Cesium Formate and Zinc Bromide

Comparative Hazard Assessment and HSE Profiles

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Third revised edition − 12 July 2017

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Executive summary

This work presents a comparative overview of the physico-chemical and biological properties of cesium formate and zinc bromide, the prime constituents of the two oilfield high-density brines. Properties are then related to the chemical health, safety and environmental hazard posed by these products. The data presented supports HSE risk profiling of these chemicals for offshore oilfield use.

The content has been condensed from test results mainly supplied by formate manufacturers, an extensive review of publicly available literature, and independent research reports. The first edition of this assessment has been peer reviewed by two world-class scientists, Dr. Derek A. James, previously of the UK's Health and Safety Executive, and Professor Jussi Kukkonen, of the University of Joensuu, Finland. In this third revised edition, revisions relate to research conducted on cesium formate since the previous edition was published in December 2012. In addition, a brief review of zinc bromide-related toxicity and ecotoxicity data was carried out and related references updated.

The behaviour, movement, likely fate and effects of the two chemicals in different environmental compartments have been assessed. The results are condensed into comparative HSE profiles for cesium formate and zinc bromide, which can then be used in fluid selection.

HSE PROFILES: The properties of the two high-density brines, cesium formate and zinc bromide, are presented and collated as HSE profiles. The aim is to provide an informed picture of how these two chemicals behave and interact in the physical and chemical environment. The HSE profiles provide a baseline for the analysis of effects of incidents to people and the environment. The HSE profiles are free-standing parts of the report.

HEALTH: Human health concerns in the oilfield would mainly be limited to acute exposure during handling. Basic cesium formate is an eye irritant. Direct contact with liquid or powder forms of cesium formate may cause skin irritation, but does not lead to skin burns. The effect of the acidic and highly corrosive zinc bromide is likely to extend to severe chemical skin burns, necrosis and extensive eye damage, while also causing skin sensitisation. This is particularly pertinent, as contact with bromide brine does not lead to immediate pain. Several cases of such incidents are reported in the literature[1,2,3]. The acute inhalation effects of zinc bromide brine are estimated to be more severe than those created by exposure to cesium formate, although no test data on cesium inhalation is available. Both chemicals are harmful if swallowed.

Zinc bromide exhibits some potential for chronic effects from repeated exposure, such as damage to lungs and mucous membranes, and anemia. There is some evidence of the effect on fertility from long-term repeated exposure to bromides in high doses[4]. Repeated oral doses of cesium formate are suspected of affecting fertility and damaging organs, such as kidneys and adrenals, the nervous system and blood[5].

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1   Sagi et al. (1985)
2   Singer et al. (1992)
3   Saeed et al. (1997)
4   European Chemicals Bureau (2000b) 5.8 Toxicity to Reproduction
5   Cabot (2017) Cesium Formate Solution Safety Data Sheet 18.04.2017

Table A: Acute toxicity of cesium formate and zinc bromide to aquatic invertebrates

Organism	Endpoint	Cs formate	Zn bromide
Marine environment: Copepod (*Acartia tonsa*)	EC50 (48 h)	340 mg/l[7]	1.6 mg/l[8] 2.4 mg/l[9]
Brackish water: Mysid shrimp (*Americamysis bahia*)	Cesium formate EC50 (48 h) Zinc bromide EC50 (96 h)	521 mg/l[10]	1.5 mg/l[11]
Freshwater: Water flea (*Daphnia magna*)	EC50 (48 h)	> 100 mg/l[12]	8.8 mg/l[13] 1.22 mg/l[14]

SAFETY: Neither chemical is in itself flammable, oxidising or explosive. The corrosiveness of zinc bromide requires more specialist equipment during storage and transport. Safety in this context has not been extended to downhole operations and technical considerations.

ENVIRONMENT: Cesium formate brine has been relatively extensively tested, in particular for aquatic toxicity, but the available information for zinc bromide is scarce. The available aquatic invertebrate data for both brines has been collated into Table A. Toxicity of zinc bromide to the test species is clearly at least two orders of magnitude higher than that of cesium formate. In the freshwater environment, the difference is in the order of one magnitude. In freshwater, the lethal effects from cesium formate in laboratory conditions are, in fact, expected to be attributable to nutrient depletion due to weak complexation of formate with divalent nutrient ions rather than direct toxic effects on the organisms[6].

SPILLS AND DISCHARGES: The data indicate that immediate acute toxicity of discharges or spills of cesium formate to water bodies will be significantly lower than for zinc bromide. The formate part of the chemical is rapidly degraded by micro-organisms in the environment and no significant effects are to be expected. Results from environmental surveys following formate discharges support this conclusion[15]. No severe effects of elevated cesium levels in the environment have been reported. The environmental effects of zinc bromide are expected to be more serious – in particular, the zinc ion has the potential to cause long-term chronic effects in organisms. Exposure to even small amounts of zinc (<1 mg/l) has resulted in inhibition and disturbance of, for example, growth (e.g. common mussel[16]) and reproduction (e.g. sea urchins[17]) in laboratory conditions. In the long term, such effects may result in highly disturbed biotic communities in the environment. On the other hand, bromide ions in seawater may contribute to the concentration of ozone depleting bromine in the air[18].

6   NICNAS (2001)
7   Cabot (2017)
8   Hydro ASA internal testing
9   ICL Industrial (2012)
10 Environmental Enterprises USA, Inc. (2011a). Test report on cesium formate and Mysidopsis bahia test, 17.11.2011
11 Hydro ASA internal testing
12 Harlan Laboratories (2011a). Test report on cesium formate and Daphnia magna test, 08.02.2011
13 ICL Industrial (2012)
14 Magliette et al. (1995)
15 Zuvo et al. (2005)
16 Strömgren (1982), as quoted in WHO (2001)
17 Dinnel et al. (1989), as quoted in WHO (2001)
18 Sander et al. (2003)aaa

1 Background

The design of a well includes consideration of which combination of chemicals in the form of the well construction fluid (WCF) will be most suitable for the drilling and completion operations, i.e. which suite of chemicals will do the required job. Where more than one option is available, the technical performance advantage of the chemical solutions on hand must be balanced against the cost of their purchase and the risk associated with their deployment, maintenance and disposal.

During the operations, unwanted incidents may cause delays, increase direct costs or lead to liabilities – all of which can affect the return on investment. As any manager of complex technical projects knows, there is no such thing as incident-free operations. Incorporating a thorough evaluation of HSE risk against cost at the design stage allows better informed decisions. Realised HSE risks can be both costly and time consuming or lead to future liabilities. However, the assessment of the HSE risk may be fragmented between different consent requirements, such as occupational health or structural safety and the overall picture of the HSE risk scenery of an operation may never be compiled.

There are numerous technical solutions and fluid alternatives available for drilling and completion operations. This report provides an overview of the issues to consider when making a comparative HSE assessment and presents the available data for two high-density WCF brines: Cesium formate and zinc bromide.

- Cesium formate is marketed as an eco-friendly fluid with high technical performance standards, suitable for complex and demanding drilling and completion work.

- Zinc bromide is a traditional solution for a high-density, solids-free completion fluid. This bromide brine completion fluid is sold in high volumes by many manufacturers.

Absolute risk evaluations are often plagued with uncertainties arising from problems associated with lack of sufficient statistical data on incidents to determine probabilities. In order to avoid this, the approach taken here is comparative: Comparing a formate solution with a conventional operational solution using bromide brine provides an excellent overview of the importance of HSE aspects. The comparative approach supports the design of a methodology, which allows managers to take into account the overall HSE risk and, at the point of well design, method selection. In essence, the objective is to present how chemical choices influence risk in a way that facilitates the identification of the most cost-efficient option.

From a management point of view, the challenge is to implement corporate policies that reflect both ethical policies and legal boundaries, irrespective of where on the globe the operations are carried out. In this report, the aim is to provide the manager with sufficient data to allow informed HSE decisions and hopefully to support the creation of guidelines for how HSE properties should be taken into account in the method selection process.

2 Aim, objective, methodology and coverage

2.1 AIM AND OBJECTIVE

This report presents an overview of the physico-chemical and biological properties of cesium formate and zinc bromide and relates these to the degree of chemical hazard from an overall HSE point of view. HSE aspects are often overlapping and interdependent with linkages to several scientific branches, as indicated in Figure 1.

The aim has been to collate an overview of the available data from the literature. At the same time, the type of data and understanding required to compare chemical HSE risk profiles is systematically presented. The objective of the review has been to construct comparative HSE profiles of cesium formate and zinc bromide and present these in a manner which is understandable

also to non-experts. The aim is to facilitate informed decision making, which incorporates HSE when selecting fluids for well construction.

2.2 METHODOLOGY AND SCOPE

The content has been condensed from test results mainly supplied by formate manufacturers, an extensive review of publicly available literature and independent research reports. As any omissions are unintentional, profiles should be amended if new data becomes available. In order to minimise this possibility, peer-reviewed data from scientific journals or government reports have been preferentially used. This has been complemented with data provided by chemical

Figure 1: HSE hazards and associated scientific branches included in the study
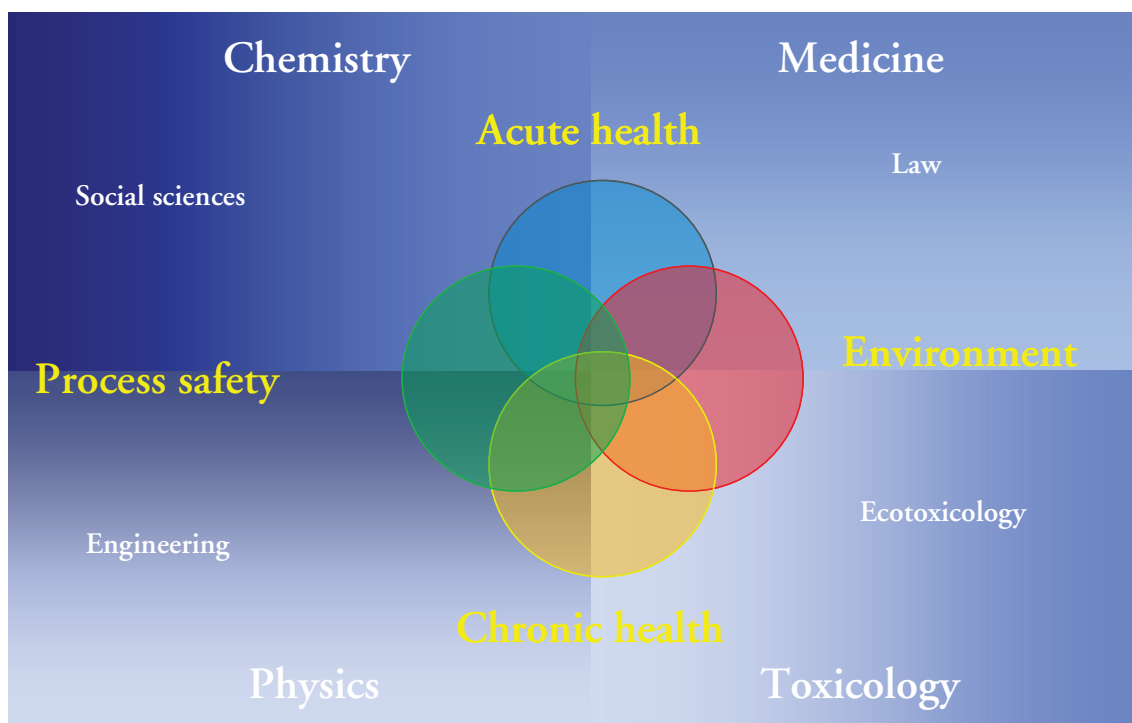
manufacturers and distributors, including data from safety data sheets (SDSs).

The behaviour and movement of the substances in different environmental compartments (seawater, marine sediment and soil) is addressed and the possible biological fate and effects of the substances is discussed. Using the available information, a comparative hazard assessment was carried out and illustrative HSE profiles created for both substances.

2.3 LIMITATIONS

It should be noted that whilst data for cesium formate has been sourced from the manufacturer, all the data used relating to zinc bromide is from publicly available sources and preferentially sourced from independent reviews. Where manufacturer-specific data has been included, this is mainly to highlight differences in how certain properties are described.

When building a drilling or completion fluid, various additives, such as corrosion inhibitors, biocides or oxygen scavengers can be included. These additives may represent a significant increase in toxicity of the fluid. The effect of these additives has not been included in this assessment.

It's beneficial to use SDSs as a data source as these are given to operators by their chemical suppliers. However, there are some differences between the SDS data for zinc bromide products. Following the precautionary principle, several different SDSs have been used to source information.

The data presented is the result of an independent literature review and the first edition has been verified through a thorough peer review by independent, world-class scientists.

3 Physico-chemical profiling

3.1 PHYSICAL AND CHEMICAL PROPERTIES

Cesium formate (CsCOOH) is an inorganic salt of the monovalent alkali metal cesium (Cs) and the anionic form of formic acid (HCO_2H). Cesium formate is highly soluble in aqueous solutions, forming high-density, alkaline brines. In aqueous solutions, it rapidly dissociates into its ionic constituents, the cesium cation (Cs^+) and the formate anion ($HCOO^-$).

Zinc bromide ($ZnBr_2$) is an inorganic salt of the divalent heavy metal zinc cation (Zn^{2+}) and two bromide anions ($2Br^-$). Zinc bromide is highly soluble in aqueous solution, forming high-density acidic brines. In aqueous solutions, it dissociates into zinc cation (Zn^{2+}) and bromide anions (Br^-).

The physical and chemical properties of the two brines are summarised in Table 1, quoting two sources of information for zinc bromide data. Both chemicals listed in the table are oilfield products containing 70 to 80% zinc bromide. Data were sourced from SDSs. Notable is the difference in the pH values of these two solutions. The pH value varies between products, which may be due to other ingredients, e.g. buffers or additives. One laboratory chemical has a pH of 4[19].

Table 1: Physical and chemical properties of cesium formate and zinc bromide

	Cs formate[20]	Zinc bromide[21]	Zinc bromide[22]
CAS number	3495-36-1	7699-45-8	7699-45-8
Chemical formula	CsCOOH	$ZnBr_2$	$ZnBr_2$
Chemical structure	$HCOO^-Cs^+$	$Zn^{2+}Br_2^{2-}$	$Zn^{2+}Br_2^{2-}$
Molecular weight	177.92	NA	NA
Appearance	Colourless liquid	Clear, colourless viscous liquid	Odourless, colourless to yellow liquid
Boiling point	112–145°C	136°C	135°C (for 75% solution)
pH	9–11 (1:10 dilution with water)	5–6 (1:10 dilution)	1–2
Viscosity	1.7–10 cp (at 20°C)	NA	NA
Solubility in water	84.6–86.6% soluble at 20 ± 0.5°C	Soluble	Complete
Vapour pressure	400–2250 Pa	5.2 mm Hg (25°C)	NA
Density	Specific gravity 1.05–2.40 g/cm³ (at 15.6°C)	Specific gravity 2.3–2.51 g/cm³	Specific gravity 2.3 g/cm³ (for 75% solution at 25°C)

19 Fisher Scientific (2017)
20 Cabot (2017)
21 ICL Industrial (2012)
22 Tetra Technologies (2015)

3.2 SPECIATION, BEHAVIOUR AND MOBILITY IN SEAWATER

3.2.1 The process

Chemical speciation describes the chemical form in which the substance exists. Speciation in turn influences the behaviour and mobility of the substance and, in fact, these are all interdependent properties of substances. These properties largely determine the fate and effects of a substance in the environment.

3.2.2 Cesium formate

In seawater, cesium formate dissociates into its ionic constituents Cs^+ and $HCOO^-$. Cesium is a natural component of seawater and its average concentration is approximately 0.3 μg/l[23]. Alkali metals exist as hydrated ions in aqueous solutions. For the cesium ion, the arrangement of water molecules around the cation is probably octahedral[24]. A very small proportion (max 1%) of the cesium in seawater exists as ion paired with sulphate $(CsSO_4^-)$[25].

In seawater, the formate anion may form weak association complexes with cations. In an aqueous solution a very small proportion of the formate ions will react with water molecules and formic acid will be formed. The equilibrium reaction between formic acid and formate is:

$HCO_2^- + H_2O \Leftrightarrow HCO_2H + OH$ (**1a**)

More commonly written as:

$HCO_2^- + H_3O^+ \Leftrightarrow HCO_2H + H_2O$ (**1b**)

Or the shorter version:

$HCO_2^- + H^+ \Leftrightarrow HCO_2H$ (**1c**)

Removal of formate ions from the water column through biodegradation[26] will change the equilibrium and the reaction equation to the left will dominate until new equilibrium is obtained. However, once in the sea, the formate is diluted and then fairly rapidly degraded by the ocean's micro-organisms. Hence the formate anion's behaviour and mobility in seawater is limited.

In highly illuminated surface waters the oxidation of formate ions by hydroxyl radicals is possible. Hydroxyl radicals (•OH) are formed by the action of sunlight on the water molecules and are found in surface waters in very low concentrations. Carbon dioxide, hydroxide ions and hydroperoxyl radicals are formed as a result of formate oxidation[27].

During extended exposure of formate brine to high-temperature conditions (> 200°C) a small amount of decomposition might occur. The degree of formate decomposition that takes place depends on the amount of carbonate/bicarbonate pH buffer that has been added to the formate brine and the temperature. The rate at which the decomposition happens depends on the availability of catalytic surfaces. The main decomposition product of formate decomposition is bicarbonate. Bicarbonate is formed according to the decarboxylation reaction:

$COOH\ (aq) + H_2O \Leftrightarrow HCO_3\ (aq) + H_2\ (g)$ (**2**)
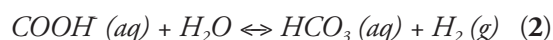
This reaction will reach equilibrium when the bicarbonate concentration reaches a certain level. A well-buffered formate brine will therefore decompose less than a formate brine with less carbonate/bicarbonate buffer. Another reaction that takes place to a smaller extent is the

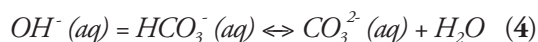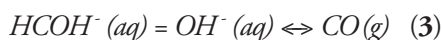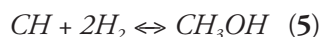23 Turekian K.K. (1968) Oceans, Prentice-Hall
24 Sharpe (1986)
25 Byrne (2002)
26 OECD (1992a)
27 Gilbert et al. (2003), Section 5.3.5

dehydration of formate according to the following reactions, producing carbon monoxide and carbonate:

$$HCOH^- \ (aq) = OH^- \ (aq) \Leftrightarrow CO \ (g) \quad (3)$$

$$OH^- \ (aq) = HCO_3^- \ (aq) \Leftrightarrow CO_3^{2-} \ (aq) + H_2O \quad (4)$$

Carbon monoxide can react further with hydrogen gas from reaction (2) and form methanol.

$$CH + 2H_2 \Leftrightarrow CH_3OH \quad (5)$$

Small amounts of methanol have been found in formate brines that have been left in HPHT wells for extended periods of time. Trace amounts of oxalate has also been measured in formate brines that have been exposed to HPHT conditions.[28]

3.2.3 Zinc bromide

$ZnBr_2$ dissociates in aqueous solution into a zinc cation (Zn^{2+}) and two bromide anions (Br^-). Average baseline zinc concentrations in seawater are in the range 0.0005 to 0.026 µg/l[29]. In deep waters, zinc concentrations are markedly higher, ranging between 0.002 µg/l and 0.1 µg/l[30].

Zinc is reported to exist in water in seven different forms[31] (for details see Appendix 1). In open-sea surface waters of the North-eastern Atlantic, less than 4 % of the existing zinc exists as inorganic species[32]. The remainder forms complexes with unidentified organic ligands. Speciation by complexation also dominates in deep waters. The inorganic proportion of zinc exists mainly as free hydrated Zn^{2+} ions, and only to a smaller extent as weakly ion paired with chloride ions ($ZnCl^+$)[33].

The solubility of zinc is strongly dependent on pH. In low pH environments, zinc may be present in the aqueous phase in its ionic form, but at pH values over 8.0 it is likely to precipitate[34].

Bromine is also a natural constituent of seawater. Bromide is one of the 11 major ions of seawater. It exists in seawater as free monovalent inorganic bromide anions (Br^-) and its average concentration is 65 mg/l[35]. Formation of more harmful bromine compounds such as bromate and hypobromous acid is unlikely, but possible under specific conditions. It has also been reported that bromide ions from seawater may form elemental bromine (Br_2) in seawater aerosols[36].

3.3 SPECIATION, BEHAVIOUR AND MOBILITY IN MARINE SEDIMENT

3.3.1 The process

Adsorption is a key element when approaching the behaviour and mobility of substances in sediments and soils. The term refers to the adherence of molecules or particles to a certain surface. The composition of the sediment plays a vital role in the reactions occurring on the sediment-water interface. For example, in the case of metal cations, adsorption to marine sediments is determined by:

- the sediment-water partitioning coefficient

- the cation exchange capacity of the sediment

- the existing levels of cations already present in sediments and pore waters

- the amount of organic matter in sediment

28 Howard et al. (2016), Formate Technical Manual, Section A13 Thermal Stability
29 Sprague (1986), as quoted in WHO (2001)
30 Yeats (1988), as quoted in WHO (2001)
31 Florence (1980), as quoted in WHO (2001)
32 Ellwood and Van den Berg (2000)
33 WHO (2001), 1.4 Environmental transport, distribution and transformation
34 Byrne (2002)
35 Sander et al. (2003)
36 Byrne (2002)

3.3.2 Cesium formate

The behaviour of the ^{137}Cs radionuclide of cesium in marine sediments has been extensively studied. Note that the cesium used to manufacture cesium formate is non-radioactive ^{133}Cs. However, the movement of ^{133}Cs in the marine sediments should be similar to that of radioactive ^{137}Cs. When entering the water column, the cesium ion is strongly adsorbed to suspended solids within the water column. When adsorbed to such particles, it may precipitate and accumulate in sediments.

Experiments on Cs^+ and sediment clay have shown three types of cesium-binding sites[37], namely:

1. Sorption to surface and planar sites (Cs^+ is generally exchangeable)

2. Sorption to wedge sites (Cs^+ exchange sterically limited to cations of similar size and charge)

3. Sorption to interlayer sites (Cs^+ is not readily exchangeable)

It could be assumed that adsorption of formate to sediment would be negligible, as formate already undergoes rapid degradation in the water column. Formate ending up in the sediment would be dissolved in the sediment pore water or adsorbed to the anion exchange sites of the sediment. Degradation of formate ions, even in cold marine anaerobic sediments, can be anticipated according to methanogenesis studies[38].

3.3.3 Zinc bromide

Zinc partitions strongly to the suspended sediment particles of the water column as compared to the bed sediment[39]. Suspended sediment is the sediment that is maintained in suspension by the upward components of turbulent currents or that exists in suspension as a colloid. The interaction of zinc with dissolved organic carbon is controlled by pH and this process also determinates the bioavailability of zinc. An increase in pH tends to increase the zinc concentration in the sediment colloidal material, making it less bioavailable[40].

Bromide ions exist in marine sediments mainly in the pore waters and their concentration decreases with depth. Coal and organic matter of the sediment tend to accumulate bromide.

3.4 SPECIATION, BEHAVIOUR AND MOBILITY IN SOIL

3.4.1 The process

The speciation, behaviour and mobility of cesium formate and zinc bromide in soil are discussed here due to their possible interaction with soil in case of transportation accidents or disposal of cuttings or waste in landfill sites. Mobility of chemicals in soils is affected by their dissociation into the immobile soil solids phase and the mobile soil water and gaseous phases[41].

The sorption-desorption process in soil is greatly affected by the soil type and concentration of the chemical. The interactions of cations with soils are controlled by cation ion exchange, surface adsorption and reactions with organic matter[42]. In the case of anion adsorption, pH of the soil greatly impacts its anion exchange capacity by

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37 Clark and Evans (1983), as quoted by Borretzen and Salbu (2001)
38 Kendall and Boone (2006)
39 WHO (2001), 4.1.2.5 Sediment
40 Cantwell and Burgess (2001)
41 Essington (2003), Chapter 1.1
42 Bohn et al. (2001), Chapter 2 Important ions

affecting the dissociation of functional groups. In European and North American neutral, weakly weathered soils, anion exchange capacity is often much less than its cation exchange capacity[43]. However, soils anion exchange is important, e.g. in Australia, where some soils have low organic matter content and pH.

3.4.2 Cesium formate

Cesium exists in soil solution as hydrated ions[44]. The adsorption of cesium is concentration dependent and the value of Kd (soil/water adsorption coefficient) decreases with an increase in the cesium ion concentration. At trace concentrations the Cs^+ adsorption is significantly influenced by soil pH due to competitive exchange reactions[45]. The mineral composition of the soil also affects the mobility of cesium. It has been reported that certain clay minerals (e.g. micas and hydrobiotite) adsorb Cs^+ irreversibly, whilst others (e.g. vermiculite and montmorillite) hold it much less strongly[46]. The presence of soil organic matter may decrease the adsorption of Cs^+ to clay, thus making it more bioavailable[47].

Cesium adsorption has been determined to be maximal at pH 7–8[48]. Cesium does not form any complexes, precipitates or colloids[49].

Significant adsorption of formate anions from cesium formate solution to various soils has been reported earlier[50]. However, Lakefield Research found the experimental design of the study inadequate and thus the results should be treated with caution. In contrast, a study on the adsorption of formate on a type of silica (quartz) and a clay mineral (kaolinite) reported only slight affinity for formate[51].

3.4.3 Zinc bromide

The amount of zinc present in adsorbed soil fractions is much higher than the soluble fraction in the pore waters and soil solution under most conditions[52]. Zinc is adsorbed on clay and organic matter and thus leaching of zinc from soils is unlikely. However, this equilibrium will be changed if, for example, the pH of soil changes. A decrease in soil pH will increase the proportion of zinc in the soil solution. Acidic soils or sandy soils with low organic carbon content have a reduced capacity for zinc absorption and here mobility of zinc could be an issue. The soluble proportion of zinc is also the potentially bioavailable part of zinc.

Bromide ions are repelled or only weakly retained by soil, thus bromide that enters soil can be anticipated to stay mainly in the soil water phase[53]. This assumption is supported by leaching experiments conducted with methyl bromide in natural soil columns, which indicated that all added bromide leached from the soil columns during artificial rain events[54].

43 Bohn et al. (2001), Chapter 9 Anion and molecular retention
44 Essington (2003), Chapter 5.2
45 Poinssot et al. (1999), as quoted by Gilbert et al. (2003)
46 Livens and Loveland (1988)
47 Staunton and Levacic (1999)
48 Livens and Loveland (1988)
49 Hakem et al. (2000)
50 Lakefield Research (1998), as quoted by Gilbert et al. (2003)
51 Ward and Brady (1998), as quoted by Gilbert et al. (2003)
52 WHO (2001), 4.1.3 Soil
53 Bohn et al. (2001), Chapter 9 Anion and molecular retention
54 Rice et al. (1996)

3.5 PHYSICO-CHEMICAL EFFECTS ON THE RECEIVING ENVIRONMENT

3.5.1 Seawater

The pH of seawater is approximately 8.2. Discharge of bicarbonate-buffered pH 9–11 cesium formate brine would raise the pH of the seawater temporarily in the vicinity of the discharge point. However, rapid dilution by the surrounding water masses and the buffering capacity of seawater should prevent any significant change in ocean pH. Buffering capacity refers to the ability of a solution to resist changes in pH upon the addition of acids or bases. In oceans the capacity is based on the carbon dioxide system, bicarbonate being the dominant form at normal seawater pH. No pH impacts have been reported following discharges of formate brines with cuttings when used as drilling fluids[55].

In the case of zinc bromide, the hydrolysed zinc compounds produce hydrated zinc ions, zinc hydroxide and hydrated zinc oxides. These reactions decrease pH of the water, but it can be assumed that the natural buffering capacity of seawater prevents significant pH changes[56]. This assumption is not supported by titration experiments on seawater and zinc bromide, which showed that the pH of seawater changes already with small zinc bromide additions (pH changed from 7.26 to 6.12 when 1 ml $ZnBr_2$ was added to 1000 ml of seawater)[57].

The discharge of high-density brines will increase the concentration of the respective ionic constituents in seawater, and thus raise the salinity. As previously mentioned, cesium, bromine and zinc are natural constituents of seawater, and thus their discharge brings no new factors into the composition of seawater. However, the ionic balance of the seawater will be changed – the proportion of these ions will be increased. Elevated concentration of ions in seawater may also affect the atmospheric concentrations of the same elements. In fact, it has been recorded that the bromine concentration in the marine air of the North Sea is elevated when compared to more remote areas[58]. Bromine in these seawater aerosols originates from inorganic bromine present in seawater. The anthropogenic source of these elevated bromine levels is not yet known.

Organic formate ions will disappear rapidly from the water column, as micro-organisms degrade them into water and carbon dioxide[59]. Thus, both due to the dilution factor and biodegradation, the concentration of formate ions will be elevated only temporarily. However, biodegradation of organic substances consumes oxygen, and the biodegradation process could decrease the oxygen concentration of the water column locally. Theoretically this could cause problems in the deeper layers of highly stratified water masses, where mixing with the oxygen rich upper layer is minimal.

The density of seawater is affected by the increase of ion concentration, salinity and temperature. The more ions are present in the same volume of water, the higher the density will be. Density plays a vital role in the circulation of water masses. Release of large amounts of high-density drilling brines in the deep waters of a halocline

55 Zuvo et al. (2005)
56 US DHHS (1994), as quoted in WHO (2001)
57 Cabot (2007a)
58 Sander et al. (2003)
59 OECD (1992a)

water column could therefore theoretically strengthen the stratification, as the dense deeper layer and the less dense upper layer of the water column are not easily mixed.

3.5.2 Sediment

Discharges of the said brines would result in locally elevated concentrations of zinc and cesium in the sediment, which both act as sinkers, i.e. they have a tendency to accumulate in the sediment through sorption. Accidental release of zinc bromides would raise the bromide ion concentration and lead to locally increased levels of bromine in the sediment pore water.

The formate anion will be rapidly degraded by micro-organisms and assimilated into the biomass. This is also supported by the environmental survey conducted in the Barents Sea, as no elevated levels of formate were found in local sediments after drilling with potassium formate[60]. However, biodegradation utilises oxygen, and the process could in extreme cases decrease the oxygen concentration in the sediment. Theoretically, this could cause problems in highly stratified water masses. In reality, the effect would be highly localised and short termed due to dilution through water movement, even within stratified layers.

3.5.3 Soil

The terrestrial effects for both compounds could be more severe, as any discharges (transport accidents, leaching from landfills) remain relatively concentrated and are not diluted in the same manner as in the marine environment.

Aerobic and anaerobic degradation of formate anions by soil micro-organisms diminishes the formate concentration in soil. Aerobic degradation is fairly rapid (in the order of days), whereas anaerobic degradation takes longer (in the order of months). Extensive research in Finland on the biodegradation and leaching of formate-based road de-icing formulations in soil has revealed that formate will be biodegraded long before it reaches the ground water and aquifers. Therefore it presents no direct risk for the ground water quality. However, in soils where the formate spill has led to high localised concentrations the growth and activity of the micro-organisms could be inhibited. Aerobic degradation of formate ions consumes oxygen and produces water and carbon dioxide[61].

The inorganic ions (Cs^+, Zn^{2+} and Br^-) will not be degraded and their local concentrations could be elevated markedly. Leaching of zinc from soils rich in organic matter and clay is unlikely[62] and, thus, at least zinc concentrations will remain elevated unless decontamination processes are conducted. However, adsorption of zinc and cesium may in turn result in other ions being leached. In the case of anionic bromide, which stays mainly in the mobile soil water phase, leaching into ground water is more likely.

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60 Zuvo et al. (2005)
61 Hellsten et al. (2005)
62 Joutti et al. (2004)

4 Ecotoxicology

4.1 BIODEGRADATION

Biodegradation is the process by which organic substances are broken down by living organisms. At this point we refer to aerobic degradation, which results finally in the mineralisation of organic carbon into carbon dioxide (CO_2). The biodegradation rate of substances can be measured using laboratory tests that simulate different types of receiving environment, i.e. freshwater[63] and marine environment[64].

The formate part of cesium formate is readily biodegradable. In two separate biodegradation tests, 79% and 66% of formate was degraded within 28 days when tested in seawater[65]. In freshwater, 83% and 79% degradation of the chemical has been measured in the same time span[66]. Biodegradation as a concept is not applicable to inorganic zinc, bromide or cesium in elemental or ionic form.

4.2 BIOACCUMULATION AND BIOCONCENTRATION

Bioaccumulation and bioconcentration are terms used to define the uptake of a chemical by an organism. Bioconcentration is a measure of the uptake from the surrounding media, i.e. water, whereas bioaccumulation takes into account various exposure routes (e.g. respiration, food intake, epidermis).

The determinations of actual bioconcentration factors (BCFs) are laborious test procedures that are relatively seldom performed. BCF is a ratio between the concentration of a chemical in biota and in water. However, in the literature, both cesium and zinc are mentioned. The mean bioconcentration factors for marine species of plants, fish, crustacea, molluscs and fish for cesium range from 15 to 51 and for zinc between 150 to 9900. Results for freshwater species show tissue concentrations of cesium in algae and invertebrates around 1000 times higher than ambient and concentrations in fish up to 5000 times higher than ambient. No adverse effects on the organisms have been observed[67].

Cesium formate is unlikely to bioaccumulate, because the logarithmic Pow is below -2.20. For example, under the OSPAR regime chemicals with log Pow ≥ 3 are considered as bioaccumulative, unless experimental BCF tests indicate the opposite[68].

Approaching zinc bioaccumulation and bioconcentration is not altogether straightforward, as, for example, zinc is an essential element for many marine organisms, i.e. it is taken up and accumulated by organisms for biological processes. In general, animals are capable of regulating their internal zinc concentrations by various means, but at higher exposure concentrations the process is disturbed, which results in influx of zinc. Based on rainbow trout exposure to zinc for 30 days, zinc seems to accumulate in the gills, liver, kidneys and opercular bone, but not in the muscle[69].

63 OECD (1992b)
64 OECD (1992a)
65 Cabot (2017)
66 Cabot (2017)
67 Jorgensen et al. (1991), as quoted by Downs et al. (1994)
68 OSPAR (2005), § 2.1 Partitioning and bioaccumulation potential
69 ICL Industrial (2012)

The zinc concentration that disturbs the regulation depends, for example, on the species and temperature. These issues complicate the calculation of BCF, because the zinc taken up by the organisms is reflected in the BCF, but the concentrations in the tissues may be of no direct toxicological significance. Thus, applying BCF for zinc can be misleading. In case of bioaccumulation factors, both the inherently accumulated essential zinc proportion and the accumulation of excess zinc have influence on the results. Measured zinc concentrations in aquatic organisms vary a lot. For example, the baseline zinc levels in invertebrates have been reported to be in the range of 50 to 300 mg/kg of dry weight, whereas in mussel (*Mytilus edulis*) and scallop (*Pecten sp.*) kidneys as high as 3410 and 32 000 mg/kg dw concentrations have been measured respectively[70].

Hence the direct utilisation of bioaccumulation factors for management choices is not straight forward. A good approximation frequently used for both bioconcentration and bioaccumulation of a substance is through its octanol-water partition coefficient (Kow or Pow). It is used as a measure of the lipophilicity (or hydrophobicity) of the chemicals, and indicates the ratio of the equilibrium concentration of a chemical in octanol (representing organisms) and in water at a specified temperature. The higher the coefficient, the higher the potential for the chemical to bioaccumulate (i.e. enter an organism and stay there).

4.3 BIOAVAILABILITY

Bioavailability refers to the proportion of a substance that can be potentially taken up by organisms from a certain environment. The bioavailability of a chemical is strongly influenced by the physical-chemical factors of the environment. Two important factors affecting the bioavailability are pH and dissolved organic carbon. Bioavailability can be estimated using two different approaches: correlative (e.g. measuring the free ion concentrations in the aquatic environment) and predictive (modelling of bioavailability at a certain uptake spot)[71]. Therefore, bioavailabilities for compounds cannot be given as universally applicable values, as they are case specific.

4.4 BIOMAGNIFICATION

Biomagnification is the increase in concentration of a substance in the food chain. This means that the uptake is higher than the excretion or degradation. Biomagnificable substances are lipophilic and persistent organic substances or metals, which are not degradable as they are elements. The formate anion does not fall into this category.

Biomagnification of zinc is often assumed not to happen in the aquatic food web[72, 73]. However, some studies indicate that the concentration of zinc may increase with the trophic level, which means that zinc would indeed biomagnify[74, 75].

Because no biological role for cesium is known, it could also be extrapolated that no specific excretion pathway exists. Thus, biomagnification of cesium cannot be ruled out and references to food-chain transfer of radioactive cesium isotopes exist[76]. However, according to some sources[77],

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70 WHO 2001, 4.3.2 Bioaccumulation
71 WHO 2001, 4.2 Bioavailability
72 Suedel et al. (1994)
73 Barwick and Maher (2003)
74 Chen et al. (2000)
75 Borgå et al. (2006)
76 Gilbert et al. (2003)
77 Argonne National Laboratory, EVS (2005)

cesium can enter the body through ingestion or inhalation and once in the body, behaves in a manner similar to potassium and distributes uniformly throughout the body. Gastrointestinal absorption from food or water is the principal source of internally deposited cesium in the general population. Essentially all cesium that is ingested is absorbed into the bloodstream through the intestines. Cesium tends to concentrate in muscles because of their relatively large mass. However, like potassium, cesium is quoted as being excreted reasonably rapidly. 10% is excreted within two days and the reminder with a biological half-life (e.g. half of the compound is excreted) of 110 days for adults.

Thus, both exposure to cesium and zinc may lead to accumulation, but if the source of exposure is removed, much will readily clear the body along the normal pathways.

4.5 ECOTOXICITY OF THE COMPOUNDS

4.5.1 Tests and terminology

Ecotoxicology is a study of the effects of chemicals on the environment and organisms living in it. These effects can be predicted by simple laboratory test methods called ecotoxicity tests. In order to assess the chemical impacts in more detail, micro- and mesocosm studies can also be used. They are experimental designs simulating a certain environmental compartment allowing evaluations at ecosystem level. However, such designs are expensive and not reported in the literature for either cesium formate or zinc bromide. Hence this report focuses on the laboratory ecotoxicity tests, which are used also as regulatory tools by the authorities. Still, it has to be kept in mind that ecotoxicity tests are

usually performed on one chemical at a time and in actual environmental conditions the effects are caused by a combination of all surrounding components. These other components can have antagonistic, synergistic or additive effects on the toxic potential of a chemical.

Different types of test methods exist for various purposes, i.e. the test organisms can be aquatic or terrestrial. Acute tests usually measure short-term effects (e.g. lethality, inhibition of growth) and the test duration is often also relatively short (from minutes to a few days). On the other hand, chronic tests measure the effects of long-term and low-level exposures to the organisms. Chronic exposure can, for example, affect an organism's reproduction ability. The results of ecotoxicity tests are often expressed as the sample concentration that affects 50% of the test organisms (e.g. LC50 or EC50 values). Also LOEC (lowest observed effect concentration) and NOEC (no observed effect concentration) values are used.

4.5.2 Marine ecotoxicity

The test results from marine ecotoxicity tests are expressed in Table 2. In contrast to the relatively extensively tested cesium formate, the availability of public information on zinc bromide is scarcer.

Of the tested marine species, juvenile turbot *Scopthalmus maximus* was most susceptible to cesium formate. Comparable information for zinc bromide is approximately half, which indicates some difference in toxicity. However, when comparing cesium formate and zinc bromide toxicities using other test organisms, e.g. the marine copepod (*Acartia tonsa*), it is clear that the toxicity of cesium formate brine is markedly lower than the toxicity of zinc bromide. The EC50 values in *Acartia tonsa* test

Table 2: Marine ecotoxicity data

Organism	Endpoint	Cs formate	Zn bromide
Marine copepod (*Acartia tonsa*)	EC50 (48 h)	340 mg/l[78]	1.6 mg/l[79] 2.4 mg/l[80]
Marine algae (*Skeletonema costatum*)	EC50 (72 h)	710 mg/l[81] 1600 mg/l[83]	0.32 mg/l[82] 6.6 mg/l[84]
Brown shrimp (*Crangon crangon*)	LC50 (96 h)	875 mg/l[85]	
Juvenile turbot (*Scopthalmus maximus*)	LC50 (96 h)	260 mg/l[86]	115.9 mg/l[87]
Larval turbot (*Scopthalmus maximus*)	LC50 (96 h)	1400 mg/l[88]	7.6 mg/l[89]
Ide (*Leuciscus idus*)	EC50 (48 h)		21 mg/l[90]
Pacific oyster embryos (*Crassostrea gigas*)	LC50 (24 h)	1200 mg/l[91]	0.33 mg/l[92]
Amphipod (*Corophium volutator*)	LC50 (10 d)	6653 mg/kg[93]	
Sharp-nosed sand goby (*Ctenogobius gymnauchen*)	LC50 (96 h)	862 mg/l[94]	
Inland silverside (*Menidia beryllina*)	LC50 (96 h)	787 mg/l[95]	

for cesium formate and zinc bromide are 340 mg/l and 1.6 mg/l respectively.

4.5.3 Estuarine ecotoxicity

Estuaries are bodies of water adjacent to where rivers or streams flow into the sea. They are mixtures of freshwater and saltier seawater, i.e. they are brackish waters. The environmental properties and condition of estuaries differ widely depending, for example, on the river that feeds the estuary and the ocean from which it derives its salinity.

The mysid shrimp *Americamysis bahia* is commonly used as a test organism in ecotoxicity tests. It is an epibenthic shallow water organism, which is able to acclimatize to different seawater salinities, i.e. it is a euryhaline species. *A. bahia* is found in greatest amounts at salinities near 30 ppt (average seawater salinity is 38 ppt), but they commonly occur at salinities above 15 ppt[96]. Acute toxicity test results using *A. bahia* exist for both cesium formate and zinc bromide. The toxicity of zinc bromide to this organism is two orders of magnitude higher when compared to the toxicity of cesium formate (Table 3). These acute toxicity results for *A. bahia* are very similar to the LC50 values found for *Acartia tonsa*, a marine copepod that co-exists with *A. bahia* in marine environments.

78 Shell Research (1995)
79 Downs et al. (1994)
80 Bromine Compounds Ltd (2000b)
81 Shell Research (1995)
82 Downs et al. (1994)
83 Downs et al. (1994)
84 Bromine Compounds Ltd (2000a)
85 Chemex Environmental International Ltd (2011)
86 Huntingdon Research Centre (1992)
87 Bromine Compounds Ltd (2000c)

88 Downs et al. (1994)
89 Howard (1995)
90 Fisher Scientific (2007)
91 Downs et al. (1994)
92 Howard (1995)
93 Cabot internal test results
94 Quangdong Laboratory Animals Monitoring Institute (2010)
95 Environmental Enterprises USA, Inc. (2011b)
96 Price (1982)

Table 3: Comparative brackish water ecotoxicity data

Organism	Endpoint	Cs formate	Zn bromide
Mysid shrimp *(Americamysis bahia)*	Cesium formate EC50 (48 h) Zinc bromide EC50 (96 h)	521 mg/l[97]	1.5 mg/l[98]

Table 4: Comparative freshwater ecotoxicity data

Organism	Endpoint	Cs formate	Zn bromide
Freshwater algae *(Scenedesmus subspicatus)*	EC50 (72 h)	110 mg/l[99]	
Freshwater algae *(Pseudokirchneriella subcapitata)*	EC50 (72 h)	110 mg/l[100]	0.41 mg/l[101]
Invertebrate *(Daphnia magna)*	EC50 (48 h)	> 100 mg/l[102]	8.8 mg/l solution[103] 0.86 mg/l solid[104] 1.22 mg/l[105]
Invertebrate *(Ceriodaphnia dubia)*	EC50 (48 h)		0.5 mg/l[106]
Fish, Rainbow trout *(Oncorhynchus mykiss)*	LC50 (96 h)	2100 mg/l[107]	2.4 mg/l (7 d-LC50, Zn)[108]
Fathead minnow *(Pimephalas promelas)*	LC50 (7 d)		0.78 mg/l[109]
Zebra fish *(Brachydanio rerio)*	LC50 (96 h)	> 100 mg/l[110]	

4.5.4 Freshwater ecotoxicity

The limited test data available indicate that freshwater algae and invertebrates appear to be somewhat more sensitive to cesium formate than their marine cousins in acute toxicity tests (Table 4). Cesium formate is, however, still orders of magnitude less toxic to these freshwater organisms than zinc bromide. Freshwater fish seem to have a high tolerance for cesium formate, but are very sensitive to zinc.

The slightly higher toxicity of cesium formate in the freshwater medium compared to that in seawater has been explained by possible nutrient depletion due to weak complexation of formate with divalent nutrient ions, rather than any direct toxicity[111]. Formates biodegrade relatively rapidly (see Chapter 4.1).

97   Environmental Enterprises USA, Inc. (2011a)
98   Hydro ASA internal testing
99   Harlan Laboratories (2010a)
100 Harlan Laboratories (2010b)
101 Howard (1995)
102 Harlan Laboratories (2011)
103 ICL Industrial (2012)
104 Fisher Scientific (2007)
105 Magliette et al. (1995)
106 Magliette et al. (1995)
107 Huntingdon Research Centre (1992)

108 WHO (2001), Table 39 b, result for zinc not zinc bromide
109 Magliette et al. (1995)
110 Supervision and test center for pesticide safety evaluation and quality control (2008)
111 NICNAS (2001), 10.3 Summary of Aquatic Toxicology

4.5.5 Terrestrial ecotoxicity

Terrestrial ecotoxicological data on cesium formate and zinc bromide could not be found in the literature. Thus, their terrestrial impacts have been extrapolated from ecotoxicity tests on their ionic constituents or similar compounds, e.g. for cesium formate, tests on potassium formate are used. These results are presented in chapter 4.6. Terrestrial ecotoxicity tests are most often performed with different earthworm species (endpoint survival, reproduction, etc.) and various plants (endpoint seed germination, root growth, etc.).

4.6 ECOTOXICITY OF THE CONSTITUENT IONS

Selected ecotoxicity test results for the constituent ions are presented in the following four sub-chapters (4.6.1–4.6.4).

4.6.1 Cesium

The Arabidopsis plant (*Arabidopsis thaliana*) has been used to understand the toxicity mechanism of cesium. It is known that Cs^+ ions compete with K^+ ions for K^+-binding sites on essential proteins. The toxic action of cesium is related to its similarities with K^+ ion. However, the Cs ion does not act exactly in the same manner as K, which results in the inactivation of many K-activated enzymes, i.e. giving a toxic effect[112, 113].

4.6.2 Formate

Toxicity of potassium formate has been studied with various ecotoxicity tests, including species living in aquatic environments, as well as species from terrestrial environments[114]. Test results purely on formate ions are not possible to obtain from the results, because it is not clear what contribution the potassium ions had on toxicity. Still, tests with potassium acetate have resulted in lower toxicity (i.e. higher EC50 values) when compared to potassium formate, indicating that formate ions can have some negative impacts on the test organisms.

4.6.3 Zinc

Although zinc is an essential trace element required by many living organisms, excess concentrations have acute and chronic toxic effects. The LC50 values vary between test species and also the counter ion has its own contribution to the test results. The use of different test protocols and both nominal and measured zinc concentrations in the tests increase the diversity of the results further. In addition, the toxicity of zinc is strongly affected by the pH of the test system[115].

Zinc appears to be toxic to simple marine species at levels of less than one mg/l in water. Effects of zinc on marine species have been studied with various test organisms. Data on marine algae exist only from test set-ups using nominal zinc concentrations. Zinc inhibited the growth of marine diatoms (*Nitzschia closterium*) and the reported EC50 values using zinc sulphate and zinc chloride were 0.271 mg/l and 0.065 mg/l respectively[116, 117].

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112 Hampton et al. (2004)
113 Avery (1995)
114 Joutti et al. (2003)
115 Ho et al. (1999)
116 Rosko and Rachlin (1975), as quoted in WHO (2001)
117 Stauber and Florence (1990), as quoted in WHO (2001)

Ecotoxicity data on the effects of zinc on marine invertebrates is abundant. Exposure to zinc has resulted in, for example, reduced growth (common mussel *Mytilus edulis*)[118], disruption in larval development and metamorphosis (red abalone *Haliotis rufescens*)[119], and interference in fertilisation (sea urchins)[120]. Using zinc chloride as the test chemical, the lowest measured LC50 values (96 hours) are approximately 0.58 mg/l (amphipod *Allorchestes compressa* and crab *Cancer magister*). With zinc sulphate the most toxic LC50 value was 0.097 mg/l (mysid *Holmesimysis costata*). For bottom dwelling organisms it has been estimated that zinc can pose a hazard at concentrations above 123 mg/kg[121].

Some ecotoxicological data on marine fish species and zinc does exist. A study on mummichog *Fundulus heteroclitus* using zinc chloride as the test sample showed that approximately 50 percent of mummichogs are killed within two days if they are exposed to chemical concentrations near 100 mg/l (LC50 = 96.5 mg/l)[122]. In another study, the LC50 value for grey mullet *Chelon labrosus* was 21.5 mg/l when zinc sulphate was tested[123].

Extensive field and laboratory tests on metals and their effects on earthworms (*Aporrectodea tuberculata, Eissenia fetida*) have been conducted and they show detrimental impacts on the test organisms[124, 125]. If it is possible, the earthworms try to avoid soils that are contaminated with metals such as zinc. However, if the exposure can not be prevented, increasing zinc concentration results in reduced earthworm activity, disturbed reproduction, decreased biomass and finally

mortality. Also other terrestrial invertebrate studies show negative impacts caused by zinc[126].

Toxicity of zinc towards vertebrates has also been reported. Exposure to zinc has resulted, for example, in reduced growth rate and anaemia in hens (zinc in diet 2000 mg/kg)[127] and increased incidence of gizzard, pancreatic lesions and mortality in chicks (zinc in diet 6000 mg/kg)[128].

Toxicity of zinc towards plants has also been studied extensively. Zinc affects the general physiological processes of plants, such as transpiration, respiration and photosynthesis. Strong zinc toxicity results in visible symptoms, such as stunted growth and chlorosis, but at lower degrees of zinc toxicity the symptoms may be at cellular level and not so obvious. Critical level for leaf tissue concentration of zinc, which affects plant growth, is in the range 200 to 300 mg/kg dry matter for many plant species. The effects of zinc on the root lengths of plants have been studied with zinc compounds in solution and in soil. EC50 values for solution tests with different plant species (*Lolium perenne, Allium cepa, Lepidivium sativum*) vary from 1.6 mg/l to 547 mg/l. Tests with tree roots (*Acer rubrum, Picea abies, Pinus strobus*) in soil matrix indicate that the EC50 value is above 165 mg/kg soil[129].

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118 Strömgren (1982), as quoted in WHO (2001)
119 Hunt and Anderson (1989), as quoted in WHO (2001)
120 Dinnel et al. (1989), as quoted in WHO (2001)
121 Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (2002)
122 Burton and Fischer (1990), as quoted in WHO (2001)
123 Taylor et al. (1985), as quoted in WHO (2001)

124 Lukkari et al. (2005)
125 Lukkari and Haimi (2005)
126 Lock and Janssen (2001)
127 Stahl et al. (1989), as quoted in WHO (2001)
128 Dewar et al. (1983), as quoted in WHO (2001)
129 WHO (2001)

4.6.4 Bromide

Although bromide ions are essential nutrient ions to many organisms, at higher concentrations they can become toxic. This toxic property of bromide compounds has been utilised in, for example, crop protection. Excessive levels of bromide ions have been reported to cause, for example, inhibition of cell multiplication of green algae, immobilisation of invertebrates and mortality of fish.

Most laboratory test results have been conducted with sodium bromide (NaBr). The EC50 value for green algae *Scenedesmus subspicatus* growth inhibition test is 4.7 g/l (96-hour test)[130] and for *Scenedesmus pannocinus* 5.8 g/l (24 hours) and 10.0 g/l (96 hours)[131].

The two-day LC50 of sodium bromide to the brackish water invertebrate, mysid shrimp (*Americamysis bahia*), is 8.0 g/l. Several ecotoxicity tests with marine fish indicate that the highest LC50 value for vertebrates would be around 20 g/l (for example inland silverside *Menidia beryllina* 48-h LC50 = 18.3 g/l). The common laboratory test fish medaka (*Oryzias latipes*) is more sensitive to bromide, the LC50 value being 1.5 g/l[132].

Terrestrial ecotoxicity data on potassium bromide using flatworm *Dugesia tigrina* was available from the literature. LC50 value for juvenile flatworms was 30 mg/l (96-hour test). Another laboratory test has shown that exposure to calcium bromide results in root growth inhibition and decreased mitotic activity in root tip cells of bulb onion *Allium cepa*[133].

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130 Kühn and Pattard (1990)
131 Canton et al. (1983), as quoted by Pillard et al. (1999)
132 Pillard et al. (1999)
133 Vidaković-Cifrek et al. (2002)

5 Human health

5.1 THE CONSIDERED EFFECTS

Acute health effects are related to potential routes of worker exposure to high-density brines in the oilfield working environment: ingestion, inhalation and surface contact (skin or eye). Exposure to the substance is often sudden and would be based on a single, potentially large exposure area through a spill or splash.

Chronic health effects are characterised by prolonged or repeated exposures over days, months or even years. The symptoms may not be immediately apparent and the effects are often

Table 5: Reported potential health effects as presented in safety data sheets

	Cesium formate[134]	Zinc bromide[135]
Eyes	Causes serious eye irritation.	Corrosive. Causes eye damage (e.g. burns).
Skin	May cause irritation. Avoid contact with skin.	Corrosive. Causes severe skin burns. Dermal sensitiser. May cause an allergic reaction.
Ingestion	Harmful if swallowed. Adverse effects on multiple organ systems were observed in animals following repeated oral exposure to cesium formate. However, these effects are not expected under normal handling conditions.	Harmful if swallowed. Causes burns to mucous membranes. Possible symptoms include abdominal pain, nausea and vomiting. May also cause central nervous system and brain effects, such as drowsiness, hallucinations, irritability, muscular incoordination, respiratory depression and coma.
Inhalation	Due to its liquid state, this material is not expected to be a significant inhalation hazard. Aerosols or dried product may be irritating to respiratory tract. Do not breathe dust, vapours or mist.	Can cause severe irritation of mucous membranes and respiratory system.
Chronic	In a 28-day oral study in rats, effects were seen in multiple organ systems at the high dose (500 mg/kg/d). Signs of neurotoxicity were also observed. Elevated reticulocyte count and effects on the heart, liver, spleen and serum biochemistry were observed at the middle dose (150 mg/kg/d). Elevated reticulocyte count was the only effect observed at the low dose (15 mg/kg/d). (OECD 407). Based on a 90-day oral repeated-dose toxicity study (OECD 408) on a similar substance (cesium chloride), this product is classified as STOT-RE Category 2 – may cause damage to multiple organs (kidneys and adrenals) through prolonged or repeated exposure. The No Observed Adverse Effect Level (NOAEL) for kidney and adrenal effects is equivalent to 10 mg Cs/kg bodyweight/day. This study also indicated that the substance is suspected of damaging fertility. Not classified as carcinogenic by OSHA, NTP, IARC or ACGIH.	Repeated exposure may cause skin rash (dermatitis). Repeated or prolonged ingestion can cause digestive and/or renal disorders. Repeated or prolonged inhalation may cause bronchitis. Chronic exposure may cause central nervous system effects. Mutagenic and reproductive effects have occurred in test animals. Not classified as carcinogenic by OSHA, NTP, IARC or ACGIH.
Aggravation of pre-existing conditions	Respiratory disorder, adrenal gland disorders.	Persons suffering from debilitation, depression, alcoholism, neurological or psychological disorders may be more susceptible to the effects of this compound[136].

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134 Cabot (2017)
135 Summarised based on Fisher Scientific (2017), Sigma Aldrich (2016), Tetra Technologies (2015), Spectrum Chemical (2015), ICL Industrial (2012)
136 J.T. Baker (2011)

irreversible. The possible effects on human health are often extrapolated from laboratory toxicity tests, which are performed using, for example, rats and mice as test animals.

Acute and chronic human health effects of the brines are discussed in more detail in the following two subchapters and compiled toxicity test results are presented in Appendix 2. The health effects and precautions given in various SDSs by the manufacturers are summarised in Table 5 as an indication of how the danger is presented to management and users.

5.2 ACUTE HEALTH EFFECTS

Protection against acute health hazards should be provided by appropriate training and the use of appropriate personal protective equipment. The differences between the recommended personal protective equipment (PPE) is summarised in Table 6.

Table 6: Recommended PPE for cesium formate and zinc bromide

	Cesium formate[137]	Zinc bromide[138]
Eyes	Wear eye/face protection, such as safety glasses with side shields, goggles or a face shield if splashes are likely to occur.	Wear tightly fitting chemical safety goggles and/or face shield. Safety showers and/or eyewash stations should be provided.
Clothing	Wear chemical impervious protective clothing if skin contact may occur. Wear suitable gloves, such as impervious gloves, nitrile rubber gloves, PVC or other plastic material gloves.	Wear protective, long-sleeved, bodycovering clothing, boots and appropriate gloves. In case of accidental release, full protective clothing, including self-contained breathing apparatus, must be used.
Respirators	Approved respirator may be necessary if local exhaust ventilation is inadequate.	Respiratory protection is required when workplace conditions warrant it. Self-contained breathing apparatus, respirator with dust filter or respirator with full facepiece may be required. Follow applicable regulations (e.g. OHSA, NIOSH or European standards).

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137 Cabot (2017)
138 Summarised based on Fisher Scientific (2017), Sigma Aldrich (2016), Tetra Technologies (2015), ICL Industrial (2012)

5.2.1 Inhalation

The inhalation of the dry powder forms of formates and bromides could occur during operations involving mixing powder into brines. This is most likely to occur when the powder is mixed into brine at a mixing plant or rig site. There is no evidence of damage from inhalation of cesium formate. However, the inhalation of formic acid has been shown to lead to methanol type poisoning, where the toxic metabolite appears to be formate[139]. This indicates that the inhalation of formate could lead to poisoning. However, should inhalation occur, the effects are likely to be much more severe with the corrosive bromide powder. The dust particles would likely cause burns in the mouth, throat and lungs.

Inhalation exposure to another zinc halide, zinc chloride, has been reported to cause, for example, interstitial oedema and fibrosis, pneumonitis, bronchial mucosal oedema, and even death[140].

5.2.2 Ingestion

This is an unlikely route of exposure for professional workers in an oilfield situation and there appears to be no documented cases of any high-density brines causing poisoning by accidental ingestion. However, should ingestion occur, both brines may be harmful.

Single or short-term exposures to elevated zinc concentrations through water and beverages have been reported. The symptoms have been gastrointestinal stress, nausea and diarrhoea. Zinc concentrations in the digested articles varied between 1000 to 2500 mg/l[141].

5.2.3 Skin or eye contact

Exposure through skin or eye contact is the most probable exposure scenario in offshore activities. Exposure for workers is possible, for example, through splashing or spills.

Here, the hazard is clearly several times greater with bromide brines. Several cases of chemical burn injuries caused by contact with bromides (calcium bromide) have been documented in the literature[142, 143, 144]. These injuries resulted in skin necrosis and were in some cases further complicated by the initial lack of any sensation of pain (allowing longer exposure time) and skin-graft loss or a slow healing process. Corrosive halide brines, such as zinc bromide, may also cause permanent eye damage.

In most cases, dermal exposure to zinc on its own does not result in any noticeable toxic effects in humans[145].

Cesium formate may cause serious eye irritation, but no significant skin or eye injuries (e.g. chemical burns) are known to have been caused by cesium formate or other formate brines.

5.3 CHRONIC HEALTH EFFECTS

The cesium formate SDS states that the material does not contain any known carcinogenic substances[146], but first-hand test data was not available. Neither is there any comparative data on the bromide brines in the literature. Some data has been collated into a table in Appendix 2.

A 28-day oral repeated-dose toxicity study in

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139 NIH (1992)
140 WHO (2001), 8.4.1 Acute toxicity
141 WHO (2001), 8.3.1 Poisoning incidents
142 Sagi A. et al. (1985)
143 Singer A. et al. (1992)
144 Saeed W.R. et al. (1997)
145 US DHHS (2005), 2.2 Summary of health effects
146 As listed by a number of relevant organisations; i.e. IARC (International Agency for Research on Cancer), NTP (National Toxicology Program), OSHA (Occupational Safety and Health Administration), ACGIH (American Conference for Governmental Industrial Hygienists) or EU (European Union)

Figure 2: Photograph of two patches of blackened full thickness skin necrosis on the right side of the neck of an oil worker who had splashed calcium bromide solution over his right forearm and face[147].

rats showed that repeated exposure to cesium formate through ingestion can, however, have an effect on their organ systems at high doses (500 mg powder/kg/day). Such doses can affect, for example, the reproductive organs if exposure duration is four weeks. Based on the results of long-duration testing on rats, neurotoxicity effects might also be exhibited in mammals exposed to high doses. At low doses (15 mg/kg/day) such effects are not to be expected, but may result in elevated reticulocyte count.

Information on the possible long-term effects of the dissociation products of cesium formate and zinc bromide are presented in the following paragraphs. This allows predictions on the potential outcomes of exposure to these brines, as toxicological data on the brines are scarce.

Cesium does not have a known biological function. A 90-day repeated-dose oral toxicity study in rats on cesium chloride showed that it may cause damage to multiple organs, including adrenals, kidneys and reproductive organs, at levels of 30 mg Cs/kg bw/d and above. The medical literature provides a single report of a man who ingested approximately 34 mg/kg cesium (as cesium chloride) after morning and evening meals for 36 days. This resulted in decreased appetite, nausea, diarrhoea and apparent transient neurological changes 15 minutes after dosing[148]. Cardiac arrhythmias have been described in patients who have ingested large doses of cesium chloride as components of homeopathic remedies[149].

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147 Saeed et al. (1997)
148 Neulieb R. (1984)
149 U.S. DHHS (2004)

Formate is rapidly oxidised to CO_2 in mammals. Sustained high-plasma formate concentrations (e.g. in the case of methanol poisoning) are toxic to the retina and optic nerve. Humans are less able than rodents to oxidise formate and are thus more sensitive to methanol (and formate) intoxication[150]. Formic acid itself is a mitochondrial toxin, of which formate is the suspected toxic metabolite[151].

Zinc is an essential nutrient associated with normal growth, immune and reproductive functions. Disruption of these functions can occur following excessive exposure to zinc, but only at high doses[152]. Zinc is usually not toxic via dermal exposure. Inhalation of large amounts of zinc (as dust or fumes, e.g. during welding or smelting) can cause metal-fume fever. Even in such cases, long-term respiratory effects are usually not caused[153].

Long-term exposure to zinc by ingestion has been reported to cause a wide range of symptoms, of which some are neutropenia, leucopenia and sideroblastic anemia[154]. Ingestion may also cause damage to the pancreas, lowered HDL cholesterol levels, inhibition of copper uptake resulting in copper deficiency and, in animal studies, even reproductive effects at doses > 200 mg/kg/day[153]. However, the blood zinc level recovers to normal after cessation of zinc uptake. In *in vitro*-studies, zinc has shown to cause, for example, gene mutations in human lymphocyte cultures[155].

Bromide in the ionic form may be viewed with some concern due to its potential connection with reproductive toxicity. Sodium bromide has been demonstrated to cause both male and female infertility in laboratory animals albeit at relatively elevated doses (19.2 g/kg)[156]. Bromides also produce depression, emaciation and, in severe cases, psychosis and mental deterioration. Skin rashes (dermatitis) may occur when bromide exposure is prolonged or repeated[157].

In addition bromate (BrO_3^-), which can be formed from bromides under certain circumstances, has been classified as a possible carcinogen by the International Agency of Research on Cancer (IARC)[158].

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150 Hanzlik et al. (2004)
151 Treichel et al. (2003)
152 U.S. DHHS (2005)
153 Agency for Toxic Substances and Disease Registry ATSDR (2005)
154 WHO (2001), 8.3.5.2 Case reports
155 WHO (2001), 7.6.1 In-vitro studies
156 European Chemicals Bureau (2000b) 5.8 Toxicity to Reproduction
157 ICL Industrial (2012), Spectrum Chemical (2015)
158 IARC (1999) Group 2B: Possibly carcinogenic to humans, potassium bromate

6 Structural safety aspects

Zinc bromide is a very corrosive fluid with acidic pH. If unprotected by additives, it will corrode metals, which may lead to significant structural problems.

Cesium formate is a strong base, with pH in the range of 9–10. Corrosion does not occur under normal circumstances. However, some concern has been raised about structural integrity of stressed duplex stainless steel after extended exposure to formate brine at high temperature followed by cooling to below 100°C[159].

This report does not probe the structural safety aspects related to fluid choices. However, in order to highlight that chemical choice must also take into account structural safety, some examples are briefly discussed.

Certain elastomers used in rubber seals may harden and crack under high pH conditions, others under low pH. The main issue is that fluid choice determines which elastomers are compatible. This may require meticulous planning, as the wrong type of seals used in safety-critical applications (e.g. seals on blow out preventers, wirelines, tubing hangers, certain pumps, valves, etc.), may present a safety-critical issue and potentially lead to spills.

The chosen fluids have to be compatible with all aspects of the well design. However, in this report, technical issues are not considered in detail. Sufficient to say that should safety-critical issues not be considered, this could lead to increased risk of large-scale risk realisation. Comparative details for fluid options should always be considered in detail with the relevant fluid sales organisation's technical support.

The potential structural safety issues encountered with formates are easily countered through taking potential issues into account during the well design phase. Weighed against the overall technical performance, the structural issues can be engineered out of the well at the design phase. However, should the potential safety issues not be taken into account, realisation of the risk may lead to significant cost.

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159 Howard, S., & Chrenowski, M. (2014, March 25). Corrosion in Formate Brines – 20 Years of Laboratory Testing and Field Experience. Offshore Technology Conference. Doi: 10.4043/24983-MS

7 Comparative analysis and results

7.1 ACUTE ENVIRONMENTAL TOXICITY

Cesium formate has been extensively tested for aquatic ecotoxicity and the available data give a reasonably informed picture of the environmental hazard. Unfortunately there is limited amount of aquatic toxicity data for zinc bromide in the public domain and thus a comparison of the two substances is not straightforward. However, the available information demonstrates clearly that **zinc bromide toxicity is two orders of magnitude higher than that of cesium formate** for marine and brackish water species (see chapters 4.5.2 and 4.5.3). The results are supported by an evaluation of the toxicity of the dissociation products.

Zinc bromide also appears to be very toxic towards freshwater organisms, both from acute and chronic perspectives (see chapter 4.5.4). The higher toxicity of cesium formate towards freshwater algae than towards marine species is most likely explained by nutrient depletion, which is caused by formate ions that form weak association complexes with essential divalent cations, such as calcium and magnesium[160]. The concentration of these ions is much higher in seawater and thus growth-limiting depletions are not easily obtained.

In a terrestrial environment the acute effects caused by both high-density brines would be more severe as the pollution would be more localised as the dilutive effect of seawater is absent. Exposure of the terrestrial environment to offshore chemicals could, for example, be due to rail or road transportation accidents or leaching from landfills. In case of large point exposures, e.g. due to transportation accidents, both chemicals will cause mortality of soil microbes, plants, etc. However, as the acute toxicity of zinc bromide is significantly higher, **relatively small discharge of zinc bromide will cause detrimental effects.** Thus, it could also be expected that the spatial extent of the most severely affected area (all organisms dead) would be significantly smaller with cesium formate.

With lesser terrestrial exposures, e.g. due to leaching from landfills, any effects would be less severe. In the case of cesium formate, the formate ion would degrade rapidly and sorption of cesium would minimise its bioavailability. Similarly adsorption of zinc on organic material is assumed, but bromide ions would not be degraded like formate.

7.2 POTENTIAL LONG-TERM EFFECTS IN THE ENVIRONMENT

The long-term effects of chemicals are always more difficult to predict. However, an extensive survey on the effects of formate brines on the seabed environment in the Barents Sea, Norway, demonstrated that the use of a mixture of potassium and sodium formate in drilling resulted in only minor environmental alterations[161]. The seabed survey was conducted **three years after the drilling operations** had finished and in a chemical assessment **no elevated formate concentrations** were found. In the same study, the biological diversity of the nearby fauna was

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160   NICNAS (2001)
161   Zuvo et al. (2005)

concluded to be high and only minor disturbances were observed. Only tube builders and filter-feeders, which are sensitive to sediment surface disturbance, were present in lower abundances at some study points. However, the experimental design did not allow speculation on the mutual roles of the chemical exposure and the overall disturbance of the sea bottom due to drilling operations on the slightly disturbed fauna. The study did not include cesium, but **no long-term environmental effects of cesium in the marine environment have been reported** in the literature. However, cesium cannot be degraded, which means that it stays in the environment. Thus long-term effects through, for example, biomagnification, cannot be excluded totally.

No environmental impact survey data are available for zinc bromide brine. However, **it can be assumed that zinc bromide could, in the long-term, have effects on the aquatic environment**, as neither of the constituent ions are biodegradable (i.e. they will stay in the environment). If present in sufficient concentration the ions will interfere with the growth, reproduction and developmental processes of any organisms that they contact, resulting in **disturbed biodiversity**, perhaps with an increased abundance of opportunistic species. Also the increase of zinc concentration along the food chain is possible.

In the case of severe transportation accidents, the long-term effects might include the chemical sterilisation of all water and soil/sediment in areas of severe exposure. The restoration of life might take quite a while at such sites. The majority of the cesium and zinc ions are likely to remain bound to the soil or sediment unless active remediation processes are initiated.

Thus, biomagnification of both cesium and zinc in the food chain in the immediate vicinity of the accident site could happen. Contamination of soil can act as a selective criterion for an emerging new population, as it is known that certain terrestrial organisms are capable of living in soils with elevated metal concentrations. In addition, it has been observed that herbivorous insects avoid such zinc-tolerant plants due to the elevated zinc concentrations in the plant tissues[162]. **Thus, terrestrial long-term effects are likely to be expected, especially in the case of zinc bromide accidents.**

Another long-term effect in the terrestrial environment is the possible leaching of compounds in soil, which can result in the contamination of ground water that is often used as a source for human drinking water. The European Directive on the quality of water intended for human consumption sets limits for certain substances, but neither cesium formate or zinc bromide (or their constituent ions) are included in the directive[163]. However, bromate, the ozonation product of bromide, is included and its concentration in drinking water may not exceed 10 µg/l. Bromate is formed from bromide at drinking water facilities, which use ozonation as a disinfection method. The phenomenon is common, but it usually only reaches alarming levels when the bromide concentration of aquifer waters is elevated for some reason. **Thus, accidental release of zinc bromine near ground water areas could ultimately cause prohibition in the use of ground water for human consumption.**

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162 Ernst et al. (1990), as quoted in WHO (2001)
163 Council Directive 98/83/EC

7.3 SAFETY ISSUES

Both fluids have certain structural safety issues related with their use. Incorporating these aspects in the design phase of the well construction projects will avoid such risk factors. However, safety-critical risk should always be considered separately and in detail for each well. Hence, no common conclusions are attempted.

7.4 ACUTE HEALTH EFFECTS

The risk of creating acute health problems is greater with zinc bromide than with cesium formate brine because of the corrosive nature of zinc bromide. **Zinc bromide is known to cause severe damage to skin and eyes** and for humans the most likely route of exposure to both brines is, in fact, through skin or eye contact.

7.5 CHRONIC HEALTH EFFECTS

Chronic health effects from human exposure to the two brines are unknown. In the case of zinc bromide, available toxicity data are particularly scarce. However, it could be assumed from data on the constituent ions, zinc and bromide, that the most significant chronic health effect from zinc bromide might be damage to reproductive organs and processes, although the classification of the substance does not indicate this and reproductive effects are only mentioned in some SDSs. For cesium formate, more data are available. From tests on rats, repeated oral doses of cesium (as formate or chloride) could result in damage to multiple organs, including kidneys, adrenals and reproductive organs in humans. Repeated high oral exposure to cesium formate could also have other chronic effects (e.g. neurotoxicity) in humans.

7.6 COMPARATIVE OVERVIEW OF DESIGNATED RISK AND SAFETY PHRASES

For cesium formate, the following classification applies according to CLP (Regulation (EC) No 1272/2008:

- Acute Tox. 4, H302 (Harmful if swallowed)

- Eye Irrit. 2, H319 (Causes serious eye irritation)

- Repro 2, H361f (Suspected of damaging fertility)

- STOT RE 2, H373 (May cause damage to organs (kidneys, adrenals), nervous system and blood through prolonged or repeated exposure)

Similarly for zinc bromide, the following classifications are found in ECHA's classification and labelling inventory:

- Acute Tox. 4, H302 (Harmful if swallowed)

- Eye Dam. 1, H318 (Causes serious eye damage)

- Skin Corr. 1B, H314 (Causes severe skin burns and eye damage)

- Aquatic Acute 1, H400 (Very toxic to aquatic life)

- Aquatic Chronic 1, H410 (Very toxic to aquatic life with long-lasting effects)

- Skin Sens. 1, H317 (May cause an allergic skin reaction)

A comparative overview of the GHS (Globally Harmonized System of Classification and Labelling of Chemicals) provided by three suppliers of zinc bromide is summarised on the next page. Of the three SDSs, one refers to a product used in the oilfield and the other two to products used in laboratories. This illustrates the large variety in classifications and, thus, the information provided by manufacturers.

For example, powders are not classified as 'dangerous to the environment'. The comparison also highlights the difference in hazardous properties of cesium formate compared to zinc bromide.

Table 7: GHS classifications for cesium formate and different zinc bromide products

	Cesium formate[164]	Zinc bromide		
Type of product	Oilfield product	Oilfield product[165]	Laboratory solution[166]	Laboratory powder[167]
CsCOOH / ZnBr$_2$ amount	60–84%	72–80%	70–90%	100%
SDS	US version	US version	US version	US version
Classification				
Acute toxicity (oral), Category 4	X	X	X	X
Skin corrosion/irritation, Category 1B		X	X	
Skin corrosion/irritation, Category 1C				X
Sensitization – Skin, Category 1		X	X	
Serious eye damage, Category 1			X	X
Serious eye damage, Category 2A	X			
Reproductive toxicity, Category 2	X			
Specific target organ toxicity (repeated exposure), Category 2	X			
Acute aquatic toxicity, Category 2			X	
Chronic aquatic toxicity, Category 2		X	X	
Hazard statements				
H302 – Harmful if swallowed	X	X	X	X
H314 – Causes severe skin burns and eye damage		X	X	X
H317 – May cause an allergic skin reaction		X	X	
H318 – Causes serious eye damage			X	
H319 – Causes serious eye irritation	X			
H361f – Suspected of damaging fertility	X			
H373 – May cause damage to organs (kidneys, adrenals), nervous system and blood through prolonged or repeated exposure	X			
H411 – Toxic to aquatic life with long-lasting effects		X	X	

164 Cabot (2017)
165 Tetra Technologies (2015)
166 Sigma Aldrich (2016)
167 Spectrum Chemical (2015)

HSE profile – cesium formate

Human health

PPE: Wear eye/face protection, such as safety glasses with side shields, googles or face shields if splashes are likely to occur. Wear suitable gloves (impervious, nitrile rubber, rubber, PVC or other plastic material gloves). Wear chemical impervious protective clothing if skin contact may occur. Approved respirator may be necessary if local exhaust ventilation is inadequate.

Skin & eye
Irritating to eyes. May irritate skin.

Ingestion
Harmful if swallowed.

Inhalation
Aerosols or dried product may be irritating to respiratory tract. Do not breathe dust, vapours or mist.

Chronic
Based on studies with rats, repeated ingestion could result in damage to multiple organs, including kidneys, adrenals and reproductive organs. Repeated high doses could also cause neurotoxicity. Not mutagenic (AMES, chromosome aberration, and mouse lymphoma assays). Not classified as carcinogenic by OSHA, NTP, IARC, ACGIH or EU.

Acute Tox. 4, H302 (harmful if swallowed); **Eye Irrit. 2, H319** (causes serious eye irritation); **STOT RE 2, H373** (may cause damage to organs (kidneys, adrenals, nervous system, blood) through prolonged or repeated exposure); **Repro 2, H361f** (suspected of damaging fertility)

Hazard classification and labelling for transport

NOT classified as dangerous goods for the purposes of transport by rail, road or in packed form by sea (ADR, RID, IMDG)

Has no UN number nor requires any specific labelling for transport requirements.

Has been classified being subject to the IBC code (ship type 3 and pollution category Z) with additional requirement 15.19.6.

Label elements

WARNING!

Environment – practically non-toxic or non-toxic to marine organisms, slightly toxic or practically non-toxic to freshwater organisms
(adapted from GESAMP rating scheme, GESAMP reports and studies No 64, 2002)

Acute toxicity:

Seawater:	Copepod (*Acartia tonsa*)	EC50 (48h) = 340 mg/l
Brackish water:	Mysid shrimp (*Mysidopsis bahia*)	EC50 (48h) = 521 mg/l
Fresh water:	Water flea (*Daphnia magna*)	EC50 (48h) > 100 mg/l

Chronic toxicity:
Long-term adverse effects in marine environment NOT to be expected.

Photo © Polina-Petrenko / iStockphoto

HSE profile – zinc bromide

Human health

PPE: Wear safety goggles and/or face shield. Wear protective, long-sleeved, body-covering clothing, boots and appropriate gloves. In case of accidental release, full protective clothing, including self-contained breathing apparatus, must be used. Respiratory protection is required when workplace conditions warrant it. Self-contained breathing apparatus, respirator with dust filter or respirator with full face-piece may be required. Follow applicable regulations (e.g. OHSA, NIOSH or European standards).

Skin & eye
Corrosive, causes severe burns on skin and eye damage.

Ingestion
Causes burns to mucous membranes.

Inhalation
If inhaled (vapour, mist) can cause severe irritation of mucous membranes and respiratory system.

Chronic
Repeated or prolonged exposure may cause following symptoms:
Skin: Dermatitis.
Ingestion:
Digestive/renal disorders.
Inhalation: Bronchitis.
All routes:
Central nervous system effects. Mutagenic and reproductive effects have occurred in test animals. Not classified as carcinogenic by OSHA, NTP, IARC or ACGIH.

Acute Tox. 4, H302 (harmful if swallowed); **Skin Corr. 1B, H314** (causes severe skin burns and eye damage); **Skin Sens. 1, H317** (may cause an allergic skin reaction); **Aquatic Chronic 1, H410** (very toxic to aquatic life with long-lasting effects)
Some products additionally: **Eye Dam. 1, H318** (causes serious eye damage); **Aquatic Acute 1, H400** (very toxic to aquatic life)

Hazard classification and labelling for transport

Dangerous goods class, proper shipping name, UN Number and note "marine pollutant" on the documentation are required.

Labelling with "Class 8 – corrosive substances" and "marine pollutant" label required.

Has been classified being subject to the IBC code (ship type 2 and pollution category X).

Label elements

DANGER!

Environment – moderately to highly toxic for aquatic environment

Acute toxicity:

Seawater:	Copepod (*Acartia tonsa*)	EC50 (48h) = 1.6 mg/l
Brackish water:	Mysid shrimp (*Americamysis bahia*)	EC50 (96h) = 1.5 mg/l
Fresh water:	Water flea (*Daphnia magna*)	EC50 (48h) = 8.8 mg/l

Chronic toxicity:
Potential to cause long-term adverse effects in the aquatic environment. Sublethal effects such as interference with reproduction and developmental processes possible.

Photo © endopack / iStockphoto

Glossary of terms

A

Acute Toxicity Test	A toxicity test involving short-term exposure of an organism to a potential toxicant. The exposure is generally not more than 96 hours and the effect is often measured by mortality
Acute	Having a sudden onset, severe enough to induce a rapid response
Adsorption	Accumulation of a substance at the boundary of two phases, usually between solid and liquid phases
Anaerobic	Conditions under which no oxygen is available
Anion	An ion with a negative electrical charge
Assimilable	Available for absorption and utilisation
ASTM	American Society for Testing and Materials

B

BCF	Bioconcentration Factor determined according to OECD 305 or ASTM E 1022 guidelines
Bioaccumulation	The tendency of substances to accumulate in the body of exposed organisms with increases over time or with age through various exposure routes
Bioavailable	Chemical in a form that is assimilable by living organisms
Bioconcentration	A process by which there is a net accumulation of a chemical directly from water into aquatic organisms resulting from simultaneous uptake and elimination
Biodegradable	Capable of being decomposed of by natural means
Buffering capacity	The ability of a chemical system to neutralise excess acid or base

C

CAS	Chemical Abstract Service
Cation	An ion with a positive electrical charge
Chemical	The term 'chemical' is used here to mean both substances and preparations
Chemical speciation	A distribution of the chemical forms in which an element can exist, e.g. free ion, complex, solid
Chronic	Involving a stimulus that is lingering over a long period of time
Chronic Toxicity Test	A toxicity test involving an organism that is exposed to a potential toxicant for a long period of time. The exposure time depends on the normal development and life span of the organism, and can range from days and weeks to years. The effects of the toxicant are commonly measured in terms other than mortality, such as growth rate or reproductive ability
Clay	This is a term generally reserved for material which is plastic when wet, and has no well developed parting along the bedding planes, although it may display banding
CO	Carbon monoxide
CO$_2$	Carbon dioxide
Complexation	The formation of chemical complexes
-COOC-	Esters
Crustacea	A large, diverse arthropod taxon including crabs, lobsters, crayfish, shrimp and krill.
Cs	Cesium or caesium
CsCOOH	Cesium formate

D

Discharge	The operational release of offshore chemicals or their degradation and transformation products in the maritime area
Disorption	The release of an ion from a compound into solution or onto another compound
Dissociate	When a compound breaks up and forms separate compounds
Divalent	An ion with an electrical charge of +2 or -2

E

EC50	Median Effective Concentration: A toxicant concentration that has an effect on 50% of the test organisms
Ecotoxicology	The study of toxicity and the effects it has on an ecosystem

H

H_2	Hydrogen
H_2O	Water
$HCOO^-$	Formate anion
HCO_2H	Methanoic (formic) acid
HCO_2K	Potassium formate
HOCNF	Harmonised Offshore Chemical Notification Format
HCO_3^-	Bicarbonate
HPHT	High Pressure High Temperature
Humic substances	Organic polyelectrolytic compounds which have complex structures and vary in composition. They occur naturally on sediment and soil particles and may be composed of humic acid, fulvic acid and humin
Hydrolysis	A chemical reaction involving water
Hydrophobic	Water hating

I

Ion	An atom or molecule that has had electrons either removed or added to it, producing a positively charged or negatively charged particle

K

K_b	Equilibrium/dissociation constant
K_d	Distribution coefficient
KOH	Potassium hydroxide
Kow	See "Pow"

L

LC50	Median Lethal Concentration: A toxicant concentration that is lethal to 50% of the test organisms
Ligand	A complexing group in co-ordination chemistry. Generally the entity for which electrons are donated

M

Micro-organism	An unicellular organism of microscopic size, such as bacteria
Monovalent	An ion with a single electrical charge of +1 or -1

N

Na	Sodium
NICNAS	National Industrial Chemicals Notification and Assessment Scheme
NOEC	No Observed Effect Concentration

O

OECD	The Organisation for Economic Co-operation and Development
Offshore chemicals	All chemicals intentionally used in connection with offshore exploration and production activities in the marine area
OSPAR	The Oslo-Paris Convention for the protection of the Marine Environment of the North-East Atlantic

P

Partition coefficient	The ratio of chemical concentration in two different compartments or phases under steady state conditions
Pow	Octanol-water partitioning coefficient
Preparation	Preparation is a mixture or solution consisting of two or more substances

S

Salinity
The content of dissolved salts in a water body. Can be determined, for example, from the empirical formula $S = 0.030 + (1.805 \times \text{chlorinity})$

SDS
Safety Data Sheet

Substance
Substance is defined in OSPAR guidelines for completing the HOCNF as a chemical element or compound in the natural state or obtained by any production process, including any additives necessary to preserve the stability of the preparation and any impurity deriving form the process used, but excluding any solvent which may be separated without affecting the stability of the substance or changing its composition

T

Toxicity
The inherent potential or capacity of an agent to cause adverse effects to a living organism when the organism is exposed to it

Z

ZnBr$_2$
Zinc bromide

References and bibliography

A

Argonne National Laboratory, EVS (2005). Human Health Fact Sheet, Cesium.

Avery S.V. (1995). Caesium accumulation by microorganisms: uptake mechanisms, cation competition, compartmentalization and toxicity. Journal of Industrial Microbiology 14(2), 76-84.

B

Barwick M. and Maher W. (2003). Biotransference and biomagnification of selenium copper, cadmium, zinc, arsenic and lead in a temperate seagrass ecosystem from Lake Macquarie Estuary, NSW, Australia. Marine Environmental Research, 56: 471-502.

Benton W., Harris M., Magri N., Downs J. and Braaten J. (2003). Chemistry of Formate Based Fluids. SPE 80212.

Bohn H.L., McNeal B.L. and O'Connor G.A. (2001). Soil Chemistry, Second edition. John Wiley & Sons, Inc. UK, pp307.

Borgå K, Campbell L, Gabrielsen G.W., Norstrom R.J., Muir D.C. and Fisk A.T. (2006). Regional and species specific accumulation of major and trace elements in Arctic seabirds. Environmental Toxicology and Chemistry, 25(11): 2927-2936.

Borretzen P. and Salbu B. (2001). Fixation of Cs to marine sediments estimated by a stochastic modelling approach. Journal of Environmental Radioactivity, 61:1-20.

Bromine Compounds Ltd (2000a). Hyder Laboratories Study no. HE990748. (Accessed through IMO).

Bromine Compounds Ltd (2000b). Hyder Laboratories Study no. HE990749. (Accessed through IMO).

Bromine Compounds Ltd (2000c). Hyder Laboratories Study no. HE990750. (Accessed through IMO).

Byrne R.H. (2002). Inorganic spesiation of dissolved elements in seawater: the influence of pH on concentration ratios. Geochemical Transactions 3: 11-16.

C

Cabot. Internal test results.

Cabot (2007). Internal data on zinc bromide titration.

Cabot (2017). Cesium Formate Solution Safety Data Sheet. 18.04.2017.

Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (2002). Summary tables.

Cantwell M.G. and Burgess R.M. (2001). Metal-colloid partitioning in artificial interstitial waters of marine sediments: influences of salinity, pH, and colloidal organic carbon concentration. Environmental Toxicology and Chemistry, Vol 20(11): 2420-2427.

CDH Finechemical. Material Safety Data Sheet, Zinc Bromide. Available at: http://www.cdhfinechemical.com/images/product/msds/115_253762230_ZincBromide-CASNO-7699-45-8-MSDS.pdf (accessed on 4.07.2017).

Chemex Environmental International Ltd (2011). The acute toxicity of Cesium Formate to Brown Shrimp (*Crangon crangon*) over a 96-hour exposure period. Report for Cabot Corporation. ENV9587/061101.

Chen C.Y., Stemberger R.S., Klaue B., Blum J.D., Pickhardt P.C. and Folt C.L. (2000). Accumulation of Heavy Metals in Food Web Components across a Gradient of Lakes. Limnology and Oceanography, Vol. 45(7): 1525-1536.

Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption.

D

Downs J.D, Killie Siv, Whale G.F. and Inglesfield C. (1994). Development of Environmentally Benign Formate-Based Drilling and Completion Fluids. SPE 27143: 419-428.

E

Ellwood M.J. and Van den Berg, C.M.G. (2000). Zinc speciation in the Northeastern Atlantic Ocean. Marine Chemistry, 68: 295-306.

Environmental Enterprises USA, INC. (2011a). Test report on cesium formate and *Mysidopsis bahia* test, 17.11.2011.

Environmental Enterprises USA, INC. (2011b). Test report on cesium formate and *Menidia beryllina* test, 17.11.2011.

Essington M.E. (2003). Soil and water chemistry: an integrative approach. CRC Press, Boca Raton, FL.

European Chemicals Bureau (2000b). IUCLID Dataset. Substance ID: 7647-15-6, Sodium Bromide.

F

Fisher Scientific (2017). Safety Data Sheet, Zinc bromide. Revision dated 25.05.2017. Available at: https://www.fishersci.com/shop/msdsproxy?productName=AC212770500&productDescription=ZINC+BROMIDE+99.999%25+EXTRA+PUR&catNo=AC212770500&vendorId=VN00032119&storeId=10652&keyword=true (accessed on 3.07.2017).

Fisher Scientific (2007). Material Safety Data Sheet, Zinc bromide. Revision dated 23.05.2007. Available at https://fscimage.fishersci.com/msds/25320.htm (accessed on 31.05.2017).

G

Gilbert Y., Wemyss P., Gaches P., Smith D., Pipe R. and Stutt E. (2003). Formate Brines Environmental Assessment. Metoc plc.

H

Hakem N.L. Al M., Apps J.A. and Moridis G.J. (2000). Sorption of cesium and strontium on Hanford soil. Journal of Radioanalytical and Nuclear Chemistry 246(2): 275-278.

Hampton C.R., Bowen H.C., Broadley M.R., Hammond J.P., Mead A., Payne K.A., Pritchard J. and White P.J. (2004). Cesium Toxicity in Arabidopsis. Plant physiology 136: 3824-3837.

Handbook of Chemistry and Physics (2007). 88th edition, David R. Lide (ed.), CRC.

Hanzlik R., Fowler C. and Eells, J. (2004). Absorption and elimination of formate following oral administration of calcium formate in female human subjects. Drug Metabolism and Disposition Fast Forward. DOI: 10.1124/dmd.104.001289.

Harlan laboratories (2011). Test report on cesium formate and *Daphnia magna* test, 8.02.2011.

Harlan laboratories (2010a). Test report on cesium formate and *Desmodesmus subspicatus* test, 11.11.2010.

Harlan laboratories (2010b). Test report on cesium formate and *Pseudokirchmeriella subcapitata* test, 24.12.2010.

Hellstén P.P., Kivimäki A.-L., Miettinen I.T., Mäkinen R.P., Salminen J.M., and Nystén T.H. (2005). Degradation of potassium formate in the unsaturated zone of a sandy aquifer. Journal of Environmental Quality 34(5): 1665-1671.

Ho K.T., Kuhn A., Pelletier M.C., Hendricks T.L. and Helmstetter A. (1999). pH dependent toxicity of five metals to three marine organisms. Environmental Toxicology 13(2): 235-240.

Howard et al. (2016). Formate Technical Manual, Section A13 Thermal Stability.

Howard, S., & Chrenowski, M. (2014, March 25). Corrosion in Formate Brines – 20 Years of Laboratory Testing and Field Experience. Offshore Technology Conference. Doi: 10.4043/24983-MS.

Howard, Siv K. (1995). Formate Brines for Drilling and Completion: State of the Art. SPE 30498.

Huntingdon Research Centre (1992). The Acute Toxicity of Caesium Formate to Juvenile Turbot (*Scophthalmus maximus*), SLL 239(f)920927, 16.11.1992.

Huntingdon Research Centre (1992). The Acute Toxicity of Caesium Formate to Rainbow Trout (*Oncorhynchus mykiss*), SLL 239(e)/920752, 02.12.1992.

Hydro ASA internal testing.

I

IARC (1999). Group 2B: Possibly carcinogenic to humans, Potassium bromate.
Latest classifications available at http://monographs.iarc.fr/ENG/Classification/latest_classif.php (accessed on 27.06.2017).

ICL Industrial (2012). Material Safety Data Sheet, Zinc Bromide Solution. Revision dated 4.11.2012. Available at http://icl-ip.com/wp-content/uploads/2012/02/2650_uszincbromidesolution.pdf (accessed on 27.06.2017).

J

Joutti A., Schultz E., Martikainen E., Räisänen M.L., Lintinen P. and Lehto O. (2004). Extractablility of metals and ecotoxicity of soils from two old wood impregnation sites in Finland. Science of the Total Environment, 326(1/3): 71-84.

Joutti A., Schultz E., Pessala P., Nystén T. & Hellstén P. (2003). Ecotoxicity of Alternative De-icers. J Soils & Sediments 3(4): 269-272.

J.T. Baker (2011). Material Safety Data Sheet, Zinc Bromide. Revision dated 15.03.2011. Available at https://us.vwr.com/store/asset?assetURI=https://us.vwr.com/stibo/hi_res/eng_us/93/40/9469340.pdf (accessed on 04.07.2017).

K

Kendall M.M. and Boone D.R. (2006). Cultivation of methanogens from shallow marine sediments at Hydrate Ridge, Oregon. Archaea 2: 31-38.

Kühn R. and Pattard M. (1990). Results of the harmful effects of water pollutants to green algae (*Scenedesmus subspicatus*) in the cell multiplication inhibition test. Water Research 24(1): 31-38.

L

Livens F.R. and Loveland P.J. (1988). The influence of soil properties on the environmental mobility of caesium in Cumbria. Soil Use and Management 4(3): 69-75.

Lock K. and Janssen C.R. (2001). Modelling zinc toxicity for terrestrial invertebrates. Environmental Toxicology and Chemistry 20: 1901-1908.

Lukkari T., Aatsinki M., Väisänen A. and Haimi J. (2005). Toxicity of copper and zinc assessed with three different earthworm tests. Applied Soil Ecology 30: 133-146.

Lukkari T. and Haimi J. (2005). Avoidance of Cu- and Zn-contaminated soil by three ecologically different earthworm species. Ecotoxicology and Environmental Safety 62: 35-41.

M

Magliette R.J., Doherty F.G., McKinney D., and Venkataramani E.S. (1995). Need for environmental quality guidelines based on ambient freshwater quality criteria in natural waters – case study "zinc". Bull Environ Contam Toxicol, 54: 626-632.

N

Neulieb R. (1984). Effects of oral intake of cesium chloride: A single case report. Pharmacol Biochem Behav 21(Suppl. 1):15-16.

NICNAS (2001). Full Public Report – Cesium Formate – File No NA/811, National Industrial Chemicals Notification and Assessment Scheme, Sydney.

NIH (1992). NTP technical report on Toxicity Studies of Formic Acid (CAS No: 64-18-6) Administered by Inhalation to F344/N Rats and B6C3F1 Mice. National Toxicology Program, NIH Publication 92-3342, July 1992.

O

OECD (1992a). Biodegradability in Seawater, Closed bottle test. OECD Method 306.

OECD (1992b). Ready Biodegradability, Closed bottle test. OECD Method 301D.

OSPAR (2005). OSPAR Guidelines for completing the Harmonised Offshore Chemical Notification Format (HOCNF). Agreement 2005-13.

P

Pillard D.A., Hockett J.R. and DiBiona D.R. (1999). The Toxicity of Common Ions to Freshwater and Marine Organisms. American Petroleum Institute, Publication Number 4666. API Publishing Services, Washington D.C.

Price W.W. (1982). Key to the shallow water Mysidacea of the Texas coast with notes on their ecology. Hydrobiol. 93(1/2): 9-21.

Q

Quangdong Laboratory Animals Monitoring Institute (2010). Test report on cesium formate and *Ctenogobius gymnauchen* test, 28.04.2010.

R

Rice P.J., Anderson T.A., Cink J.H. and Coats J.R. (1996). The influence of soil environmental variables on the degradation and volatility of methyl bromide in soil. Environmental Toxicology and Chemistry 15(10): 1723-1729.

S

Saeed W.R., Distante S., Holmes J.D. and Kolhe P.S. (1997). Skin injuries afflicting three oil workers following contact with calcium bromide and/or calcium chloride. Burns 23(7-8): 634-637.

Sagi A., Baruchin A.M., Ben-Yakar Y., Kon M., Eyal A. and Mahler D. (1985). Burns caused by bromine and some of its compounds. Burns 11: 343-350.

Sander R., Keene W.C., Pszenny A.A.P., Arimoto R., Ayers G.P., Baboukas E., Cainey J.M., Crutzen P.J., Duce R.A., Hönninger G., Huebert B.J., Maenhaut W., Mihalopoulos N., Turekian V.C. and Van Dingenen R. (2003). Inorganic bromine in the marine boundary layer: a critical review. Atmospheric Chemistry and Physics, 3: 1301-1336.

Sharpe A.G. (1986). Inorganic Chemistry. Longman Scientific and Technical, Harlow, UK.

Shell Research (1995). Acute toxicity of caesium formate monohydrate to *Acartia tonsa* and *Skeletonema costatum*. SBER.95.003, March 1995.

Sigma-Aldrich (2016). Safety Data Sheet, Zinc Bromide solution (product number 02135). Revision dated 02.06.2016. Available at: http://www.sigmaaldrich.com (accessed on 30.06.2017).

Singer A., Sagi A., Ben Meir P. and Rosenberg L. (1992). Chemical burns: our 10-year experience. Burns 18(3): 250-252.

Spectrum Chemical (2015). Safety Data Sheet, Zinc Bromide, anhydrous reagent. Revision dated 11.02.2015. Available at https://www.spectrumchemical.com/MSDS/Z1048-AGHS.pdf (accessed on 3.07.2017).

Staunton S. and Levacic P. (1999). Cs adsorption on the clay-sized fraction of various soils: effect of organic matter destruction and charge compensation. Journal of Environmental Radioactivity 45: 161-172.

Suedel B.C., Boraczek J.A., Peddicord R.K., Clifford P.A. and Dillon T.M. (1994). Trophic transfer and biomagnification potential of contaminants in aquatic ecosystems. Reviews of Environmental Contamination and Toxicology 136: 21-89.

Supervision and test center for pesticide safety evaluation and quality control (2008). Test report on cesium formate and *Brachydanio rerio* test, 02.07.2008.

T

Tetra Technologies (2015). Safety Data Sheet, Zinc Bromide Solution. Revision dated 20.02.2015. Available at http://www.tetrachemicals.com/Products/Bromides/Zinc_Bromide.aqf (accessed on 03.07.2017).

Treichel J., Henry M., Skumatz C., Eells J., and Burke J. (2003). Formate, the Toxic Metabolite of Methanol, in Cultured Ocular Cells. Neuro Toxicology, Vol 24(6): 825-834.

Turekian K.K. (1968). Oceans, Prentice-Hall.

U

U.S. Department of Health and Human Services (US DHHS). (2004) Public Health Service. Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Cesium.

U.S. Department of Health and Human Services (US DHHS). (2005) Public Health Service. Agency for Toxic Substances and Disease Registry (ATSDR). Toxicological Profile for Zinc.

V

Vidaković-Cifrek M., Pavlica M., Regula I. and Pape D. (2002). Cytogenic Damage in Shallot (Allium cepa) Root Meristems Induced by Oil Industry High-Density Brines. Archives of Environmental Contamination and Toxicology, Vol. 43(3): 284-291.

W

WHO (2001). Environmental Health Criteria 221, Zinc. Geneva, pp 254 (available at: http://www.who.int/ipcs/publications/ehc/ehc_221/en/index.html) (accessed on 31.05.2017).

Z

Zuvo M., Bjornbom E., Ellingsen B., Buffagni M., Kelley A. and Trannum H.C. (2005). High-resolution environmental survey around an exploration well drilled with formate brine in the Barents Sea, Norway. SPE 94477.

Appendix 1 Speciation of zinc in water

Different possible forms for zinc in water:

1. Simple hydrated metal ion
   a) e.g. $Zn(H_2O)_6^{2+}$
   b) diameter 0.8 nm

2. Simple inorganic complexes
   a) e.g. $Zn(H_2O)5Cl^+$, $Zn(H_2O)5OH^+$
   b) diameter 1 nm

3. Simple organic complexes
   a) e.g. Zn-citrate, Zn-glycinate
   b) diameter 1–2 nm

4. Stable inorganic complexes
   a) e.g. ZnS, $ZnCO_3$, Zn^2SiO_4
   b) diameter 1–2 nm

5. Stable organic complexes
   a) e.g. Zn-humate, Zn-cysteinate
   b) diameter 2–4 nm

6. Adsorbed on organic colloids,
   a) e.g. $Zn^{2+}Fe_2O_3$, $Zn^{2+}SiO_2$
   b) diameter 100–500 nm

7. Adsorbed on organic colloids
   a) e.g. Zn^{2+}-humic acid, Zn^{2+}-organic detritus
   b) diameter 100–500 nm

8. Particulate matter
   a) diameter > 450 nm

Appendix 2 Toxicology test results for cesium formate and zinc bromide as presented in SDSs

	Cs formate[168]	Zn bromide[169]
Acute oral toxicity	Rat LD50 = > 300mg/kg and < 2000mg/kg (harmful)	Rat LD50 = 1477 mg/kg (harmful)[170]
Acute dermal toxicity	Rabbit LD50 > 2000 mg/kg (non-toxic)	Rabbit LD50 > 2000 mg/kg (non-toxic)[171]
Eye irritation	Primary eye irritation test in rabbit: Irritating to eyes	Rabbit: Severe eye irritation[172]
Skin irritation	Skin irritation test in rabbit: Not irritating	Rabbit: Corrosive Guinea pig (maximisation study): May cause sensitisation by skin contact[173]
Chronic effects (including mutagenic and reproductive effects)	Not mutagenic in Ames test. Negative in chromosome aberration test in human lymphocytes. Negative in mouse lymphoma assay. Rat: Repeated oral exposure over long periods (28–90 days) may cause damage to multiple organs, including reproductive organs at levels of 30 mg Cs/kg bw/d and above, and in higher doses (500 mg/kg/d over 28 days) even neurotoxicity.	Not mutagenic in AMES test[174]. Mutagenic effects have occurred in experiments with bacteria and/or yeast[175], as well as animals[176]. Animal test data suggest that zinc bromide may cause cancer[177] and adverse reproductive, developmental and teratogenic effects[178].

168 Cabot (2017)
169 Summarised from several SDSs, see detailed references
170 Fisher Scientific (2017), Spectrum Chemical (2015), ICL Industries (2012), CDH Finechemical
171 Spectrum Chemical (2015), CDH Finechemical
172 CDH Finechemical
173 CDH Finechemical
174 ICL Industries (2012)
175 Spectrum Chemical (2015)
176 Fisher Scientific (2017)
177 Spectrum Chemical (2015), CDH Finechemical
178 Spectrum Chemical (2015)

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