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FORMATE FLUIDS HAZARD ASSESSMENT

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Executive Summary

This work presents a comparative overview of the physico-chemical and biological properties of cesium and potassium formate. The properties are then related to the level of chemical health, safety and environmental hazard posed by these products in oilfield operations. The data presented supports EHS risk profiling of cesium formate and potassium formate in offshore oilfield environments. In aqueous solutions these chemicals make technically superior, solids free drilling fluids with very low hazard properties for environment or people.

The content of this report has been condensed from an extensive review of publicly available literature, supplemented by previous independent research reports and test results. A previous edition, where the properties of cesium formate were compared to that of a traditional heavy brine, zinc bromide, was 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.

The behaviour, movement, likely fate and effects of formate brines in different environmental compartments have been assessed. The aim is to provide a detailed picture of how these two chemicals, as aqueous solutions (brines) and powders, behave and interact in the physical and chemical environment. The EHS profiles provide a baseline for the analysis of effects of incidents to people and the environment.

ACUTE HEALTH: The human health effects of these products have been considered, both short and long term. A main consideration is acute exposure during handling. Direct contact with liquid or powder forms of any chemical may lead to various degrees of skin irritation. The cesium formate is a skin irritant after extended contact, but evidently does not lead to skin burns. The potassium formate is a potential irritant with no evidence of skin burns found.

CHRONIC HEALTH: High repeated oral doses of cesium formate may result in neurotoxicity and can affect multiple organ systems. However, this exposure route is considered unlikely in a working environment. There is no evidence of chronic health issues from dermal exposure to either fluid.

SAFETY: Neither fluid is flammable, oxidising or explosive. Neither fluid is corrosive. The high density of the cesium formate fluid is an important safety factor, as the fluid is designed to provide pressure control in hazardous oil/gas wells and prevent catastrophic well blow-outs.

ENVIRONMENT: Both potassium and cesium formates have been relatively extensively tested, in particular for aquatic toxicity, in accordance with testing requirements for different regulative areas. Neither fluid is considered to be environmentally hazardous under GHS requirements. Potassium formate is used extensively for example as a de-icer for roads and airport pavements and as a growth promoter in animal feed, indicating little potential for acute or chronic toxicity to flora or fauna.

SPILLS and DISCHARGES: The data indicate that immediate acute toxicity of discharges or spills of cesium or potassium formate to water bodies is very limited. 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.

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1 Background

As any manager of complex technical projects knows, there is no such thing as incident-free operations. Unplanned incidents can happen during well construction operations and may cause delays, increase direct costs or lead to liabilities – all of which can affect the return on investment. Incorporating a thorough evaluation of environmental, health and safety (EHS) risk against cost at the design stage allows better-informed decision-making. Realized EHS risks can lead to immediate damage as well as long term potential damage and liability. Both may be costly, and damage to the marine environment in particular may be very difficult to mitigate or remedy. However, the assessment of the EHS risk may be fragmented between different consent bodies, such as those responsible for occupational health or structural safety or environmental permits and the overall picture of the EHS 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 EHS assessment, and presents the available data, for high-density formate brines. The highest density formate brines are aqueous solutions of potassium formate and/or cesium formate. These innovative fluids enable oil companies to safely construct more productive oil and gas wells, particularly those accessing very deep reservoirs. The formate anion is readily biodegradable, while the cation (alkali metal) constituents of the formate brines fluids are already present in the seawater. For example, potassium is the 6th most common ion in seawater.

From a corporate management point of view, the challenge is to implement consistent company EHS policies that reflect both ethical policies and legal boundaries, irrespective of where in the world the operations are carried out. In this report the aim is to provide sufficient data to allow informed EHS decisions in well construction fluid selection that take into account both acute and long term environmental effects as well as the contribution of fluid choice to overall safety of the operation. A life cycle type of approach has been taken to present the data and results from observations of the environment following product use and discharge. This gives a holistic picture of the overall consequences that reaches far beyond the consideration of a single ecotoxicity test.

2 Aim, objectives, methodology and coverage

2.1 Aim and objective

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

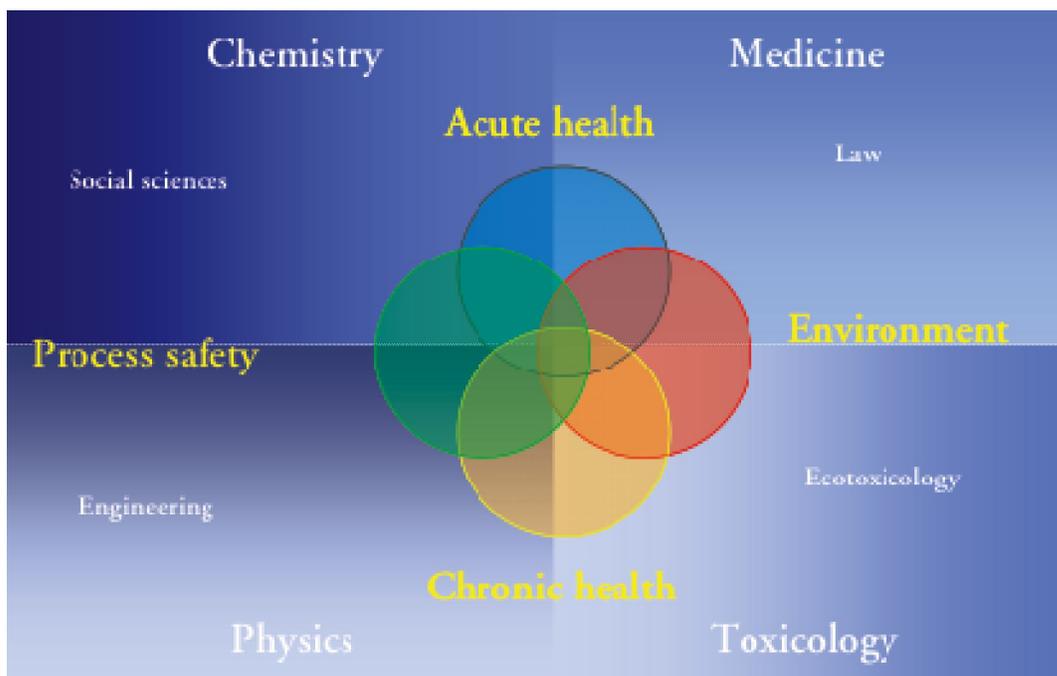


Figure 1: EHS hazards and associated scientific branches included in the study

2.2 Methodology and scope

The analysis is based on EHS data for formates from an extensive review of the open literature, supplemented by previous independent research reports and test results from the manufacturers. Any omissions are unintentional and, should new data emerge, the EHS profiles should be amended accordingly. In order to minimize this possibility, peer reviewed data from scientific journals or government reports have been preferentially used.

The behaviour and movement of potassium and cesium formate in different environmental compartments (seawater, marine sediment and soil) is addressed and the possible biological fate and effects of the substances are discussed. Using the available information, a hazard assessment has been carried out and illustrative EHS profiles created for both chemicals and their aqueous solutions.



When formulating conventional WCF various toxic additives, such as corrosion inhibitors, biocides or oxygen scavengers may be included to mitigate the deficiencies of the other formulation components. These additives may significantly increase the toxicity of the fluids. Fortunately, formate brines do not require additives of this kind and so their toxic contributions have not been examined in this study.

3 Physico-chemical profiling

3.1 Physical and chemical properties

Formates (also known as methanoates) are esters and salts of formic (methanoic) acid. Formic acid is the simplest and strongest of the organic carboxylic acids and is unique as it can behave as both an acid and an aldehyde. Formic acid is a colorless liquid which fumes slightly and has a distinctive, pungent penetrating odor. It is found naturally in sweat, urine, nettles and the stings of ants, bees and wasps. It is miscible with water and many organic solvents. Formic acid is produced by the oxidation of methanol or formaldehyde.

Cesium formate (CsCOOH) and potassium formate (KCOOH) are inorganic salts of monovalent alkali metal cesium (Cs) or potassium (K) and the anionic form of formic acid (HCO₂H). These particular formate salts are highly soluble in aqueous solutions, forming high-density, alkaline brines. In aqueous solutions both rapidly dissociate into ionic constituents, the cesium (Cs⁺) or potassium (K⁺) cations and the formate anion (HCOO⁻). The structural formula of the formate anion is shown in Figure 2 and a summary of selected physico-chemical properties of the alkali metal formate salts and their brines (highly concentrated aqueous solutions) are presented in Table 1.

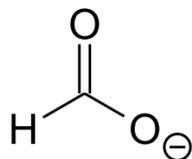


Figure 2. Structural formula of the formate anion

Table 1. Selected physico-chemical properties of Formate Brines¹

	Sodium formate	Potassium formate	Cesium formate
CAS no.	141-53-7	590-29-4	3495-36-1
Molecular weight	68.01	84.11	177.94
Melting point	253°C	167°C	
Solubility	434 gl ⁻¹ 972 gl ⁻¹ (at 20°C)	714 gl ⁻¹	1906 gl ⁻¹ (at 20°C)
Formate Log Kow	-4.27	-4.27	<-1.28
Density of pure Formate Brine ²	1.33 gcm ⁻³	1.59 gcm ⁻³	2.3 gcm ⁻³

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 The cations and existing concentrations in seawater

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. Alkali metals exist as hydrated ions in aqueous solutions. For the cesium ion, the arrangement of water molecules around the cation is probably octahedral³. A very small proportion (max 1 %) of the cesium in seawater exists as ion paired with sulphate (CsSO₄)⁴.

¹ Gilbert et al. (2003)

² Measured at fluid saturation at 20°C . Units equivalent to specific gravity, SG (unitless)

³ Sharpe A.G. (1986) Inorganic Chemistry. Longman Scientific and Technical, Harlow, UK.

⁴ Byrne R.H. (2002) Inorganic speciation of dissolved elements in seawater: the influence of pH on concentration ratios. *Geochemical Transactions* 3: 11-16.

The same dissociation reaction occurs with potassium formate. Potassium is one of the major components in seawater with an average concentration of 0.38 g/kg.⁵ Potassium cations are surrounded by four water molecules in a tetrahedral arrangement.⁶

The alkali metal ions (M⁺) are all prevalent in seawater, and the average concentration and overall abundance of the ionic constituents are detailed in Table 2.

Table 2. Average alkali metal ion abundance in seawater⁷

Element	Probable species	Concentration (mg l ⁻¹)	Ranking from most abundant	Abundance (Tonnes)
Potassium	K ⁺	3.8 x 10 ²	6	5.02 x 10 ¹⁴
Cesium	Cs ⁺	4 x 10 ⁻⁴	29	5.29 x 10 ⁸

Both cations are naturally abundant in seawater, with sodium and potassium regarded as major constituents⁷. The average concentration of the major transformation product of formate, the bicarbonate ion, HCO₃⁻, is 140 mg l⁻¹.⁸

Potassium is in sufficient abundance (380 mg l⁻¹) in seawater to be regarded as a major constituent⁹. To put this into perspective, one cubic mile of seawater will contain some 1.7 million tonnes of potassium ions¹⁰. The release of up to 500 tonnes (the full contents of an average wellbore, over 250 m³) – representing a catastrophic loss of potassium formate brine containing some 46 % (230 tonnes) of potassium ions - would increase the ionic levels in the surrounding seawater within the nearest 1 km³ area by approximately 0.25 mg l⁻¹, an increase of some 0.065% above base level.

Some examples of calculated potassium ion concentration increases within different radii water columns following a 230 MT discharge of 75% w/w potassium formate brine are shown in Table 3. This table assumes an average water depth of 100 m, representative of shallow seas, following the precautionary principle. If the same spill occurred in a water depth of 1 km, the concentration increases are of course much less. These are illustrated in Table 4.

⁵ Wright (1995)

⁶ Byrne (2002)

⁷ Wright (1995)

⁸ Pillard et al. (1999)

⁹ Wright (1995)

¹⁰ Clark (1994)

Table 3. Effects of discharge of 250 tonnes of potassium formate brine on potassium levels in sea body of 100 m depth

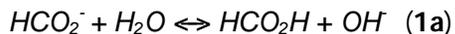
Radius from discharge point (m)	Surface area	Volume of water	Increase in potassium concentration (mg/l-1)	Total concentration (mg/l-1) potassium ions
5.64	100 m ²	10,000 m ³	25,000	25,380
17.84	1,000 m ²	100,000 m ³	2,500	2,880
56.42	10,000 m ²	1,000,000 m ³	250	630
178.41	100,000 m ²	10,000,000 m ³	25	405
564.19	1 km ²	100,000,000 m ³	2.5	382.5
1784.12	10 km ²	1 km ³	0.25	380.25

Table 4. Effects of discharge of 250 tonnes of potassium formate brine on potassium levels in sea body of 1000 m depth.

Radius (m)	Surface area	Volume of water	Increase in potassium concentration increase (mg/l-1)	Total concentration (mg/l-1) potassium ions
5.64	100 m ²	100,000 m ³	1720	2100
17.84	1,000 m ²	1,000,000 m ³	172.5	552.5
56.42	10,000 m ²	10,000,000 m ³	17.25	397.25
178.41	100,000 m ²	100,000,000 m ³	1.725	382.725
564.19	1 km ²	1 km ³	0.172	380.172
1784.12	10 km ²	10 km ³	0.017	380.017

3.2.3 The anion

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:



More commonly written as:



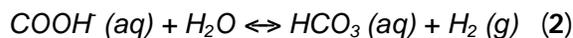
Or the shorter version:



Removal of formate ions from the water column through biodegradation¹¹ 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 micro-organisms. Hence the formate anion's behaviour and mobility in seawater is limited.

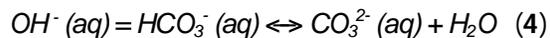
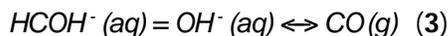
In highly illuminated surface waters the oxidation of formate ions by hydroxyl radicals is possible. Hydroxyl radicals ($\cdot\text{OH}$) are formed by the action of sunlight on the water molecules and they are found in surface waters in very low concentrations. Carbon dioxide, hydroxide ions and hydroperoxyl radicals are formed as a result of formate oxidation¹².

During extended exposure of formate brine to high-temperature conditions (e.g. > 130°C), as might happen during use in deep gas well drilling, a small amount of decomposition might occur. The degree of formate decomposition that takes place depends on the amount of carbonate/bicarbonate pH buffer present in solution, the pressure, the temperature and the amount of exposed catalytic surfaces. The main decomposition product of formate decomposition is bicarbonate. Bicarbonate is formed according to the decarboxylation reaction:



This reaction will reach equilibrium when the local bicarbonate and hydrogen concentration reach a certain level. A formate brine containing bicarbonate as a pH buffering agent will therefore decompose less than a straight formate brine. In normal use in well construction operations very little formate is converted to bicarbonate (probably less than 1%).

Another reaction that could take place to a smaller extent is the dehydration of formate according to the following reactions, producing carbon monoxide and carbonate.



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



Small amounts of methanol have occasionally been found in formate brines that have been left in HPHT wells for very extended periods of time (i.e. years) Trace amounts of oxalate are sometimes found in formate brines that have been exposed to HPHT conditions.¹³

¹¹ OECD (1992a)

¹² Gilbert et al. (2003), section 5.3.5

¹³ Howard et al. (1996), chapter A13 Thermal Stability

3.3 Speciation, behaviour and mobility in marine sediment

Adsorption is a key factor determining 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

Ion preference or selectivity is defined as the potential of a charged surface to demonstrate preferential adsorption of one ion over another. Such ion preference is described by the 'lyotropic series'. For alkali metal cations and calcium (an alkali earth metal) this usually follows the trend $\text{Cs}^+ > \text{K}^+ > \text{Na}^+ > \text{Ca}^{2+}$. The sorption of ions by soils is influenced by the size of the hydrated ion radius (smallest preferred) and the least negative heat of hydration. This indicates that all three alkali metal cations derived from formate brines will be sorbed by soil and sediments to some extent but that caesium will be adsorbed to a considerably greater extent.¹⁴

The behavior of the ^{137}Cs radionuclide of caesium in marine sediments has been extensively studied. **Note that the caesium used to manufacture caesium formate is the non-radioactive ^{133}Cs .** However, the movement of the benign ^{133}Cs in the marine sediments should be similar to that of the radioactive ^{137}Cs . When entering the water column, the caesium 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 caesium binding sites¹⁵, namely:

1. Sorption to surface and planar sites (Cs^+ is generally exchangeable)
2. Sorption to wedge sites (Cs^+ exchange is 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 studies¹⁶.

¹⁴ Gilbert et al. (2003)

¹⁵ Clark and Evans (1983), as quoted by Borretzen and Salbu (2001)

¹⁶ Kendall and Boone (2006)

3.4 Speciation, behaviour and mobility in soil

3.4.1 The process

The speciation, behaviour and mobility of cesium and potassium formate 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 phases¹⁷.

The sorption-desorption process in soil is greatly affected by the soil type and the concentration of the chemical. The interactions of cations with soils are controlled by cation ion exchange, surface adsorption and reactions with organic matter¹⁸. In the case of anion adsorption, the pH of the soil greatly impacts its anion exchange capacity by 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 capacity¹⁹.

Due to the ionic nature of the constituents of formate brines (alkali metal cations and the formate anion) their transport and mobility in the environment will be greatly influenced by their electrostatic interactions with the functional groups of sediment and soil components such as clay minerals and organic matter. Sediment and soil-surface electrochemical properties vary between soil/sediment types and depend on factors such as parent material, input of organic matter and climatic conditions. Therefore different soils and sediments will have different abilities to adsorb various ionic species. Ion preference or selectivity is defined as the potential of a charged surface to demonstrate preferential adsorption of one ion over another. Such ion preference is described by the 'lyotropic series'. For alkali metal cations and calcium (an alkali earth metal) this usually follows the trend $Cs^+ > K^+ > Na^+ > Ca^{2+}$.²⁰

The sorption of ions by soils is influenced by the size of the hydrated ion radius (smallest preferred) and the least negative heat of hydration. This indicates that all three alkali metal cations derived from formate brines will be sorbed by soil and sediments to some extent but cesium will be adsorbed to a considerably greater extent.

The availability of sites where ionic interactions can occur is an important factor in determining ion exchange. Various micro-structural environments on the mineral complexes such as faults, cleavages, cracks, frayed edge sites (FES) and stepped edges increase the availability of sites. The process of cation exchange involves the replacement of a given cation by another cation and the cation exchange capacity (CEC) of a soil/sediment its capacity to retain cations. As a consequence of their structure, clay minerals in sediment and suspended particulate matter are effective ion exchangers. When a clay particle is suspended in water, some of the interlayer cations pass into solution, result-

¹⁷ Essington (2003), chapter 1.1

¹⁸ Bohn et al. (2001), chapter 2 Important ions

¹⁹ Bohn et al. (2001), chapter 9 Anion and molecular retention

²⁰ Cabot (2002)



ing in a negatively charged silicate framework surrounded by a diffuse cloud of cations. The charged surfaces and diffused cloud of oppositely charged ions are called a double layer. The stability of colloidal suspension and the ion exchange properties of solids are closely related to the behaviour of the double layer. It consists of ions more or less attached to the solid surface and outside that a diffuse layer in which ions are free to move.

The octanol-water partitioning coefficient is a measure of a chemical's lipophilicity (affinity for the organic/lipid phase) in a two-phased system – measured as the equilibrium distribution between octanol and water. The octanol water partitioning coefficient, Powh is usually reported as the Log-Pow. The LogPow (also known as LogKow) of ionic species is low due to the high affinity of such species for the aqueous phase. LogPow is correlated with bioaccumulation and gives an indication of both the likelihood that the chemical will potentially bioaccumulate in the lipid (fatty) layers, as well as the likely adsorption to organic material in sediments. The octanol-water partitioning coefficient of the formate anion, derived from cesium formate, has been measured at less than 0.0533 and the corresponding LogKow is less than -1.28. This value indicates that only small amounts of the salts would be expected to adhere to the sediments. The partition coefficients of the formate anion derived from sodium and potassium formate solutions have been estimated at -4.27. The LogPow for the Formate Brines reported in the HOCNF are less than zero for Sodium and Potassium Formate, and less than -2.2 for Cesium Formate. These negative values for LogPow indicate that only minute amounts of the formate anion would partition to an organic/lipid phase or adhere to sediments.

3.4.2 Cesium

Cesium is relatively rare in the earth's crust and seawater, occurring at concentrations of 3 mg/kg and 3×10^4 mg/l, respectively²¹. Cesium is the most electropositive and alkaline metal occurring typically in pegmatite deposits where it occurs as the mineral pollucite. Cesium metal is a liquid and extremely reactive. Cesium exists in soil solution as hydrated ions²². 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 reactions²³. 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 strongly²⁴. It seems also that the presence of soil organic matter decreases the adsorption of Cs⁺, thus making it more bioavailable²⁵. Cesium adsorption has been determined to be maximal at pH 7-8⁴⁸. Cesium does not form any complexes or precipitates or colloids²⁶.

²¹ Gilbert et al. (2003)

²² Essington (2003), chapter 5.2

²³ Poinssot et al. (1999), as quoted by Gilbert et al. (2003)

²⁴ Livens and Loveland (1988)

²⁵ Staunton and Levacic (1999)

²⁶ Hakem et al.(2000)

3.4.3 Potassium

Potassium is the eighth most abundant element in the earth's crust, making up 2.1% by weight (2.09 x 10⁴ mg/kg, CRC 2000). It is widely distributed in silicate rocks, plants and sea water. Most potassium minerals are insoluble and the metal is obtained from them with great difficulty. It is one of the most reactive and electropositive metals. Potassium is an essential constituent for plant growth and is found in most soils but, as it can be a limiting element, there is also a great demand for potassium fertilisers.

3.4.4 Formate

Significant adsorption of formate anions from cesium formate solution to various soils has been reported earlier²⁷. However, the experimental design of the study is considered to be inadequate and thus the results should be treated with caution. In contrast, another study on the adsorption of formate on a type of silica (quartz) and a clay mineral (kaolinite) found that these minerals had only slight affinity for formate²⁸.

Simplifying, this means that when formate fluids are added to soil, the cesium ions and to a lesser extent the potassium will be absorbed but the formate will stay in the soil solution until it biodegrades.

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 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 fluids²⁹.

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 and potassium are natural constituents of seawater, and thus their discharge introduces no new elements into the composition of seawater. However, the ionic balance of the seawater will be changed – the proportion of these ions will be increased temporarily in a limited body of water.

²⁷ Lakefield Research (1998), as quoted by Gilbert et al. (2003)

²⁸ Ward and Brady (1998), as quoted by Gilbert et al. (2003)

²⁹ Zuvo et al. (2005)

Organic formate ions will disappear rapidly from the water column, as micro-organisms degrade them into water and carbon dioxide³⁰. Thus, both due to the dilution factor and biodegradation, the concentration of formate ions will be elevated only temporarily. However, the aerobic 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 halocline 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. However, this is not considered to be possible for the volumes of these fluids used for any single well.

3.5.2 Sediment

Discharges of the formates would result in locally elevated concentrations of cesium in the sediment. Cesium acts as a sinker, i.e. it has a tendency to accumulate in the sediment through sorption. Potassium on the other hand is more likely to dissolve into the seawater and does not have as strong a sorption tendency as cesium.

The formate anion will be rapidly degraded by micro-organisms and assimilated into the biomass. This is supported by an environmental survey conducted in the Barents Sea in which only natural background levels of formate were found in local sediments after drilling with potassium formate³¹. However, biodegradation utilizes 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 localized and of short duration due to dilution through water movement, even within stratified layers.

3.5.3 Soil

The terrestrial effects for both compounds could be more negative, 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 potassium formate-based road de-icing formulations in soil has revealed that

³⁰ OECD (1992a)

³¹ Zuvo et al.(2005)

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 dioxide³².

The inorganic ions (Cs^+ , K^+) will not be degraded and their local concentrations could be elevated markedly.

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 mineralization 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. freshwater³³ and marine environment³⁴.

Cesium formate is readily biodegradable, i.e. in 28 days 79 % of formate is degraded when tested in seawater³⁵. In a freshwater medium 83 % of the chemical is degraded in the same time span³⁵.

Potassium formate is readily biodegradable, i.e. in 28 days 71.3% of formate is degraded when tested in seawater³⁶. In a freshwater medium 92 % of the chemical is degraded in the same time span³⁷.

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 literature³⁸, cesium is mentioned. The mean bioconcentration factors for

³² Hellsten et al. (2005)

³³ OECD (1992b)

³⁴ OECD (1992a)

³⁵ Cabot (2007)

³⁶ Gilbert et al. (2003)

³⁷ Cabot (2007)

³⁸ Jorgensen et al. (1991), as quoted by Downs et al. (1994)

marine species of plants, fish, crustacea, molluscs and fish for cesium range from 15-51 and for zinc between 150-9900. 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.

The potassium alkali metal cations are essential to animals. Because of this, they are often readily bioaccumulated in plasma and tissues. Organisms are, in general, adapted for absorbing, storing and excreting essential ions through physiological mechanisms³⁹. Note that these ions occur naturally, and do not pose the same bioaccumulative risks that some other toxicants do. This is largely due to existing, efficient excretion systems.

Cesium formate is unlikely to bioaccumulate, because the logarithmic Pow is below -2.20. For potassium formate the logarithmic Pow is below 0. For example, under the OSPAR regime chemicals with $\log \text{Pow} \geq 3$ are considered as bioaccumulative, unless experimental BCF tests indicate the opposite⁴⁰.

The very low octanol-water partitioning coefficients (LogPow) established for the Formate Brines are indicative of a very low tendency to bioaccumulate. In general, bioaccumulation is only significant for lipophilic (fat-loving) compounds, such as the higher molecular weight hydrocarbons. The hydrophilic (water-loving) nature is further confirmed by the high aqueous solubility of the formate brines.

The direct utilization of bioaccumulation factors in the ranking and selection of drilling fluids 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 hydrophilicity) of the chemicals, and it indicates the ratio of the equilibrium concentration of a chemical in octanol (and hence in an organism) 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 and biomagnification

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)⁴¹. Therefore, bioavailabilities for compounds cannot be given as universally applicable values, as they are case specific.

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. Biomagnifiable substances are lipophilic and

³⁹ Pillard et al. (1999)

⁴⁰ OSPAR (2005), § 2.1 Partitioning and bioaccumulation potential

⁴¹ WHO (2001), chapter 4.3.2 Bioaccumulation

persistent organic substances or metals, which are not degradable as they are elements. The formate anion does not fall into this category. Potassium is an essential part of many biological systems and there are specific excretion pathways for potassium. Potassium is therefore not regarded to as having biomagnification potential.

The highly soluble nature of the formate brines and the biodegradation of the formate anion make it unlikely that these chemicals have a significant potential for bioconcentration.⁴² However, the possibility of bioconcentration and biomagnification of cesium ions cannot be dismissed.

Biomagnification of cesium is a possibility and references to food chain transfer of radio-active cesium isotopes exist⁴³. However, according to some sources⁴⁴, 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 2 days and the remainder with a biological half-life (e.g. half of the compound is excreted) of 110 days for adults. Thus, exposure may lead to accumulation of cesium, but once the source is removed, it will readily clear from the body along the normal pathways.

4.4 Ecotoxicity of the compounds

4.4.1 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 chemical. 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,

⁴² NICNAS (2001)

⁴³ Gilbert et al. (2003)

⁴⁴ Agronne National Laboratory, EVS (2005)

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.

4.4.2 Marine ecotoxicity

The test results from marine ecotoxicity tests are expressed in Table 5.

Table 5. Marine ecotoxicity data

Organism	Test	Endpoint	Cesium formate (mg/l)	Potassium formate (mg/l)
<i>Menidia beryllina</i> ^{45, 46}	7 d chronic, definitive	Survival NOEC	420	1200
	7 d chronic, definitive	Survival LOEC	700	2000
	7 d chronic, definitive	Growth NOEC	252	432
	7 d chronic, definitive	Growth LOEC	420	720
	7 d chronic, definitive	Survival IC25	471	1430
	7 d chronic, definitive	Growth IC25	440	1270
	7 d chronic, definitive	Survival IC50	553	1670
	7 d chronic, definitive	Growth IC50	532	1540
	96 h, definitive	Survival IC50	787	
<i>Acartia tonsa</i> ^{47, 48}	48 h	EC50	340	300
<i>Skeletonema costatum</i> ⁴⁹	72 h	EC50	710	3400
	72 h	EC50	1600	
<i>Scophthalmus maximus</i> ⁵⁰	96 h, Juvenile Turbot	LC50	260	
	96 h, Larval turbot	LC50	1400	1700 ⁵¹
<i>Corophium volutator</i> ⁵²	10 d	LC50	6653	
<i>Crangon crangon</i> ⁵³	96-hour	LC50	875	1300 ⁵⁴
<i>Ctenogobius gymnauchen</i> ⁵⁵	96-h, acute	LC50	862	
<i>Crassostrea gigas</i> ⁵⁶	24 h	LC50	1100	

⁴⁵ ENVIRONMENTAL ENTERPRISES USA, INC. (2011) Test report on cesium formate and *Menidia beryllina* test, 17.11.2011

⁴⁶ ENVIRONMENTAL ENTERPRISES USA, INC. (2011) Test report on potassium formate and *Menidia beryllina* test, 17.11.2011

⁴⁷ Cabot (2007b) Material Safety Data Sheet. Cesium Formate Solution. 10.4.2007

Available online: <http://www.cabot-corp.com/cws/product.nsf/MSDSKEY/>

⁴⁸ Gilbert et al. (2003)

⁴⁹ Cabot (2007b)

⁵⁰ Cabot (2007b)

⁵¹ Gilbert et al. (2003), test method unknown

⁵² Cabot (2007b)

⁵³ Cabot (2011) test data

⁵⁴ Gilbert et al. (2003)

⁵⁵ Quangdong Laboratory Animals monitoring institute (2010) Test report on cesium formate and *Ctenogobius gymnauchen* test, 28.4.2010

⁵⁶ Cabot (2007b)

4.4.3 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 *Mysidopsis 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. *M. 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 ppt⁵⁷. The 48-hour LC₅₀ acute toxicity test results for *M. bahia* with formate brines are 521 mg/l (cesium formate) and 883 mg/l (potassium formate). These acute toxicity results for *M. bahia* are slightly better than the 48-hour LC₅₀ values for *Acartia tonsa*, a marine copepod that co-exists with *M. bahia* in marine environments.

Table 6. Chronic ecotoxicity data for a brackish water species – *Mysidopsis bahia*

Organism	Test	Endpoint	Cesium formate (mg/l) ⁵⁸	Potassium formate (mg/l) ⁵⁹
<i>Mysidopsis bahia</i>	7 d chronic, definitive	Survival NOEC	420	720
	7 d chronic, definitive	Survival LOEC	700	1200
	7 d chronic, definitive	Growth NOEC	252	432
	7 d chronic, definitive	Growth LOEC	420	720
	7 d chronic, definitive	Survival IC25	369	760
	7 d chronic, definitive	Growth IC25	260	551
	7 d chronic, definitive	Survival IC50	481	908
	7 d chronic, definitive	Growth IC50	392	796

The *Mysidopsis bahia* test⁶⁰ conducted on the suspended particulate phase of the drilling fluids resulted in following 96-hour LC50 values: Cesium formate 1700 mg/l⁶¹ and for potassium formate 6900 mg/l⁶².

⁵⁷ Price (1982)

⁵⁸ ENVIRONMENTAL ENTERPRISES USA, INC. (2011) Test report on cesium formate and *Mysidopsis bahia* test, 17.11.2011

⁵⁹ ENVIRONMENTAL ENTERPRISES USA, INC. (2011) Test report on potassium formate and *Mysidopsis bahia* test, 17.11.2011

⁶⁰ Appendix 2 to Subpart A of Part 435—Drilling Fluids Toxicity Test

⁶¹ ENVIRONMENTAL ENTERPRISES USA, INC. (2011) Test report on cesium formate drilling fluid and *Mysidopsis bahia* test, 17.11.2011

⁶² ENVIRONMENTAL ENTERPRISES USA, INC. (2011) Test report on potassium formate drilling fluid and *Mysidopsis bahia* test, 17.11.2011

Table 7. Freshwater ecotoxicity data

Organism	Test	Endpoint	Cesium formate (mg/l)	Potassium formate (mg/l)
<i>Pseudokirchneriella subcapitata</i> ⁶³	72-h	LC50, growth rate	110	
	72-h	NOEC, growth rate	18	
	72-h	LOEC, growth rate	56	
	72-h	LC50, yield	33	
	72-h	NOEC, yield	18	
	72-h	LOEC, yield	56	
<i>Desmodesmus subspicatus</i> ⁶⁴	72-h	LC50	110 (growth rate)	>1000 ⁶⁵
	72-h	NOEC, growth rate	56	
	72-h	LOEC, growth rate	180	
	72-h	LC50, yield	67	
	72-h	NOEC, yield	56	
	72-h	LOEC, yield	180	
<i>Onchorhynchus mykiss</i>	96 h	LC50	>1000 ⁶⁶	3500 ⁶⁷
<i>Daphnia magna</i> ⁶⁸	24 h	LC50	>100	
	48 h	LC50	>100	540 ⁶⁹
<i>Brachydanio rerio</i> ⁷⁰	96-hour	LC50	>100	

4.4.4 Freshwater ecotoxicity

The limited test data available for freshwater organisms indicate that fresh-water algae may be more sensitive to cesium formate than their marine cousins in acute toxicity tests (Table 5). Freshwater fish, represented here by rainbow trout, seem to have a high tolerance for cesium formate and potassium formate.

The relatively higher toxicity of cesium formate in the freshwater medium compared to that in seawater, has been explained by the possible nutrient depletion due to weak complexation of formate with divalent nutrient ions rather than any direct toxicity⁷¹. Formates biodegrade relatively rapidly (see Chapter 4.1).

⁶³ Harlan laboratories (2010) Test report on cesium formate and *Pseudokirchneriella subcapitata* test, 24.12.2010

⁶⁴ Harlan laboratories (2010) Test report on cesium formate and *Desmodesmus subspicatus* test, 11.11.2010

⁶⁵ BASF (2011) Safety data sheet Katalysator 93650, 14.11.2011

⁶⁶ Cabot (2007b)

⁶⁷ BASF (2011)

⁶⁸ Harlan laboratories (2011) Test report on cesium formate and *Daphnia magna* test, 8.2.2011

⁶⁹ BASF (2011)

⁷⁰ Supervision and test center for pesticide safety evaluation and quality control (2008) Test report on cesium formate and *Brachydanio rerio* test, 2.7.2008

⁷¹ NICNAS (2001), chapter 10.3 Summary of Aquatic Toxicology

4.4.5 Terrestrial ecotoxicity

Terrestrial ecotoxicity tests are most often performed with different earthworm species (endpoint survival, reproduction) and various plants (endpoint seed germination, root growth). Toxicity of the formates to terrestrial organisms has been studied with a very few tests. Ecotoxicological data on cesium formate could not be found in the literature and thus, their terrestrial impacts have been extrapolated from ecotoxicity tests on the ionic constituents and similar compounds such as potassium formate.

The *Arabidopsis* plant (*Arabidopsis thaliana*) has been used in order to understand the toxicity mechanism of cesium, and 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^{72,73}.

Toxicity of potassium formate using the bulb onion *Allium cepa* has been reported. The EC_{50} value was 50 mg/l, being slightly lower (i.e. more toxic) than obtained for potassium acetate. A similar trend was observed when aquatic floating plants were exposed to potassium formate and acetate.⁷⁴

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). The 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 characterized by prolonged or repeated exposures over days, months or even years. The symptoms may not be immediately apparent and the effects are often 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. Similarly, as with ecotoxicity testing, often the concentration that causes death in half of the test population (LD_{50}) is determined.

Acute and chronic human health effects of the brines are discussed in more detail in the following two subchapters.

⁷² Hampton et al. (2004)

⁷³ Avery (1995)

⁷⁴ Joutti et al. (2003)



Table 8. Reported potential health effects as per MSDS

	Potassium formate ⁷⁵	Cesium formate solution ⁷⁶
Eyes	May cause irritation. Avoid contact with eyes.	Irritating to eyes. Avoid contact with eyes.
Skin	May cause irritation. Avoid contact with skin.	Irritating to skin. Avoid contact with skin.
Ingestion	Ingestion may cause gastrointestinal irritation, nausea, vomiting and diarrhoea. Low hazard for usual industrial or commercial handling.	Harmful if swallowed.
Inhalation	Dried product may be irritating to respiratory tract. Do not breathe dust.	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.
Chronic	Does not contain any substances listed by 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).	Effects were observed in multiple organ systems at the high oral dose (500 mg/kg/d) over a period of 28 days. Signs of neurotoxicity were also observed. Elevated reticulocyte count and effects on the heart, liver, spleen and serum biochemistry were observed at the intermediate dose rate (150 mg/kg/d). Elevated reticulocyte count was the only effect observed at the low dose (15 mg/kg/d). Effects were observed in ovaries and testes at 500 mg/kg/d in a 28-day repeated oral dose study in rats. No effects were observed in rat reproductive organs at the intermediate and low doses (150 and 15 mg/kg/d).
Aggravation of pre-existing conditions		

⁷⁵ Cabot (2007)

⁷⁶ Cabot (2007)



Table 9. Recommended PPE for potassium formate and cesium formate

	Potassium formate ⁷⁷	Cesium formate solution ⁷⁸
Eyes	Wear eye/face protection. Safety glasses with side-shields. Goggles. Wear faceshield if splashes are likely to occur.	Wear eye/face protection. Safety glasses with side-shields. Goggles. Wear faceshield if splashes are likely to occur.
Clothing	Wear chemical impervious protective clothing if skin contact may occur. Wear gloves as appropriate (impervious gloves, neoprene gloves, nitrile rubber gloves, rubber gloves, PVC or other plastic material gloves.)	Wear chemical impervious protective clothing if skin contact may occur. Wear gloves as appropriate (impervious gloves, neoprene gloves, nitrile rubber gloves, rubber gloves, PVC or other plastic material gloves).
Respirator	Approved respirator may be necessary if local exhaust ventilation is not adequate.	Approved respirator may be necessary if local exhaust ventilation is not adequate.

5.2 Acute health

Protection against acute health hazards should be provided by appropriate training and the use of appropriate personal protective equipment. The recommended personal protective equipment (PPE) is summarised in Table 9.

5.2.1 Inhalation

The inhalation of the dry powder forms of formates 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. Generally the product is manufactured, stored and transported to the well sit in its brine (solution) form. 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. This could indicate that the inhalation of formate could lead to poisoning.

5.2.2 Ingestion

This is an unlikely route of exposure for professional workers in an oilfield situation and there appear to be no documented cases of any high-density brines causing poisoning by accidental ingestion. For example, sodium formate is reported to have a low toxicity, with 10 grams given orally in humans producing no toxic effects⁷⁹.

⁷⁷ BASF Safety data sheet

⁷⁸ Cabot (2007)

⁷⁹ Toxnet Hazardous substances databank

5.2.3 Skin or eye contact

Exposure through skin or eye contact, through splashes and spills, is the most probable exposure scenario in well construction operations. No significant skin injuries (e.g. chemical burns) have been recorded for formates.

5.3 Chronic health

For both the potassium formate and cesium formate the MSDS state that the materials do not contain any known carcinogenic substances⁸⁰, but first-hand test data was not available. Tests on rats show 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 potassium formate are presented in the following paragraphs. This allows predictions on the potential outcomes of exposure to these brines, as toxicological data on the brines themselves are scarce.

Cesium does not have a known biological function. 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 dosing⁸¹. Cardiac arrhythmias have been described in patients who have ingested large doses of cesium chloride as components of homeopathic remedies⁸². A test on oyster embryos (*Crassostrea gigas*) over 24 hours (24 hour/LC 50 = 1,200 mg/l) indicate that cesium formate is not significantly toxic to these species during periods of intense cellular activity.⁸³

Potassium on the other hand is an essential ion for cellular functioning. Potassium Formate is not mutagenic, either in the presence or absence of liver S-9 fraction in two strains of *S. typhimurium*.⁸³

Formate is rapidly oxidized to CO₂ 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 oxidize formate and are thus more sensitive to methanol (and formate) intoxication⁸⁴. Formic acid itself is a mitochondrial toxin, of which formate is the suspected toxic metabolite⁸⁵.

⁸⁰ 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)

⁸¹ Neulieb (1984)

⁸² U.S. DHHS (2004)

⁸³ NICNAS (2001)

⁸⁴ Hanzlik et al. (2004)

⁸⁵ Treichel et al. (2003)

5.4 Overview of designated risk and safety phrases

Potassium formate is not classified. For cesium formate solution only two risk phrases and two safety phrases are stated in the classification according to Directive 67/548/EEC⁸⁶:

R36 - Irritating to eyes.

R48/22 - Harmful: danger of serious damage to health by prolonged exposure if swallowed

S22 - Do not breathe dust.

S24/25 - Avoid contact with skin and eyes

The following hazard statements and precautionary statements have been assigned to cesium formate according to CLP (Regulation (EC) No 1272/2008:

H302 - Harmful if swallowed

H319 - Causes serious eye irritation

H371 - May cause damage to nervous system

H373 - May cause damage to multiple organs, nervous system, and blood through prolonged or repeated exposure

P260 - Do not breathe dust

P264 - Wash your hands thoroughly after handling

P280 - Wear eye protection

P305+P351+P338 - IF IN EYES: rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.

P337+P313 - If eye irritation persists, get medical advice

P270 - Do not eat, drink or smoke when using this product

P301+P312 - IF SWALLOWED: call a poison centre or a physician if you feel unwell

P330 - Rinse mouth

P405 - Store locked up

P501 - Dispose of contents/container in accordance with local, regional, national and international regulations

⁸⁶ Cabot (2011)

6 Structural safety aspects

Cesium formate in aqueous solution is a slightly alkaline fluid, with a pH in the range of 9-10. Potassium formate in aqueous solution is also slightly alkaline, with a pH in the range 8-10 pH range. Corrosion does not occur under normal circumstances. However, some concern has been raised related to structural integrity of certain CRAs (Corrosion Resistant Alloys) after an extended period of exposure to halide and formate brines and HPHT conditions in the presence of acid gases. At the time of writing this is not yet resolved or confirmed.

This report does not probe the structural safety aspects related to fluid choices. However, in order to highlight that the choice of chemicals 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 do it under low pH. The main issue is that the choice of fluids determines the choice of elastomers that 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 safety structural issues encountered with formates are easily countered through taking the 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.

7 Analysis

7.1 Acute environmental toxicity

Both potassium and Cesium formate has been extensively tested for aquatic ecotoxicity and the available data give a reasonably informed picture of the environmental hazard.

From available acute toxicity tests results, the study shows that the toxicity of the formate brines increases in the order: Sodium Formate < Potassium Formate < Cesium Formate. This indicates that it is the alkali metal cation that has a profound impact on the overall toxicity. The results of the tests carried out indicate that both freshwater and marine crustacea are moderately sensitive to Formate Brines. Overall, it has to be noted that all the compounds are less toxic to marine species than to freshwater species.

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 magnesium⁸⁷. 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 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, cesium formate will cause mortality of soil microbes, plants, etc.

With lesser terrestrial exposures, e.g. due to leaching from landfills, any effects would be less severe. The formate ion would degrade rapidly and sorption of cesium and to a lesser extent potassium would minimize its bioavailability.

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 alterations⁸⁸. The seabed survey was conducted **three years after the drilling operations** had finished and in chemical assessment **no elevated formate concentrations** were found. In the same study the biological diversity of the nearby fauna was concluded to be high and only minor disturbances were observed. Only tube builders and filter-feeders, which are sensitive to sediment

⁸⁷ NICNAS (2001)

⁸⁸ Zuvo et al. (2005)

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 was based on potassium formate and 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.

In the case of severe transportation accidents the long-term effects might include the chemical sterilization 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 are likely to remain bound to the soil or sediment unless active remediation processes are initiated. Thus, biomagnification of cesium in the food chain in the immediate vicinity of the accident site could happen. Potassium in excessive amounts would be less harmful as most organisms have effective excretion pathways for potassium. However, the effect on fauna is dependent on the species ability to regulate the level of salts in the body.

7.3 Safety

There are certain aspects, as with most technological solutions, that have to be taken into account when using these clear, solid free fluids for drilling. Being solids free, the inclusion of weighting agents is not needed, reducing the potential for well control problems.

Compatibility with other materials has to be assured and the fluids should, if used as well completion fluids, not be left for extended periods of time (e.g. measured in years) downhole.

Compatibility of the drilling fluids (generally mainly potassium formates for top sections, cesium formate for reservoir sections) with each other, minimizing the need for spacers. Cesium formate is a high density fluid that can effectively be used to prevent blowouts as fast "kill pills".

7.4 Acute health effects

The acute health effects would be minor, if any. No acute inhalation or dermal hazards beyond "possible irritant" or "irritant" were found. These are on par level with, for example, numerous household chemicals such as laundry detergents.

7.5 Chronic health effects

For cesium formate more data are available. From reference to tests with rats, high repeated oral doses of cesium formate on humans could result in damage to reproductive organs. Repeated high oral exposure to cesium formate could also have other chronic effects (e.g. neurotoxicity) in humans.

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 response rapidly
Adsorption	Accumulation of a substance at the boundary of two phases, usually between solid and liquid phases
Anaerobic	Conditions under which no oxygen is required
Anion	An ion with a negative electrical charge

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
CEC	Cation exchange capacity; inversely related to ionic strength becoming equal to the total fixed charge at great dilution
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
Chemical use	Application of any offshore chemicals in connection with offshore exploration and production activities in the maritime area that might result in a discharge
Chronic	Involving a stimulus that is lingering over a long period of time
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
CO₂	Carbon dioxide
Complexation	The formation of chemical complexes
Crustacea	Animal with hard outer shell
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
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

H₂	Hydrogen
H₂O	Water
HCOO⁻	Formate anion
HCO₂Cs	Cesium formate
HCO₂H	Methanoic (formic) acid



HCO₂K	Potassium formate
HCO₃⁻	Bicarbonate
HCOOH	Methanoic (formic) acid

I

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

K	Potassium
K_b	Equilibrium/dissociation constant
KCl	Potassium chloride
KCOOH	Potassium formate
K_d	Distribution coefficient
K_{oc}	Sediment–water partitioning coefficient
KOH	Potassium hydroxide

L

LC50	Median Lethal Concentration: A toxicant concentration that is lethal to 50 % of the test organisms
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M

M⁺	Alkali metal ion
Micro-organism	An unicellular organism of microscopic size, such as bacteria
Monovalent	An ion with a single electrical charge of +1 or -1
MSDS	Material safety data sheet

N

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



O

O₂	Oxygen
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
PNEC	Predicted No Effect Concentration
Pow	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 $S = 0.030 + (1.805 \times \text{chlorinity})$
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 from 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
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