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**NATIONAL INDUSTRIAL CHEMICALS NOTIFICATION  
AND ASSESSMENT SCHEME**

**FULL PUBLIC REPORT**

**Caesium Formate**

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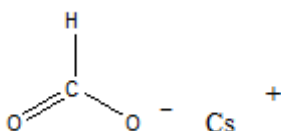
**FULL PUBLIC REPORT****Caesium Formate****1. APPLICANT**

Central Chemical Consulting Ltd of 7 Silica Road, Carine 6020, West Australia and Cabot Australasia of 300 Millers Road, Altona, Victoria, 3018 have submitted a joint standard notification statement in support of their application for an assessment certificate for caesium formate.

**2. IDENTITY OF THE CHEMICAL**

The notified chemical is derived from salt mineral deposits in Canada, which also have high levels of magnesium, calcium and other bivalent metals. These are removed through precipitation of their carbonates, and this accounts for the relatively high level of potassium carbonate in the notified chemical. The high levels of alkali metals (sodium, potassium and rubidium) in the product are in accord with its origin in lake salt deposits.

|   |   |
|---|---|
| <b>Chemical Name:</b>                                 | Caesium formate                                   |
| <b>Chemical Abstracts Service (CAS) Registry No.:</b> | 3495-36-1   |
| <b>Other Names:</b>                                   | Formic acid, caesium salt                         |
| <b>Marketing Name:</b>                                | caesium formate solution<br>caesium formate brine |
| <b>Molecular Formula:</b>                             | CsCHO <sub>2</sub>                                |
| <b>Structural Formula:</b>                            |   |



|   |   |
|---|---|
| <b>Molecular Weight:</b>                      | 177.94  |
| <b>Method of Detection and Determination:</b> | Infrared (IR)   |
| <b>Spectral Data:</b>                         | IR spectrum: 3422 (water), 2805, 1631, 1593, 1383, 1349, and 762 cm <sup>-1</sup> |

### 3. PHYSICAL AND CHEMICAL PROPERTIES

The following data refer to a stock solution of caesium formate (72 wt %) in water.

|  |   |
|--|---|
| <b>Appearance at 20 °C &amp; 101.3 kPa:</b>      | colourless to very pale yellow solution with a mild odour   |
| <b>Boiling Point:</b>                            | 110°C (solution decomposes above 190°C)   |
| <b>Density:</b>                                  | 2320 kg/m <sup>3</sup> (saturated solution)   |
| <b>Vapour Pressure:</b>                          | 0.466 kPa at 20°C, 0.732 kPa at 25°C – see comments below   |
| <b>Water Solubility:</b>                         | 4.88 g of CsHCO <sub>2</sub> dissolve in 1 g water at 20°C; (density = 2.3 g/mL) – see comments below           |
| <b>Partition Co-efficient (n-octanol/water):</b> | log K <sub>ow</sub> < -1.28 – see comments below  |
| <b>Hydrolysis as a Function of pH:</b>           | stable to hydrolysis at pH 4, 7 and 9; Method OECD TG 111 – see comments below.                                 |
| <b>Adsorption/Desorption:</b>                    | log K <sub>oc</sub> = 1.87-2.93. Method OECD TG 106 – see comments below.                                       |
| <b>Dissociation Constant:</b>                    | pK <sub>a</sub> = 3.74 ± 0.06; Method OECD TG 112 – see comments below  |
| <b>Flash Point:</b>                              | not applicable  |
| <b>Flammability Limits:</b>                      | not flammable; combustible  |
| <b>Autoignition Temperature:</b>                 | not determined  |
| <b>Explosive Properties:</b>                     | not expected to be explosive  |
| <b>Reactivity/Stability:</b>                     | stable up to 190°C; classed as a mild reducing agent, which when in contact with oxidants, can react vigorously |

#### 3.1. Comments on Physico-Chemical Properties

The boiling point of concentrated aqueous salt solutions is significantly elevated above that of water, and the measured value is in keeping with this. The notifier also indicated that the solution decomposes above 190°C, and this presumably refers to decomposition of the formate anion to form CO<sub>2</sub> and hydroxide ion.

The report on determination of vapour pressure indicated that the melting point of the solution should be 17°C, but that the commercial solution remained supersaturated down to 1°C. This may be due to the presence of relatively high concentrations of other ionic salt impurities which stabilise the solution in the metastable supersaturated state.

The vapour pressure of the commercial solution was determined (Pelletier, 1998) between 1 and 39°C using a calibrated pressure transducer and, for those temperatures between 17 and 39°C, the data provided a linear relationship between pressure and reciprocal temperature (degrees K).

Caesium formate is highly water soluble and a saturated solution at 20°C containing 4.88 kg of solid CsHCO<sub>2</sub> in 1 L of water has a volume of 2.56 L and a density of 2.297 kg/L.

Hydrolysis of the notified chemical was examined as a function of solution pH (Gibb and Benton, 1998a) using a 0.08 M solution held for 5 days at 50°C in buffer solutions of pH 4, 7 and 9. After the 5 day period, the concentration of formate in the solutions was analysed using High Performance Liquid Chromatography (HPLC), and compared with that in controls held at 5°C in a refrigerator. No significant decrease in formate concentration was observed between any of the test solutions and the controls, with the maximum decrease recorded being 2.3 %. These results indicate insignificant hydrolytic degradation at 50°C under the test conditions, and even less degradation is expected at ambient temperatures.

The *n*-octanol/water partition coefficient of ionic materials such as caesium formate is expected to be low due to the very high affinity for the aqueous phase. The partition coefficient was determined (Boeri *et al.*, 1997) through direct measurement of the caesium formate concentration in water and *n*-octanol after an aqueous solution containing 0.00075 mol/L (133.4 mg/L) of CsHCO<sub>2</sub> was equilibrated for 6 hours at 25°C with water saturated *n*-octanol at volume ratios 1:5, 1:10 and 1:20 (water: *n*-octanol). Analysis was performed using HPLC, and in all three cases the concentration of caesium formate in the octanol was less than 0.000040 mol/L. The partition coefficient ( $P_{ow}$ ) was consequently determined as  $< 0.0533$ , and the corresponding  $\log P_{ow} < -1.28$ .

A report on the adsorption and desorption of caesium formate on three soil types was submitted (Gibb and Benton, 1998b). The three soil types used were an Aridisol, an Ultisol and an Alfisol and are characterised by different relative contents of clay, organic matter and cation exchange capacity (CEC).

| Soil     | Organic Matter (%) | Clay Content (%) | CEC (Cmol/kg) |
|----------|--------------------|------------------|---------------|
| Aridisol | 0.79               | 13.0             | 8.7           |
| Ultisol  | 1.95               | 33.0             | 26.2          |
| Alfisol  | 0.70               | 8.8              | 7.7           |

Eight grams of each soil sample was agitated for 48 hours with solutions containing known concentrations of caesium formate, and the percent adsorption onto the soil monitored over the test period through analysis of the residual formate concentrations in the solution. The results were analysed to provide a  $\log K_{oc}$  of 1.87 for the Ultisol, 2.74 for the Aridisol and 2.93 for the Alfisol respectively. From the physico-chemical properties of the soil supplied there appeared to be an inverse correlation between  $\log K_{oc}$  and the organic content of the soil, clay content of

the soil and cation exchange capacity of the soil. Consequently it is difficult to interpret the apparent adsorption data with the usual soil physico-chemical parameters, but the measured log  $K_{oc}$  for the formate ion are moderate, and indicate that this ion may be reasonably mobile in soil media.

However, subsequent studies on desorption of the formate from the soils with either  $CaCl_2$  solution or dilute hydrochloric acid failed to detect any formate ion in either aqueous phase, and the formate ion may be rapidly degraded once associated with the soil.

The dissociation constant of the formate anion in 0.01 M caesium formate was determined (Gibb and Benton, 1998c) by titration with dilute (0.2 M) HCl as 3.74.

#### 4. PURITY OF THE CHEMICAL

**Degree of Purity:** > 98 %

**Hazardous and Non-hazardous Impurities (> 1% by weight)** The impurities found in a 72 % w/w aqueous caesium formate solution, and their reported concentrations, are listed below.

| Species   | Concentration (ppm) | Species            | Concentration (ppm) |
|-----------|---------------------|--------------------|---------------------|
| K         | 6100                | Si                 | < 1                 |
| Na        | 5300                | B                  | 2                   |
| Rb        | 3200                | P                  | < 1                 |
| Li        | 301                 | Mo                 | < 1                 |
| Al        | < 1                 | Tl                 | 10                  |
| Ba        | 1                   | Cu                 | < 1                 |
| Ca        | 1                   | Cr, Mn, Mg, Ni, Pb | < 1                 |
| Fe        | < 1                 | SO <sub>4</sub>    | 23                  |
| Sr        | < 1                 | Cl                 | 407                 |
| Insoluble | < 100               |                    |                     |

#### Additives/Adjuvants:

*Chemical name:* water

*CAS No.:* 7732-18-5

*Weight percentage:* variable, depending upon the required solution density

*Chemical name:* potassium carbonate

*CAS No.:* 584-08-7

|                           |  |
|---------------------------|--|
| <i>Weight percentage:</i> | 2800 ppm; used to precipitate out transition metal impurities and provide a buffering for the final solution (to pH 10.00 ±0.5). |
| <i>Chemical name:</i>     | citric acid  |
| <i>Weight percentage:</i> | 150 ppm; added as a clarifier.   |
| <i>CAS No.:</i>           | 77-92-9  |

## 5. USE, VOLUME AND FORMULATION

### *Use and Formulation*

Caesium formate solution will be manufactured in Canada and imported for two uses. Some of the notified chemical will be used in coal laboratories where it will be used to prepare media of different densities and used to classify coal on the basis of whether the coal fractions sink or float in the different density media. The remainder will be used as a drilling fluid in the development of oil and natural gas wells worldwide. The notified chemical will be imported either as a concentrated aqueous solution (72 % w/w) in 70 L drums or as a solid in 25 kg heat sealed polyethylene sacks.

Formate based drilling fluids will be formulated by mixing sodium, potassium and caesium formates in water to achieve a clear solution with a specified density. The notified chemical will be added either as a *ca.* 83 % caesium formate solution in water, or as the dry powder.

Caesium formate has been registered under the *Harmonised Offshore and Chemical Notification Format* (HOCNF) developed under the *Oslo and Paris Conventions for the Prevention of Marine Pollution Programmes and Measures Committee* (PARCOM) for use as a drilling fluid in the North Sea oil field.

### *Coal Classification*

When used in classification of coal, samples of the washed coal are immersed in solutions of different concentrations, hence different densities, of caesium formate, and the coal classified according to the fractions which sink or float in the different media. It was stated in the dossier that around 15 coal testing laboratories in NSW and Queensland may use caesium formate for classification purposes.

Typically testing is conducted on 1 kg samples of coal, and after the test the caesium formate solution separated from the coal using filtration, and recovered for re-use. Some of the caesium formate remains entrained with fine coal particles and otherwise adsorbed into pores in the coal. The majority of this is removed through washing the coal with water prior to the coal being returned to stockpiles, or possibly being sent to landfill. The wash water is reconcentrated through evaporation to its original density, and used in subsequent testing. Nevertheless, despite the high level of re-use of these variable density fluids, some losses are incurred. A typical laboratory may lose 110 L of the 72 % (specific gravity 2.14) caesium formate solution each year. Since there may be 15 laboratories using the new chemical, this leads to an annual loss estimate of around 1650 L, amounting to *ca.* 2.54 tonnes of solid caesium formate.

### *Oil / Gas Drilling*

Large quantities of the caesium formate solution will be used in oil/gas drilling operations on off shore drilling platforms. In particular, the solution will be used during completion phases of the drilling operation when breaching of the actual oil/gas reservoirs occurs. During drilling operations, a drilling fluid (often also called “drilling mud”) is pumped down the drill shaft and functions as a lubricant for the drills, and also acts as a carrier fluid for removing the solid cuttings (*i.e.* the rock removed from the bore hole). The drilling fluid must possess certain density and rheological properties to function effectively under the conditions encountered in wells, and conventionally such fluids are prepared from oil based products supplemented with barium sulphate (as a weighting agent) and other organic additives. In certain circumstances, the use of aqueous caesium formate solutions (whose density can be adjusted through dilution with water) dispenses with large scale use of organic materials and barium sulphate in this role. This lessens potential release of organic material to the environment, and is also claimed to offer other practical engineering advantages during well drilling (Howard, 1995).

During the development of a well, the drilling fluid is pumped down the centre of the (hollow) drilling rods and is extruded through holes in the cutting head, which is of larger bore than the shaft of drill rods. The fluid then fills the annular region between the bore hole (typically 21.6 cm to 31.1 cm in diameter – see Cobby and Craddock, 1999) and the drilling shaft, and as it is pushed back towards the surface and carries the drill cuttings with it. The bore hole is cased and fitted with appropriate valves and plumbing to allow for the return of the fluid and cuttings back to the drilling platform or drilling rig. Here the solid cuttings are separated from the fluid through a series of shaker tables, centrifugation and filtration units so that, apart from operational losses, the drilling fluid is contained within a closed loop.

The cuttings are then automatically dumped overboard, while the fluid itself is returned to the storage tank for reuse. It is usual that on off shore drilling platforms the tailings (cuttings) are discharged through a pipe set a little below the sea surface, but far above the sea floor.

In the submission, the company indicated that the discarded drill cuttings may contain up to 15 % (w/w) of the drilling fluid, although when centrifugation is employed this may be dramatically reduced, and residual fluid levels as low as 1 % have been recorded. It was not indicated in the notification whether centrifugation will be used on the North West shelf operations but, regardless of the efficiency of the recovery operations employed, some fluid will be ultimately discharged overboard with the drill cuttings and enter the marine environment.

The percentage of drilling fluid recovered as described above was not indicated but, due to the anticipated high cost of the caesium formate solution, is expected to be high. The notifier included a copy of a detailed *Loss Management Manual* for the use of drill rig operators and personnel involved in transporting and transferring the chemical to the drilling platforms. However the company has not specified the recovery technologies to be used on Australian drilling platforms, or expected quantities of the notified chemical likely to be released with discarded drill cuttings. Accordingly, for the purposes of this report it will be assumed that discarded cuttings will contain 10 % by weight of entrained drilling fluid.

The quantity of drilling fluid used in drilling the wells is variable (depends on drill well depth and location), but the notifier stated that a typical oil/gas drilling platform may use 1500 barrels of the notified chemical (around 160 tonnes of solid caesium formate) during drilling



each new well. The company indicated that up to four wells may be drilled each year using the new caesium formate based fluids, and so in excess of 600 tonnes of the chemical may be in use at any one time.

#### *Volume*

It is anticipated that up to 2250 tonnes per annum will be imported for all uses. The company indicated that up to 3 tonnes of the notified chemical would be imported for coal sink use in the first year, and that subsequent imports of 1 tonne per annum could be anticipated in order to replenish losses. However, this may be conservative and, from indicative losses given in the notification, the required replenishment quantities appear to be closer to 2.5 tonnes per annum.

The major use for the chemical will be in oil/gas drilling on off shore drilling platforms, and here the notifier indicated that a typical well may use up to 1500 drums (10500 L) of the 72 % caesium formate solution which equates to the use of *ca.* 162 tonnes of solid caesium formate. Since it is likely that stockpile of material sufficient for developing at least two wells would be kept in Australia at any time, likely annual imports of caesium formate for this purpose may exceed 300 tonnes. Every attempt is made to recover and reuse the drilling fluid after completion of the well, but some losses are inevitable and will require replacement through import of replacement stocks.

## **6. OCCUPATIONAL EXPOSURE**

#### *Transport and Storage*

Estimates of the numbers of workers involved in these activities were not provided. No exposure of workers involved in transport or storage of drums of caesium formate solution or sacks of dry powder is expected except in the case of an accident involving damage to the packaging. Due to the hygroscopic nature of the notified chemical, storage will always be in enclosed, airtight packaging.

#### *Coal Classification*

Approximately 3 people in each of four coal laboratories will use caesium formate at one time. Coal samples will be placed in caesium formate solutions of specified density manually. The grains which float are removed, the excess solution is drained off and the grains which sank are placed in a solution of higher density. Once the coal has been separated into its density fractions, the coal fractions are thoroughly washed with water to remove any residual formate. The washed coal is then oven dried. All formate washings are collected and re-concentrated to the original density (2.14 g/L) by water evaporation.

Dermal exposure to the notified chemical in aqueous solution may occur at a number of points during this process. There is also the possibility of splashing resulting in ocular contact. The notifier stated that laboratory staff will be required to wear goggles and rubber or nitrile gloves during these activities. As the notified chemical is hygroscopic, spills will not dry to produce dust.

#### *Oil / Gas Drilling*

During the use of caesium formate as a drilling and completion fluid, the total number of industry persons who will be exposed to the caesium formate during the period of its initial testing will be less than 200 persons worldwide. The team involved in drilling generally

includes a person who directs the overall operations on behalf of the operator, the drilling superintendent who directs the day to day operations, drillers, toolpushers, roustabouts and fluid people. The fluids team involve at least two people who mix, test and control the drilling fluid properties while drilling operations are in progress. There will also be use of the notified chemical solution by the completion team. The activities of the completion team were not specified by the notifier, but are expected to involve similar exposure scenarios for the notified chemical. All workers will be experienced personnel trained in the handling, mixing and application of such drilling fluids, either in laboratory settings or in field applications for drilling and completing oil and gas wells.

The notified chemical will be used by drilling contractors in closed-loop systems at the wellhead therefore worker exposure to the caesium formate solution will be restricted to exposure to drips and spills when the notified chemical solution is decanted or pumped from the importation drum into the enclosed drilling system. There may also be exposure during sampling of the fluid for testing of viscosity or other properties, and when the fluid is transferred for storage during recovery operations. When dry powder is used to prepare the drilling fluids, it will dissolve rapidly into drilling fluid formulations. Any dusts are expected to absorb water from the atmosphere and minimal exposure to the dry powder form of the notified chemical is therefore expected. There may be exposure of workers to significant volumes of the notified chemical when the drill bit is manipulated during replacement or removal from the drill hole. No worker exposure is anticipated during transfer of the notified chemical from storage to the drilling site or during storage on a drilling rig.

The protection measures used to prevent exposure of these workers were not specified by the notifier, however the Material Safety Data Sheet (MSDS) for the notified chemical indicates that appropriate clothing, gloves and eye protection (goggles or face shield) should be worn. The workers involved in testing, mixing and application of fluids are generally petroleum engineers with specific skills and training in the design and application of drilling and completion fluids.

## **7. PUBLIC EXPOSURE**

It is expected that during transport, formulation, storage, and use, exposure of the public to the notified chemical will be low.

Given that the use of the notified chemical will be restricted to coal testing laboratories and onshore/offshore drilling operations, no public exposure is anticipated except in the event of an accidental spill during transport from the docks to the drilling sites and coal testing laboratories.

## **8. ENVIRONMENTAL EXPOSURE**

### **8.1 Release**

#### *Coal Classification*

Approximately 2.5 tonnes of caesium formate may be released each year from use of the notified chemical in coal classification laboratories, primarily in NSW and Queensland. Most of this material will be associated with the coal samples used for the tests, with the bulk

returned to coal stockpiles for sale. Once the coal is burnt, the caesium component will be associated with the ash which would most probably be placed into a landfill. The caesium would most likely be in the form of soluble salts such as oxides or carbonates, and would consequently be susceptible to leaching from the landfill. However, the associated release will be diffuse and at very low levels.

Some of the unburnt test coal containing entrained caesium formate may be placed into landfill, but the likely quantity was not specified. The fate of any entrained caesium formate would be similar to that for the coal ash.

### *Oil / Gas Drilling*

Much of the notified chemical used in drilling fluids (or muds) is expected to be released with the waste drill cuttings to the marine environment. While no quantitative estimates or examples of these releases were provided in the notification it will be assumed that the drill cuttings contain up to 10 % of the new chemical. The tailings are discharged through a pipe just below the surface and, once discharged from the drilling rig, it is expected that the solid drill cuttings coated with residual drilling fluid would eventually settle to the sea floor. However, depending on factors such as particle size, sea conditions, weather conditions and ocean currents, the deposition may take some time. Also, it is likely that the distribution would be disperse, and that the discarded cuttings would be spread over a wide area of the sea floor.

Caesium formate solution will be used for development of the wells near the vicinity of the reservoirs, *ie* drilling holes from the main well shaft into the rock formations which actually contain the oil and gas. No information on the length, diameter and number of such development holes for any given well was provided in the notification, but it will be assumed that the waste generated is equivalent to that of the major well drilling operation. On a typical production drilling platform, each bore hole may be between 1 and 4 km in length. Given that the typical diameter of a production hole is 31.1 cm, it is estimated that each well may produce between 75 and 300 m<sup>3</sup> of rock cuttings with a weight of approximately 150-600 tonnes. Assuming that the cuttings contain 10 % of drilling fluid, each well may be responsible for release of up to 60 tonnes of the drilling fluid containing an estimated 42 tonnes of caesium formate. Since caesium formate brines may be used in drilling up to four wells each year, an annual release of around 170 tonnes of caesium formate is anticipated, *ie* around 130 tonnes of caesium.

## **8.2 Fate**

### *Coal Classification*

When the coal containing residual material is burnt, the formate component of the notified chemical will be destroyed (producing CO<sub>2</sub> and water vapour), while the caesium will become associated with the ash, probably as an oxide or carbonate. Coal ash would normally be disposed of into landfill. It is likely that the residual caesium salts would be susceptible to leaching as ground water percolates through these structures, consequently releasing this element to the aquatic environment.

### *Drilling Fluid*

It is difficult to estimate the quantity of caesium formate likely to be released to the marine environment with well drill cuttings but, assuming four wells are drilled each year, up to 170 tonnes of caesium formate may be released each year to the marine environment in association with discarded drill cuttings.

However, due to the high solubility of the material, the notified chemical is expected to diffuse into the surrounding sea water and is not expected to remain adsorbed to the drill cuttings. The formate component will be degraded through abiotic and biotic processes, while the caesium (*ca.* 130 tonnes per annum) would remain in solution. Since the caesium formate will be released in high concentration around each drilling rig, the caesium levels in the surrounding water will be significantly elevated above ambient concentrations.

### *Biodegradation*

The notifier provided a test report on the ready biodegradation of the chemical (Douglas and King, 1992b) which was performed using the closed bottle procedure of OECD TG 301 D. This test measures the decay of dissolved oxygen in a closed vessel containing the test material (initial concentration 45 mg/L) inoculated with sewage bacteria over a 28 day period. The results indicated that 83 % of the test compound had degraded after 28 days, and also since 60 % degradation had occurred within 10 days of the 10 % degradation point being reached, the notified chemical passes the criteria for ready biodegradability. In a parallel study using sodium benzoate, this reference compound was degraded 92 % after 28 days, which indicates that the bacterial culture used in the test was viable.

Only the formate anion component of the notified chemical is degraded, and the caesium will be unaffected by bacterial action.

### *Bioaccumulation*

The highly soluble nature of the notified chemical, together with its biodegradability, indicates that it is not likely to have significant potential for bioaccumulation.

## **9. EVALUATION OF TOXICOLOGICAL DATA**

### **9.1 Acute Toxicity**

A number of toxicological studies have been carried out on the notified chemical, however data supporting some of these tests were not available. Some data reported is given as a summary originating from internal Shell reports undertaken in 1994.

#### **Summary of the acute toxicity of caesium formate solution (83 %)**

| <i>Test</i>                        | <i>Species</i> | <i>Outcome</i>                | <i>Reference</i> |
|------------------------------------|----------------|-------------------------------|------------------|
| acute oral toxicity                | rat            | LD <sub>50</sub> = 1780 mg/kg | (Harrod (1997a)  |
| acute dermal toxicity<br>(summary) | rat            | LD <sub>50</sub> > 2000 mg/kg | (Shell, 1994)    |
| skin irritation                    | rabbit         | slight irritant               | (Harrod, 1997b)  |
| eye irritation                     | rabbit         | moderate irritant             | (Harrod, 1997c)  |
| skin sensitisation                 | rabbit         | non-sensitiser                | (Shell, 1994)    |

### 9.1.1 Acute Oral Toxicity (Harrod, 1997a)

|                                  |  |
|----------------------------------|--|
| <i>Species/strain:</i>           | rat/Sprague-Dawley   |
| <i>Number/sex of animals:</i>    | 5/sex/dose   |
| <i>Observation period:</i>       | 14 days  |
| <i>Method of administration:</i> | gavage; 1250, 1580, 2000 and 5000 mg/kg  |
| <i>Test method:</i>              | OECD TG 401  |
| <i>Mortality:</i>                | all animals at 5000 mg/kg and 9/10 animals at 2000 mg/kg died within the first day after treatment   |
| <i>Clinical observations:</i>    | <p>animals at dose levels of 1580 mg/kg and above exhibited varying degrees of depression, convulsions, respiratory distress, ataxia, excessive salivation, masticatory movements and gross signs of distress and external staining; faecal stains were noted at the 1250 mg/kg dose level</p> <p>all surviving animals exhibited body weight gain at day 14</p> |
| <i>Morphological findings:</i>   | gross necropsy findings for animals that died during the observation period included those generally seen in agonal animals, with indications of gastro-intestinal irritation and external staining; there were no gross pathological changes observed in animals which survived the 14 day observation period   |
| <i>LD<sub>50</sub>:</i>          | 1780 mg/kg   |
| <i>Result:</i>                   | the notified chemical was of low acute oral toxicity in rats.  |

### 9.1.2 Dermal Toxicity

No test reports concerning the acute dermal toxicity of the notified chemical were submitted. A summary of toxicology testing on the notified chemical (Shell, 1994) included data on dermal toxicity testing. Doses of 50, 400 and 2000 mg/kg were administered to groups of 2 male and 2 female rats. Sites of application showed erythema on day 2, or on days 2 and 3. The acute dermal toxicity of caesium formate monohydrate was greater than 2000 mg/kg.

### 9.1.3 Acute Inhalational Toxicity

No test reports were submitted.

### 9.1.4 Skin Irritation (Harrod, 1997b)

*Species/strain:* rabbit/New Zealand White

*Number/sex of animals:* 3/sex

*Observation period:* 7 days

*Method of administration:* 500 µL of undiluted caesium formate was applied by a closed patch method to intact skin for 4 hrs

*Test method:* OECD TG 404

#### *Draize scores:*

| <i>Time after treatment (days)</i> | <i>Animal #</i> |           |           |           |           |           |
|------------------------------------|-----------------|-----------|-----------|-----------|-----------|-----------|
|                                    | <i>1♂</i>       | <i>2♂</i> | <i>3♂</i> | <i>4♀</i> | <i>5♀</i> | <i>6♀</i> |
| <b><i>Erythema</i></b>             |                 |           |           |           |           |           |
| 1 hour                             | 2 <sup>a</sup>  | 2         | 2         | 1         | 2         | 1         |
| 1                                  | 1               | 1         | 1         | 1         | 2         | 1         |
| 2                                  | 1               | 1         | 0         | 1         | 1         | 1         |
| 3                                  | 1               | 0         | 0         | 1         | 1         | 0         |
| 7                                  | 0               |           |           | 0         | 0         |           |
| <b><i>Oedema</i></b>               |                 |           |           |           |           |           |
| 1 hour                             | 2               | 2         | 1         | 1         | 2         | 2         |
| 1                                  | 1               | 1         | 0         | 0         | 1         | 1         |
| 2                                  | 1               | 1         | 0         | 0         | 1         | 0         |
| 3                                  | 1               | 0         | 0         | 0         | 1         | 0         |
| 7                                  | 0               |           |           | 0         | 0         |           |

<sup>a</sup> see Attachment 1 for Draize scales

*Comment:* partial recovery in three animals and full recovery in three animals were noted at 72 hours; full recovery was noted in the remaining animals by day 7; two animals showed desquamation at day 7; the Primary Irritation Index was calculated to be 1.8

*Result:* the notified chemical was a slight irritant to the skin of rabbits.

### 9.1.5 Eye Irritation (Harrod, 1997c)

*Species/strain:* rabbit/New Zealand White

*Number/sex of animals:* 3/sex

*Observation period:* 14 days

*Method of administration:* 100 µL undiluted caesium formate delivered into the right eye of each animal

*Test method:* OECD TG 405

*Draize scores of unirrigated eyes:*

| <i>Time after instillation</i> |                             |          |          |                |          |          |                |          |          |                |          |          |
|--------------------------------|-----------------------------|----------|----------|----------------|----------|----------|----------------|----------|----------|----------------|----------|----------|
| <i>Animal</i>                  | <i>1 hour</i>               |          |          | <i>1 day</i>   |          |          | <i>2 days</i>  |          |          | <i>3 days</i>  |          |          |
| <i>Cornea</i>                  | all Draize scores were zero |          |          |                |          |          |                |          |          |                |          |          |
| <i>Iris</i>                    |                             |          |          |                |          |          |                |          |          |                |          |          |
| 1♂                             | 1                           |          |          | 0              |          |          | 0              |          |          | 0              |          |          |
| 2♂                             | 1                           |          |          | 0              |          |          | 0              |          |          | 0              |          |          |
| 3♂                             | 1                           |          |          | 0              |          |          | 0              |          |          | 0              |          |          |
| 4♀                             | 1                           |          |          | 0              |          |          | 0              |          |          | 0              |          |          |
| 5♀                             | 1                           |          |          | 0              |          |          | 0              |          |          | 0              |          |          |
| 6♀                             | 1                           |          |          | 0              |          |          | 0              |          |          | 0              |          |          |
| <i>Conjunctiva</i>             | <i>r</i>                    | <i>c</i> | <i>d</i> | <i>r</i>       | <i>c</i> | <i>d</i> | <i>r</i>       | <i>c</i> | <i>d</i> | <i>r</i>       | <i>c</i> | <i>d</i> |
| 1♂                             | 1 <sup>a</sup>              | 2        | 3        | 2 <sup>a</sup> | 2        | 2        | 2 <sup>a</sup> | 1        | 0        | 2 <sup>a</sup> | 1        | 0        |
| 2♂                             | 2 <sup>a</sup>              | 3        | 3        | 2 <sup>a</sup> | 2        | 3        | 2 <sup>a</sup> | 2        | 1        | 2 <sup>a</sup> | 1        | 0        |
| 3♂                             | 1 <sup>a</sup>              | 2        | 2        | 2 <sup>a</sup> | 2        | 2        | 2 <sup>a</sup> | 1        | 0        | 1              | 1        | 0        |
| 4♀                             | 1 <sup>a</sup>              | 2        | 3        | 2 <sup>a</sup> | 2        | 2        | 2 <sup>a</sup> | 2        | 0        | 2 <sup>a</sup> | 1        | 0        |
| 5♀                             | 1 <sup>a</sup>              | 2        | 3        | 2 <sup>a</sup> | 2        | 1        | 2 <sup>a</sup> | 2        | 1        | 2 <sup>a</sup> | 1        | 0        |
| 6♀                             | 2 <sup>a</sup>              | 2        | 3        | 2 <sup>a</sup> | 2        | 1        | 2 <sup>a</sup> | 2        | 0        | 2 <sup>a</sup> | 1        | 0        |

| <i>Animal</i>      | <i>Time after instillation</i> |          |          |                |          |          |                |          |          |
|--------------------|--------------------------------|----------|----------|----------------|----------|----------|----------------|----------|----------|
|                    | <i>4 days</i>                  |          |          | <i>7 days</i>  |          |          | <i>14 days</i> |          |          |
| <i>Conjunctiva</i> | <i>r</i>                       | <i>c</i> | <i>d</i> | <i>r</i>       | <i>c</i> | <i>d</i> | <i>r</i>       | <i>c</i> | <i>d</i> |
| 1♂                 | 2 <sup>a</sup>                 | 1        | 0        | 1              | 1        | 0        | 0              | 0        | 0        |
| 2♂                 | 1 <sup>a</sup>                 | 1        | 0        | 1 <sup>a</sup> | 1        | 0        | 0              | 0        | 0        |
| 3♂                 | 1                              | 1        | 0        | 0              | 0        | 0        |                |          |          |
| 4♀                 | 1 <sup>a</sup>                 | 1        | 0        | 1 <sup>a</sup> | 1        | 0        | 0              | 0        | 0        |
| 5♀                 | 1 <sup>a</sup>                 | 1        | 0        | 1 <sup>a</sup> | 1        | 0        | 0              | 0        | 0        |
| 6♀                 | 1 <sup>a</sup>                 | 1        | 0        | 1 <sup>a</sup> | 1        | 0        | 0              | 0        | 0        |

<sup>1</sup> see Attachment 1 for Draize scales  
r = redness    c = chemosis    d = discharge

a = one or more of the additional observations discussed below were also reported

*Comment:* iritis in all animals cleared by 24 hours; no corneal opacity was observed

additional observations included a blistered appearance to the conjunctiva or nictitating membrane, areas of conjunctiva or nictitating membrane appeared haemorrhagic, and areas of nictitating membrane appeared blanched

*Result:* the notified chemical was moderately irritating to the eyes of rabbits.

### **9.1.6 Skin Sensitisation**

No test reports concerning the skin sensitizing potential of the notified chemical were submitted. A summary of toxicology testing on the notified chemical (Shell, 1994) included data on a Buchler test with induction and challenge by occluded topical application of 80 % w/v caesium formate in water. None of the 20 test animals showed any overt reaction to treatment.

## **9.2. Repeated Dose Toxicity**

Repeated dose toxicity data for caesium formate were not available. The subchronic effects of the notified chemical are expected to be those of the constituent parts, the formate anion and the caesium cation. In the stomach, these are likely to be in the form of formic acid and caesium chloride, respectively.

Formic acid did not demonstrate any significant toxicity in rats when administered in their drinking water 4 (0.5% and 1.0%) for 2 to 27 weeks (Sollman, 1921). In a 6 week test in rats, the same doses are reported to have resulted in reduction in organ weights and body weight gain (Gangolli, 1999). The caesium cation is reported to be of higher toxicity than Na<sup>+</sup>, but lower toxicity than K<sup>+</sup>, Li<sup>+</sup> or Rb<sup>+</sup> (Burt, 1986). It is further stated by Burt that the toxicology of caesium compounds results from the anion rather than the caesium cation.

## **9.3 Genotoxicity**

### **9.3.1 *Salmonella typhimurium* Reverse Mutation Assay**

No test reports concerning the genotoxicity of the notified chemical were submitted. A summary of toxicology testing on the notified chemical (Shell, 1994) included data on a point mutation test. The notified chemical was not mutagenic in both the presence and absence of liver S-9 fraction in two strains. The tests were not performed in duplicate.

### **9.3.2 Chromosomal Aberration Assay in Human lymphocytes (Akhurst, 1995)**



*Cells:* human lymphocytes

*Metabolic system:* activation S-9 mix (rat liver)

*Dosing schedule:* 625, 1250, 2500 and 5000 µg/mL

| Metabolic Activation | Experiment/ Study Number | Test concentration (µg/mL)                                  | Controls        |
|----------------------|--------------------------|---|-----------------|
| -S9                  | 1                        | treatment time = 18 hour harvest (625, 1250 and 2500 µg/mL) | Positive: EMS   |
|                      | 2                        | treatment time = 18 hour harvest (625, 1250 and 2500 µg/mL) | Negative: DMSO  |
|                      |                          | treatment time = 32 hour harvest (1250 µg/mL)               |                 |
| +S9                  | 1                        | treatment time = 18 hour harvest (625, 2500 and 5000 µg/mL) | Positive: CP    |
|                      | 2                        | treatment time = 18 hour harvest (625, 2500 and 5000 µg/mL) | Negative: water |
|                      |                          | treatment time = 32 hour harvest (500 µg/mL)                |                 |

EMS - ethyl methanesulphonate ; CP - cyclophosphamide ; DMSO – dimethylsulphoxide; - cultures selected for metaphase analysis

*Test method:* OECD TG 473

*Comment:* no precipitation was observed; without S9 activation, the notified chemical was cytotoxic at 5000 µg/plate; slight toxicity was observed at this dose with S9 metabolic activation

the notified chemical caused no substantial increase in the proportion of metaphase cells containing chromosomal aberrations at any dose level when compared with the solvent control

in the absence of metabolic activation, there was a statistically significant increase in the proportion of aberrant cells at 2500 µg/mL, 18 hour harvest in the second test, however the proportion was marginally above the historical control value and no similar increase was observed in the first test

all positive control compounds caused large, statistically significant increases in the proportion of aberrant cells

*Result:* the notified chemical was non clastogenic under the conditions of the test

## 9.4 Overall Assessment of Toxicological Data

Caesium formate solution (83%) had low acute oral toxicity in rats ( $LD_{50} = 1780$  mg/kg), with clinical signs including depression, convulsions, respiratory distress, ataxia, excessive salivation, masticatory movements, and signs of distress and external staining at  $> 1250$  mg/kg, faecal stains were, evident at 1250 mg/kg. Caesium formate solution (83 %) was a slight skin irritant and a moderate eye irritant. In the eye irritation study, iritis was seen in all rabbits at 1 hour, with resolution at 24 hours. Conjunctival erythema and oedema occurred in all rabbits from 1 hour to 7 days after instillation. Conjunctival chemosis was evident in all rabbits at 1 to 48 hours after instillation. Some or all of the following observations occurred in all rabbits from 1 hour up to 7 days after instillation; blistering of the conjunctiva, blanching and/or blistering of the nictitating membrane, and haemorrhagic areas in the conjunctiva and/or nictitating membrane, All signs of irritation had cleared by day 14.

Summaries of experimental findings were submitted for the following endpoints. Caesium formate monohydrate had low dermal ( $LD_{50} > 2000$  mg/kg) toxicity in rats, with signs of erythema, noted at sites of application on days 2 and 3. Aqueous Caesium formate (80 % w/v) was not sensitising to guinea pigs in a Buehler test. An acute inhalation study was not submitted.

A repeat-dose toxicity test for the notified chemical was not submitted. Formic acid did not cause significant toxicity to rats when administered in their drinking water at 0.5 and 1 % for 2 to 27 weeks. The caesium cation is not expected to produce significant chronic toxicity.

The notified chemical was not mutagenic in a microscreen test (2 strains of *S. typhimurium*, no repeat test). In a chromosome aberration assay in human lymphocytes, an increase in aberrant cells at 2500 pg/mL in the absence of S9 at an 18 hour harvest time was not considered to be evidence of clastogenicity because the increase was only slightly higher than the historical control value and it was not reproducible in a duplicate test.

Based on the studies provided, the notified chemical is classified as a hazardous substance in accordance with the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1999) and the following risk phrases apply: R22 'Harmful if swallowed' and R36 'Irritating to eyes'.

## 10. ASSESSMENT OF ENVIRONMENTAL EFFECTS

The following ecotoxicity data for caesium formate solutions against both freshwater and marine aquatic organisms were submitted.

### Fresh Water Species Summary

| <i>Test</i>               | <i>Species</i>                              | <i>Results</i> (nominal)                                |
|---------------------------|---|---|
| acute toxicity [OECD 203] | rainbow trout<br><i>Oncorhynchus mykiss</i> | $LC_{50}$ (96 h) = 2100 mg/L<br>NOEC (96 h) = 1000 mg/L |

|  |                                  |   |
|--|----------------------------------|---|
| acute immobilisation of freshwater invertebrates [OECD TG 202] | <i>Daphnia magna</i>             | EC <sub>50</sub> (48 h) = 35 mg/L<br>NOEC (48 h) = 10 mg/L                                      |
| inhibition of freshwater algal growth [OECD TG 201]            | <i>Selenastrum capricornutum</i> | E <sub>b</sub> C <sub>50</sub> (72 h) = 2.0<br>E <sub>r</sub> C <sub>50</sub> (72 h) = 3.4 mg/L |
| inhibition of freshwater algal growth [OECD TG 201]            | <i>Scenedesmus subspicatus</i>   | E <sub>b</sub> C <sub>50</sub> (72 h) = 1.6<br>NOEC (72 h) = 1.0 mg/L                           |

\* NOEC - no observable effect concentration

## Marine Species Summary

| <i>Test</i>  | <i>Species</i>                                     | <i>Results</i> (nominal)  |
|--|--|---|
| acute toxicity to marine fish [UK Ministry of Agriculture] | Turbot<br><i>Scophthalmus maximus</i>              | LC <sub>50</sub> (96 h) = 260 mg/L  |
| acute toxicity to marine molluscs                          | Pacific oyster embryos<br><i>Crassostrea gigas</i> | LC <sub>50</sub> (24 h) = 1200 mg/L   |
| acute immobilisation to marine invertebrates               | Copepod<br><i>Acartia tonsa</i>                    | EC <sub>50</sub> (48 h) = 340 mg/L  |
| acute immobilisation to marine invertebrates               | Mysid<br><i>Mysidopsis bahia</i>                   | sl EC <sub>50</sub> (48 h) < 30000<br>See notes below   |
| acute toxicity to marine invertebrates                     | Brown<br><i>Crangon crangon</i>                    | sl LC <sub>50</sub> (96 h) = 91 mg/L  |
| inhibition of marine algal growth [OECD TG 201]            | <i>Skeletonema costatum</i>                        | E <sub>b</sub> C <sub>50</sub> (72 h) = 710<br>E <sub>r</sub> C <sub>50</sub> (72 h) = 1600<br>NOEC (72 h) = 320 mg/L |

\* NOEC - no observable effect concentration

## 10.1 Freshwater Species

### *Fish*

The tests on rainbow trout were conducted under semi static conditions over a 96 hour test period at 14±1°C with daily renewal of the test media (Douglas and King, 1992a). The nominal concentrations of the chemical were 0 (control), 320, 560, 1000, 1800, 3200 and 5600 mg/L. Ten fish were used in each test. The pH and dissolved oxygen levels of the test media were 7.6-8.3 and 9.9-10.1 mg/L respectively. No mortalities or aberrant behaviour of the test animals was observed for exposures less than 72 hours at the (nominal) 1800 mg/L concentration, but after 72 hours exposure at this test concentration some of the fish (2 of the surviving 7) showed increased pigmentation, and one was dead after 96 hours exposure. At higher exposures the fish exhibited increased pigmentation, loss of equilibrium and lethargy, and after 96 hours exposure at 3200 mg/L (nominal) only 2 of the original 10 fish survived. The data was analysed using the methods of Thompson and Weil to provide the 96 hour LC<sub>50</sub> of 2100 mg/L and the associated No Observed Effect Concentration (NOEC) of (nominally) 1000 mg/L. These data indicate that the chemical is not toxic to this species.

### *Invertebrates*

An acute toxicity test of notified chemical against *Daphnia magna* was conducted under static conditions over a 48 hour period using one control and nine test solutions made up at nominal concentrations of 0 (control), 5.6, 10, 18, 32, 56, 100, 180, 320 and 560 mg/L at a temperature maintained at  $21 \pm 1^\circ\text{C}$  (Douglas and Ffrench, 1992). The test was conducted in duplicate using 10 *Daphnia* in each test vessel. During the tests the water hardness was between 150 and 200 mg/L (as  $\text{CaCO}_3$ ), the pH between 7.6 and 8.2 and the dissolved oxygen levels between 8.3 and 8.9 mg/L. No immobility was observed over the 48 hour test period for the lowest nominal test concentrations of 5.6 mg/L, but after 48 hours exposure at (nominal) 10 mg/L one of the test animals was observed to be immobile, while after 48 hours exposure at 100 mg/L all animals were dead. The data were analysed using the methods of Thompson and Weil to provide the 48 hour  $\text{EC}_{50}$  of 35 mg/L and the associated NOEC of (nominally) 10 mg/L. These results indicate that the caesium formate is slightly toxic to this species.

Analysis of the mortality data using the preferred probit analysis is not possible due to the very steep dose response curve and lack of data points where particular solution concentrations correspond to partial mortality of the *Daphnia* population.

### *Algae*

Tests on algal growth inhibition (*Selenastrum capricornutum*) were performed with solutions of the notified chemical made up in nutrient media at nominal concentrations of 0 (control), 0.2, 0.4, 0.8, 1.5, 3, 6 and 12 mg/L, and three replicate tests were conducted at each concentration over a 72 hour test period (Whale, 1995a). The mean temperature throughout the test was between  $21.4$  and  $25.5^\circ\text{C}$ , and the pH of the media containing algae was between 7.3 and 8.3 during the test. Growth of algal biomass was monitored by counting the cell density over the 72 hour test period, and while a lag in growth was noted for all test solutions and the control for the first 24 hours, the algae grew well in the ensuing 48 hours in the control and lower concentration solutions. Nevertheless, significant inhibition of growth in algal biomass was observed at all test concentrations, and the data analysed using probit analysis to furnish the 72 hour  $\text{E}_b\text{C}_{50}$  of 2.0 mg/L and corresponding  $\text{E}_r\text{C}_{50}$  (inhibition of rate of biomass growth) of 3.4 mg/L. These results indicate that the notified chemical is moderately toxic to this species of green algae.

A report on the toxicity of caesium formate to a second species of fresh water green algae (*Scenedesmus subspicatus*) was also submitted (Douglas and King, 1992c). This test was conducted over 72 hour period at  $24 \pm 1^\circ\text{C}$  using nominal compound test concentrations of 0 (control), 1.0, 2.0, 4.0, 8.0, 16.0 and 32.0 mg/L. Similar observations and analysis indicated that the notified chemical is also moderately toxic to this species, with  $\text{E}_b\text{C}_{50}$  of 1.6 mg/L and  $\text{E}_r\text{C}_{50}$  of 1.8 mg/L. The No Observed Effect Level (NOEL) was 1.0 mg/L.

## **10.2 Marine Species**

### *Fish*

The tests on juvenile turbot were conducted under semi static conditions over a 96 hour test period at  $14 \pm 1^\circ\text{C}$  in test media made up in synthetic sea water (Douglas and King, 1992d). The nominal concentrations of the chemical were 0 (control), 56, 100, 180, 320, 560 and 1000 mg/L, and 10 fish were used in each test. The pH and dissolved oxygen levels of the test media were  $8.5 \pm 0.1$  and 8.1-8.5 mg/L respectively. No mortalities or aberrant behaviour of the test animals were observed for exposures less than 24 hours at the (nominal) 100 mg/L concentration, but after 48 hours exposure at this test concentration two of the fish were dead.

No further mortalities occurred in the ensuing 3 days. However, increased mortality was observed at the higher nominal concentrations and, after 72 hours exposure to the nominal 560 mg/L solution, all fish were dead. The only sublethal effect noted on the fish was loss of equilibrium. The data were analysed to provide the results tabulated above, although the methodology used was not specified. The 96 hour LC<sub>50</sub> indicates that the notified chemical is practically non toxic to this species.

#### *Molluscs*

A test on the toxicity of the notified chemical to marine molluscs was conducted using Pacific Oyster Embryos (Whale, 1995b). The test conducted against *Crassostrea gigas* embryos (*ca.* 100 per test) over 24 hours using eight solutions of the compound prepared in natural sea water made up at nominal concentrations between 1 and 3200 mg/L. The number of embryos which failed to develop normally were noted and compared with the control, and the data analysed to provide the results tabulated above. These indicate that caesium formate is non toxic to this species at the crucial period of intense cellular activity.

#### *Invertebrates*

An acute toxicity test (immobilisation) of notified chemical against the marine copepod *Acartia tonsa* was conducted over a 48 hour test period using a control and five solutions of caesium formate made up in sea water at nominal concentrations between 10 and 1000 mg/L (Whale, 1995c). Significant immobilisation (13 of the original 30 animals) was noted after 48 hours exposure to a solution containing nominally 330 mg/L of the test compound. All 30 animals were dead (immobile) after 24 hours exposure to the nominally 1000 mg/L solution. The data were analysed to give the results in the table above, and the 48 hour EC<sub>50</sub> of 340 mg/L indicates that caesium formate is practically non toxic to this species of marine invertebrate.

A very synoptic summary report of a range finding study on the toxicity of the material to Mysid shrimp was also submitted (Lang, 1997). This test was conducted at 20 ± 2°C in artificial sea water using solution test concentrations between 30000 mg/L and 1000000 mg/L. No further details were provided except that the 96 hour LC<sub>50</sub> was stated as being less than 30000 mg/L (the least concentrated test solution).

A report on the toxicity of the material to Brown shrimp was also submitted with the notification (Douglas and King, 1992e). This test was performed under static conditions over a 96 hour period at 14 ± 2°C using nominal test concentrations of caesium formate in sea water of 0 (control), 56, 100, 180, 320, 560 and 1000 mg/L. Twenty test animals were used at each concentration and significant mortality relative to the control was first apparent after 24 hours at 320 mg/L with 3 of the original 20 animals dead. Increased mortality was noted as the exposure increased; after 72 hours exposure to the 560 mg/L solution, all animals were dead. The data were analysed using a proprietary laboratory method (not described) to give the 96 hour LC<sub>50</sub> of 91 mg/L. This result indicates that the test material is slightly toxic to this species of marine invertebrate.

#### *Algae*

Tests on growth inhibition of the marine diatom *Skeletonema costatum* were performed with solutions of the notified chemical made up in nutrient media at nominal concentrations of 0 (control), 100, 320, 1000 and 3200 mg/L (Whale, 1992c). Six replicate tests were conducted at each concentration over a 72 hour test period, and the algal growth data obtained using a

Coulter counter analysed to provide the toxicity end points tabulated above. The results of this test indicate that the notified chemical is practically non toxic to this species of green algae.

Duplicate tests were run in test solutions containing both high (1 g/L) and low concentrations of EDTA in order to ascertain whether possible complex formation between this chelating ligand and caesium influenced toxicity. Comparison of the growth data between the two sets of data indicated no significant differences in the algal growth rate curves obtained in the two media, and that complex formation does not appear to influence toxicity of the chemical.

### **10.3 Summary of Aquatic Toxicity**

The notified chemical is at worst slightly toxic to those marine aquatic organisms against which it has been tested with the 48 hour LC<sub>50</sub> of the most sensitive species (brown shrimp) being 91 mg/L. It also shows slight toxicity to freshwater invertebrates with the 48 hour LC<sub>50</sub> for *Daphnia* of 35 mg/L, but has been shown to be moderately toxic to two species of fresh water green algae, with 72 hour E<sub>b</sub>C<sub>50</sub> (72 h) values of 1.6 and 2.0 mg/L respectively.

The large difference between the toxicity of the notified chemical to freshwater algae compared with the marine counterparts may be due to the ability of the formate ion to form weak association complexes with divalent ions such as calcium and magnesium, which are essential micronutrients for algae. In sea water these elements are present in relatively high concentrations, with Mg present at around 1270 mg/L and Ca at around 400 mg/L (CRC, 1977), while in the nutrient media used in fresh water algal growth studies the levels are very much lower, and are typically less than 10 mg/L for both elements. If the availability of these elements to the algae is reduced through association with the formate ions, this will impair algal growth and this would be the cause of the measured toxicity. The very much higher concentrations of the divalent elements in sea water mean that greater concentrations of caesium formate would be required to significantly reduce their availability to the marine algae and diatoms.

The formate component of the notified chemical is readily biodegradable, and will consequently be removed from the aquatic environment quickly. However the caesium component will be persistent. The chemical is assessed to have little potential for bioaccumulation.

## **11. ASSESSMENT OF ENVIRONMENTAL HAZARD**

The environmental hazard resulting from use of the notified chemical in coal classification laboratories is considered to be low since little release to the aquatic compartment is likely. It is estimated that around 2.5 tonnes of the notified chemical may be released each year from this activity, and most is expected to become assimilated into coal ash after the coal has been burnt.

However, far larger releases of the chemical are likely from its use in off shore oil/gas drilling operations, and localised high concentrations of caesium may consequently result from the disposal of drill cuttings to the marine environment where the drill cuttings form mounds under the drilling platforms. It is estimated that up to 170 tonnes of the notified chemical may be released each year in this manner, and up to *ca.* 42 tonnes (containing 32 tonnes of caesium metal) from any particular well. Since the notified chemical is highly water soluble the

caesium is expected to eventually diffuse into the surrounding water column. Sea water has an ambient caesium concentration of 0.002 mg/L (CRC, 1985), and so assuming a release of 42 tonnes of CsHCO<sub>2</sub> in the cuttings from a given well, the liberated caesium will require diffusion into approximately 160 cubic kilometres of water to bring the concentration to within 10 % of the ambient<sup>1</sup>. If it is assumed that the average water depth around a given off shore well is 1 km, then the water around the well for a radius of approximately 7 km could have significantly elevated concentrations of this element. When water depth is less than 1 km, a larger area of ocean will have higher than ambient caesium levels.

The notified chemical has been shown to exhibit slight toxicity to the brown shrimp (96 hour LC<sub>50</sub> = 91 mg/L), so sensitive organisms may be exposed to toxic concentrations of the chemical in the immediate vicinity of the cutting mounds as the chemical diffuses into the surrounding sea water. However, without a detailed analysis of the relevant diffusion rates (taking into account likely current strengths and other localised factors), it is impossible to further quantify the risk to susceptible organisms. Due to the high water solubility it may be expected that, once desorbed from the cuttings, diffusion would be rapid.

The formate component of the notified chemical is readily biodegradable, although the caesium will be persistent. The chemical is assessed as having low potential for bioaccumulation, and also is not expected to have large affinity for the organic component of soils or sediments. The high water solubility indicates that the chemical should be very mobile in soils and sediments.

The notified chemical is not likely to present a hazard to the environment when it is used as a variable density medium for coal classification since little release to the water compartment is likely as a result of this use.

However, large quantities of the notified chemical may be used in off shore oil/gas drilling operations and much of this is likely to be discarded onto the sea floor with drilling wastes. These wastes form mounds on the sea floor under the drilling platforms, and since there is uncertainty regarding the rate of diffusion of the entrained caesium from these mounds, some exposure to marine organisms is considered likely. Some toxic effects have also been observed in marine test animals exposed to high levels of the chemical, and consequently it is concluded that the new material may pose an environmental hazard to marine ecosystems.

## **12. ASSESSMENT OF PUBLIC AND OCCUPATIONAL HEALTH AND SAFETY EFFECTS**

### *Hazard Assessment*

The notified chemical was found to be of low acute oral toxicity to rats (LD<sub>50</sub> = 1780 mg/kg), low dermal toxicity in rats, a slight skin irritant and a moderate eye irritant in rabbits, and non-sensitising to the skin of guinea pigs. The results of genotoxicity testing were equivocal. The notified chemical is not expected to cause significant chronic effects based on the known properties of the formate anion and caesium cation. The notified chemical is classified as a

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<sup>1</sup> Assuming ambient Cs concentration in sea water is 0.002 mg/L, and that 32 tonnes of Cs are released around each well, the required volume of water which would raise this concentration by 10 % (*ie* by 0.0002 mg/L) = 32 X 10<sup>9</sup> (mg)/0.0002 mg/L

= 16 X 10<sup>13</sup> L = 16 X 10<sup>10</sup> m<sup>3</sup>  
= 160 cubic kilometres

hazardous substance in accordance with the NOHSC *Approved Criteria for Classifying Hazardous Substances* (NOHSC, 1999) and the following risk phrases apply: R22 'Harmful if swallowed' and R36 'Irritating to eyes'.

#### *Occupational Health and Safety*

The notified chemical will be used in Australia only in the form of concentrated aqueous solutions. Due to the hygroscopic nature of the notified chemical, it is unlikely to be isolated in solid form. Approximately 12 laboratory workers may be exposed to solutions of the notified chemical during coal classification procedures. An unspecified number of workers in Australia may be exposed to the notified chemical on oil platforms, although the notifier estimates that the total worldwide will be of the order of 200 workers. Exposure is expected to be primarily dermal, through drips, spills and splashes while transferring the solutions.

The main risk on exposure to the notified chemical is associated with ocular exposure. Precautions to prevent ocular exposure to splashes of the solutions should be taken whenever the solutions are handled. To minimise the risk of eye irritation, eye protection (goggles or face shield) should be worn.

#### *Public Health*

Given that the intended use of the notified chemical will be restricted to coal testing laboratories and onshore/offshore drilling operations, no public exposure is anticipated except in the event of an accidental spill, during transport from the docks to drilling sites or laboratories. Based on this information, the notified chemical is unlikely to pose a significant hazard to public health when used in the proposed manner.

### **13. RECOMMENDATIONS**

#### *Regulatory controls*

- The NOHSC Chemicals Standards Sub-committee should consider the following health hazard classification for the notified chemical:
  - R22 Harmful if swallowed
  - R36 Irritating to eyes

#### *Control Measures*

##### **Occupational Health and Safety**

- Employers should ensure that the following personal protective equipment is used by workers to minimise occupational exposure to the notified chemical in solution:
  - eye protection should be worn at all times when the solutions are handled; impervious gloves (rubber or nitrile), and industrial clothing and footwear should be worn.

Guidance in selection of personal protective equipment can be obtained from Australian, Australian/New Zealand or other approved standards.

- A copy of the MSDS should be easily accessible to employees.



- As concentrated solutions of the notified chemical are classified as hazardous to health in accordance with the NOHSC *Approved Criteria for Classifying Hazardous Substances*, workplace practices and control procedures consistent with provisions of State and Territory hazardous substances legislation must be in operation.

## Environment

- Special efforts should be made to bring the contents of the final reports on the present chemical, and other drilling mud components, to the attention of relevant State Authorities. In particular the WA Department of Minerals and Energy conduct their own assessment on formulated drilling fluids prior to granting approval for the use of these materials. This authority requires data on toxicity test performed against local marine species prior to granting approval for use.

### 13.1 Secondary notification

The Director of Chemicals Notification and Assessment must be notified in writing within 28 days by the notifier, other importer or manufacturer:

- (1) Under Section 64(2) of the Act:
  - if any of the circumstances listed in the subsection arise.

The Director will then decide whether secondary notification is required.

No additional secondary notification conditions are stipulated.

## 14. MATERIAL SAFETY DATA SHEET

The MSDS for the notified chemical was provided in a format consistent with the *National Code of Practice for the Preparation of Material Safety Data Sheets* (NOHSC, 1994).

This MSDS was provided by the applicant as part of the notification statement. It is reproduced here as a matter of public record. The accuracy of this information remains the responsibility of the applicant.

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## Attachment 1

The Draize Scale (Draize, 1959) for evaluation of skin reactions is as follows:

| <i>Erythema Formation</i>                 | <i>Rating</i> | <i>Oedema Formation</i>   | <i>Rating</i> |
|---|---------------|---|---------------|
| No erythema                               | 0             | No oedema   | 0             |
| Very slight erythema (barely perceptible) | 1             | Very slight oedema (barely perceptible)                                     | 1             |
| Well-defined erythema                     | 2             | Slight oedema (edges of area well-defined by definite raising)              | 2             |
| Moderate to severe erythema               | 3             | Moderate oedema (raised approx. 1 mm)                                       | 3             |
| Severe erythema (beet redness)            | 4             | Severe oedema (raised more than 1 mm and extending beyond area of exposure) | 4             |

The Draize scale (Draize *et al.*, 1944) for evaluation of eye reactions is as follows:

### *CORNEA*

| <i>Opacity</i>   | <i>Rating</i> | <i>Area of Cornea involved</i> | <i>Rating</i> |
|--|---------------|--------------------------------|---------------|
| No opacity   | 0 none        | 25% or less (not zero)         | 1             |
| Diffuse area, details of iris clearly visible                                  | 1 slight      | 25% to 50%                     | 2             |
| Easily visible translucent areas, details of iris slightly obscure             | 2 mild        | 50% to 75%                     | 3             |
| Opalescent areas, no details of iris visible, size of pupil barely discernible | 3 moderate    | Greater than 75%               | 4             |
| Opaque, iris invisible   | 4 severe      |                                |               |

### *CONJUNCTIVAE*

| <i>Redness</i>  | <i>Rating</i> | <i>Chemosis</i>                                     | <i>Rating</i> | <i>Discharge</i>   | <i>Rating</i> |
|---|---------------|---|---------------|--|---------------|
| Vessels normal  | 0 none        | No swelling   | 0 none        | No discharge   | 0 none        |
| Vessels definitely injected above normal  | 1 slight      | Any swelling above normal                           | 1 slight      | Any amount different from normal   | 1 slight      |
| More diffuse, deeper crimson red with individual vessels not easily discernible | 2 mod.        | Obvious swelling with partial eversion of lids      | 2 mild        | Discharge with moistening of lids and adjacent hairs                         | 2 mod.        |
| Diffuse beefy red   | 3 severe      | Swelling with lids half-closed                      | 3 mod.        | Discharge with moistening of lids and hairs and considerable area around eye | 3 severe      |
|   |               | Swelling with lids half-closed to completely closed | 4 severe      |  |               |

### *IRIS*

| <i>Values</i>   | <i>Rating</i> |
|---|---------------|
| Normal  | 0 none        |
| Folds above normal, congestion, swelling, circumcorneal injection, iris reacts to light | 1 slight      |
| No reaction to light, haemorrhage, gross destruction                                    | 2 severe      |

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