smoothly, rather than in bursts;
- use of written procedures;
- summaries of MSDS and/or procedures posted at workstation;

- restricted access to area where HF is used, through signs or barriers;
- area kept very clean;
- work with HF carried out outside normal working hours;
- only skilled workers such as qualified chemist or experienced employee allowed to handle HF;
- HF ordered from supplier just before use, avoiding storage at site;
- deliveries of HF not accepted unless drums and pallet in good condition;
- acid tanks covered when not in use;
- presence of at least one other person when HF is being used. It has been recommended that workers should not work alone with HF of > 10% concentration. (WorkSafe Western Australia, 1996);
- scrupulous attention to washing down all equipment and surfaces that have been in contact with HF, in order to avoid future accidental contact with the material.
- gravity feed systems used by several formulators for filling containers from a mixing tank, in order to avoid pumping the product;
- unused HF returned to the supplier when use ceased; and,
- good design and correct choice of packaging to assist users with safety. Two widely used fabric rust removers, one of which is also available to the public, have dispensing nozzles which only allow a few drops at a time.

In the USA there is a requirement that open containers e.g. buckets, be replaced by suitable closed containers for transporting HF during formulation (OSHA, 1989).

Responses to the survey indicated that users and suppliers are attempting to control the risks by specifying more closely than usual how, where, when and by whom HF is used.

10.1.5 Personal protective equipment

Where other control measures are not practicable or adequate to control exposure, personal protective equipment (PPE) should be used. For HF, PPE is chosen to prevent routine exposure and to protect workers in the case of accidental spillage or release.

The degree of protection required in order to avoid exposure to HF may vary with the nature of the work carried out and concentration and form of HF. Some workplaces specify different degrees of PPE, depending on the task to be carried out. Responses to the survey of industry indicate that some PPE is used in almost all cases, but the range of protection is wide.

Systems of PPE for different tasks are most formalised at alkylation sites using anhydrous HF. One site has a brochure for staff with colour photographs of each combination and the suitable combinations for the various tasks. PPE used at alkylation sites range from a minimum of goggles and long sleeve gloves to a selfcontained pressurised body suit used in the case of an HF release. Items of PPE are carefully cleaned after use to prevent them becoming a source of exposure to HF. For aqueous HF, 67 replies were received from those handling more concentrated HF (35% to 70%). All reported wearing gloves and varying eye/face protection. About one quarter used respiratory protection, and the same proportion mentioned footwear. Full body suit or protection was reported by 8 (12%). An apron or overalls was mentioned by 46 (68%) but the latter may have been made of normal fabric.

For users of more dilute HF (< 35%), a high proportion of gloves and eye/face protection was reported, with fewer other precautions. Safety glasses or goggles were more common than face shields.

For HF the efficacy of the PPE would depend on whether the combinations chosen combine to give full protection to all skin. Where respiratory protection against fumes is required, one formulator found it difficult to combine this with full face and head protection against splashes. Other problems reported with the use of PPE are that it is difficult to work in full PPE for a long period of time, face protection may reduce visibility and that thicker and more resistant gloves reduce dexterity.

Gloves are an important element of PPE, even when lower concentrations are used. More dilute HF solutions may not cause irritation initially. If they penetrate PPE through gaps or through pinholes in gloves, the consequence may be a serious delayed burn.

Information on permeation of 30 to 70% HF solutions with different materials is available (OSHA, 1998). This information, in conjunction with manufacturers' recommendations, can be used to select PPE.

10.2 Hazard communication

10.2.1 Labels

Under the NOHSC National Model Regulations and Code of Practice for the Control of Workplace Hazardous Substances (NOHSC, 1994c) and the corresponding State and Territory legislation, suppliers and employers of hazardous chemicals used at work are obliged to label hazardous substances in the workplace in accordance with the NOHSC Code of Practice for the Labelling of Hazardous Substances (Labelling Code) (NOHSC, 1994d). These requirements also apply to laboratory use, process intermediates, bulk solutions and hazardous substances which are decanted and not consumed immediately. Where products containing HF are intended for domestic end-use, they need only comply with the SUSDP labelling requirements (Australian Health Ministers' Advisory Council, Products used domestically and industrially need to comply with both 1997). codes ie with SUSDP along with additional information in accordance with the Other labelling requirements, such as those required by the Labelling Code. Australian Dangerous Goods (ADG) Code, would also apply. (See Section 10.3.5).

Mixtures containing HF are classified as hazardous substances at concentrations of 0.1% and above, and require the appropriate risk and safety phrases. For concentrations of 7% and above, the current risk and safety phrases in Australia are in Table 27 below:

 Table 27 - Risk and Safety Phrases for HF

 From: Designated List of Hazardous Substances (NOHSC, 1999)

Classification and Risk phrases	Safety phrases
T+: R26/27/28	S1/2
Very toxic by inhalation, in contact with skin and if	Keep locked up and out of the reach of children - S7/9
swallowed.	Keep container tightly closed and in a well ventilated place. S26
C: R35	In case of contact with eyes, rinse immediately with plenty
Causes severe burns.	of water and seek medical advice. S36/37
	Wear suitable protective clothing and gloves.
	S45
	In case of accident or if you feel unwell, seek medical advice immediately (show the label whenever possible).

The risk phrases are modified for concentrations of hydrofluoric acid between 7% and 1%, and for concentrations between 1% and 0.1%. Safety phrases would remain as above. See Table 28 below:

FIOM. Designated List of Hazardous Substances (NOHSC, 1999)				
	Hydrofluoric acid in % w/w			
Risk phrases	≥0.1% but <1%	≥1% but <7%	≥7%	
R20/21/22: Harmful by inhalation, in contact with skin and if swallowed.	v			
R36: Irritating to eyes	~			
R23/24/25: Toxic by inhalation, in contact with skin and if swallowed.		~		
R34: Causes burns.		~		
R26/27/28: Very toxic by inhalation, in contact with skin and if swallowed.			~	
R35: Causes severe burns.			~	

 Table 28 - Risk Phrases for dilutions and mixtures of HF

 From: Designated List of Hazardous Substances (NOHSC, 1999)

In October 1998 the EU Working Group on the Classification and Labelling of Dangerous Substances recommended a change to the risk phrases to be used in the most dilute concentration range ($\geq 0.1\%$ but < 1%). The Group recommended that the risk phrase R36 (Irritating to eyes) be replaced by R36/37/38 (Irritating to eyes, respiratory system and skin). If this change is made to the EU classification documents, then, in accordance with NOHSC procedures, the EU classification will be adopted by NOHSC.

Both EU and Australian classification lists have separate entries for hydrogen fluoride and for aqueous solutions as hydrofluoric acid. No specific concentration limits are set for the former in the EU classification, but have been set in Australia, in order to allow for non-aqueous dilutions and mixtures that may be prepared. The specific concentration limits for non-aqueous dilutions are based on the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1994e) and differ from those set for aqueous solutions.

Labels were obtained during the course of the assessment. A formal evaluation of their compliance with the Labelling Code was not carried out. However the following deficiencies were noted in some labels:

- presence of HF not disclosed;
- incorrect identification of the active ingredient as hydrochloric acid, rather than HF;
- ingredients identified only as "strong acids";
- percentage of HF not stated.
- risk and safety phrases not present, or incomplete.
- under the Labelling Code, concentration ranges can be given if the exact amount is commercially confidential and suggested concentration ranges are given as: >60%, 30 to 60%, 10 to 30% and <10%. It was found that other concentration ranges were also used, and one label declared 10 to 59% hydrofluoric acid. In this case the same label was probably used on several dilutions of HF; and
- incorrect Hazchem code

Several companies use extra labelling, as part of their precautions for using HF. One laboratory supplier uses additional red octagonal labels, and supplies extra labels of different colours if requested by the customer. "STOP – Hydrofluoric Acid" labels are used by a formulator on all drums and intermediate bulk containers in addition to normal labelling. These are especially useful on large packs where the label is small in comparison with the size of the pack. A distinctive extra label is recommended in the PACIA Code of Practice.

10.2.2 Material Safety Data Sheets

Material Safety Data Sheets (MSDS) are the primary source of information for workers involved in the handling of chemical substances. Under the NOHSC *National Model Regulations for the Control of Workplace Hazardous Substances* (NOHSC, 1994a) and the corresponding State and Territory legislation, suppliers are obliged to provide an MSDS to their customers for all hazardous substances.

MSDS for HF and products containing it were requested from applicants, notifiers and questionnaire respondents as part of the assessment It was noted that at least one importing company was operating without an MSDS, before obtaining one from overseas principals. Some questionnaire respondents also indicated that they had not been supplied with a MSDS.

Site visits to car detailing businesses suggested that the MSDS are not always easily available to those using the chemicals. Even if held by the company, they may be stored in offices away from the main work area. No formal evaluation was carried out of the MSDS received, but the following deficiencies were noted in the supply and quality of MSDS:

- some users did not hold MSDS;
- some MSDS were quite old (many dated 1992-93, with the oldest dated 1986) and varied from the more recent versions supplied for the assessment. One MSDS referred to a superseded formulation, and listed acid fluorides instead of HF;
- one repacker had been supplying customers with the technical data sheet rather than the MSDS, as he did not appreciate the difference between the two documents. Another questionnaire respondent supplied an emergency procedure guide instead of an MSDS;
- percentage strength of HF not included, or declaration of strength only as low, medium etc. In some MSDS HF was only identified by CAS number;
- formal statement of hazardous nature omitted;
- no clear statement of the hazards of HF or appropriate emergency and first aid procedures;
- overseas MSDS in particular gave poor and incomplete information. They were less likely to clearly state the health effects, or to recommend calcium gluconate products
- no local contact address and emergency number; and,
- incorrect Chemical Abstracts Service (CAS) number for HF, incorrect exposure standard or statement that exposure standard had not been determined.

It is believed that many people are unaware that solutions of bifluoride salts, or acidified solutions of fluoride salts, contain HF, as this information was not included in the MSDS seen for some products.

10.2.3 Other methods of hazard communication

Labels and MSDS are the major channels for hazard communication of a chemical or mixture. Information from industry reveals that several companies have taken initiatives to give additional information to workers, customers and others handling HF. Examples are:

- Small laminated information cards supplied to the driver of any truck transporting HF products from the premises.
- An information sheet provided to customers with the effects of HF, possible substitute formulations that do not contain HF and the efficacy of those formulations.

HF has been the subject of extra guidance material because of the acknowledged dangers it presents.

Guidance material available in Australia includes:

- NOHSC Guidance Note "Hydrogen Fluoride", 1989;
- Workcover Corporation, SA "Hazard Alert: Hydrofluoric Acid Burns" No 3, November 1995;

- ACT Workcover "Hazard Alert No 9: Hydrofluoric Acid Burns from Aluminium Cleaner" Sept 1995;
- WA Dept of Occupational Health, Safety and Welfare lift-out "Hydrofluoric Acid" from SafetyLine 29, Feb 1996; and,
- The Plastics and Chemicals Industries Association (PACIA) "Hydrofluoric Acid Code of Practice" (1997) includes guidance material and useful information on Australian legislation.

Additional information is used in transport via the Standards Australia series of "Emergency Procedure Guides – Transport". A guide is available for aqueous solutions of HF.

10.2.4 Education and training

Guidelines for the induction and training of workers potentially exposed to hazardous substances are provided in the NOHSC *Model Regulations and Code of Practice for the Control of Workplace Hazardous Substances* (NOHSC, 1994c).

A specific training session on HF is carried out at one oil refinery, for all workers and contractors working near HF-containing process equipment. This session is to be repeated every two years. Other applicants and notifiers indicated that they carried out training.

The WA SafetyLine internet information service includes "Case Study: Hydrofluoric Acid", as a SafetyLine Institute lecture, based on a real incident. (WorkSafe Western Australia, 1998a). The aim of the lecture is to:

- explain the physical, chemical and toxicological properties of 70% HF;
- apply the principles of hazard identification, risk assessment and control to the case study; and,
- identify the significant faults that led to the accident and emphasise the importance of the hierarchy of controls in preventing further accidents.

Several formulators reported that worker training relevant to the handling of HF and other chemicals was provided by local TAFE colleges. In one case, the employer had contributed a module specifically covering HF and encouraged workers to undergo training.

10.3 Other workplace regulatory controls

10.3.1 Monitoring

Under the NOHSC Model Regulations and Code of Practice for the Control of Workplace Hazardous Substances (NOHSC, 1994c), employers are required to carry out an assessment of the workplace for all hazardous substances, the methodology of which is provided in the NOHSC Guidance Note for the Assessment of Health Risks Arising from the Use of Hazardous Substances in the Workplace (NOHSC, 1994). When the assessment indicates that the risk of exposure is significant, atmospheric monitoring for HF should be conducted in the workplace as a precursor to the implementation of suitable control measures to reduce exposure.

No atmosphoric monitoring data was supplied for those sites using HF industrially, although four companies stated that it had been carried out and two of these indicated that results were below the exposure standard. Data was supplied from an aluminium smelter and phosphate fertiliser manufacturer, where HF is generated incidentally.

Biological monitoring is the assessment of exposure through measurement of the chemical or its metabolites in biological specimens. For HF, estimation of fluoride in urine is a non-specific indicator, as it will include fluoride from other sources such as fluorine and fluoride salts. Levels will be affected by non-occupational exposure from food and water.

10.3.2 Exposure standard

The current occupational exposure standard for hydrogen fluoride (as F) in Australia is 3 ppm (2.6 mg/m³) (NOHSC, 1995) and this value is also the peak limitation. The standard was adopted from the American Conference of Governmental Industrial Hygienists (ACGIH). Comparative occupational exposure standards are presented in Table 29.

In Australia fluorides (as F) also have an exposure standard of 2.5 mg/m^3 , with no peak limitation, adopted from ACGIH. The ACGIH are awaiting further toxicological data and industrial hygiene experience before setting a short term limit for fluorides (ACGIH, 2000).

The USA, in addition to exposure standards, has a measure which reflects the acute hazards of HF. The concentration set by the US National Institute for Occupational Safety and Health (NIOSH) as Immediately Dangerous to Life or Health (IDLH) is 30 ppm (24 mg/m³) (NIOSH, 1996). Recently the USEPA has proposed short-term exposure limits for HF and several other chemicals. The current proposed Acute Exposure Guideline Levels (AEGL's) for HF, still under review (EPA, 2000); (Bureau of National Affairs, 2000) are in Table 30.

Country	TWA	STEL	Source
Australia	3 ppm (2.6 mg/m ³) as F	Ceiling, as for TWA	(NOHSC, 1995)
European Union	1.8 ppm (1.5 mg/m ³) 8 h Indicative Occupational Exposure Level	3 ppm short-term Indicative Occupational Exposure Level	(LOLI, 2000)
Germany	3 ppm (2.5 mg/m ³)	6 ppm peak limitation, momentary value which should not be exceeded more than 8 times per shift. (Sampling for 5 minutes)	(Deutsche Forschungsgemeinschaft, 1999)
Norway	0.8 ppm (0.6 mg/m ³)		(RTECS, 2000)
Sweden		2 ppm (1.7 mg/m ³) ceiling, 15 min reference period	(LOLI, 2000)
United Kingdom	No current TWA but propose to adopt the European Union value above (UK HSC, 2000)	3 ppm (2.5 mg/m ³) as F, 15 minutes.	(HSE, 1999)
USA – ACGIH	3 ppm (2.6 mg/m ³) as F	Ceiling, as for TWA	(LOLI, 2000)
USA - OSHA	3 ppm 8 hr TWA as F	Short term level vacated	(LOLI, 2000)
USA - NIOSH	3 ppm (2.5 mg/m ³) 10 h TWA as F	6 ppm, (5 mg/m ³) 15 minutes	(LOLI, 2000)

Table 29 – Occupational exposure limits

 Table 30 - Proposed US EPA Acute Exposure Guideline Levels for HF

	10 min	30 min	60 min	4 hr	8 hr
AEGL 1	1 ppm	1 ppm	1 ppm	0.5 ppm	0.5 ppm
AEGL 2	95 ppm	34 ppm	24 ppm	12 ppm	8.6 ppm
AEGL 3	170 ppm	62 ppm	44 ppm	22 ppm	15 ppm

AEGL 1 - Level of detection; effects are reversible and non-disabling

AEGL 2 - Effects are disabling and irreversible

AEGL 3 - Level at which death is expected.

Recommended levels for biological monitoring are as follows:

- The ACGIH current recommended Biological Exposure Index (BEI) for fluoride in urine is 3 mg/g creatinine prior to shift (preferably two days without exposure), and 10 mg/g creatinine post shift (ACGIH, 2000). Measurements in pre-shift samples indicate the amount of fluoride accumulated in the body over a long period of time and are an indicator of skeletal burden. Post-shift samples indicate the magnitude of recent exposure. The recommended BEIs are based on a no-effect level of 5 mg/g creatinine (5 mg/L) in 24 h specimens and an environmental background level of 1 mg/L. ACGIH estimate that these BEI are likely to be exceeded if workers are exposed to water soluble fluorides at the Threshold Limit Value (TLV) of 3 ppm ceiling limit, equivalent to 2.6 mg F/m³.
- In 1979 NIOSH recommended maximum concentrations for fluoride in urine of 4 mg/L for pre-shift samples and 7 mg/L for post-shift samples. (Lauwerys & Hoet, 1993).
- German Biological Tolerance (Biologischer Arbeitsstoff-Toleranz-Wert or BAT) values for hydrogen fluoride and inorganic fluorine compounds (fluorides) are 7.0 mg/g creatinine urinary fluoride at the end of a shift or end of exposure, and 4.0 mg/g creatinine at the beginning of the next shift (Deutsche Forschungsgemeinschaft, 1999).
- The EU Scientific Committee for occupational exposure limits to chemical agents (SCOEL) has recommended (European Commission, 1998) an end of shift urinary limit of 8 mg F/L in order to protect against the systemic effects of fluoride. They estimate that this urinary level will not be exceeded if 8 h TWA exposure to HF is 1.5 mg/m³ or 8 h TWA exposure to mixed HF and inorganic fluorides (gas and particulate) is 2.5 mg/m³.

10.3.3 Health surveillance

HF or fluorides are not listed in Schedule 3 of the NOHSC *Model Regulations for the Control of Workplace Hazardous Substances* (NOHSC, 1994a) as substances requiring health surveillance. However, in accordance with these model regulations, employers have a responsibility to provide health surveillance in those workplaces where the workplace assessment indicates that exposure to a hazardous substance may lead to an identifiable substance-related disease or adverse health effect. Health surveillance for fluorides was reported by one formulator, and is carried out in the aluminium and fertiliser industries where incidental exposure to HF can occur.

10.3.4 Standard for major hazard facilities

Anhydrous hydrogen fluoride and hydrofluoric acid solutions > 50% are specifically listed in Schedule 1 of the *National Standard for the Control of Major Hazard Facilities* (NOHSC, 1996a) with a threshold of 50 tonnes. This standard has been under consideration by all States and Territories, and has been taken up in the legislation of Western Australia and Victoria. Queensland are currently preparing legislation.

The standard covers areas such as hazard identification, safety reports, training and education, emergency planning and accident reporting for identified facilities. The NOHSC *Code of Practice for the Control of Major Hazard Facilities* (NOHSC,

1996) provides practical guidance on how to meet these requirements. Under the standard, if substances listed in the schedules are held at a facility in quantities that either exceed the threshold level on their own or when aggregated with other listed substances, the facility is automatically classified as a major hazard facility (MHF). If the threshold is not reached, but substances are present that exceed 10% of the threshold level, then the relevant public authority responsible for regulating major hazard facilities may consider classifying the facility, based on their assessment of hazard and risk.

10.3.5 Australian Code for the Transport of Dangerous Goods by Road and Rail

Anhydrous hydrogen fluoride (UN Number 1052) and hydrofluoric acid (UN Number 1790) are both listed in the *Australian Code for the Transport of Dangerous Goods by Road and Rail* (ADG Code) (FORS, 1998). Concentrated mixtures of hydrofluoric acid and sulfuric acid are separately listed (UN Number 1786). It is expected that a range of formulations and mixtures containing HF would be classified in "Not Otherwise Specified" (N.O.S) categories such as 2922 or 3264, based on toxicity and/or corrosivity, especially where HF and other acids are both present.

Both forms of HF are listed as Corrosive, in Class 8, and have a subsidiary listing in Class 6.1, as Toxic. Anhydrous HF and concentrations of hydrofluoric acid > 60% are in Packing Group I, and concentrations of hydrofluoric acid < 60% are in Packing Group II. In dilutions which do not meet the criteria for Corrosive, the Dangerous Goods Classification would not apply. Data on the corrosive cut-off concentrations for HF are not available. However, it has been suggested (WorkCover New South Wales, 2000) that the level may be as low as 1%.

Criteria for the classification of mixtures and unlisted chemicals are set out in Chapter 2, Volume 1 of the ADG code.

The ADG Code contains detailed provisions for the packaging and marking of containers in Class 8. In addition, the entries in Appendix 2 note that anhydrous HF is corrosive to metals and glass in the presence of water. Hydrofluoric acid is highly corrosive to glass, other siliceous materials and most metals. Only concentrations containing more than 60% acid may be packed in unlined metal drums.

For bulk containers such as the isotainers used to transport anhydrous HF, adherence to design and construction standards is mandated. The technical requirements for intermediate bulk containers (IBCs) used for Dangerous Goods are specified in a supplement to the ADG.

Hazchem codes are assigned to bulk Dangerous Goods in transport to reflect the initial emergency response recommended in situations such as spillage, leakage or fire. Where anhydrous HF is transported, the number "2" of the code 2XE denotes that water fog or fine water spray should be used for dispersing spillages. "X" indicates that full protective clothing should be worn. At a minimum, this equipment involves breathing apparatus, protective gloves, appropriate boots and a splash suit. A fully sealed gas suit may be required. The spillage should be contained so that the material is prevented from entering drains and watercourses. The letter "E" denotes that evacuation of people from the neighbourhood of an

incident should be considered. Bulk isotainers should themselves be placarded, and for smaller containers the road vehicle should be similarly marked.

The Hazchem 2XE code is also applicable to hydrofluoric acid in Packing Group I, but for Packing Group II the E is not used.

Mixtures of hydrofluoric acid and sulfuric acid containing between 70% and 80% by mass of acids and not less than 25% HF are coded under UN Number 1786. The applicable Hazchem code of 2WE differs from HF in warning that a violent reaction or explosion can occur.

Other requirements of the ADG Code for bulk loads include appropriate documentation, procedures for transfer of bulk product, safety equipment to be carried and procedures and responsibilities in case of emergency. An emergency procedure guide that is required to be carried may be in the form of those published by Standards Australia.

Much of the volume of HF and HF products carried within Australia would be in smaller quantities that do not attract the requirements of a "placard load". Controls for these quantities are based primarily on package and labelling requirements.

Replies to the industry survey concerning accidents in transport suggest that few respondents were aware of any incidents. The small number reported were attributed to isolated faults in packaging or damage to packaging in transport. Some additional incidents were identified through other information sources. The survey also specifically asked if HF or HF products had been supplied in faulty packaging. A large majority of respondents to this section indicated that this had not occurred. In the small number of cases where this was reported, it was considered to be a "one-off" problem and quickly rectified.

10.3.6 Standard for the Uniform Scheduling of Drugs and Poisons

For application of this standard to occupational use, see information in Section 10.5 and Table 31.

10.3.7 Other regulatory controls

The Stored Chemicals Information Database (SCID), maintained by WorkCover NSW, now requires licensing in that State of premises holding corrosive and toxic material above certain threshold quantities. The information in the database is used to inform emergency services staff such as firefighters.

Under the Chemical Safety in Schools (CSIS) package produced by the NSW Department of Education and Training, hydrofluoric acid is banned from use in NSW government schools, may not be stored on site, nor produced by any chemical reaction. Implementation of the package is mandatory for NSW government schools, and it has been purchased for many other NSW schools.

Regulations in place overseas for the safe use of HF include:

The EU Directive 96/82/EC (Seveso II) is aimed at control of major-accident hazards involving dangerous substances;

The Control of Major Accident Hazards (COMAH) Regulations, introduced by UK in 1999 and based on the EU directive. Hydrogen fluoride is not listed in COMAH as a separate substance in the Schedule, but is picked up in the groupings of substances;

The US EPA Risk Management Program (RMP) rule covers facilities using anhydrous HF and hydrofluoric acid of concentrations of 50% and above, if the quantity exceeds the threshold of 1000 lb. Part of the Clean Air Act, these regulations are aimed at preventing accidental releases of chemicals that could cause serious harm to human health or the environment and to reduce the severity of releases that do occur.

The US Occupational Safety and Health Administration (OSHA) "Final Rule on Process Safety Management of Highly Hazardous Chemicals; Explosives and Blasting Agents" covers use of anhydrous HF of quantities > 1000 lb; and,

EU Council Directive 94/33/EC of 22 June 1994 places restrictions on the work which can be carried out by young people (under 18 years of age), including work involving harmful exposure to some chemical agents. Concentrations of hydrofluoric acid of 1% and above would be covered by these provisions.

10.4 **Product stewardship**

The PACIA Code of Practice on HF (PACIA, 1997) introduces several voluntary initiatives related to industry product stewardship of aqueous solutions of HF, as well as guidance on labelling, emergency procedures etc. The development of such a code was requested by the Western Australian OHS authority, after an accidental death in that State in 1994. The Code places more responsibility on suppliers to take steps beyond the legal requirements, in order to promote safe and appropriate use of HF. Topics covered include minimisation of use, advice to customers, packaging, storage, transport, first aid and medical treatment, education and training, and reporting of incidents. A total of 40 applicants and survey respondents reported that they hold a copy; some of these were alerted to its existence through the HF survey.

Signatories to the PACIA Code of Practice agree to support the safe use of HF by their own companies and their customers through action in the following areas:

- Minimisation of use by ensuring that customers do not overuse hydrofluoric acid, or use it inappropriately and, where possible by suggesting safer alternative chemicals or methods to customers.
- Advice to customers this includes a number of measures in addition to those required by law. For example, the supplier should verify that safe handling can be carried out by the customer, that the end-use is suitable if the chemical is to be formulated or onsold and that appropriate first aid and medical procedures are in place. Customers should be reminded by letter every six months of the dangers of the chemical and should acknowledge receipt of the letter. Packs > 500 mL should only be supplied to laboratories if safe dispensing arrangements are in place. Suppliers should formally withhold supply if not satisfied that appropriate arrangements are in place and advise the customer, the PACIA HF Taskforce and the relevant local authority.
- Packaging As well as complying with legal requirements, packaging should be distinctive, through shape or colour, so that it can be identified at a distance

of 3 metres or more. Outer packs or drums should have an additional warning label emphasising that HF is present.

- Storage and transport The storage areas holding HF and products containing it should be clearly identified, so that the material cannot be confused with other chemicals e.g. hydrochloric acid. Suppliers should provide advice and instruction to those transporting hydrofluoric acid in drums. A specific emergency procedure guide should be used rather than the Initial Emergency Response Guide (which covers HF as part of a generic entry). A first aid kit containing calcium gluconate should be carried if a large quantity of hydrofluoric acid is being transported.
- First aid and medical treatment First aid kits containing calcium gluconate should be kept in all areas where exposure could occur, including workplaces, storage and transport. Calcium gluconate gel should be replaced when it reaches its expiry date. If hydrofluoric acid is used or handled regularly, the appropriate local hospital should be informed in writing, to ensure that effective treatment will occur in the case of exposure. This liaison should be renewed annually, in order to keep new hospital staff up to date. (The Code of Practice also contains detailed first aid and treatment information).
- Formulated products Suppliers should advise formulators of the hazards of HF and where appropriate recommend alternatives. Formulators of products of > 10% strength should be encouraged to themselves become signatories to the Code. Formulations of > 10% strength should not be sold to the general public. Formulations should not be designed to be atomised, sprayed or heated except under strictly controlled conditions, and the design of the pack should facilitate safe dispensing. Threaded valves are recommended for packs over 5 L. Labels should state the exact percentage of hydrofluoric acid.
- Education and training Signatories should provide their staff with comprehensive training on all aspects of hydrofluoric acid, including precautions, legal requirements and the obligations of the Code. Records of training should be kept for 5 years.
- Reporting of incidents Signatories and other parties are encouraged to report in writing to PACIA all incidents involving hydrofluoric acid and a sample incident report form is provided. This information is to be circulated to signatories.

The organisation representing scientific suppliers, Science Industry Australia, is a signatory to the Code and encourages its members to abide by the principles as detailed in the Code.

PACIA were asked to supply information for this assessment on the take-up of the Code of Practice and experience with various aspects. They were not able to provide any information, except that incident reports for HF had not been received.

Two respondents to the HF survey reported that they voluntarily restricted the concentration of HF products they were prepared to sell and others would sell only dilute concentrations to purchasers they did not know. It was found to be difficult to do this without the support of regulatory controls, especially when it was known that competitors would supply the higher percentage.

Other examples of product stewardship reported by survey respondents include:

• Inspection of customer premises;

- verbal and written advice on hazard;
- supply of first aid products or advice on obtaining them;
- supply of gloves to customers;
- laminated first aid card provided;
- product delivered by hand; and
- consultations with technical staff available.

10.5 Public health regulatory controls

Hydrofluoric acid has been considered by the National Drugs and Poisons Scheduling Committee (NDPSC) for inclusion into the Standard for the Uniform Scheduling of Drugs and Poisons (SUSDP). Hydrofluoric acid (excluding its salts and derivatives) is included in Schedule 7 of the SUSDP except when included in Schedule 5 or 6 [i.e. Schedule 6 : Hydrofluoric acid (excluding its salts and derivatives) in preparations containing 10 per cent or less of hydrogen fluoride except when included in Schedule 5; Schedule 5 : Hydrofluoric acid (excluding its salts and derivatives) in preparations containing 0.5 per cent or less of hydrogen fluoride]. Concentrations of HF covered under Schedule 7 have an entry in Appendix J of the SUSDP regarding Conditions for Availability and Use of Schedule 7 Poisons. In the case of HF, the condition is "Not to be available except to authorised or licensed persons".

While most of the Standard for the Uniform Scheduling of Drugs and Poisons (SUSDP) is aimed at protection of the public, the Schedule 7 requirements which apply to concentration of HF of 10% and above are also relevant to occupational use. Licensing applies in this Schedule, and the type varies between States, as shown in Table 31.

State or Territory	Licence required to sell Sc 7 HF	Licence required to purchase Sc 7 HF	Other information
ACT	Yes	No	Records of each purchase and the purchaser must be kept.
NSW	Yes, although not compulsory if buyer is a wholesaler.	Yes, with an exemption for a scientifically trained person purchasing for laboratory use.	Licence is not issued, rather an authority issued to allow supply and use for a specified period of time, usually 1 year. Information is recorded on quantity, strength and nature of use.
NT	Yes	Yes	Users must be able to demonstrate a genuine industrial or research need in order to obtain a written authorisation to possess and use the substance, which must be stored in a manner to prevent unauthorised access. MSDS recommendations must be followed and retailers encouraged purchase of calcium gluconate gel. Suppliers must sight the authorisation. A register is maintained of purchasers' details by the Poisons Branch.
QLD	Yes	No	Records of sales must be kept and material for sale kept under lock and key.
SA	Yes	No	-
TAS	Yes	Yes	Licence required to sell or supply. Authorisation required in order to obtain, possess and use.
VIC	Licence required to sell or supply by wholesale, but this is not chemical- specific.	No	Applicants must be fit and proper persons and the premises must be suitable, sanitary and adequate for the purposes applied for.
WA	Yes	Yes	Comprehensive controls. Licences not issued to sell by retail.

In 1998 the NDPSC undertook a review of the SUSDP labelling requirements for HF and related substances such as hydrosilicofluoric acid, sodium bifluoride and ammonium bifluoride. As a result of this review, amendments were made to ensure consistency between these chemicals in their requirements especially for warning statements, safety directions and first aid instructions.

Table 32 lists current requirements for these statements.

Chemical			Warning Statements	Safety Directions	First Aid Instructions	
Hydrofluoric acid in Schedule 5			2.	1, 4.	а.	
Hydrosilicofluoric acid acid) in Schedule 5	Hydrosilicofluoric acid (Fluorosilicic acid) in Schedule 5					
Ammonium bifluoride i	in Schedu	ule 5				
Sodium bifluoride in S	chedule 5	5				
Hydrofluoric acid in So	chedule 6	or 7	1, 17.	1, 4, 5. 8, 29.	f, s, c, a, t.	
Hydrosilicofluoric acid acid) in Schedule 6 or	(Fluorosil 7	licic				
Ammonium bifluoride i	in Schedu	ule 6				
Sodium bifluoride in S	chedule 6	6				
Fluorides (including sil	licofluorid	es)	-	1, 4.	a (Schedule 5)	
when in Schedule 5 or separately specified	6 except	when			a, b, s (Schedule 6)	
Warning statement Safety directions	1 2 17 1 4	Highly Corro Conta blindr Avoid Avoid	y corrosive. osive. act with eyes even ness. I contact with eye I contact with skir	n for short periods s.	can cause	
	5	Wear	r protective gloves	s when mixing or u	using.	
a Avo 29 If us gel.			If used frequently, obtain a supply of calcium gluconate gel.			
First aid instructions a If poisoning occurs, co Information Centre. Pl Zealand 03 47470000			ntact a doctor or I none <i>(e.g. Australi</i>	Poisons a 13 1126; New		
	If swallowed, and if more than 15 minutes from a hospital, induce vomiting, preferably using lpecac Syrup APF.					
	С	If swallowed, do NOT induce vomiting. Give a glass of water.				
	f	If skin contact occurs, remove contaminated clothing and wash skin thoroughly.			ated clothing and	
	S	lf in e minut	eyes, hold eyes op tes and see a doo	pen flood with wat	er for at least 15	
	t	lf ava	ilable, apply calci	ium gluconate gel	to affected skin.	

Table 32 - Warning Statements, Safety Directions and First Aid Instructions required under the SUSDP

Currently child-proof closures are not required for HF under the SUSDP. Under the EU Directive 90/35/EEC, containers of any capacity containing preparations offered or sold to the general public and classified as very toxic, toxic or corrosive must be fitted with child-resistant fastenings and carry a tactile warning of danger. HF at concentrations of 1% or above would currently be covered by this Directive.

In 1998 the US Consumer Product Safety Commission (CPSC) issued a requirement for child-resistant packaging for household products containing more than the equivalent of 50 mg of elemental fluoride and more than the equivalent of 0.5% elemental fluoride. HF products would be covered by this rule.

EU Council Directive 76/768/EEC of 27 July 1976 prohibits the use of hydrofluoric acid in cosmetics.

10.6 Environmental controls

10.6.1 Environmental regulatory controls

Most States and Territories have regulations that would require sites using, storing or manufacturing chemicals to possess a discharge licence issued by their State or Territory EPA. These regulations would encompass HF. Each licence would be site-specific and include operational constraints, monitoring requirements, measures to ensure maximum reductions of discharges to the environment and concentration limits on such discharges.

In 1990 the Australian and New Zealand Environment and Conservation Council (ANZECC) set national goals for fluoride in ambient air and forage (ANZECC, 1990).

10.6.2 Spillage and disposal

Because of the hazardous nature of HF, emergency and spill procedures must be effective in avoiding both human and environmental exposure. Due to the wide end-uses and products containing HF, not all MSDS have been viewed for spillage and disposal statements. Generally, those seen are satisfactory. The following procedures were reflected in MSDS for control of spills.

Anhydrous hydrofluoric acid

Do not allow chemical to enter drains and waterways or surrounding soil. Extracted air contaminated with large amounts of fumes should be scrubbed prior to release to the atmosphere.

Where possible, upturn leaky containers to allow gas rather than liquid to be released. Contain leaks with sand, earth or other absorbent material. Dilute with water and neutralise with lime. Keep waste out of drains and waterways.

Hydrofluoric acid solution

Do not allow chemical to enter drains and waterways. Contain spills with sand, earth or other absorbent material. Dilute with water, and where possible, neutralise with lime.

10.6.2.1 Use of silica-containing materials in spills

Although sand, soil or vermiculite are often recommended as materials to contain and covers HF spills, it should be noted that these materials may react to form silicon tetrafluoride gas. A manufacturer of HF recommends polyacrylamide, which can sprayed onto spills and which is effective in reducing fumes. It reacts with the spill to form a solid gel for disposal, but has the disadvantage of being very slippery. If polyacrylamide is not available, the same manufacturer recommends soaking the spill with sand and neutralising with a dilute alkali, as an emergency measure.

10.7 Emergency procedures

Emergency procedures are an extremely important part of HF management. This is especially so because early treatment of HF burns and use of calcium gluconate antidote for dermal exposure reduce the effect of such burns (WorkSafe Western Australia, 1998a). Good management of accidental releases can also prevent exposure of workers and the environment.

Three important requirements for emergency plans are that the identity of the chemical be acknowledged, that all relevant people are aware of what should be done in an emergency, and that the means of doing it should be available. The people and organisations who may be involved in an emergency include various departments of the organisation where the exposure occurs, ambulance, medical practitioner or clinic, hospitals and other emergency services.

At workplaces which use, store or transport HF, preparations for the handling of incidents should be part of the risk assessment and should facilitate the prompt application of further medical treatment as well as first aid on site.

Aspects of chemical control relevant to emergency response are covered under some of the requirements mentioned in earlier sections e.g. the NOHSC *National Code of Practice for the Control of Workplace Hazardous Substances* requires established emergency procedures, inclusion of this topic in induction programs, procedures for safe disposal of a spill and suitable PPE to allow an uncontrolled release to be safely identified and repairs made. Dangerous Goods requirements also cover many relevant aspects, with one section of the ADG Code covering emergency procedures. State or Territory licensing requirements for storage of dangerous goods provide information that can be used in emergencies.

A major importer of anhydrous HF reported detailed response plans for any emergency that may occur in transport or at the storage site. The main features of the transport plan for its range of chemicals are 24-hour telephone response, incident attendance, and technical response to any emergency. Only designated contractors handle HF. The procedures for the storage site are general ones that can be used for a range of emergencies. In case of an accidental release of anhydrous HF, a modelling system is available to estimate the effect.

Details of the precautions used in transport from the dockyard to the petroleum refinery were also provided by an importer and user of anhydrous HF. The driver is trained about HF and other refinery hazards by the refinery and carries the MSDS and appropriate first aid in the truck. Police and fire services are informed when a delivery is to be made and meetings have been held between these services, the transport company and refinery staff.

MSDS would be the main source of information on emergency procedures in Australia for those handling HF. Emergency responders would have access to further information to aid the handling of spills etc. Schemes such as the NSW SCID database on storage of hazardous chemicals would assist in a coordinated response.

In 1999 the US EPA issued an alert (USEPA, 1999) stating that MSDS alone may not be an adequate source of information for responding effectively and safely to accidental releases of chemicals. The alert identified additional sources of information and procedures that would assist first responders to an emergency. Suggested resources include chemical use inventories, pre-planning with industry, training, and specialised assistance from chemists and health professionals.

10.7.1 First aid protocols and antidotes

Although calcium gluconate products are generally considered the preferred treatment, other materials such as magnesium salts and benzalkonium chloride products are also recommended by some suppliers.

Protocols for first aid treatment and advice to doctors on further treatment are described in the Worksafe Australia Guide (NOHSC, 1989) and the PACIA Code of Practice (PACIA, 1997). The latter document also lists Australian suppliers of calcium gluconate products.

There is no consensus on the length of time a skin burn should be rinsed with water, before calcium gluconate gel is applied. MSDS recommendations range from "thoroughly, as quickly as possible" to "at least 20 minutes". Longer rinsing may remove the material from the skin more thoroughly, if contaminated clothing is quickly removed. However, this protocol will delay the application of calcium gluconate and transfer of the patient to hospital and may cause the patient to be chilled if the burn is extensive. It is expected that the pressure of the water stream would affect the efficiency of rinsing and that optimal protocols may vary for different concentrations of HF. Segal (1998, 2000) has noted that recent practice in the USA is to recommend 5 minute rinsing time before other treatment.

Some MSDS recommend eye-drops as part of first aid treatment for eye splashes. It should be noted that 10% calcium gluconate (gel or solution) should not be used at all for eye injury (WorkSafe Western Australia, 1998b) because of the risk of damage to the eyes. Current recommendations for immediate treatment (NOHSC, 1989); (PACIA, 1997) emphasise flushing the eyes thoroughly and obtaining medical attention. Specialist eye treatment is likely to be needed. Some MSDS warn that gel for skin treatment should not be used in eyes. More dilute solutions of calcium gluconate (1%) may be part of later medical treatment. As calcium gluconate is supplied in ampoules at 10% and must be diluted accurately it is not suitable for workplace first aid treatment of the eyes unless in-house medical or nursing staff are available.

Hexafluorine is a new proprietary antidote to HF. It is claimed to be a very effective first aid treatment for skin and eye splashes of hydrofluoric acid. High cost (> \$1500 for a fire extinguisher type dispenser) is a drawback to its use (Segal, 1998). *In vitro* and animal testing (Hall et al., 1999) and successful use as the primary first aid measure in 11 incidents at a metal treatment plant (Mathieu et al., 2000) have been reported. A spokesman for the manufacturers has advised that

Hexafluorine is commercially available in some countries, but has not been introduced or approved for use in Australia (Prevor, 1999).

10.7.2 First aid on site

On-site recognition of and response to a HF injury requires advance organisation and training. Equipment needed in case of emergency includes calcium gluconate gel, which has a limited shelf life, eye wash basins and safety showers. A major supplier of calcium gluconate gel in Australia advised that the shelf life of their product is one year, with the expiry date stamped on the crimped end of the tube. This product is available through pharmacies as well as industrial channels. In order to increase the availability of calcium gluconate to their customers, some suppliers of HF also supply the gel.

Rehearsed procedures for first aid, arranging further medical treatment, and minimisation of further harm to workers or the public are also necessary for the optimal handling of accidents.

The HF survey questionnaire asked specifically about first aid arrangements and possession of calcium gluconate products. Other comments relevant to emergency management were received. The 139 replies to this section of the survey are summarised in Table 33, representing replies from users, formulators and repackers of aqueous HF. Replies from resellers were not included, as very few of this group reported any first aid precautions.

First aid measure reported	Number and % of respondents		Details
Calcium gluconate products	93	(67%)	Gel or cream was most commonly reported. Tablets and ampoules also mentioned.
Safety shower	28	(20%)	
Eye wash basin or bottle	24	(17%)	
Running water	14	(10%)	
Medical aid / hospital access	10	(7%)	
Other	26	(19%)	Measures reported included first aid stations and trained staff, nurse on site, MSDS or notices with first aid instructions and milk.
No first aid	2	(1%)	

Table 33 - First Aid measures at workplaces

Access to calcium gluconate products can be taken as one measure of awareness of the hazards of HF. Of the 139 who completed this section of the survey 93 (67%) reported that they held supplies of calcium gluconate, mainly the gel, and 46 (33%) did not.

Respondents were more likely to have calcium gluconate if they were importers or direct customers of importers, ie were closer to the top of the distribution chain (Figure 10.1).

An analysis was made of the 38 replies from further down the distribution chain where calcium gluconate <u>was</u> held, in order to identify any common factors. It was found that many of this group bought from the same suppliers, suggesting that some supplier chains have been more successful in passing information to their customers. In particular 10 (26%) of these 38 respondents purchased from the same laboratory distributor.

Where respondents close to the top of the distribution chain <u>did not</u> possess calcium gluconate, it was noted that their supplier's MSDS often did not recommend it clearly as the antidote, or did not mention it at all. One respondent in this group had an empty tube of calcium gluconate gel, which had not been replaced for a long time.



10.7.3 First aid off site

For workplaces that use HF, it is recommended in the PACIA Code of Practice that contact be made with a local hospital, in order to facilitate any future emergency treatment. One company sends any injured worker to the hospital accompanied by an information pack, which confirms the identity of the chemical. It is reported that other companies use the MSDS for the same purpose.

Ambulance services are an important link between first aid on site and hospital treatment, and can facilitate swift treatment of injuries. In a fatal injury from HF in 1994, ambulance response was delayed, possibly because the chemical was inaccurately noted by phone as hydrochloric acid. Arrangements for ambulance services vary between States, but in Victoria there is one central training authority, allowing good coordination.

It is reported that both hospitals and medical practitioners consult the National and State Poisons Information Centres when necessary, for advice on the treatment of HF burns, and information on hospitals with specialist knowledge of HF treatment.

Some questionnaire respondents have arrangements where workers are supplied with calcium gluconate gel to take home, in case a delayed burn becomes apparent. In one case gel taken from the premises was formally issued and signed for, so that the shelf life of the gel could be monitored, and replaced when it became too old.

Two companies reported that they held calcium gluconate injections that could be administered by medical practitioners.

Hospital management

All HF exposures that do not become completely painless after application of appropriate first aid measures or where the pain returns, should be referred for medical opinion. If a patient requires further medical evaluation it is usual to refer the patient to a Hospital Emergency Department. If there is any doubt as to the nature of the exposure, prompt referral for specialist examination is required.

Hospitals may vary in their expertise and experience in handling HF injuries. Those catering to industrial areas may develop more familiarity with the treatment of HF than others. Serious HF burns in Victoria are now referred to Austin and Repatriation Medical Centre, and it has been suggested that regional hospitals with expertise and those with Medical Toxicology Units be used more widely, in order to provide a uniform treatment protocol for such cases. Hospitals may also be able to access databases such as POISINDEX.

If the patient has received adequate first aid, there is nothing additional that a general practitioner can provide outside the hospital setting. In hospital the patient can be considered for specific treatment regimes such as the administration of calcium gluconate by the intra-arterial route, a Bier's Block, or the use of alternative agents such as magnesium salts. These therapies are administered under the supervision of a Medical Toxicologist. If there is any doubt as to the nature of the exposure, prompt referral for a specialist examination is required.

It was reported (Beulke, 1998) that on some occasions hospital pharmacies in Australia did not hold calcium gluconate gel when it was required to treat burns patients, a matter of concern because the care of the patients may have been compromised. If prepared gel is not available, a substitute can be prepared from calcium gluconate solution and K-YTM Jelly Personal Lubricant

11. Discussion and Conclusions

11.1 Import, manufacture and use

Substantial quantities of both anhydrous HF and aqueous solutions are imported into Australia, but manufacture (excluding *in situ* manufacture) does not take place in Australia. HF can also be incidentally produced in a range of processes, in quantities larger than the amount consumed deliberately.

Approximately 350 tonnes/year of anhydrous (100%) HF is imported, primarily as an alkylation catalyst for petroleum refining. As a low-boiling liquid, it is transported in isotainers or cylinders, and exists as a gas above 19.5 °C. Minor uses are for surface treatment of plastics, in excimer laser gas mixtures and for research.

Aqueous dilutions of HF, commonly known as hydrofluoric acid, are imported in strengths of 35% to 70% in drums or bottles. Yearly import quantity is approximately 350 tonnes. Formulated products for niche markets are also imported.

Some of the aqueous HF is used at the higher concentrations at which it is imported e.g. for laboratory analysis or chemical synthesis. Most is diluted by end-users or formulated into products that are resold for particular uses e.g. metal treatment or cleaning, fabric rust removal, floor and wall treatment. Repackaging and relabelling also occurs. Tables 4 and 5 summarise information on types of use from the NICNAS survey.

HF can also be formed in aqueous solution from acids and fluoride salts, or from bifluoride salts. Such solutions are known to be used in Australia for metal treatment and cleaning, oil well stimulation, glass etching and fabric rust removal.

Incidental production of HF occurs through the processes of aluminium smelting, phosphate fertiliser production, the production of ceramic materials such as bricks and tiles, in steel production, in burning coal for fuel, and heating or burning of other fluoride-containing chemicals. HF may also occur as an impurity in other chemicals or be produced through the reaction of other chemicals.

11.2 Environment

It is not the role of a preliminary assessment to undertake a risk characterisation of the chemical. However, a crude calculation can be made. The most sensitive validated result was 120 h EC $_{50} = 20$ mg/L for the marine invertebrate *Perna perna*, (brown mussel). This is several orders of magnitude higher than the predicted environmental concentration of 0.92 µg/L in receiving waters. The lowest result from an unvalidated test was LC $_{50} = 2.3$ ppm for rainbow trout, which is still several orders of magnitude higher than the PEC. Based on these, a low aquatic environmental hazard can be predicted.

Potentially of more concern is the quantity of HF being released to the atmosphere through end use, and particularly through incidental production. While figures quoted in this report with respect to incidental production are considered to be overestimations, in the absence of more reliable data they indicate substantially higher release through incidental production than can be expected through end use. While it is recognised that the chemical does not persist in the atmosphere, plants have been shown to take up HF while it is present in the atmosphere. Plants growing near HF producing facilities may be expected to have higher F levels than those found in less polluted areas, and this may increase the risk of fluorosis to animals consuming foliage from these areas. The PNEC determined for a point source emission was 0.7 μ g/m³. With prolonged exposure, plants have been shown to suffer adverse effects at concentrations less than this. Air concentrations could reasonably be expected to be higher than this around sites where HF is produced incidentally such as coal burning power stations and aluminium smelters, indicating that susceptible plants in these areas will be adversely affected.

This preliminary report for hydrofluoric acid has not highlighted any significant concern for the environment through normal end use of the chemical, however there is the potential for impacts on the environment as the result of HF produced incidentally. Fluorides accumulate primarily in the skeletal tissues of terrestrial animals that consume fluoride containing foliage and the possibility of biomagnification is unclear. Additionally, some plant species have been shown to be very susceptible to fluoride effects. Further data on emissions from industries known to incidentally produce HF is essential to be able to more adequately assess potential impacts and the NPI may be expected to generate such information. With additional information further assessment of HF may need to be considered to better determine the potential for adverse environmental impacts.

11.3 Health hazards

Inhaled HF is completely absorbed in the upper respiratory tract and distributed rapidly to the blood. When in contact with the skin it is also absorbed but the extent of absorption is not known, and would vary with time of exposure, concentration, and corrosive effects on the skin. Once in the body, HF ionises to fluoride and its effects are the same as other sources of fluoride.

HF is both corrosive and toxic, with higher concentrations causing greater harm. Acute exposure results in burns and respiratory damage, and in systemic effects that can be fatal. Systemic effects of HF include disturbance of calcium and other electrolyte balance. Hypocalcemia can produce ventricular fibrillation and death. Exposure through either inhalation or dermal contact has led to deaths in humans.

It has been estimated that contact of even 1% of body surface area (BSA) with HF of 50% or above may cause systemic effects and 2.5% BSA may be fatal.

Skin contact with HF can cause painful second and third degree burns that heal very slowly. Lower concentrations of HF may not have an immediate irritant effect on the skin but can cause delayed burns, and injury can be caused by even dilute solutions (0.1%) if not treated promptly.

Inhalation of low concentrations of HF (1 to 2 mg/m³) caused upper airway and eye/skin irritation in volunteers. The no observed adverse effect level (NOAEL) in animals as determined in the OECD assessment is 0.72 mg/m^3 .

Chronic exposure to HF may cause skeletal fluorosis. In humans this is a known effect of prolonged exposure to fluoride through inhalational or oral routes. HF is not believed to be a sensitiser, genotoxic or carcinogenic. Some studies have found reproductive effects.

HF is not flammable, explosive or oxidising. However its high chemical reactivity means that particular care must be taken in choosing packaging materials and controlling corrosion in processing equipment. Contact with metals can lead to the formation of hydrogen gas which forms explosive mixtures in air, and can build up pressure in closed containers. HF solutions of < 65% react with metals, as can higher concentrations on prolonged storage. Anhydrous HF is a low boiling liquid and at ambient temperatures < 19.5 $^{\circ}$ C at 1013 hPa has substantial vapour pressure. If released, it can form a mobile cloud under some conditions. Concentrated aqueous solutions can fume in air and heat is produced on dilution.

11.4 Occupational health and safety

Occupational exposure to HF may occur during transport and storage, *in situ* manufacture, processing or use of the chemical. This may include re-packing and simple dilution of hydrofluoric acid solutions, formulation of products and use of solutions and products containing the chemical. Occupational exposure may also occur during the disposal of contaminated waste or as a result of contact with HF formed incidentally in other processes. For both aqueous and anhydrous HF in the occupational environment, the relevant routes of exposure are inhalation and dermal contact.

In order to assess accidental acute exposure to HF, information on incidents and injuries in Australia was gathered from varied sources (Appendix 3). The data gathered for the assessment would not be complete and may not be representative of the real pattern of incidents and injuries, but do indicate situations in which problems can occur. Approximately 10% of the respondents to the HF survey reported one or more incidents.

Chronic exposure can also occur under certain conditions when HF is used deliberately, and is the main area of concern when it is produced incidentally. Because of the corrosive nature of HF, chronic exposure through dermal and inhalation routes is likely to occur only from exposure to low concentrations. Inhalational exposure may be increased in dispersive uses such as masonry cleaning or non-dip metal treatment. As monitoring is not commonly carried out in industries using HF, estimates of chronic exposure were conducted via modelling.

Transport

Both anhydrous and aqueous HF are controlled under the ADG code for transport by road or rail in Australia, and for storage in New South Wales under the requirements of the SCID database. Few incidents in transport or storage were reported during the assessment, suggesting that these controls are generally working well. However the consequences of large-scale spillage or loss of containment are high for anhydrous HF and aqueous solutions of high concentrations. It is also noted that the legal controls on small quantities in storage and transport are not as rigorous as for bulk amounts, relying on packaging standards and package labelling.

Anhydrous HF

Approximately 350 tonnes/year of anhydrous HF is used at 5 petroleum refineries in Australia as a catalyst in the alkylation process. Smaller quantities are used as part of the process for surface treatment of plastics and have been reported as a component of gas mixtures for excimer lasers. Very small and variable quantities are used in research.

The major use of anhydrous HF is petroleum alkylation. This is a closed process and is carried out at five sites in Australia. HF would exist as a gas at the alkylation temperatures of 20 to 40° C (Hammershaimb et al., 1992) and can also contaminate other parts of the product stream. Leaks, equipment failures and maintenance processes in the complex refinery environment are possible sources of exposure. Both inhalation and skin contact are possible routes of exposure for anhydrous HF.

The challenges posed by the control of anhydrous HF in large-scale processing have led petroleum refiners to put comprehensive controls in place. Considerable resources are directed to this, but the corrosive nature of HF to equipment, the low boiling point of anhydrous HF, the systems needed to avoid secondary contamination, and the complex plant all mean that the potential for exposure remains. Because of the large quantity of anhydrous HF used, the transport, storage and use of HF in this industry sector has the greatest potential for large-scale releases. The controls used in this sector are however amongst the strongest.

Of the other uses known for anhydrous HF, fluorination of plastic is carried out in one plant, with significant controls. Little information was obtained on the small-scale uses in research or in excimer gas mixtures.

Modelling and limited monitoring of exposures during alkylation suggest that chronic exposure is not of concern because it is a closed process that is rarely breached. Personal monitoring (Brown, 1985) in 1985 found air concentrations of 0.2 ppm and below. EASE modelling resulted in values of 0 to 0.1 ppm for a closed system.

Aqueous HF

Approximately 350 tonnes/year HF is imported as aqueous solutions, primarily of 35% to 70% strength. Smaller quantities of specialty products containing HF are imported.

The majority of this material is formulated into lower strength solutions and products to which other chemicals, often other acids, are added. Because of the processes of dilution, formulating, packing and repacking, the total volume of HF product in use is substantially more than the volume imported and there is a large range of products in commerce. Most of the products are directed at industrial users, but some are available to the public.

The major potential for exposure occurs during formulation, the various end-uses, and the associated transport and storage. Use of aqueous HF varies in type and location of use, concentration and quantities handled. Occupations, industry sectors, and size of businesses involved also vary. Processes are either open or partially closed. The largest use of aqueous HF in Australia is metal treatment and cleaning.

Skin contact and inhalation are possible routes of exposure for aqueous HF. Inhalation is more likely at higher concentrations because they have a higher vapour pressure, but can occur with lower concentrations, especially if ventilation is poor or aerosols are formed. The potential for dermal exposure is relevant at all concentrations.

During formulation, concentrations of 35% to 70% are commonly used as starting materials. EASE estimates of exposure are 20 to 100 ppm for 70% HF, depending on the level of controls in the non-dispersive system. For 35% HF the corresponding estimates are 0.5 to 5 ppm (Table 10 and Appendix 2).

EASE estimates were also carried out for metal treatment and cleaning, a major end-use of aqueous HF. Typical metal treatment uses dip baths or more open processes. Cleaning is likely to be an open process. EASE estimations were carried out for different scenarios of metal treatment and cleaning with a 8 to 10% product (Table 10 and Appendix 2). For a non-dispersive use with local exhaust ventilation, estimated air concentrations of 0.5 to 1 ppm are similar to the values measured overseas near dip tanks of 0.17 to 3.4 ppm. EASE estimations were significantly higher if engineering controls were reduced, if the use was a wide dispersive one, or if aerosols were formed. For a wide dispersive use similar to an open cleaning process, with direct handling and dilution ventilation, air concentrations of 100 to 140 ppm were predicted.

The EASE estimates in Table 10 can also be extrapolated to other end-uses of HF if concentration, methods of handling and engineering controls are similar.

Dermal exposure calculations are included in Table 10, but may not be relevant to most normal use because of the corrosive properties of HF. Dermal exposure is likely to occur only accidentally for most concentrations of HF. However exposure to dilute solutions may occur in some uses e.g. mag wheel cleaning. It has also been reported (Queensland. Department of Employment, Training and Industrial Relations, 1999) that HF solutions used for cleaning down the decks of fishing vessels are being used in some cases with bare feet, which would be in contact with the diluted solution.

As well as accidental exposure to HF solutions or products, secondary exposure may occur from objects contaminated with HF unless all potentially contaminated surfaces are cleansed. Secondary exposure is particularly likely from HF treatment of building surfaces and fabrics, but may be relevant to other applications e.g. boat and vehicle cleaning.

Exposure may occur if it is not known that HF is being handled. A major concern identified during the assessment is that organisations and people using HF may not be aware of its identity, thus nullifying all control measures aimed at the chemical. This may occur when HF is formed *in situ* from fluoride or bifluoride salts, or in other situations where hazard communication and workplace systems are not in place.

Accidental spillage is a major cause of acute injury from HF. Transfer of HF from one container to another is considered a critical step where accidents can occur. For larger scale operations, there is ambivalence about the advantages of mechanical pumps. One formulator added concentrated solutions of HF to tanks manually from smaller containers to avoid the chance of a pump blocking as this could cause hose breakage and spillage. However, in manual handling the worker is closer to the chemical during the transfer operation, and at risk if any accidental spills occur. If the top of the tank is significantly above ground level, the worker would need to lift the drum above shoulder height in manual filling.

The ergonomic aspects of transfer are also significant in smaller scale operations and were considered to be an important contributor to the accident which led to the death of a laboratory worker in 1994. Factors in this accident included the working space available, height of the bench, and the fact that lightweight containers were not secured to prevent them tipping over.

Aqueous HF or hydrofluoric acid is used in many different concentrations, types of use and methods of application. Situations of higher concern for acute exposure are considered to be:

- Uses requiring concentrations of 40% or above, as inhalation exposure is increased at high concentrations, and skin contact over relatively small areas will cause more harm. These uses include all uses of anhydrous HF, formulation, laboratory work, cleaning gold nuggets, etching of flash glass, and other applications where concentrated HF is diluted for use or used to "top-up" dip tanks;
- Dispersive uses where it is difficult to avoid human contact, and personal protective equipment (PPE) is relied upon to protect the worker. Many cleaning processes would fall into this category. Aerosol formation and proximity to thin films may also increase inhalational exposure in these scenarios;
- Applications that must be carried out "on-site" or in isolated locations, where it may be difficult to provide control measures e.g. building cleaning, floor etching, bathtub stripping, graffiti removal, oil well stimulation, cleaning gold nuggets, vehicle and marine cleaning;
- Use indoors without exhaust ventilation, unless low concentrations are used; and
- Uses where hazardous transfer of solutions must be carried out.

Chronic exposure is possible for any use of aqueous HF carried out over a long period of time. Modelling data suggest that inhalational exposure, especially to aerosols, and dermal contact with very dilute solutions could both be contributors to levels of intake of concern.

HF produced in situ

HF can also be produced in aqueous solution if formulations contain both fluoride salts and other acids, or bifluoride salts. The amount formed is dependent on the quantity of the salt and the pH in the mixture (Appendix 1). HF produced *in situ* may be used for most applications suitable for aqueous HF. When formed in this way, its identity may not be recognised, and appropriate labelling and safety precautions may not be implemented.

Incidentally produced HF

Two major sources of incidentally produced HF are smelting of aluminium and production of phosphate fertilisers. Each of these processes is believed to be carried out at several sites in Australia.

HF can also be formed through the thermal decomposition of fluorine-containing chemicals and polymers. It can be an impurity in other chemicals and also formed as a decomposition product of some chemicals.

In the aluminium and phosphate fertiliser industries, controls are focussed on the prevention of chronic health effects that may occur from exposure to the low levels of HF produced as a byproduct of the production processes, and from other emissions. Air and biological monitoring are carried out in these industries.

Industries such as phosphate fertiliser production and aluminium smelting emit HF along with other particulate and/or gaseous fluorides. The exact quantities are in general not known because analytical methods measure only the fluoride ion and will therefore include chemicals other than HF. In aluminium smelting other non-fluoride exposures also occur. In such mixed exposures it is difficult to attribute observed health effects to a particular chemical or to compare exposures with predetermined standards. However, the limited monitoring data received from these industry sectors (from one company only in each industry) and the NOAEL identified as part of the OECD assessment suggest that exposure may be close to the level that may cause chronic health effects. Therefore caution is required for any processes where there is potential for inhalation exposure over whole shifts.

No exposure data was received on HF/fluoride emissions in the brick/tile and steel production industries, and the extent of occupational exposure is not known.

Other incidental production scenarios such as thermal degradation during fires, welding, brazing or processing of fluoropolymers are likely to produce varied exposures, and the individual situations should be investigated.

Based on the information received during the assessment, two fire scenarios may be the source of significant amounts of HF, which could make re-entry to the scene of a fire hazardous. The first is the use of total flooding fire extinguishant systems, most likely to be used in confined spaces. The second is decomposition of significant quantities of refrigerant in a fire. However, other scenarios may also be hazardous for either acute or chronic exposure.

HF may also be an impurity in other chemicals, or formed from reactive chemicals. Fluorosilicic acid, used in large quantities in Australia, has both these characteristics.

Occupational controls

For HF there are substantial regulatory controls in Australia in the form of a number of national standards and codes, implemented through State and Territory legislation. These include the ADG code, the NOHSC Hazardous Substances regulatory package, and the SUSDP. The major concentration cutoff levels differ between SUSDP and the NOHSC *Designated List of Hazardous* Substances, leading to complex labelling requirements. The occupational exposure standard is 3 ppm (2.6 mg/m³) 8 h TWA and this is also the peak limitation. The PACIA Code of Practice on HF, prepared by industry, introduced several additional initiatives aimed at improving the safe use of aqueous HF.

Humans are exposed to fluoride via a variety of sources including the diet and drinking water, and assessment of the effects of total fluoride in humans is a complex area. The dose at which no adverse effects were seen in animals on repeated exposure to HF (agreed by the OECD) is less than the current exposure

standard. It may be that biological monitoring is more appropriate than an exposure standard in some sectors of industry. In addition available exposure data for assessment are insufficient to confirm that all industry sectors are able to meet the current exposure standard. On the basis of this preliminary assessment, it is not possible to draw conclusions regarding review of the exposure standard.

Implementation of controls at the workplace level is crucial to their effectiveness. Because of the characteristics of HF, few occupational use scenarios are low hazard, and the safe use of the chemical depends on the consistent application of effective combinations of controls. Information obtained during the assessment suggests that this is more difficult for some uses and some sectors of industry. In the use of anhydrous HF, the major workplace control is use of a closed system, supplemented by other measures. The varied uses and concentrations of aqueous HF are reflected in differing control mechanisms.

Multiple lines of defense need to be implemented to manage the acute toxicity and corrosivity of anhydrous HF and higher concentrations of aqueous HF. Many workplace controls, including the elimination of the use of HF, have been implemented by industry and are detailed in Section 10.

The importance of controlling higher concentrations should not overshadow the fact that similarly complete systems of control are needed to avoid injuries from lesser concentrations, and that dilutions of HF are hazardous down to low concentrations.

The implementation of many controls is dependent on hazard communication. This is threatened if information is not accurately conveyed down the distribution chain. For many aqueous HF products and dilutions, this chain is quite long and involves very small businesses or "micro-firms", described as being notoriously difficult to reach (Reid, 1999). The large and varied workforce and industry sectors using HF mean that many are not familiar with the processes and precautions needed to ensure safety in handling, and may not make these controls an inherent part of their use of the substance.

During this assessment it was found to be difficult to make direct contact with franchisees using HF, and they may be dependent on franchisors for relevant health and safety information. Some importers of finished products containing HF were not familiar with chemical issues and did not hold MSDS for their products.

For HF, emergency arrangements are a particularly important control. The effects of accidental exposure can be influenced by the nature and speed of treatment of injuries. First aid and medical arrangements to handle an emergency should be in place in advance, and be able to be quickly and reliably implemented. During the assessment it was found that many companies had not made these arrangements. Treatment protocols and antidote supplies may not be readily available to all medical personnel. NICNAS will supply copies of this assessment report to health authorities responsible for hospital and emergency treatment in order to raise awareness of these issues.

The reactivity of HF makes management of spills more difficult. One large manufacturer recommends a polyacrylate homopolymer that can be sprayed onto spills of HF, and reacts to form a solid but slippery gel. Other measures recommended involve silica containing materials that may react with HF to form

silicon tetrafluoride. However under emergency conditions these may be the most readily obtainable materials.

In occupational use of HF, compliance with both regulatory and voluntary controls was found to be lacking in a number of areas:

- defects in MSDS and labels;
- hazard communication systems failing to alert workers that HF is present in a workplace product;
- potential exposure of workers to life-threatening concentrations of HF, because of inadequate engineering controls and personal protective equipment;
- lack of monitoring conducted to inform workplace risk assessment ie whether exposures meet the exposure standard;
- many formulators not aware of the PACIA Code of Practice, and its recommendations not generally taken up;
- SUSDP requirements re licensing of Schedule 7 HF not taken up by all States and Territories;
- inadequate emergency procedures and first aid arrangements; and
- in some cases a poor system of workplace control measures such that use of HF could not be confirmed.

The quality and completeness of control measures varied between companies and industry sectors.

11.5 Public health

The general public may be exposed to HF via skin absorption, inhalation and ingestion. HF and fluoride salts found in products such as metal/toilet cleaners, rust removers, and etching creams, can dissociate fluoride ions leading to penetrating tissue destruction and systemic poisoning. Although there is potential for exposure of the public to products containing HF, most of the products sold to the public contain concentrations of less than 10% HF and are covered in relation to labelling for safety directions and first aid instructions under Schedules 5 or 6 of the SUSDP. A limited number of products (rust removers and metal cleaners) which contain greater than 10% HF are available to the general public, although these are covered under Schedule 7 of the SUSDP with an entry in Appendix J limiting the sale and access to HF to licensed and authorised users. This may reflect difficulties in the implementation of control programs in States or Territories that have taken up the SUSDP recommendations.

The public will mostly come into contact with products containing HF where they are used as rust removers and for cleaning purposes such as on stainless steel, aluminium, tiles and bricks. Since the range of uses of products containing HF is relatively small, the likelihood of large scale public exposure is relatively low. The history of use of products containing HF indicates that the "worst case" exposure scenario is mainly from accidental exposure. Under these circumstances the hazard is very high and is dependent on the strength of the acid, the percentage of the body exposed, and the length of the exposure.

Public exposure to HF could occur through large-scale releases or inappropriate occupational use. This possibility will be minimised by comprehensive application of occupational controls in the transport and use of HF.

No significant exposure should occur during consumer use provided products containing HF are appropriately packaged and labelled and where existing safety directions and first aid instructions covered under Schedules 5 and 6 of the SUSDP for less than 10% HF, and Schedule 7 with an Appendix J entry for greater than 10% HF, are strictly adhered to. Currently in Australia there are around 120 calls annually to Poisons Information Centres regarding HF poisoning, with most exposures being dermal or inhalational. Accidental ingestion and ocular exposure are less common. Almost all calls regarding HF require referral to hospital for assessment and treatment. The number of incidents involving HF is of concern, and is currently under consideration by the National Drugs and Poisons Schedule Committee.

Secondary exposures to HF, via contact with items treated with the acid (such as clothes treated with a rust remover) are likely to produce skin irritation and burns if the HF is not completely removed. Secondary exposure to HF may also occur where products are used in the domestic situation by tradespeople and not adequately removed following use. The development of systemic toxicity will depend on the amount and concentration of HF remaining in the treated area or on the treated article. If instructions for use are adhered to, the possibility for secondary exposure is reduced.

11.6 Data gaps

Data gaps identified on the effects of HF are:

- Testing to identify rate of absorption of dilute HF through the skin;
- Concentration of aqueous HF that is not irritant to skin;
- Two generation reprotoxicity studies (final results based on sodium fluoride not yet published);
- Additive effect of other acids on the effect of HF through the skin; and
- Local effects from chronic dermal exposure to low concentrations of aqueous HF.

Some of this data may be forthcoming as a result of regulatory action in the USA.

Other data gaps identified are:

- Data on extent of emissions from industries that produce HF incidentally, which is needed to more adequately assess potential impacts. The National Pollutant Inventory may be expected to generate such information;
- Additional data to quantify air fluoride concentrations and concentrations in vegetation in areas around industries known to incidentally produce HF;
- Range of sources of incidental production that involve occupational exposure;
- Use and exposure information for some niche applications of HF e.g. bathtub stripping; and
- Full exposure information on building cleaning, where a range of use scenarios may be occurring.

11.7 Conclusions

This preliminary assessment concludes:

- Accidental exposure to HF is a major concern through inhalation or skin contact. Concentrated aqueous solutions and anhydrous HF can cause death from spills or loss of containment. Lower concentrations also cause harm, even at very low levels, where delayed burns can occur from skin contact.
- Health effects from chronic exposure cannot be ruled out for incidental production and some use scenarios, based on the NOAEL and the exposure standard.
- The use of high concentrations, use "on-site" rather than in fixed facilities, or use in remote areas may make it difficult to implement adequate controls.
- Under some circumstances large releases of anhydrous HF or concentrated aqueous HF can form a mobile cloud.
- Despite public health controls, serious incidents arising from public use continue to occur. Existing public health controls are not uniformly applied.
- There is potential for impacts on the environment arising from incidental production of HF.
- There is poor compliance with occupational regulatory and voluntary controls in some areas, as identified in Section 11.4.
- Many controls have been implemented at the workplace level to reduce or eliminate exposure, including eliminating the use of HF or reducing the concentration used, and these measures could be implemented where appropriate in other workplaces.

11.8 Need for further assessment

OECD countries including Australia have agreed to the SIDS Initial Assessment Profile for HF (Appendix 6). This profile includes the results of the EU risk assessment - that there is need to limit the risks to workers, consumers and for exposure via the environment for some sites.

It is clear that occupational and public exposures are significant for risk. However there is a substantial amount of use, exposure and exposure control information in this assessment report to facilitate risk management action by industry and regulatory authorities. Further assessment may be necessary if control measures to reduce exposure are not implemented fully or may be triggered by new toxicological data from planned regulatory action in the USA. Additional information on incidental releases of HF to the environment would be required in order to undertake a full (risk) assessment of environmental impact.

It is considered that further assessment in the form of a detailed risk assessment by NICNAS is not necessary at this time.
12. Recommendations

Recommendation 1: Industry review of control measures

HF is an extremely hazardous substance and OECD countries have agreed that further work is required to reduce risk arising from its use. This assessment identified failures in application of controls and measures for limiting risks to users of HF. Therefore it is recommended that:

- industry (suppliers and users of HF) review their controls for HF and ensure full compliance with existing regulation and codes of practice. The States/Territories OHS jurisdictions are responsible for ensuring industry compliance with regulatory requirements.
- industry should also implement additional voluntary measures such as outlined in the PACIA Hydrofluoric Acid Code of Practice where appropriate.
- OHS jurisdictions and industry work in partnership to ensure take-up of the voluntary initiatives aimed at ensuring safe use of HF, including the Code Obligations in the PACIA Code of Practice. Updating of the information in this Code, and monitoring of its take-up and effectiveness should also be carried out.
- suppliers assist their customers in this regard, via provision of advice for safe use.

NICNAS will evaluate implementation by industry of the recommendations in this report 12 to 18 months after the publication of the report. If voluntary measures to reduce exposure are not effective, NICNAS may proceed to a full (risk) assessment, with associated risk reduction recommendations to regulatory authorities.

Occupational health and safety

Recommendation 2: Hazard classification

HF is classified as a hazardous substance by NOHSC. It is recommended that:

- NOHSC adopt the same concentration cut-off levels for hydrogen fluoride and hydrofluoric acid in the *List of Designated Hazardous Substances*. It is recommended that the current cut-off levels for hydrofluoric acid be adopted for both entries.
- suppliers and employers take note of the amended risk phrases agreed by the EC Working Group on the Classification and Labelling of Dangerous Substances in October 1998. This amendment should be taken up in the NOHSC *List of Designated Hazardous Substances* as soon as possible, to provide the following classification for solutions ≥0.1% and <1%:
 - R20/21/22 Harmful by inhalation, in contact with skin and if swallowed
 - R36/37/38 Irritating to eyes, respiratory system and skin

MSDS, labels and training materials should be amended to incorporate this change, applicable to the lowest concentrations of HF that are classified as hazardous substances.

Recommendation 3: Material Safety Data Sheets (MSDS)

Suppliers of HF and HF products must comply with the NOHSC requirements for hazardous substances. Non-compliance with MSDS requirements in relation to supply, content and accessibility to workers was identified in this assessment.

- It is recommended that all suppliers and employers review their MSDS compliance.
- Given the significant hazard of HF, and the lack of compliance with regulatory requirements for MSDS, it is recommended that this be followed up by the OHS jurisdictions. It is recommended that OHS jurisdictions undertake compliance reviews for MSDS on HF and products containing HF, 6 months after the publication of this report.

In addition it is recommended that suppliers and employers pay particular attention to the following, that will assist in the safe use of HF:

- All suppliers of HF and HF products should ensure that up-to-date MSDS are supplied to customers.
- As HF is a Type I hazardous ingredient (NOHSC, 1994f) its identity must be disclosed on the MSDS by its common chemical name and CAS number. It is recommended that the exact percentage of HF in mixtures be disclosed in the MSDS and that concentration ranges should not be used. The disclosure of exact concentration of HF will assist in first aid and medical treatment and other emergency measures. It is unlikely that the concentration of HF in mixtures is critical to the commercial confidentiality of these mixtures.
- Except for dilute solutions, the health effects section of the MSDS should state that exposure may cause death. For all aqueous solutions it should warn of the possibility of delayed burns from dilute material.
- Information on the reactivity of HF, including formation of hydrogen and safe methods for acid dilution, should be included (Section 5.3).
- Employers should ensure that employees have good access to accurate and up to date MSDS.
- Where solutions of fluoride or bifluoride salts are used in a mixture at pH < 5 the MSDS should state that the mixture contains HF and include appropriate first aid and emergency procedures.
- MSDS for chemicals that can react to form HF should include this information (see Section 6.1.2).
- First aid instructions on MSDS for dermal exposure should specify application of calcium gluconate on-site, as well as in the Advice to Doctor section.

Recommendation 4: Workplace labels

- Suppliers must comply with NOHSC labelling requirements. As noncompliance was identified in this assessment it is recommended that all suppliers review their labels for compliance.
- Given the significant hazard of HF, and the lack of compliance with regulatory requirements for labels, it is recommended that this be followed up by the OHS

jurisdictions. It is recommended that OHS jurisdictions undertake compliance reviews for labels on HF and products containing HF 6 months after the publication of this report.

It is also recommended that suppliers and employers pay particular attention to the following, that will assist in the safe use of HF. It is recommended that:

- The exact percentage of HF in mixtures should be disclosed on labels, and that concentration ranges should not be used.
- A distinctive extra warning label should be provided for packages of HF and HF products, of the type suggested in the PACIA Code of Practice. One such red and white octagonal label contains the wording "STOP: Hydrofluoric Acid is Dangerous. Read the MSDS and Label". This recommendation does not apply to bulk tanks, where other labelling requirements are more appropriate.
- Where solutions of fluoride or bifluoride salts are used in a mixture at pH < 5 the labelling should be as for HF.
- Labels for chemicals that can react to form HF should include this information (see Section 6.1.2).

Recommendation 5: Register of hazardous substances

The NOHSC *National Model Regulations for the Control of Workplace Hazardous Substances* require a register of hazardous substances to be kept. It is recommended that users of HF or HF products pay particular attention to this requirement, to ensure that they have effective systems in place to confirm the presence of HF in the workplace.

Recommendation 6: Education and training of workers

Training of workers is an obligation under OHS laws and Hazardous Substances Regulations. It is recommended that employers ensure that all workers potentially exposed to HF receive training appropriate for the safe handling of HF. This should form part of the induction program for all workers and be reinforced at regular training sessions. In particular the health effects, safe methods of use, disposal, personal protective equipment, first aid and emergency procedures should be emphasised. Training manuals should contain first aid information.

Recommendation 7: Other hazard communication

It is recommended that suppliers, employers and industry associations identify voluntary measures, additional linkages and resources that can be used to improve hazard communication and safe use of HF. Possible mechanisms are listed below:

- HF is used in a range of industries and it is recommended that other industry associations take note of the voluntary initiatives in the PACIA Code of Practice, which may also be relevant to their members. Science Industry Australia is already a signatory to this Code.
- Anhydrous HF is not covered by the PACIA Code of Practice. Use of anhydrous HF in petroleum alkylation is a specialised process carried out at five sites within Australia. Because of the large quantities required and the physical, chemical and toxicological properties of the chemical, its use poses particular challenges. Sharing of information on safety, emergency

arrangements etc within this small group would be of benefit to facilitate problem solving.

• Some guidance material of use in the management of HF is listed in Section 10.2.3.

NICNAS will prepare a Safety Information Sheet for HF, aimed primarily at workers, which can be distributed to workplaces. It is recommended that industry and State jurisdictions distribute this information widely.

Recommendation 8: Emergency procedures

It is recommended that emergency procedures should cover emergency response, safe disposal, first aid and medical treatment, and take special note of the points below:

- Where there is the possibility of exposure to the public as a result of an emergency, the procedures should cover this possibility. For large quantities of anhydrous HF, which may form a mobile cloud when released into the atmosphere, modelling of possible releases should be carried out.
- All facilities handling HF should have calcium gluconate antidote and trained personnel available, and should ensure that first responders, hospitals and clinics in the area are informed and equipped to treat HF exposure. Calcium gluconate gel should be within shelf life, easily available on the site, and available for workers to take home if they are likely to experience delayed burns. It is recommended that the National and State Poisons Information Centres be consulted if necessary when burns occur.
- The MSDS can be used to identify the chemical and concentration to medical personnel.
- Safety showers and eyewash basins should be available at workplaces. If this is not possible at the site, other emergency washing facilities should be identified.
- In verbal communication hydrofluoric acid is often wrongly identified as another chemical, hydrochloric acid, especially by those people not familiar with chemical names. Confusion of the two chemicals is likely to occur under emergency conditions, and procedures should stress proper identification at this time.
- Emergency Procedure Guides (EPG) are a major aid to management of emergencies in transport. It is recommended that specific EPGs for HF be carried at all times when HF or HF products are being transported, even when below the threshold quantity for this as an ADG Code requirement. A useful model EPG is Australian Standard 1678. The more general Dangerous Goods Initial Emergency Response Guide (IERG) does not contain information on the antidote and is not considered adequate.
- Choice of absorbents for clean up of spills should be made with the knowledge that silica-containing materials may react with HF.
- First aid instructions for eye injuries should <u>not</u> recommend calcium gluconate products, as some concentrations may be harmful to eyes. The correct first aid treatment is thorough flushing with normal saline or water, and obtaining medical attention. Later medical treatment may include use of 1% calcium gluconate.

Recommendation 9: Health surveillance and atmospheric monitoring

Where there may be a significant health risk to workers through exposure to HF through inhalational or dermal routes, appropriate biological monitoring and health surveillance should be carried out. Fluorosis is acknowledged as an effect of long-term exposure. All fluoride exposure should be taken into account.

Where a workplace assessment indicates that significant exposure to gaseous HF could occur, appropriate workplace monitoring must be carried out to confirm and quantify the exposure.

It is specifically recommended that workplace monitoring in phosphate fertiliser plants include all relevant areas including the areas where fertiliser is aged.

Recommendation 10: NOHSC exposure standard

On the basis of this preliminary assessment, it is not possible to draw conclusions regarding review of the exposure standard. It is recommended that NOHSC maintain awareness of developments overseas, to ensure that the Australian standard remains consistent with overseas standards and current knowledge regarding the effects of chronic exposure to HF.

Recommendation 11: NOHSC injury coding

It is recommended that NOHSC consider separate coding of HF in injury data or, alternatively, strengthen the guidance material on reporting injuries, so that all injuries from HF or HF products are included in the acid category.

Environment

Recommendation 12: Air monitoring data near emission sites

HF is toxic to vegetation. It is recommended that monitoring should be conducted by industry for HF/fluorides as described in ANZECC's National Goals for Fluoride in Ambient Air and Forage, both in the air and surrounding vegetation around sites known to incidentally produce HF.

Public health and safety

Recommendation 13: Compliance with SUSDP labelling requirements

The toxicity of HF is well established and exposure to fluoride-containing products has resulted in serious injuries and deaths. Where products containing HF are available to the general public at concentrations which are covered by Schedules 5 and 6 of the SUSDP, it is recommended that the packaging requirements, safety directions, warning statements and first aid instructions for these products are strictly adhered to. It is recommended that all hazard precautions given in data sheets supplied with HF be observed.

As required by the SUSDP, where HF is formed in solution this should be recognised and labelling should be in accordance with the requirements for HF.

Recommendation 14: Licensing of HF Schedule 7 users

It is recommended that all States and Territories take up the provisions for HF in Schedule 7 and Appendix J of the SUSDP, so that users of concentrations of HF above 10% are licensed. Liaison between State/Territory bodies implementing SUSDP and those responsible for occupational health is recommended to ensure maximum safety in the use of HF.

Recommendation 15: Referral to National Drugs and Poisons Schedule Committee

It is recommended that the following issues be raised with the NDPSC for further consideration, as part of its current review of the first aid and warning statements for HF:

- First Aid Instructions, Warning Statements and Safety Directions for potassium bifluoride, consistent with the existing statements for sodium bifluoride and ammonium bifluoride.
- The inclusion of a warning statement for HF, bifluorides and fluorosilicic acid, that skin contact may cause burns that are not evident for some time;
- Alteration of upper cutoff concentration for HF from 10% to 7%, in order to harmonise with the upper cutoff concentration under the NOHSC *Designated List of Hazardous Substances*. This would simplify labelling requirements for industry and allow similar protection to consumers as for workers.

13. Secondary Notification

Under Section 65 of the *Industrial Chemicals* (*Notification and Assessment*) Act 1989, secondary notification of hydrofluoric acid/hydrogen fluoride (HF) may be required where an introducer of the chemical becomes aware of any circumstances that may warrant a reassessment of its hazards and risks. Specific circumstances include:

- the function or use of HF has increased, or is likely to change, significantly;
- the amount of hydrofluoric acid introduced into Australia has increased, or is likely to increase, significantly;
- manufacture of HF (other than *in situ* production) has begun in Australia; and
- additional information has become available to the introducers as to the adverse health, safety or environmental effects of HF.

The Director (Chemicals Notification and Assessment) 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.

Appendix 1

Chemistry of Aqueous Solutions of Fluoride Salts

A1.1 Acidified fluoride salts

HF will be present in the aqueous solutions of inorganic fluoride salts, if the pH is low (acid). This situation will occur if the solution contains a strong (highly ionised) acid as well as the fluoride salt. Strong* acids include hydrochloric (HCl), nitric (HNO₃), perchloric (HClO₄), and sulfuric (H₂SO₄) All soluble fluoride salts, including bifluorides, can be a source of HF via this mechanism. The conjugate base of HF, which is F-, reassociates to form HF at low pH because HF is a weak (not highly ionised) acid.

The quantity of undissociated HF and of F^- in solution can be calculated at different pHs via the Henderson-Hasselbach equation (Atkins, 1989) from the known dissociation constant of HF, K_a.

In the ionization of HF, HF $\leftarrow - \rightarrow$ H⁺ + F⁻

 $K_{a} = [H^+][F^-] = 6.5 \times 10^{-4} M$ [HF]

From K_a one can write [HF] / [F⁻] = [H⁺] / K_a

then,

As the K_a of HF= 6.5 x 10^{-4} M, one calculates $pK_a = 3.2$

Then the ratio [HF] / [F-] can be calculated for any pH from the expression

 $\log ([HF / [F]) = 3.2 - pH$

For example, at pH 3.2 half of any fluoride is converted to HF, for when the log is zero the ratio is 1:1. Whereas at pH 2.2 the ratio is 10:1, ie 91% of any fluoride ion is converted to HF. (For these estimates any formation of bifluoride ion has been ignored.)

 $\log ([HF] / [F^-]) = pK_{a^-} pH$ where $pX = -\log X$

^{*} The words *strong* and *weak*, as applied to an acid, describe the extent to which its molecules undergo ionization in solution. They do not refer to the concentration of the acid, and both strong and weak acids can be prepared as dilute or concentrated solutions. The acid ionization constant of a particular acid, K_a, will be higher for a strong acid than for a weak one.

Applications

The solubility of NaF is 4.1 g/100 g or about 1 M. If a 1 M water solution of NaF is acidified to below pH 2 then about a 1 M solution of HF is formed, which is equivalent to about 2%.

The solubility of KF is higher at 10 M, so acidification of a saturated solution of KF will produce a 20% HF solution.

Ammonium bifluoride (NH₄HF₂) is very soluble in water (41.5 wt %) (Papcun, 1994). Because the molecule contains two fluorine atoms, a 1 M solution could produce up to 2 M HF. In practice, a close to quantitative conversion at pH < 2 occurs at lower concentrations. For example, from Figure A1.1 a 0.5 M or 2.8 g/100g solution of NH₄HF₂ would produce a 0.85 M or 1.7 g/100 g solution of HF at pH 1, with 85% of the fluorine atoms in the form of HF. At higher concentrations or higher pH a significant amount of the HF₂⁻ ion is present. (Figure A1.3).

Insoluble fluoride salts (such as calcium fluoride CaF_2) in aqueous solution are a poorer source of HF, as they are limited by the solubility of the salt. However, in aqueous suspensions which are acidified, solubility will be increased by the presence of the acid, and a significant quantity of HF can be formed.

It can be seen from the above examples that acidified fluorides can produce substantial quantities of HF in solution.

A1.2 Bifluoride salts

Bifluoride salts (commonly sodium, potassium and ammonium bifluoride) are a special subset of the group of soluble fluoride salts. They differ in forming acidic solutions in aqueous solution, without the addition of a strong acid. Therefore some HF is formed in aqueous solution when bifluoride salts are dissolved. For other fluoride salts, aqueous solutions contain the F^- ion, and this is only converted to HF if a strong acid is added.

The special characteristics of bifluorides occur because, in the presence of excess F^- , HF can form the bifluoride ion F-H-F or HF₂⁻.

 $HF + F \leftarrow \rightarrow HF_2^-$

 $K_2 = [HF_2^-] / [HF] [F^-] = 5 \text{ to } 25 \text{ M}^{-1}$

The formation constant for this complex is relatively small, so there is not much bifluoride formed except in concentrated solutions. As a corollary, if a bifluoride salt is dissolved in water, it will immediately dissociate into HF and F⁻. At low concentrations this dissociation is nearly complete. For example, an 0.1 M solution of a bifluoride would be over 90% dissociated to almost 0.1 M HF and 0.1 M F⁻ if the pH were controlled at pH 3.2. Only at concentrations above 0.2 M does more than half of the bifluoride remain in that form at pH 3.2. These solutions would contain HF at concentrations above 0.1 M as well.

Because of the equilibria among the various components it is not possible to specify simple formulae to calculate the relative concentrations of each species. Instead, a graphical presentation based on Excel iterative calculations shows how the species distribution changes with pH and the total fluoride concentration for typical values of the equilibrium constants (Figures A1.1, A1.2 and A1.3 for HF, F-and HF_2^- respectively). The absolute concentrations will depend on the choice of these equilibrium constants, which depend on conditions such as temperature and ionic strength, but the qualitative picture will remain the same. Note that both the pH and the total fluoride increases by a factor of 100 (from 0.1 M to 10 M) from the front to the back of the graphs.

Applications

A solution of, say, 0.5 M ammonium bifluoride NH₄HF₂ (2.8 g/100g) corresponds to a total fluoride solution concentration of 1 M, the mid-point from the front to rear of the graphs. If this solution were made in neutral water the pH would drop because the HF formed by dissociation of the HF₂⁻ would further dissociate to H⁺ and F⁻. The pH would effectively be buffered at the pK_a of pH 3.2, because the dissociation of HF₂⁻ produces equal amounts of HF and F⁻. From the graph, at pH 3.2, about 20% (0.2 M) of the total fluoride would be in the form of HF, and this would be equivalent to approximately 0.4 g / 100 g HF. This also corresponds to the maximum concentration of remaining HF₂⁻, because its concentration depends on the product [HF] [F⁻]. Any external adjustment of the pH by addition of acid or base would alter the species distribution to more HF (pH < 3.2) or more F⁻⁻ (pH > 3.2) with less HF₂⁻. Note that the concentration of NH₄HF₂ in this example is the same as in Section A1.1, but the final HF concentration is lower, (0.4 g/100 g versus 1.7 g/100 g) because of the different pH.

A 5 M (28 g / 100 g) solution of NH₄HF₂ corresponds to a total fluoride solution concentration of 10 M and log [F] is 1. From figure A1.1, at pH 3.2, only about 10% (1 M) of the total fluoride would be in the form of HF, and this would be equivalent to approximately 2.0 g / 100 g HF. Note that the concentration of NH₄HF₂ in this example is ten times higher than in the example in the previous paragraph, but the concentration of HF is only five times higher. This reflects the higher proportion of HF₂⁻ ions in more concentrated solutions of bifluorides.

It can be seen from these examples that aqueous solutions of bifluoride salts can produce HF in solution, but that the concentration is not as high as it would be if extra acidification occurred.



Figure A1.1 – Proportion of HF in aqueous solution at different pH and fluoride concentrations



Figure A1.2 – Proportion of F⁻ in aqueous solution at different pH and fluoride concentration



Figure A1.3 – Proportion of HF2⁻ in aqueous solution at different pH and fluoride concentration

A1.3 Concentration calculations

In figures A1.1, A1.2, and A1.3 concentration is expressed as log of the molarity of all fluoride in the solution (log [F]). The equivalent concentrations by weight of HF, NH₄HF₂ (ammonium bifluoride) and NaF (sodium fluoride) to some values of log [F] are in Table A1.1 below. This table and the figures can be used to predict the concentration of F^- , HF and HF⁻₂ in varying strength solutions of HF, ammonium bifluoride or sodium fluoride at different pHs.

[HF]	[NH4HF2]	[NaF]	Log [F]
HF concentration in solution	ammonium bifluoride concentration in solution*	sodium fluoride concentration in solution	
0.1 M	0.05 M	0.1 M	-1.0
(0.2 g/100g)	(0.28 g/100g)	(0.42 g/100g)	
0.31 M	0.15 M	0.31 M	-0.5
(0.62 g/100g)	(0.84 g/100g)	(1.3 g/100g)	
1 M	0.5 M	1 M	0
(2 g/100g)	(2.8 g/100g)	(4.2 g/100g)	
3.1 M	1.5 M	Not soluble	0.5
(6.2 g/100g)	(8.4 g/100g)		
10 M	5 M	Not soluble	1.0
(20 g/100g)	28 g/100g)		

Table A1.1 -	Concentration	equivalents	for Figures	A1.1, A1.2, and A1.3
	0011001101011	quarteres		

* Total fluoride concentration will be twice the concentration of the ammonium bifluoride concentration ie 0.1 M total fluoride when ammonium bifluoride concentration is 0.05 M, because this molecule contains two fluorine atoms.

For example, a solution produced from 0.84 g NH₄HF₂ in 100 g water will have a log [F] of - 0.5 (TableA1.1 above). Total fluoride concentration is 0.31 M. From the graphs (Figures A1.1, A1.2, A1.3) it can be seen that at pH 3, this solution will contain significant proportions of HF (33.2%), HF₂⁻ and F⁻.

At this pH and concentration, the amount of HF in the NH_4HF_2 solution will be: <u>33.2</u> X 0.31 M or 0.1 M HF. This corresponds to an actual concentration 100

of HF in the resulting solution of 0.2%.

Appendix 2

Calculations of Occupational Exposure Using the EASE model

A2.1 Occupational exposure

EASE modelling of inhalational exposure is based on the volatility of substances, use patterns and patterns of control. For dermal contact the model is based on "potential for dermal contact" to solids or liquids, and assumes that dermal exposure to gases and vapours is very low.

The EASE model was used to estimate exposure for varying conditions of use in alkylation, formulation and metal treatment/cleaning. The final estimates are shown in Table 10.

A2.1.1 Calculation of inhalational exposure

Inputs to the EASE model are displayed in Table 2A.1. Vapour pressures were taken from Table 2. For anhydrous HF, the nominal value of 101.3 kPa was used, as higher pressures do not operate in the EASE model. Vapour pressures were converted from mm Hg to kPa by dividing by 7.5.

The output from EASE is in ppm and was converted to mg/m^3 by multiplication by 0.82 (see Table 2).

Inhalational exposure was calculated using the following formula and parameters

$$D_{inh} = \underline{C \ x \ R \ x \ E} \ mg/kg/d$$

BW

 $D_{inh} = 0.08 - 820 \ x \ 1.3 \ x \ 8$

70

Where $C = \text{concentration in } mg/m^3$

 $R = respiration rate of 1.3 m^3/h$

E = time exposed/day in hours (8 h)

BW = body weight in kg (70 kg)

 $D_{inh} = Amount inhaled/day in mg/kg/day$

EASE Predicted inhalational exposure: 0.1– 1000 ppm or $0.08\ mg/m^3-820\ mg/m^3$

$D_{inh} = 0.012$ to 122 mg/kg/d

Note: This calculation assumes 100% inhalational uptake, which is supported by toxicokinetic data. (Section 8.1.1)

Table 2A.1: Inpu	ut to E/	ASE model use	d to estimate HF	atmospheric levels i	in various occupational	l settings	
Process		Process temperature	HF concentration	Vapour pressure kPa	Use pattern	Control pattern	HF levels (ppm)
Alkylation	(1)	20°C	100%	103.3 (nominal 101.3)	Closed, no system breaching	Full containment	0 0.1
	(2)	20°C	100%		Closed, with system breaching	Segregation	200 – 500
Formulation	(1)	20°C	20%	15.96	Non-dispersive	LEV	20 - 50
	(2)	20°C	20%		Non-dispersive	Segregation	70 - 100
	(3)	20°C	35%	0.33	Non-dispersive	LEV	0.5 – 1
	(4)	20°C	35%		Non-dispersive	Segregation	3 - 5
Metal treat/clean	Ð	20°C	8 - 10%	0.021	Non-dispersive	LEV	0.5 - 1
	(2)	20°C	8 - 10%		Non-dispersive	Direct handling with dilution ventilation	10 – 20
	(3)	20°C	8 - 10%		Wide dispersive use	Direct handling with dilution ventilation	100 140
	(4)	20°C	8 - 10%		Non-dispersive or wide dispersive use	Direct handling with dilution ventilation, aerosols formed.	500 - 1000
Closed system		The substance re the system is no	emains within the rev longer considered to	actor or is transferred fr o have full containment.	rom vessel to vessel throug	h closed pipework. Where breaching of th	e system occurs,
Wide dispersive us	Ð	Uncontrolled exp	osure may occur to	immediate workers and	d others. Examples of this (category are painting and spraying of pesti	cides.
Formation of aeros	ō	Typical aerosol g	enerating activities	are spraying, splashing	and stirring. EASE modell	ling with aerosol assumes that large quanti	ties are formed.
LEV (local exhaust ventilation)		LEV removes a s about its design €	substance at the poil effectiveness.	nt of origin or generatio	m. EASE modelling assum	es that it is appropriate for the purpose and	l operating at or
Segregation		Separating the w	orker from the subsi	tance by distance, typic	cally a few metres from the	source of exposure.	
Dilution ventilation		Natural or mecha air changes per h	anical (not local) ven nour.	tillation. Working in the	e open air is one form, as is	general mechanical ventilation with a signi	ficant number of
Direct handling		The worker hand	les the substance di	irectly without precautio	ons. The effect of personal	protective equipment needs to be judged s	eparately.

A2.1.2 Calculation of dermal exposure

Dermal exposure was estimated for 1.0% solutions. As a worst case exposure scenario, direct contact was assumed to be extensive (10 events/day) and EASE predictions were that this would result in exposure to 5 - 15 mg/square cm/day.

Intake was calculated on the basis that the area of skin exposed was 840 cm^2 (area of the hands).

Based on: liquid; wide dispersive use; direct handling; extensive contact:

EASE Predicts dermal exposure of 5 to 15 mg/cm²/day

 $D_{dermal} = \frac{5 - 15 \times 840}{70}$

= 60 - 180 mg/kg/day for 100% HF

Where: Hands only exposure = 840 cm^2

Average body Wt = 70 kg

Dermal absorption = 100%

If dermal uptake = 60-180 mg/kg/d for 100% HF

thus 1% solution = 0.6 to 1.8 mg/kg/d (av 1.2 mg/kg/day)

Note: This calculation assumes 100% dermal uptake. Dermal uptake rate for HF is not known.

A2.1.3 Calculation of combined inhalational and dermal exposure

Combined exposure through inhalational and skin contact expressed as mg/kg/day was calculated as the sum of the two exposures, for formulation and metal treatment scenarios (see Table 10).

A2.1.4 Calculation of NOAEL in OECD report

The OECD report determined a no observed adverse effect level (NOAEL) for inhalation of 0.72 mg/m^3 , based on a 90-day rat inhalation study.

This was calculated to be equivalent to approximately **0.08 mg F' /kg/b.w.**, based on exposure of 6 h/day and 5 days/week. The OECD report assumed that rat respiration rate was 0.223 m³/day and rat body weight (bw) 0.35 kg. Inhalational uptake was assumed to be 100%.

NOAEL = $0.72 \ge 0.223 \ge 6 \ge 5$

0.35 24 7

= 0.08 mg F/kg/bw

Dose of F⁻ (atomic wt 19) can be approximated to dose of HF (mol wt 20.01).

A2.1.5 Other sources of fluoride

The OECD report estimated that worst-case human exposure to fluoride through food and drink in areas of fluoridated water is 5640 μ g / day (5.64 mg/day). Based on 70 kg body weight, this is equivalent to 0.08 mg/kg/day.

The OECD report estimated a background air level of F of 0.07 μ g/m³. Based on a human respiration rate of 1.3 m³/h and 24 h/day exposure, this is equivalent to 0.002 mg/day.

Appendix 3

Occupational Incidents in Australia

Information on the data sources used for the tables below is in Section 7.2.10.

Year **Incident details Oil refineries** 1995 During routine maintenance a large cloud of HF from an HF storage vessel escaped into the atmosphere. The HF entered under the hood of the C class suit being worn by the maintenance technician who suffered an inhalation injury. Three other personnel were affected by this incident. An investigation showed the pipe work to be sloping away from the vessel thereby trapping HF. This was modified to be self- draining back to the top of the HF storage vessel. 1996 Two operators inhaled butane and HF vapours. On investigation it was found that a reflux pump seal in the alkylation unit was leaking. 1997 During the erection of a maintenance scaffold in the alkylation unit a leak was noticed. The scaffolder bent down to observe the pipe work and inhaled HF fumes. He experienced sore throat and itchy tongue and was sent to hospital for observation and discharged with no after effects. 1997 *Potential for incident reported, during laboratory analysis for HF. HF acid bomb could topple over on the bench in the fume cupboard as bench swollen and top layer chipped away to expose rotting wood. Repairs carried out. 1997 A leak of HF gas was noticed from one of the tri cock valves on the acid storage drum as a white cloud. Water was applied to the leak and operator changed into C-class protective clothing to isolate the tri cock manifold. The leak became worse when the top isolation block valve was activated. The operator then located and isolated the bottom isolation valve and curbed the leak within two minutes of the increased release. As a result of this incident, several steps were taken to improve training, engineering systems, incident response capability and other precautions for emergencies.

Table 3A.1 Incidents involving anhydrous HF in Australia reported by industry

	(continued)		
Year	Incident details		
Oil refineri	<u>es</u>		
1997	*Possible exposure to HF vapours due to a leaking valve in the laboratory sample bomb when collecting sample for routine analysis.		
1997	Maintenance crew working on alkylation unit propane stripper were engulfed in HF vapours from malfunctioning valve.		
1997	Loss of containment through HF leak into cooling water.		
1998	Leak in acid blowdown line which contained steam.		
1998	Failure of a flow transmitter tapping isolation valve in the alkylation unit feed control caused release of hydrocarbons to the atmosphere. The feedstream contained HF.		
1998	Loss of HF from the alkylation unit.		
-	Summary of several incidents: HF leaks controlled and contained on site using water deluge system. A limited number of acid burns resulted in first aid treatment.		
-	Valve body split. No injuries reported.		
-	Material containing trace HF dropped onto skin and caused an ulcerated sore.		
-	Minor burn when connecting pump line and changing spade.		
-	Leaking joint on HF isotainer transfer line.		
-	Difficulty making changeover to new isotainer as its dimensions were not standard. As a result, some HF was released.		
-	Severe burn when stripping plug valve.		
-	Contractor sustained burns and was airlifted to hospital. No further details disclosed to NICNAS.		
	* Potential burn		

Table 3A.1 - Incidents involving anhydrous HF in Australia reported by industry

Table 3A.2 - Incidents involving aqueous HF in Australia reported by industry

Year	Incident details
Transport	
-	A recycled mauser 200 L drum containing 5% w/w HF leaked whilst being transported.
1998	A transport depot worker received a burn on the hand from 35% solution of HF after touching the top of a drum, on which a pool of liquid HF had formed. Distortion and leakage of the PVC drum may have occurred when other drums were packed on top of it. The worker was immediately treated with calcium gluconate gel and taken to hospital for observation and had no ill effects.
-	In unloading, a pallet of 4x 200 L drums was dropped too fast from truck to ground and the pressure caused bung to warp with slight HF leak.
2000	Leakage of 50% HF from closure of 60 L drum was noticed by customer company shortly after receipt. Road transport company not aware of hazard of HF until contacted, and had been cleaning the truck without PPE. Several transport workers attended hospital casualty section as a precaution. Cause of leakage not determined, but drum had been opened for sampling, and lid may not have been tightened sufficiently after this, or closure may have been faulty.
-	HF product splashed into glove. The incident was not reported and no first aid administered at first. The worker received minor burns to hand.
-	Minor spillage while decanting.
-	Minor burn suffered by an operator not wearing personal protective equipment.
-	Splash with HF required injection treatment at local hospital.
-	Hole in glove caused untreated exposure to thumb.
-	An operator wiped finger on a pipette containing HF – was treated on a drip for 4 h in hospital.
-	A pinhole in a glove caused a burn from 35% HF.
1997	Leaking lids resulted in 2 workers going to hospital with minor irritations.
1997	Tap on a vat failed and resulted in 2 workers going to hospital with minor burns.
-	Operator treated with running water and calcium gluconate gel and sent to hospital for observation. Only on-site incident in 30 years.

Table 3A.2 - Incidents involving aqueous HF in Australia reported by industry (continued)

	()		
Date	Industry use	Incident details	

-	Reseller	Skin contact to fingers, treated at casualty section of local hospital.
1991	Aluminium sheet manufacture	A maintenance fitter got a small amount of 10% HF solution inside his gloves while working on a process pump. Treated at company health centre and experienced no ongoing effect.
-	Aluminium sheet manufacture	A 1000 L container arrived with lid not tightly secured. Some solution had spilt around container and onto tray truck and this was neutralised and cleaned up.
~ 1990	Metal processing	An employee accidentally knocked over a small container of acid. Some of this splashed on his toe and resulted in hospitalisation.
-	Metal manufacture	Incidents caused by burst supply hoses and leaking drums have resulted in burns requiring medical treatment including admission to hospital.
-	Lighting manufacturer (metal treatment)	Splash caused a minor burn on the operator's foot. He was not wearing boots and did not wash the acid off.
-	Printer	Worker pulled deletion pen apart resulting in acid on fingers.
-	Mining (analysis)	About once a year there is an incident of spillage of a 40 mL mixed acid mix containing HF – either a complete spill of the 40 mL or a splash.
-	Mining (analysis)	A drum containing four, 2.5 L bottles was unpacked by unauthorised personnel and the bottles transported loose in the back of a ute.
-	Mining (analysis)	HF spilt in fume cupboard (no human exposure).

Date	Industry use	Incident details
-	Research	Several incidents where HF has penetrated small holes in gloves. First aid with calcium gluconate gel and hospital observation, no permanent effects.
-	Research	Small spills of $< 10 \text{ mL}$ ($< 5 \text{ spills over 10 years}$).
-	Analytical chemistry (lab)	Crucible was placed into a furnace (800°C) before HF had been completely converted. HF fumes escaped from the furnace into the laboratory.
-	Etching silicon wafers	Minor skin contact, treated with calcium gluconate gel.
-	Maritime	Staff cleaning hot engine room deck plates with HF/sulfuric acid product had to go above deck on several occasions because of effects of fumes generated by the product.
-	Carpet and upholstery cleaning	HF penetrated fingernails and caused blackening. Operator not wearing gloves.
	Carpet cleaning	On two occasions contract cleaners experienced soreness in fingers.
1997	Carpet cleaning	Carpet cleaner rubbed 10% spotting solution into fibres of carpet with ungloved fingers, and did not wash hands. Delayed burn became evident several hours later with symptoms of tingling fingers. Attended hospital, was treated with calcium gluconate gel and continued to rub it into fingertips for 24 h. No blistering occurred.
1995	Dry cleaning plant	Loose lid on container allowed 10% HF solution to drip onto user's fingers. Hands not washed as no burn noticed. Delayed burn evident several hours later, and was treated at hospital by calcium gluconate gel and subcutaneous injection. Fingers were sore and blistered next day but no ongoing problems. Hospital required advice on treatment from manufacturer.
1999	Car detailing	Product (concentration not known) splashed in face of worker. Treatment at hospital for burns to face and eyelids did not include calcium gluconate.

Table 3A.2 - Incidents involving aqueous HF in Australia reported by industry (continued)

Tuble eine	Tustiunun meruent	
Year	User	Incident details
<u> QLD – Der</u>	ot of Emergency Servi	ces - call out incident report
1993	Chemical formulator	A spill of 70% HF occurred during decanting from a 200 L drum on a forklift truck into a 20 L container on a set of industrial scales, in the process of formulation of an aluminium cleaning solution. Area was unbunded. Fire brigade was called, homes were evacuated, spill was neutralised with soda ash and taken away by council truck, area hosed down. Fumes caused discomfort and coughing. Three people taken to hospital. One observed for fume inhalation and sent home. One splashed while putting soda ash on spill, discharged after washing for 1.5 h. One treated for burns to both legs.
<u>QLD – Der</u>	ot of Employment, Tra	aining and Industrial Relations – cases prosecuted
-	Unknown	A worker involved in transferring acid from a large storage container to smaller ones by use of a siphon wiped up a spill of acid around a drum with a rag and ungloved hand. He subsequently put his gloves back on and continued working until the acid attacked his fingers. The workplace had no calcium gluconate and had not been advised by their supplier that this would be a good strategy. The worker was hospitalised. When the hospital sought more stock of antidote from the supplier it was found that the stocks of the supplier were 4 years out of date.
-	Bull bar manufacturer	A bull bar manufacturer used diluted HF for cleaning and brightening aluminium prior to polishing. The tank was approx 2.5 m x 1.5 m x 0.35 m, and contained approx $1000 - 1200$ L. Procedure was being conducted in the public parking area in front of the business located in a commercial business area with other businesses. Deemed to be a public health risk, factors including: overflow would go directly into street drain, tank was left open during the day, the lock when on invited tampering, safety signs on the tank for skin and eye protection would not be easily interpreted by the public, amount of acid used was not insignificant.
1996	Farm	A worker suffered burns to his hands after being employed cleaning aluminium and stainless steel strips inside and outside a food van, by dipping a rag into cleaning fluid containing 15% HF and wiping. No gloves were worn for the first 0.5-1 h of the work. Treatment lasted 3 months and worker had some difficulty carrying out former employment as bricklayer. Relevant factors: the lack of PPE, lack of relevant risk and safety phrases on label, inadequate training and supervision.

Year	User	Incident details	
Wester	- NICINI		
WorkCove	er NSW		

LateRestoration of bathImprovement notice issued because workers were at risk of exposure to HF in restoration of bath tubs.1990'stubs

<u>SA – Country Fire Service – Incident</u>

1993TransportLeakage of HF from a bulk road tanker occurred in an isolated area of north South Australia. Not known if
material was anhydrous or aqueous HF. Spill resulted from overfilling of tanker, allowing no room for
expansion.

WorkSafe WA - details of prosecutions under the Occupational Health Safety and Welfare Act 1984

- 1996 Laboratory An employee received burns while performing acid digestion of mineral samples. At the time of the accident the beakers were placed on hot plates to evaporate the acids and during a visual inspection the employee knocked over 3 beakers containing the acid solution. PPE worn by the employee included full length plastic apron, safety glasses, surgical rubber gloves, steel capped leather boots and a laboratory coat. The employee informed her supervisor, hosed herself down with water, took calcium tablets and applied calcium gluconate gel. The following inadequate systems of work were noted: the beakers on the hot plate not being restrained by supports; the PPE worn by the employee was inadequate in that adequate foot protection was not worn (ie rubber boots) and no sleeve protectors were worn.
- 1995 Used car dealership A trainee salesperson received burns to his hands after cleaning wheels of cars for 6 h. The employee used a hand held spray bottle which contained a cleaning solution containing 4.2% HF and 7% sulphuric acid. The employee was not provided with a MSDS or told to dilute the chemical or that it was a hazardous chemical. No PPE or calcium gluconate gel were provided.

Date	User	Incident details
WorkSafe V	WA – Significant Inci	dent Summary Reports
18/1995 (1994)	Car detailing	A car cleaner cleaning an aluminium ute tray spilled aluminium brightener on his hands, causing painful burns. The solution contained 5% HF and was applied with a spray pack that leaked the solution onto his hand. No calcium gluconate was supplied to treat the burns. PPE including gloves was not readily available. No MSDS was available and the employee was not aware of the hazardous nature of the chemical.
04/1997 (1996)	Crayfish processing factory	An employee received burns to legs, abdomen, arms, face and eye when using a metal cleaner that contained 8% HF and 8% sulfuric acid. She required emergency treatment at a hospital. Contributing factors were: lack of enough information to use the product safely – neither employer nor employee read the label, and no MSDS was obtained. There was insufficient training and supervision and inadequate or unuseable protective equipment. Also appropriate first aid treatment for HF was not provided.
18/1994 (1994)	Laboratory	A laboratory technician knocked approximately 100 mL of 70% HF onto his thighs while sitting at a fume cupboard processing mineral samples. Immediate 10% body burns ensued. Despite rapid flushing with water and emergency hospitalisation he died 15 days later. Contributing factors to the accident were found to be: failure to protect skin from exposure; failure to restrain cups of HF in secure holders; failure to apply neutralising cream; lack of emergency planning/facilities/personnel; poor work station design.
<u>Health Dep</u>	t of WA	
~ 1995	Car detailers	Have received a number of ad hoc reports from hospital accident and emergency centres of people receiving mild burns from exposure to low strength (<10%) HF. These reports seem to reflect burns from spray packs of car detailing products which have been imported illegally from overseas. Currently these reports appear to be restricted to the motor trade industry.

Year	User	Incident details
<u>WorkCover</u>	Corporation of SA -	- raw occupational injury data of claims involving HF – to 2/3/99
1997	Spraying	Repeated spraying of Isocyanate/HF without proper respiratory protection.
1996	Metal treatment	A drop of HF on hand while treating metal work resulted in acid burn.
1995	Not known.	Spilt HF and nitric acid (pickling paste) on leg resulting in burn to leg.
1997	Aluminium treatment	Preparing aluminium in acid and chrome tanks prior to painting. Although wearing gloves, skin contact with acid occurred over a period of time. As well as HF, one tank contained sulfuric acid, the other chromic and nitric acids.
1996	Not known	Welding fumes / hydrofluoric acid caused chest cough.
1997	Cleaning coils	Product containing HF and phosphoric acid was used in trigger spray bottle to clean coil of unit without gloves. Trigger leakage occurred.
NSW Poiso	ns Information Centr	e – details of phone calls received in 1996 relating to workplace exposure to HF
1996	Not known.	Aching bones in face possibly caused by chronic inhalation of HF fumes at work : advised to see GP.
1996	Not known	Splash of a mixture of HF and sulfuric acid received 3 days prior: advised to go to hospital.
1996	Not known	Exposure to HF; acid may have gone through glove.
1996	Not known	Exposure of hand to pickling paste mixture containing 5% HF and 30% nitric acid had occurred 30 minutes prior: patient in hospital.

Table 3A.3 - Australian increase information from other sources (continued)						
Date	User	Incident details				
Tasmania Department of Health and Human Services						
1991	Not known	The Workplace Standards Authority report one recorded claim lodged relating to HF burn.				
Anecdotal	incidents reported in	unpublished study (Soroczynski, 2000)				
-	Soft drink manufacturer	A 200 L drum of descaling agent containing an unknown amount of HF was purchased from a 'back yard' cleaning chemical manufacturer. The drum exploded, blowing the bung out of the drum and a substantial amount of the product was sprayed around the area, causing property damage, including etched glass windows. Response to the incident was delayed while staff and emergency services tried to determine the contents of the drum.				
-	Cleaning contractors	Two cleaning contractors used a product containing 10% HF to clean an empty swimming pool. They used household dishwashing type gloves and no other protective equipment. Dermal exposure occurred through holes in the gloves, no calcium gluconate was available. Both men required hospitalisation for a number of days.				
-	Cleaning contractor	A contractor was etching the floor of an aluminium shipping container with an unknown concentration of HF, and complained to a chemist that his respirator was not working as he could smell the fumes. The chemist found the respirator had a cartridge approved for organic vapour.				
Austin and Repatriation Medical Centre						
-	Car dealership	A 35 year old male car dealer presented to an emergency room 24 h after a HF burn. He had used a mag wheel cleaner containing 8% HF to remove rust and had not been wearing any protective gloves because he was not aware of the potential hazard of HF. He did not receive any first aid and presented to his doctor because of pain and tingling in his fingers.				

Date	User	Incident details				
Case report: (Isbister, 2000)						
2000	Cleaning	Man's right hand and fingers burnt after using cleaning product with 4% HF and 20% H ₂ SO ₄ . Hospitalised for 5 days.				
MHIDAS Database						
1996	Transport (in Western Australia)	A trailer with 4 x 205 L drums of nitric acid and 4 cases with 6 x 500 mL bottles of hydrofluoric acid rolled over, releasing some nitric acid. Goods were in approved packaging and were secured as required. Death of driver contributed to delays in identifying chemical.				
1988	Fertiliser manufacture	Hydrogen fluoride fumes were released from the acidulation/grinding unit on changeover to a new type of starting material. Two workers were hospitalised and 20 treated on site for gas inhalation.				

Appendix 4

Health Effects of Dermal/Ocular Exposure To HF

Animal Studies

Animal	Method	Concentration	Time of	Total Quantity or Exposure	Health effects	Reference
Dermal Studies:						
Rabbit	Solutions of HF applied to shaved rabbit ear for 5 min, then washed off for 15 min.	1-50%	5 min	3 drops	 1, 2 or 4%, no reaction; 6, 8, or 10%, transitory blanching; 12, 15, 18 and 22%, crust formation in about 24 hrs, which disappeared in about a week; 25, 30%, blanching, redness, crust formation; 35, 40%, blister formation, superficial ulceration; 50%, deep ulceration. 	Klauder et al., 1955.
Rabbit	0.5 g of solid mixture of 85% sodium bisulfate, 13% sodium bifluoride and sodium chloride was dissolved in 0.2 mL water and applied to intact and abraded skin. A similar solution of sodium bisulfate was also tested.		24 h	0.7 g of mixture	 Abraded skin: severe necrosis, (skin completely destroyed); severe to mild edema. For sodium bisulfate, severe necrosis in scratches only, mild edema. Intact skin: severe to mild necrosis, mild to barely perceptible edema. For sodium bisulfate, mild erythema, barely perceptible, to no edema. 	E.I.Dupont de Nemours & Co, 1973.

Animal studies (continued)

Animal	Method	Concentration	Time of	Total Quantity	Health effects	Reference
			exposure	or Exposure		
Dermal Studie	es (cont.):					
Rats (male)	0.5 mL HF applied to lateral side of right thigh, and wiped off after 5 min. Air flow controlled so that HF could not be inhaled.	50%	5 min	Approx. 1.7% of body surface area (BSA).	Increases in ionised fluoride and decreases in total and ionised calcium were observed in sera within 30 minutes of treatment, and 80% of animals died within 24 h.	Kono et al., 1982.
Rabbit	a) Solutions applied to backs and occluded. Rinsed by swabbing after exposure period.	2%	1 h, 4 h	2 mL/kg applied	1 h, necrotic lesions of skin observed. Raised fluoride serum levels, but no symptoms of toxicity.4 h, as for 1 h group, but average number and size of lesions greater, serum fluoride higher. Reduction in weight of testes.	Derelanko et al., 1985.
	b) Solutions applied to backs and occluded. Rinsed by showering for 30 seconds after exposure period.	0.01% to 2%	1 min to 60 min.	2 mL/kg applied	0.01% and above caused visible lesions with exposure times of 5 min and above.2% non-corrosive with exposure time of 1 min. Longer exposure times produced lesions.Serum fluoride levels not reported.	

Animal studies (continued)

Animal	Method	Concentration	Time of	Total Quantity	Health effects	Reference
			exposure	or Exposure		
Dermal Studies (cont.):						
Rats	Solution applied to backs. Rinsed off with a continuous 5-minute wash.	70%	60 seconds	50 µl	Severe damage of the skin (erythema. edema, blistering and coagulative necrosis down to the dermal muscular junction). Wound healed over 35-56 d.	Bracken et al., 1985.
Rabbit	Solution applied to backs with semi- occlusive patch. Washed after exposure period. OECD Guideline 404 used	5%	4 h	5 mL	Marked eschar production and destruction of the underlying tissue observed 24 h after application. Lesions did not recover after 14 d.	Bayer, 1990, as cited in OECD 1999.
Ocular Study						
Rabbit (Ocular)	Experimental splash burn to eyes. Washing protocol not stated.	0.5%, 2%, 8%, 20%	Not stated	Not stated	 0.5%: recovery in 10 days 2%: mild persistent stromal edema and vascularization 8%: ischemia and corneal stromal edema persisting for 40-65 days, with corneal vascularization. 20%: immediate damage with total corneal opacification with conjunctival ischemia, and with corneal stromal edema within an hour, followed by necrosis of anterior ocular structures. 	McCulley et al., 1983, as cited in Grant & Schuman, 1986.

 $\overline{BSA} - Body$ surface area

HF **Conditions of exposure** Area of body Treatment Effect Reference concentration Dermal: During laboratory synthesis Second and third degree burns were 100% Estimated exposure Patient was treated on the spot, Burke et al.. of fluoroborate salt, was 5 g HF and and taken to hospital where eventually treated by plastic surgery. In 1973. connecting tube burst, and HF 2.5% BSA. burns were treated with calcium addition to these, renal abnormalities. severe nausea and stupor in the first days spilt on technician. including the right gluconate side of face. neck after exposure appeared to be due to and forearm. systemic effects of fluoride. 100% 49-year old male exposed to Patient taken to hospital and Burns caused a deep wound. Patient Approx. 5% BSA Sheridan et al.. HF in industrial accident. calcium gluconate injected into survived and recovered well. affected, primarily 1995. the lower abdomen subcutaneous tissue beneath the and right thigh. wound. The wound was excised. and later grafted. 100% 37-year old exposed to HF in 25% BSA Patient was showered in Sheridan et al., At first emergency room patient was workplace accident. noted to have conjunctival injection and exposure, primarily workplace and treated in hospital 1995. emergency room with topical mild respiratory distress, but was upper arms and calcium gluconate gel. otherwise alert and stable. On arrival at torso. Transferred to another hospital second hospital he was hypotensive and where calcium and magnesium in severe respiratory distress. Then he were replaced during cardiac suffered cardiac arrest and could not be arrest. resuscitated.

Case reports of dermal/ocular exposure to HF

HF	Conditions of exposure	Area of body	Treatment	Effect	Reference
concentration					
Dermal (cont.)	:				
100%	Petroleum refinery worker splashed while trying to remove a plug during a shutdown.	2.5% approx BSA exposure, primarily to face. Inhalation may also have occurred.	Degree of rinsing after spill not determined. Specific HF treatment with calcium gluconate started more than 1½ h after exposure.	The spill resulted in third degree skin burns, profound hypocalcaemia, hypomagnesemia and ventricular fibrillation which led to death 10 h after exposure.	Tepperman, 1980.
70%	Man exposed as a result of spill.	8% BSA burns to right leg.	Leg immediately rinsed with tap water for 15 min. Treated in local and later major hospital. Intravenous calcium given some hours after injury, and calcium levels were stabilised 10 h after injury.	Experienced extreme pain immediately. Several episodes of ventricular fibrillation occurred, resulting in death 15.5 h after injury.	Mullett et al., 1987.
70%	Details not reported.	25% BSA burns	Not reported.	Patient had dermal burns, severe hypocalcaemia, and died in cardiac arrest.	El Saadi et al., 1989.
70%	Metal process worker exposed to HF.	22% BSA burns, to scalp, neck, shoulders, anterior aspect of the torso, and both thighs and hands.	Patient showered immediately, had calcium gluconate gel applied to burns, and was taken to hospital. Intravenous fluids given, and calcium administered both intravenously and beneath the eschar (hard scab of burn). Hypercalcaemia occurred and was treated.	Two hours after injury the patient was hypocalcaemic and required ventilatory support, which continued for 3 d. Was discharged 27 d after injury.	Greco et al., 1988.

Case reports of dermal/ocular exposure to HF (continued)
HF	Conditions of exposure	Area of body	Treatment	Effect	Reference
concentration					
Dermal (cont.):					
70%	Laboratory technician performing acid digestion of mineral samples was splashed when 70% HF was spilt.	Both thighs burnt when acid dropped on lap. Estimated BSA 9%. Estimated spill 100-230 mL.	Washed with water and in swimming pool. Ambulance attended after 35-40 min, and transferred to hospital for treatment.	Initially severe pain and shock. Patient was hypothermic and hypocalcaemic on admission to intensive care unit of hospital. Despite treatment, patient died from multi-organ failure 15 d after exposure.	WorkSafe Western Australia, 1998a, Muriale et al, 1996.
70%	23-year old man burnt in HF solution spill.	9-10% BSA burn to both thighs.	Not reported	Fatal systemic fluorosis characterised by hypocalcaemia and ventricular arrhythmia. Post-mortem examination demonstrated extensive acute myocardial necrosis.	Mayer & Gross, 1985, as cited in Kirkpatrick 1985.
70%	Sanitation worker splashed and exposed to HF via fumes when plastic HF container burst during compaction.	Face and hands, plus inhalation.	Not reported.	Died in emergency room later on the day of exposure.	Greenberg, 1999; Van Gelder, 1996.
70% (assumed)	Laboratory worker burnt when beakers containing acid digestion mixture (with HF) were spilt.	Foot.	Worker hosed herself with water, took calcium tablets, and applied calcium gluconate gel. Was admitted to hospital.	Severe pain felt on foot. Was absent from work for one month.	Worksafe WA, 1996. (unpublished information).

HF	Conditions of exposure	Area of body	Treatment	Effect	Reference
concentration					
Dermal (cont.):					
60%	Pipefitter at oil refinery exposed to HF.	2.5% BSA, involving right side of face, ear and neck.	Admitted to hospital, and received calcium intravenously and below the eschar (scab at burn site).	Initially expectorated clear solutions but electrocardiogram was normal. Further pulmonary and abdominal symptoms developed and patient required ventilatory support for 2 days. Discharged from hospital 24 days after injury.	Greco et al., 1988.
48%	Two patients, details not reported.	No details reported.	Not reported.	Dermal burns but no systemic toxicity.	El Saadi et al., 1989.
30%	Patient exposed when tanker truck exploded.	44% BSA exposed.	Patient given cold shower immediately and admitted to hospital. Calcium gluconate given intravenously with dopamine infusion.	At hospital admission patient was alert but in extreme pain. Dyspnea occurred 2 h after exposure and several episodes of ventricular tachycardia and ventricular fibrillation occurred 5 h after exposure, requiring cardioversion. Patient survived and was discharged 78 d after injury.	Yamaura & et al, 1997.
18%	20-year old male working with an aluminium cleaner which penetrated his gloves.	Fingertips	Initially soaked hands in iced Epsom salts. Treated by hospital emergency room, where product was first thought to be hydrochloric acid, and later by family physician.	Chief symptom was painful erythematous fingertips. No symptoms remained 20 d after exposure.	Jordan, 1982.

HF	Conditions of exposure	Area of body	Treatment	Effect	Reference
concentration					
Dermal (cont.):					
15% HF 7.5% H ₂ SO ₄	Cleaned aluminium and stainless steel strips on van without gloves for 1½ h, and for a further ½ h with food grade gloves.	Fingers and both hands.	Exact details not given. It is likely that hands were washed with water at time injury noticed, and that hospital treatment involved calcium gluconate.	Stinging sensation at end of fingers was noticed after 1½ h and progressed to feeling that hands were on fire. Skin discoloured to reddish-brown. Treatment sought at hospital and was required every 2 d for 3 months. Worker had difficulty carrying out normal occupation as bricklayer.	Queensland. Department of Employment, Training and Industrial Relations 1999.
15%	Technician cleaning oxidation from silver soldering on a copper component was exposed through pinhole in rubber glove. Cotton liners underneath held the solution in contact with skin. Solution used for 1 h.	Fingers and hand.	Only normal washing carried out at completion of task. Burn not detected until 8 h after task completed. Treatment commenced 24 h after exposure, and calcium gluconate later injected into burned area.	Burning sensation and whitening of skin occurred 8 h after exposure. Pain increased over the next day. Three months after exposure, hand was still swollen and had reduced use and dexterity of fingers. Seven months after exposure, dexterity had returned but some swelling remained. Minor scarring remained.	Stencil & Tobin, 1987.
12%	27-year old male worked with HF for several hours without gloves	Fingers and hands.	Treatment was sought on 3 occasions, and fingernails were removed on third visit. Magnesium compound soaks and dressings were continued for 3 d.	Initial symptom was pain only, in both hands but concentrated in fingertips. Approx 14 h after exposure, the hands were painful, edematous and erythematous. Symptoms resolved by 2 weeks after exposure.	Jordan, 1982

HF	Conditions of exposure	Area of body	Treatment	Effect	Reference
concentration					
Dermal (cont.)	•				
13% or <13% (summary of 156 cases)	Dermal exposures to rust removers via secondary burns from treated clothing. Cases were reported to a USA Poisons Centre over a 1 y period, and represent 25% of total HF cases during that period. In 24% of secondary burns, clothing was washed or rinsed before use, and in 34% of cases it was machine- washed. Mean exposure time was 5 h, range 0.1-12 h.	Mean BSA burn was 2.3%, range 1- 18%.	Only 5 patients admitted to hospital (mean stay 1.7 d). Topical treatment with calcium compounds used in 79.5% of cases, and irrigation in 20.5% of cases.	Symptoms included erythema (97.4%), pain (87.2%) and blistering (31.4%). Complaints persisted for a mean of 5.6 days (range 1-90 days.	Phillips et al., 1991(a).
6% to 11% (summary of 237 cases)	Dermal exposures to rust removers, reported to a USA Poisons Centre in 1986. The majority of exposures $(\geq 64\%)$ occurred in the home.	Fingers affected in 72% of cases. Highest BSA reported (3-4% and 8-10%) were in 2 children who mistakenly used a solution as a sun tan lotion.	Topical calcium gluconate gel used in 49% of patients, and early initial application appeared to hasten recovery. Subcutaneous calcium gluconate injection used in one patient.	No systemic toxicity was reported, even with the largest BSA exposures. Reported symptoms included dermal swelling, redness, blistering, blackish discoloration under fingernail, pain without dermal changes. Onset of symptoms delayed by ½ h to more than 24 h after exposure. Complications of infection or fingertip dermal necrosis occurred in a small number of cases.	El Saadi et al., 1989.

HF	Conditions of exposure	Area of body	Treatment	Effect	Reference
concentration					
Dermal (cont.):					
10%	HF solution used to clean heavy equipment, splashed on gloves and forearm of worker who was filling a garden sprayer with it.	Hand and forearm (assumed).	Treatment sought on the evening of the exposure because of pain.	Hand and forearm started to ache on evening of exposure, and pain intensified. Tissue and bones of hand had been damaged, and part of hand was amputated.	Oregon OSHA, 1999.
10%	HF spilt on fingers from stopper of bottle, while removing rust stains from sweaters.	Fingers.	Not known when HF rinsed from skin. Calcium gluconate treatment started after 4 days.	1 h after use, fingers became red and swollen, and later marble-white. The pain became increasingly severe overnight and for several days until treatment. Complete healing occurred after 1 month, with slight scar formation.	Klauder et al., 1955.
10%	Leaking stain remover spilt on fingers and not washed off.	Fingers.	Symptoms occurred several hours later and were treated at hospital by subcutaneous injection of calcium gluconate, followed by calcium gluconate gel.	Fingers were sore and blistered the next day but there were no ongoing problems with the hand.	Orica, 1999.
10%	Carpet cleaner used product without gloves for short time, and did not wash off.	Fingers.	Symptoms occurred several hours later and were treated at hospital with calcium gluconate gel for 24 h.	No blisters developed.	Orica, 1999.

HF concentration	Conditions of exposure	Area of body	Treatment	Effect	Reference
Dermal:					
7-10%	Woman exposed to Whink Rust Stain Remover for 8 h.	Not stated.	Medical treatment delayed for 24 h. Initial treatment not specified. Physical therapy and systemic anti-inflammatory agents required.	Developed a flexion contracture of the index finger, and could not resume work for 2 weeks. Other exposures to this product, via wet rags in contact with hands or wrists, has led to flexor contractions of the hand, and in some cases a carpal tunnel-like syndrome.	Edelman, 1986.
9.8%	Used rust remover without gloves for 15 min.	Three fingers.	Treated for 3 days in hospital intensive care with intravenous calcium gluconate. After discharge, calcium gluconate gel was used to give relief.	1 h after use, three fingers were burning, and the pain later rose to the shoulder. Admitted to hospital with severe pain, which was not relieved by intravenous morphine. Three finger nails lost.	Warland-Brown, 1997.
8%	Service station manager had used unlabelled preparation to clean aluminium wheels of his car.	Right hand and fingers.	Treatment for acute irritant contact dermatitis and infection started 24 h after exposure. Treatment did not include calcium gluconate. Not known when HF rinsed from skin.	Pain, considerable oedema of right hand, erythema affecting the fingers and thumb and a pustule on the right middle finger 24 h after exposure. Dermatitis cleared within 7 d of treatment.	Apted, 1997.

HF	Conditions of exposure	Area of body	Treatment	Effect	Reference
concentration					
Dermal (cont.):					
8% HF 23% HCl	14-month old boy spilt rust remover on himself from a bottle.	11% BSA affected, comprising both anterior thighs and knees, and the right scapular region.	Taken to hospital immediately. Treatment included mechanical ventilation, intravenous calcium supplementation, local treatment of burns. Skin grafts carried out on third day.	On arrival at hospital, patient was lethargic, with systolic blood pressure of 60 mm Hg and heart rate of 140 /minute. During the period 4-6 h after exposure, 5 episodes of ventricular fibrillation were successfully treated. Required mechanical ventilation till 16 th day, and was discharged from hospital on 19 th day. One month after exposure, grafted burn wounds were healing normally.	Bordelon, 1993 Worksafe 56.
8% HF 8% H ₂ SO ₄	Worker in crayfish processing factory burnt while using metal cleaner in undiluted form.	Legs, abdomen, arms, face, eye.	Did not apply first aid when acid first contacted skin. Required emergency treatment at hospital. No further details given.	Painful burns. No further information given.	WorkSafe Western Australia, 1997a.
5%	40-year old male carpet layer had used rust remover without gloves.	Fingers of left hand.	Treatment by soaking hand in calcium gluconate commenced 48 hrs after exposure, and continued for a further 24 h.	Main symptom 48 h after exposure was unremitting pain in fingertips, which was alleviated by calcium gluconate soak. Tissue changes were later evident, and soft- tissue irregularity in the small finger persisted 9 m later.	Lukinuk et al., 1997.
5%	Car cleaner who was cleaning aluminium ute tray was exposed when solution leaked from the spray pack.	Hand.	First aid not applied immediately. No further details.	Painful burns. No further details given.	WorkSafe Western Australia, 1995.

Case reports of dermal/ocular exposure to HF (continued)

HF	Conditions of exposure	Area of body	Treatment	Effect	Reference
concentration					
Dermal (cont.):					
4.2% HF 7% H ₂ SO ₄	Employee of used car lot cleaned car wheels for 6 h without PPE.	Hands.	Calcium gluconate gel not available at workplace. No further details of treatment.	Chemical burns to hands. No further details provided.	WorkSafe Western Australia, 1997b.
4% HF 20% H ₂ SO ₄	Man (26 y) exposed while using cleaning solution.	Right hand, primarily fingers.	Initially treated with analgesic at clinic and at hospital 5 h later with intravenous and topical calcium gluconate, and later Bier block. Fingernails removed.	Used solution for 2 h before tingling occurred, which progressed to severe pain over 1 h. Treatment did not resolve pain and intramuscular analgesic needed for 72 h. Discharged from hospital after 5 days.	Isbister, 2000.
10% ammonium bifluoride and 27.5% phosphoric acid (H ₃ PO ₄)	Exposed when used solution to clean aluminium window frames for 4-5 h without gloves.	Fingers.	Treatment with diuretics and prednisone tablets commenced 24 h after exposure.	Fingers began to tingle 2 h after exposure started. They became painful that evening, with swelling during the night. Gross oedema and reduced sensation of the fingers, which disappeared within 4 d, were noted after 24 h, but no skin lesions. Some nails were lost after 4-6 weeks, but re-grew normally.	Pedersen, 1980.
2%	63-year old man used metal cleaner with a cloth, and without gloves.	Hands.	Treatment probably sought approx. 20 h after exposure, and involved application of calcium gluconate gel dressings every 2 h.	One hour after exposure, patient developed a burning sensation in his palms, and associated deep bone pain, which intensified over the next 20 h. Treatment resolved symptoms rapidly.	Smith, 1992.

Case reports of dermal/ocular exposure to HF (continued)

HF	Conditions of exposure	Area of body	Treatment	Effect	Reference
concentration					
Dermal (cont.)	:				
Not stated	15-year old boy was mixing aluminium rim cleaning solution for use in a spray machine, and splashed undiluted product on the back of his pant leg.	Spill affected back of leg.	Patient initially washed pant leg and boots with water. Irritation was felt after 1 h and leg rinsed with soap and water. After pain worsened, patient was taken to hospital.	Seven hours after exposure, patient was found to have significant deep tissue HF burn, and underwent 13 separate grafting surgeries. He was not able to attend school for 1 y, and has limited use of right leg.	Bureau of National Affairs, 1998.
Ocular:					
13% or < 13%	Review of 8 ocular exposures to HF during 1990. Total HF cases during this time was 619.7/8 exposures were due to splashes.	One eye only affected in 6/7 splashes.	Home irrigation was carried out in all cases, and was followed up by emergency dept irrigation of 10-30 m. Antibiotics were also used in 2/8 and steroids in 1/8.	All patients reported pain, 7 developed conjunctivitis, and 1 suffered transient corneal clouding.	Phillips et al., 1991(b).

BSA – Body surface area

Appendix 5



HYDROFLUORIC ACID (HYDROGEN FLUORIDE) QUESTIONNAIRE

Who should complete this questionnaire?

This questionnaire is relevant to anyone who imports, manufactures, buys, repacks, re-sells, formulates or uses hydrofluoric acid or products containing hydrofluoric acid. For common uses of this chemical, see list on page 7.

The last section of the questionnaire (Section H) also asks about your use of some other fluoride chemicals.

Hydrofluoric acid is also known as hydrogen fluoride or HF, and its Chemical Abstracts Service Number (CAS Number) is 7664-39-3.

Please complete each section of this questionnaire which is relevant to you and return it by Wednesday 23rd December, 1998 (with the MSDS and labels requested) to:

HF Survey NICNAS - Existing Chemicals
GPO Box 58
Sydney NSW 2001

If you have any queries about the questionnaire or any of the questions, please contact:

Rosemary Sager	Phone 02 9577 9476
	Fax: 02 9577 9465
	Email: sagerr@worksafe.gov.au

Company Information

_Fax:

Hfaues6.doc 12/11/98

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Please answer this sect fluoride, or if it is produ as they are covered in c	tion if y ced in other s	ou ma cident ection	anufacture hydrofluoric acid or hydrogen ally. (Do not count dilution or formulation steps s.)
A1. Do you manufactu Yes	re hydr	ofluori	c acid (hydrogen fluoride) in a deliberate process? No
If yes, please give quanti	ty and o	details	if applicable (kg/per annum)
	-		
	-		
A2. Is hydrofluoric acid	d (hydro	ogen flu	uoride) incidentally produced as part of another
process?			Ne
res			
If yes, please give quantit	ty and o	details	if applicable (kg/per annum)
(Please include disposal deta	ls for this	s materi	al in Part G)
(Please include disposal deta	ls for this	s materi	al in Part G)
(Please include disposal deta Part B: Purchase In	ils for this forma	s materi tion	al in Part G)
(Please include disposal deta Part B: Purchase In Please answer this sect contains hydrofluoric a or products/mixtures co Please tick applicable b than one product, please	forma forma tion if y cid. Th ontaini poxes a se attac	s materi tion you bu nis inc ng HF, and fill ch sep	al in Part G) by hydrofluoric acid or any material which ludes dilute or concentrated solutions, HF gas in details as appropriate. (If you have more arate sheet.)
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(Please include disposal deta Part B: Purchase In Please answer this sect contains hydrofluoric a or products/mixtures co Please tick applicable k than one product, pleas B1. What HF-containir if necessary) Hydrofluoric acid (HF solution)	forma forma tion if y cid. Th ontaini ooxes a se attac ng mate	s materi tion you bu nis inc ng HF. and fill ch sep erial do No	al in Part G) y hydrofluoric acid or any material which ludes dilute or concentrated solutions, HF gas in details as appropriate. (If you have more arate sheet.) you buy? Please give details. (Attach extra shee Strength (percentage) Quantity (kg per month) Pack type and size
(Please include disposal deta Part B: Purchase In Please answer this sect contains hydrofluoric a or products/mixtures co Please tick applicable b than one product, pleas B1. What HF-containir if necessary) Hydrofluoric acid (HF solution)	Is for this forma tion if y cid. TI ontaini poxes a se attac ng mate Yes	s materi tion you bu nis inc ng HF. and fill ch sep erial do No	al in Part G) by hydrofluoric acid or any material which ludes dilute or concentrated solutions, HF gas in details as appropriate. (If you have more arate sheet.) by you buy? Please give details. (Attach extra sheet Strength (percentage) Quantity (kg per month) Pack type and size
(Please include disposal deta Part B: Purchase In Please answer this sect contains hydrofluoric a or products/mixtures co Please tick applicable b than one product, pleas B1. What HF-containir if necessary) Hydrofluoric acid (HF solution) HF gas (bydrogen fluoride gas)	Is for this forma tion if y cid. Th potaini poxes a se attac ng mate Yes	s materi tion you bu nis inc ng HF. and fill ch sep erial do No	al in Part G) by hydrofluoric acid or any material which ludes dilute or concentrated solutions, HF gas in details as appropriate. (If you have more arate sheet.) you buy? Please give details. (Attach extra sheet Strength (percentage) Quantity (kg per month) Pack type and size Quantity (kg per month) Pack type and size
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(Please include disposal deta Part B: Purchase In Please answer this sect contains hydrofluoric a or products/mixtures co Please tick applicable b than one product, pleas B1. What HF-containir if necessary) Hydrofluoric acid (HF solution) HF gas (hydrogen fluoride gas)	Is for this	s materi tion you bunis inc ng HF. and fill ch sep erial do No	al in Part G) Ty hydrofluoric acid or any material which Iudes dilute or concentrated solutions, HF gas in details as appropriate. (If you have more arate sheet.) you buy? Please give details. (Attach extra sheet Strength (percentage)

Part A:	Manufacture	Information
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Please answer this section if you manufacture hydrofluoric acid or hydrogen fluoride, or if it is produced incidentally. (Do not count dilution or formulation steps, as they are covered in other sections.)

A1. Do you manufacture hydrofluoric acid (hydrogen fluoride) in a deliberate process? Yes No

			· · · · ·		
If yes, please give	quantity and	details if applica	able (kg/per	annum)	

A2. Is hydrofluoric acid (hydrogen fluoride) incidentally produced as part of another process?

Y	íes 🛛	No
[]	
lf yes, please give qu	antity and details if applica	able (kg/per annum)

(Please include disposal details for this material in Part G)

Part B: Purchase Information

Please answer this section if you buy hydrofluoric acid or any material which contains hydrofluoric acid. This includes dilute or concentrated solutions, HF gas, or products/mixtures containing HF.

Please tick applicable boxes and fill in details as appropriate. (If you have more than one product, please attach separate sheet.)

B1. What HF-containing material do you buy? Please give details. (Attach extra sheet if necessary)

Hydrofluoric acid (HF solution)	Yes	No	Strength (percentage) Quantity (kg per month) Pack type and size
HF gas (hydrogen fluoride gas)			Quantity (kg per month) Pack type and size

B5. If you re-sell HF or HF products, what aspects of "product stewardship" do you practice? (These include precautions and guidance to customers which will help them to use the material safely)

Part C: Questions for re-sellers and re-packers of hydrofluoric acid or products containing hydrofluoric acid.

If you simply re-sell or repack hydrofluoric acid or products containing hydrofluoric acid, please provide the following details. (Do not include details of products that you formulate in this section. These are covered in Part D.)

Product Name	% HF	Typical end use	Available to public? (eg factory door, retail sales)	Annual sales volume of product

C1. Please give details of the products that you re-sell:

Please supply copies of <u>MSDS</u> and <u>labels</u> for these products

C2. If you repackage HF or HF products to re-sell, briefly describe the repackaging process.

C3. Please give details of the original and final pack size and type, including type of closure (cap or dispenser).

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C4. Please provide a complete list of contact details of your customers to whom you sell hydrofluoric acid or products containing hydrofluoric acid. This information will be **kept confidential, and used only to send questionnaires to these customers**. Attach separate list if needed.

C5. Do any of the HF products that you re-sell contain other fluorides? eg sodium, potassium or ammonium fluoride or bifluoride, hydrosilicofluoric acid, silicofluoride salts. Please give details, including identity and concentrations used:

(Section H covers fluoride chemicals which are not in HF formulations)

Part D: Questions for Formulators

If you formulate products containing HF, either for your own use or for re-sale, please answer the following questions. Simple dilution is also counted as formulation.

D1. Please provide the following details for products you formulate:

Product Name	Typical end uses	% HF	Product resold Yes/No	Annual sales volume.	Size and type of package, type of closure	Available to public? (eg retail, factory-door sales)

Please supply copies of the <u>MSDS</u> and <u>labels</u> for these products.

D2. Please describe each step of your formulating process and filling process.

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D3. Please provide a complete list of contact details of your customers to whom you sell the hydrofluoric acid products that you formulate. This information will be kept confidential, and used only to send questionnaires to these customers. Attach separate list if needed.

D4. Do any of the HF-containing products that you formulate contain other fluorides? eg sodium, potassium or ammonium fluoride or bifluoride, hydrosilicofluoric acid, silicofluoride salts, fluoroboric acid. Please give details, including name of product, fluoride used, and concentrations of fluoride used:

(Section H covers fluoride chemicals which are not in HF formulations)

Part E: Questions for users of hydrofluoric acid or products containing hydrofluoric acid

E1. Please indicate the sector of industry in which you operate eg metal processing, research and development, mining etc:

E2.	In wha	at process or processes do you use HF or products containing HF?
		Metal preparation or pickling
		Glass etching or frosting
		Ceramic/stone etching or anti-slip treatments (please specify)
		Chemical synthesis
		Laboratory processes (please specify)
		Cleaning, brightening or polishing of aluminium, stainless steel or other metal (please specify)
	_	
		Cleaning of brick, stone etc (please specify)
		Rust or stain removal in dry cleaning, laundering or carpet cleaning (please specify)
		Use as catalyst
		Other (please specify)

E3. Briefly describe how you use HF/HF products (an example for one application might be: We use "Banish" to wash graffiti from external walls. Product is applied with a squeegee, and when a 5 sq. metre area is done, it is washed off with water from a hose. Difficult areas are retreated and scrubbed with a plastic scourer)

E4. What quantity do you use per month (kg)?

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Part F: Workplace Exposure

Questions for formulators, users and repackagers of hydrofluoric acid and products containing hydrofluoric acid.

- F1. Are the processes you employ:
 - Open (eg use of HF in manual cleaning process)
 - Partially closed (eg covered tanks, hydrofluoric acid added by workers manually to tanks)
 - Closed (fully sealed process including automated addition of hydrofluoric acid to tanks)

Please supply details _____

 \square

F2. When HF or HF-containing product is transferred from one container to another, how is this done? Describe the method used and any precautions._____

F3. Please describe the skill level, number and activities of workers using HF or HF products.

Classification/ skill level	Num- ber	Description of Work	Hrs/day	Days/yr
			· ····-	

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F4. Please describe the engineering controls that are in place to reduce exposure of workers to HF (eg exhaust ventilation, barrier screens)

Engineering Controls
-

F5. Please give details of the personal protective equipment used by workers. (eg type of gloves, goggles, other protective clothing. Please state type of materia grade and manufacturer if possible).

Process/Activity	Personal Protective Equipment

F6. Please list any additional precautions taken to reduce exposure of workers to HF (eg limited access to area where used, detailed procedures to be followed, special labelling or placarding, special training).

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F11.	What calcium gluconate products do you have available for first aid?
F12.	Where are these calcium gluconate first aid products kept?
F14.	Is the hydrofluoric acid or product containing hydrofluoric acid ever held in an unlabelled container eg bucket. Please give details
F15.	Are members of the public ever nearby when HF or HF products are being used o processed (eg work in homes, buildings, streets)? If so, what precautions are taken to avoid public exposure.

Part G: Environmental Effects

Questions for all respondents------

G1. Please estimate the percentage of hydrofluoric acid lost to the atmosphere from your process or during use.

Process or end use	% lost to atmosphere

G2. What forms of <u>liquid</u> or <u>solid</u> waste do you generate which contain hydrofluoric acid? eg residues from drums, rinse water from cleaned articles. Please estimate the quantity of waste generated, and the likely concentration of hydrofluoric acid in this waste.

G3. What methods do you use to dispose of hydrofluoric acid waste?

METHOD	AMOUNT (KG/MONTH)	STRENGTH OR % HF
Commercial contractor		
Neutralisation		
Venting to atmosphere		· · · · · · · · · · · · · · · · · · ·
Scrubbing		
Discharge to soil		
Discharge to water (please give		
details eg stormwater, sewer)		
Other (please give details)		

G4. Apart from the material mentioned above, please give details of any discharges of hydrofluoric acid to land, water or air? eg accidental spills

G5. Please describe any procedures for cleaning of equipment which may generate HF waste. Include details of how residues are collected and disposed of. _____

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G6.	Please indicate how	you handle empty containers.
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□ Rinse and/or re-use □

Return to supplier

Send to landfill

- Sell to drum recycler
- Other (please specify) _____

Part H: Other fluoride chemicals

This section covers fluoride chemicals OTHER THAN hydrofluoric acid.

H1. Do you manufacture, buy, sell or use any of the following fluoride chemicals, or products containing these chemicals?

Π

	Yes	No
Sodium fluoride (CAS No 7681-49-4)		
Sodium bifluoride (CAS No 1333-83-1)		
Ammonium fluoride (CAS No 12125-01-8)		
Ammonium bifluoride (CAS No 1341-49-7)		
Potassium fluoride (CAS No 7789-23-3		
Potassium bifluoride (CAS No 7789-29-9)		
Sodium fluosilicate (CAS No 16893-85-9)		
Hydrofluorosilicic acid (CAS No 16961-83-4)		
Fluoroboric acid (CAS No 16872-11-0)		
Other inorganic fluoride chemicals (please specify name and	d CAS numbe	r)

Thank you for responding to this questionnaire

Please return it to the address on page 1, along with: <u>MSDS</u>, <u>labels</u> and <u>customer list</u> if appropriate.

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Appendix 6

SIDS INITIAL ASSESSMENT PROFILE

CAS No.	7664-39-3	
Chemical Name	Hydrogen fluoride	
Structural formula	H-F	
RECOMMENDATION		
The chemical is a candidate for further work.		
SUMMARY CONCLUSIONS OF THE SIAR		
Human Health Hazards		
In the data set for HF animal as w toxicity, mutagenicity and carcin- been taken into account, since th	ell as human studies were available. With respect to reproduction ogenicity data from studies carried out with sodium fluoride have ese studies provide insight in the possible hazard of fluoride and	

HF is very toxic by inhalation, in contact with skin and if swallowed.

thus HF as has been explained in the sections on toxicokinetics.

When applied to skin and eye HF produces severe lesions, even at low concentrations. The substance is considered corrosive.

Sensitisation studies with HF are not available. It was agreed that HF and F- are not expected to react with proteins and therefore it is assumed that the substance has no sensitising properties.

Signs of acute fluoride intoxication in humans resemble those observed in animals. Dermal contact with HF either as liquid or as gas produces severe dermal lesions. Dermal contact with HF may result in systemic (cardiac) effects including death. Inhalatory exposure is highly damaging to the respiratory tract. Exposure to HF in a concentration of 1.16 mg/m³ will possibly result in some irritation. Prolonged oral intake of excess fluoride results in skeletal fluorosis, an effect for which indications were also found after inhalatory exposure. The available animal data set for HF permits the derivation of a NOAEL for repeated subchronic inhalatory exposure. No suitable studies are available to derive a NOAEL for HF for other routes of exposure. In a study with rats, changes in body and organ weights as well as haematological and clinical signs and death were seen at actual concentrations of 7.52 mg/m³; 6 hr/d; 5 d/w for 90 days. This value is equal to a duration corrected value (DCV) of 1340 μ g/m³. Based on actual exposure levels a NOAEL of 0.72 mg/m³ is established. Because at higher dose levels apart from irritation also systemic effects occur, a duration corrected equivalent of this NOAEL is calculated. This duration corrected value (NOAEL) amounts to 128 μ g/m³.

In epidemiological studies with workers exposed to 0.48 mg total fluoride/m³ (of which 0.2 mg gaseous fluoride) no fluorosis was observed. This level can be considered as an inhalatory NOAEL for fluoride in humans. At this level slight respiratory effects were observed, but these effects were not attributable to HF, because simultaneously, exposure to other air-way irritants occurred.

It is concluded that fluoride does not induce chromosomal damage *in vivo*. However, genetic damage is observed in *in vitro* studies. Carcinogenic studies with HF are not available. From studies with sodium fluoride in rats and mice it is concluded that fluoride is not considered to be carcinogenic in animals.

Reproduction studies with HF are not available. The LOAEL for these effects was 2.26 mg F-/kg b.w./d. In a two-generation study (leading to a NOAEL of 250 mg NaF/l; equivalent to 11 mg/kg bw./d) and in an intratesticular injection study, fluoride did not induce any sign of impaired testicular functioning. There are very strong indications from the two-generation study that fluoride does not affect male or female fertility. This cannot be stated with certainty because the study has not been fully reported, yet. Despite this limitation, the NOAEL of about 10 mg/kg b.w./d derived from the two-generation study has been used in the risk assessment.

From three well-performed embryo- and developmental toxicity studies with NaF an overall NOAEL for maternal toxicity and developmental effects of 11.12 mg F-/kg b.w./d can be derived.

Hazards to the Environment

HF may enter the environment from both natural (volcanoes, weathering of minerals and marine aerosols) and anthropogenic sources. The latter includes production of HF itself, but HF is also formed as a by-product during other industrial processes (phosphate fertiliser, aluminium and steel production, ceramic industry etc.).

Once released in the environment HF is unlikely to remain in its original form for very long. In air, water and soil HF is transformed to a variety of other F-compounds.

Both short and long term toxicity data (NaF) are available for fish, crustaceans, algae and micro-organisms.

The PNEC for the freshwater compartment is extrapolated from the calculated mean NOEC-value for *Daphnia magna* (8.9 mg/l) using an extrapolation factor of 10. The extrapolation leads to a PNEC for the freshwater environment of 0.9 mg/l (PNEC_{aquar}). Long-term ecotoxicity data with fluoride for terrestrial organisms, including microbial processes, are available. The lowest available NOEC, i.e. 106 mg/kg for nitrification, was selected for deriving the PNEC for the terrestrial compartment. Applying an assessment factor of 10 gives a PNEC of 11 mg/kg.

Many experiments are available in which all kinds of plants (bean, barley, corn, garden flowers, strawberries, pine, shrubs, grass, rice etc.) are exposed to HF in fumigation experiments. Sensitive species are tulip, gladiolus, fruit crops, conifers and grasses, which are affected at concentrations ranging from 0.4 to $1.0 \ \mu\text{g/m}^3$ after exposure for several days. The PNEC_{plant-air} is set at $0.2 \ \mu\text{g/m}^3$.

Cattle were shown to be the most sensitive of domestic animals to dietary fluoride, particularly young animals. Observed effects all eventually lead to a loss of body weight and diminished meat and milk production. Atmospheric NOECs for livestock (and plants) of 0.8 μ g and 0.3 μ g/m³ (daily averages) were calculated for the grazing season and winter season, respectively. It is concluded that wild herbivores are or may be more susceptible to fluoride toxicity than domestic live stock, on a dietary F content basis. Thus the atmospheric NOECs derived for livestock may provide an insufficient guarantee for the protection of wild fauna.

Exposure

Anhydrous HF and hydrofluoric acid is used for the production of organofluor compounds and inorganic fluorides, as well as a catalyst of alkylation reactions in the petrochemical industry. It is also used for etching of glass and pickling of stainless steel. The quantitative estimate currently available for the industrial and use category distribution of HF is 60% for the synthesis of organofluor compounds, 30% as intermediate in chemical synthesis of inorganic fluorides, 4% as pickling agent of metal surfaces, 3% for etching of glass surfaces, and 2% as catalyst in alkylation reactions in the petrochemical industry (CTEF 1995). The maximum total production of HF in the European Union for 1994 is 245,000 tonnes. Consumer exposure was found in rust cleaning and stone and wood cleaning agents.

NATURE OF FURTHER WORK RECOMMENDED

There is a need for further information and further consideration of exposure and risk assessment for the environment and human health.

This substance has been agreed in the European Union Risk assessment program under Regulation EEC/793/93. The EU risk assessment concluded that there are need for specific measures to limit the risks for workers and consumers and for exposure via the environment for some sites.

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