



COMPATIBILITIES AND INTERACTIONS

SECTION B12

SOLUBILITY OF MINERALS AND SALTS IN FORMATE BRINES

B12.1 Introduction2

B12.2 Solubility of barium sulfate and barite in formate brines.....2

 B12.2.1 Mechanisms of barium sulfate dissolution in formate brines.....2

 B12.2.2 Experimental work4

 B12.2.3 Results4

 B12.2.4 Conclusions5

 B12.2.5 Relevance of experimental results for oilfield applications6

B12.3 Dissolution of shales in formate brines11

B12.4 Dissolution of silicates in formate brines.....11

B12.5 Solubility of galena, hematite, and ilmenate in formate brines11

B12.6 Solubility of calcium carbonate in formate brines11

References 12

The Formate Technical Manual is continually updated.
 To check if a newer version of this section exists please visit
cabotcorp.com/formatemanual



NOTICE AND DISCLAIMER. The data and conclusions contained herein are based on work believed to be reliable; however, CABOT cannot and does not guarantee that similar results and/or conclusions will be obtained by others. This information is provided as a convenience and for informational purposes only. No guarantee or warranty as to this information, or any product to which it relates, is given or implied. CABOT DISCLAIMS ALL WARRANTIES EXPRESS OR IMPLIED, INCLUDING MERCHANTABILITY OR FITNESS FOR A PARTICULAR PURPOSE AS TO (i) SUCH INFORMATION, (ii) ANY PRODUCT OR (iii) INTELLECTUAL PROPERTY INFRINGEMENT. In no event is CABOT responsible for, and CABOT does not accept and hereby disclaims liability for, any damages whatsoever in connection with the use of or reliance on this information or any product to which it relates.

© 2016 Cabot Corporation, MA, USA. All rights reserved. CABOT is a registered trademark of Cabot Corporation.

VERSION 2 - 09/16



B12.1 Introduction

Oil and gas wells are drilled through thousands of meters of various minerals to access hydrocarbon-bearing reservoirs. While being drilled and completed, well construction fluids circulating in the wellbore are in contact with these minerals under conditions of high temperature and pressure. Therefore, it is important to have detailed knowledge of how drilling and completion fluids interact with minerals under downhole conditions. In wells where it is necessary to drill extended sections through thick layers of salt and anhydrite, it is particularly important to know if fluids solubilize these minerals.

Formate drilling and completion fluids are also in contact with barite when used downhole. Up to 5 million metric tons of barite is added to traditional drilling fluids every year to increase their density for well control purposes. Contact with barite is unavoidable as wellbores often are lined with barite filtercake when formates are deployed and, during the displacement process, some cross-contamination between fluids always takes place. Fluids with high electrolyte content, such as oilfield brines, are known to increase solubility of alkaline earth metal sulfate minerals, like calcium sulfate (gypsum and anhydrite) and barium sulfate, which have low solubility in water. This 'salting-in' effect has been known since the early 1930's (Neuman, 1933). The effect of sodium chloride brines on barite solubility was described by Shell 30 years later (Templeton, 1960). Subsequent work (Monnin, 1999) shows that at atmospheric pressure a saturated sodium chloride brine could solubilize 50–100 mg/L of barium from barite at 50–100°C / 122–212°F, and at higher temperatures and pressures the barium solubility levels could increase to 200–400 mg/L. The same paper indicates that barite is even more soluble in calcium chloride brines. Shell continued this investigation into barite solubility in brines during its early development of formate brines in the 1990's (Howard, 1995). Shell measured the solubility of some alkaline earth metal sulfates and barite in a variety of concentrated brines, and reported very high solubilities in potassium formate brine.

This section of the Formate Technical Manual looks at what is known about the solubility of minerals and salts in formate brines. Data have been collected from various sources and full descriptions of measuring methods are not always available. Considering the difficulties associated with performing good solubility measurements in brines, the data reported here should only be used as a rough guide.

B12.2 Solubility of barium sulfate and barite in formate brines

Earlier versions of this manual present solubility data for some alkaline earth metal sulfates (and barite) measured by Shell in 1995 (Howard, 1995). The intention of Shell's research was to find out if formate brines might have sulfate scale-dissolving properties and investigate the compatibility of formate brines with barite and other common minerals. The solubilities of barium sulfate and barite were measured after 16 hours hot-rolling at 85°C / 185°F in monovalent chloride, bromide, and formate brines. Shell measured barium levels of 3,400 mg/L and 1,500 mg/L for barium sulfate ($BaSO_4$) and API-grade barite respectively in 75 wt% potassium formate brine at 85°C / 185°F.

The Shell study produced interesting results, but it neglects to look into what happens to soluble barium levels in formate brines when they are cooled down to ambient conditions found in brine tanks and mud pits. It also neglects to look at realistic buffered formate brine formulations of the type used in the field. It has been noted that soluble barium levels in formate fluids returned from the field are invariably very low, even though these fluids may have been exposed to significant amounts of barite contamination in pits, pipes, and downhole.

Due to inconsistency between barite solubility data presented by Shell and field experience by Cabot Specialty Fluids a new study was undertaken by Cabot to:

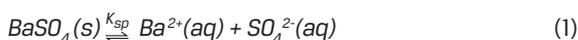
1. Determine what levels of soluble barium and sulfate are found in cooled samples of formate brines after exposure to barium sulfate under surface and downhole temperature conditions.
2. Map the impact of formate concentration and cesium / potassium ratios on the dissolution of barium and sulfate from barium sulfate.
3. Determine what impact the addition of a carbonate / bicarbonate pH buffering package has on the levels of soluble barium and sulfate in formate brines after exposure to barium sulfate under downhole temperature conditions.

B12.2.1 Mechanisms of barium sulfate dissolution in formate brines

Concentrated brines' solvencies, i.e. their ability to dissolve salts and minerals, are interesting as they often differ from those of water. During previous investigations on formate brines, Cabot has observed the following:

- Barium sulfate ($BaSO_4$) is slightly soluble in formate brine, whilst it is barely soluble in fresh water.
- Barium carbonate ($BaCO_3$) is barely soluble in formate brine and in water.
- Potassium sulfate (K_2SO_4) is only slightly soluble in formate brine, whilst it is soluble in water.
- Cesium sulfate (Cs_2SO_4) is soluble in formate brine and in water.

With these observations in mind, one can predict how various buffered and unbuffered formate brines behave when they are exposed to barium sulfate or barite. As reported by various researchers (Neuman, 1933; Templeton, 1960; Monnin, 1999), when barium sulfate is exposed to any brine very slight dissolution occurs:

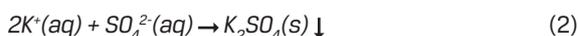


This is an equilibrium reaction. How far it goes before it reaches equilibrium depends on the solubility product constant, K_{sp} , which is dependent on the ionic strength of the brine, which again depends on brine type and concentration. How exactly the brine then reacts with the dissolved barium and sulfate ions depends on the type of brine and whether other ions are present. In the case of formate brines, it also depends on whether a carbonate buffer has been added. The following fluids are considered in this section:

1. Unbuffered potassium formate single-salt brine.
2. Single-salt potassium formate brine with carbonate / bicarbonate pH buffer.
3. Unbuffered single-salt cesium formate brine.
4. Single-salt cesium formate brine with carbonate / bicarbonate pH buffer.
5. Blended cesium potassium formate brines with and without carbonate / bicarbonate pH buffer.

Unbuffered single-salt potassium formate

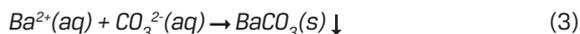
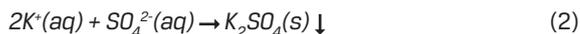
When unbuffered potassium formate single-salt brine is held in contact with barium sulfate, small amounts of soluble Ba^{2+} and SO_4^{2-} are released into solution according to Equation 1 above, and the following precipitation reaction takes place:



Removal of soluble SO_4^{2-} ions from the fluid as a result of precipitation of K_2SO_4 drives further dissolution of barium sulfate and build-up of soluble Ba^{2+} in the formate brine, according to Le Châtelier's principle. The concentration of soluble Ba^{2+} increases until the $BaSO_4$ solubilization reaction (Equation 1) reaches equilibrium.

Buffered single-salt potassium formate

When buffered potassium formate single-salt brine is held in contact with barium sulfate, small amounts of soluble Ba^{2+} and SO_4^{2-} are released according to Equation 1 above, and the following precipitation reactions take place:



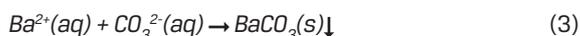
As long as there are potassium ions and carbonate ions available in the brine, these reactions continue, and concentrations of soluble Ba^{2+} or SO_4^{2-} in solution remain low. If the entire carbonate buffer is consumed, however, concentration of soluble Ba^{2+} increases until the $BaSO_4$ solubilization reaction (Equation 1) reaches equilibrium.

Unbuffered single-salt cesium formate

When unbuffered cesium formate single-salt brine is held in contact with barium sulfate, small amounts of soluble Ba^{2+} and SO_4^{2-} are released into solution according to Equation 1 above. No precipitation reactions take place, because no salts less soluble than barium sulfate can form. With no precipitation reaction driving the dissolution process forward, only very low levels of soluble barium and sulfate form according to Equation 1.

Buffered single-salt cesium formate

When buffered cesium formate single-salt brine is held in contact with barium sulfate, small amounts of soluble Ba^{2+} and SO_4^{2-} are released according to Equation 1 above and the following precipitation reaction takes place:



This means that the concentration of soluble barium remains very low, whilst the concentration of soluble SO_4^{2-} increases. The $BaCO_3$ precipitation reaction slows down when the $BaSO_4$ solubilization reaction (Equation 1) reaches equilibrium.

Blended potassium and cesium formate brines

Blended brines of cesium and potassium formate behave the same way as potassium formate (see above). This is because potassium ions precipitate out soluble sulfate as potassium sulfate (K_2SO_4) and, assuming the brine is buffered, carbonate ions precipitate out soluble barium as $BaCO_3$. If the entire carbonate buffer is consumed, however, the soluble Ba^{2+} concentration increases until the K_2SO_4 solubilization reaction (Equation 1) reaches equilibrium.

B12.2.2 Experimental work

A series of tests were performed to investigate the effect of various parameters on the dissolution of analytical-grade barium sulfate in formate brines. The parameters investigated were brine composition, brine concentration, exposure temperature and time, and addition of carbonate / bicarbonate buffer. Dissolution measurements, specifically those determining the level of soluble barium and sulfate released into solution, were performed after the fluid had cooled down to ambient temperature to simulate field conditions where fluid is exposed to high temperature downhole and then cooled in storage tanks at the surface. Analytical-grade barium sulfate powder was chosen in preference to barite as it is a more consistent product with less impurities and easier to dissolve than barite. API-grade (or drilling-grade) barite can contain many impurities such as silicates, including quartz and chert, carbonate compounds such as siderite and dolomite, and metallic oxide and sulfide compounds.

Exposure testing

All exposure testing was conducted in 316-grade stainless steel pressure cells (hot rolling cells) fitted with PTFE liners and piston end-caps. Analytical-grade barium sulfate was added at a concentration of 1.75 grams per 175 mL of formate brine, and then mixed thoroughly at ambient temperature for at least ten minutes before pouring into pressure cells. The cells were purged with nitrogen, pressurized to 200 psi, and placed in a hot rolling oven where they aged dynamically at the desired temperature for the specified amount of time. After hot rolling the cells were removed from the oven and cooled in cold water for at least one hour before pressure was released and the fluids transferred to beakers, where they were left at ambient temperature for another two hours. The samples were then filtered under vacuum through 1 μm nitrocellulose filter membranes. It should be noted that the potassium formate brines took significantly longer to filter than the cesium formate brines. This is most likely due to their higher viscosity and precipitation of fine potassium sulfate crystals, which formed a very low-permeability filter cake. To achieve an acceptable rate of filtration the potassium formate brines were first filtered through a 5 μm filter membrane before being filtered through the 1 μm membranes.

Analytical methods

The barium content of the samples was analyzed using an Agilent 4100 MP-AES optical emission spectrometer, which excites the samples using microwave-induced nitrogen plasma. The sulfate content was measured using a Metrohm Ion Chromatograph with an eluent

of 3.2 mmol/L sodium carbonate and 1 mmol/L sodium bicarbonate. Given the extremely high ionic concentrations of the brines used it was necessary to dilute the samples one thousand times before analysis could be carried out to prevent the brines from damaging the torch in the MP-AES or overloading the detector in the Ion Chromatograph. This dilution was completed in two stages, a 25-times dilution followed by a 40-times dilution for both instruments. To maintain the viability of the samples for MP-AES analysis, the initial 25-times dilution was completed using nitric acid and the following 40-times dilution with deionized water. In preparation for sulfate analysis, both dilutions were carried out with water. A 1 ml aliquot of sample was transferred via micropipette to a 25 ml volumetric flask and then made up to the mark with the appropriate diluent. A 2.5 ml aliquot of this solution was then transferred to a 100 ml flask and diluted appropriately. This process was repeated twice so that each sample was diluted and analyzed in triplicate.

In order to achieve accurate results on the Agilent 4100 MP-AES, all standards had to be properly matrix-matched with each sample. To do this, a blank sample of the appropriate formate brine was diluted 500 times using a 25-times dilution followed by a 20-times dilution. Subsequently, 5 mL aliquots of this solution were mixed with 5 mL of the appropriate barium standards, which had been prepared by serial dilution of the working standard.

Solids analyses were performed by an external test laboratory using Fourier transform infrared spectroscopy (FTIR).

B12.2.3 Results

All measured concentrations of barium and sulfate are listed in **Tables 1 to 3**, and shown in **Figures 1 to 4**.

Barium sulfate dissolution in unbuffered formate brines

Unbuffered potassium and cesium formate single-salt brines were exposed to excess barium sulfate for 16 hours at 100°C / 212°F according to the method described above. The concentrations of soluble barium (Ba^{2+}) and sulfate (SO_4^{2-}) were measured after cooling and sample preparation. Figure 1 shows the measured concentrations of soluble Ba^{2+} and SO_4^{2-} in the unbuffered brines as a function of brine concentration. As expected, and in agreement with previous research reported by Shell, a high level of barium, 3,471 mg/L, was measured in concentrated, unbuffered potassium formate brine. This is likely to have been triggered by precipitation of potassium sulfate (**Equation 2**).

Analyses of the residual solids confirm that they contain potassium sulfate. In the unbuffered cesium formate brine, significantly lower amounts of soluble barium and sulfate were measured. Analyses of the residual solids show that they only contain barium sulfate. This is in agreement with the hypothesis above, i.e. that no alkali metal sulfate precipitation reactions take place when barium sulfate is dissolved in unbuffered cesium formate brines. The concentration of soluble sulfate never exceeded about 300 mg/L in any of the unbuffered formate brines.

Effect of brine composition, buffer, and temperature on barium sulfate dissolution

It is recommended that formate brines used in the field are buffered with a carbonate / bicarbonate pH buffer. When cesium formate is used in the field it is normally blended with concentrated potassium formate brine. Only at very high densities (typically above 2.1 g/cm³ / 17.5 lb/gal) is cesium formate used on its own. Therefore, it is important to investigate the dissolution of barium sulfate in these blended brines. Single-salt potassium and cesium brines and three different blends of the two were exposed to barium sulfate for 16 hours at 100°C / 212°F. This was completed with and without 5 lb/bbl of potassium carbonate / bicarbonate buffer, which was added to give pH of about 10. The buffered brines were also exposed to 150°C / 302°F and 200°C / 392°F for the same amount of time. The results are shown in Figure 2. As can be seen, the soluble barium level stayed low in all of the buffered blends. High barium levels (up to 3,500 mg/L) were only detected in unbuffered pure potassium formate brine and in unbuffered potassium / cesium formate brine blends rich in potassium formate. As expected an elevated sulfate level (1,330 mg/L) was detected in the buffered single-salt cesium formate brine.

Effect of exposure time and temperature on barium sulfate dissolution

Single-salt potassium and cesium brines and three different blends of the two were exposed to barium sulfate for an extended time period (6.7 days / 160 hours) at 100°C / 212°F and 150°C / 302°F. All fluids were buffered with 5 lb/bbl potassium carbonate / bicarbonate buffer to give pH of about 10. The measured soluble barium and sulfate concentrations are shown in Figure 3. As can be seen, the exposure temperature doesn't have much effect on the soluble barium and sulfate concentrations after 6.7 days. This means that the dissolution rate was not high enough to consume the entire buffer even at 150°C / 302°F. Although still relatively low (327 mg/L), the measured soluble barium concentration was slightly higher in pure buffered potassium formate brine than in the blends after

exposure at 150°C / 302°F, which means that a higher buffer concentration should be considered if such brine is left in contact with such extreme levels of barium sulfate for 16 hours or more at 200°C / 392°F.

Lastly, long-term exposure testing was performed at ambient temperature to explore whether high levels of soluble barium can build up in brines stored for an elevated amount of time in contact with excess barium sulfate. Single-salt potassium and cesium brines and three different blends of the two were exposed to barium sulfate for one, two, and three weeks at ambient temperature. All fluids were buffered with 5 lb/bbl potassium carbonate / bicarbonate buffer to give pH of about 10. The measured soluble barium and sulfate levels are shown in Figure 4. Slightly elevated soluble sulfate levels were found in pure buffered cesium formate brine (up to 1050 mg/L).

B12.2.4 Conclusions

Extensive testing has been performed to establish the concentrations of soluble barium and sulfate that can be present in single-salt potassium formate brines, single-salt cesium formate brines, and their blends after they have been in contact with analytical-grade barium sulfate powder under downhole temperature conditions. The following conclusions are made:

- 16-hour exposure tests on unbuffered single-salt potassium formate brine show that barium sulfate dissolution intensified with increased potassium formate concentration. The dissolution remained low at potassium formate concentrations up to about 50 wt%. The most concentrated unbuffered potassium formate brine (75 wt%) released about 3,500 mg/L of soluble barium from barium sulfate. This finding is somewhat academic as potassium formate brines are rarely used in the field without a carbonate pH buffer.
- 16-hour exposure tests on unbuffered single-salt cesium formate brine show just a very slight increase in barium and sulfate levels as a function of increased cesium formate concentration. The concentration of both ions remained below about 300 mg/L over the entire formate concentration range.
- Tests on buffered formate brines show that when excess buffer is present in the fluids, the concentration of soluble barium remains very low (about 10 mg/L). This is because any dissolved barium precipitates out as insoluble barium carbonate.
- Elevated levels of soluble sulfate can be generated in buffered single-salt cesium formate brines exposed to excess barium sulfate.
- Increased exposure temperature (150°C / 302°F) combined with increased exposure time (6.7 days)

only slightly increases the measured level of soluble barium in buffered potassium formate brine after exposure to excess barium sulfate. No effect of increased exposure temperature or time was found in the blended potassium / cesium formate brines.

- No effect was found on the measured concentrations of soluble barium and sulfate from increasing the exposure time from one week to three weeks at ambient temperature conditions.

B12.2.5 Relevance of experimental results for oilfield applications

The current testing has confirmed previous findings by Shell that relatively high levels of soluble barium can be extracted from barium sulfate powder in highly concentrated (> 50 wt%) unbuffered potassium formate brines. The actual soluble barium concentration measured (3,471 mg/L) in an unbuffered 75 wt% potassium formate brine after 16 hours at 100°C / 212°F was similar to that reported by Shell (3,400 mg/L) after 16 hours at 85°C / 185°F.

Testing on buffered brines, however, shows that addition of soluble potassium carbonate pH buffer prevents build-up of soluble barium by precipitating barium carbonate, which is barely soluble in concentrated formate brines. High levels of barium can therefore not exist in formate brines with a properly maintained buffer level. This is in full agreement with Cabot's observation that soluble barium levels in formate fluids returned from field use are invariably very low, even though these fluids may have been exposed to significant amounts of barite contamination in pits, pipes, and downhole. Unbuffered formate brines are rarely recommended for the oilfield, and should definitely not be used in cases where the fluid could be contaminated with barite or barium sulfate.

High levels of soluble sulfate were measured in buffered cesium formate brines (up to 1,330 mg/L). Such elevated sulfate levels have never been measured in any used brines returned to Cabot from the field, despite some fluids having been in contact with barite during use. The explanation for this is most likely that the high level of contamination with barium sulfate applied during testing does not occur in real well applications, but corresponds to cases where barium sulfate is used either as weighting material or where the fluid is used to drill through sections of gypsum.

One concern regarding dissolution of barium sulfate and precipitation of barium carbonate is that barium carbonate is not as harmless as barium sulfate, and might end up in oilfield waste. If drilling waste

containing precipitated barium carbonate is discharged to the ocean, the barium will immediately recombine with sulfate as barium sulfate is extremely insoluble in water. For comparison, typical concentrations of soluble barium in produced waters from HPHT gas reservoirs discharged to the North Sea are in the 1,000 to 3,000 mg/L range (Wat, 2008). In other parts of the world, concentrations of soluble barium as high as 13,000 mg/L have been reported (Silva, 2012). Similarly, if any waste containing precipitated barium carbonate and potassium sulfate is diluted with fresh water, it recombines to form water-insoluble barium sulfate.

Even though the carbonate buffer is capable of precipitating out large amounts of barium carbonate, which prevents build-up of toxic soluble barium in highly concentrated potassium formate brine, **it is not recommended to use barite as a weighting material in formate fluids containing potassium.** This is because both the barium carbonate and the potassium sulfate precipitation reactions continue as long as there is buffer in the brine. After the buffer is depleted, concentration of soluble barium increases. Barite weighting material can theoretically be added to buffered cesium formate brine as, after some barium carbonate precipitation, no further reactions take place. This fluid would have negligible amounts of soluble barium, but a relatively high level of soluble sulfate (about 1,500 mg/L), which may be undesirable.

All testing in this study was completed on analytical grade barium sulfate. Previous testing by Shell (Howard, 1995) shows that when exposing brine to barite rather than barium sulfate, lower levels of barium were released into solution. Therefore, in real field situations where formate brines are exposed to excess barite weighting material, soluble barium concentrations should be significantly lower than reported here.

The fact that formate brines, depending on brine type and carbonate pH-buffer addition, are capable of converting insoluble barium sulfate scale to acid-soluble barium carbonate ($BaCO_3$) and / or water-soluble potassium sulfate (K_2SO_4), means that they can have potential uses as sulfate-scale dissolvers or barite filter-cake removers. For increased efficiency, a chelating agent can be added. Previous unpublished research (J.D. Downs personal communication) has shown that addition of 0.5 molar diethylenetriamine penta-acetic acid (DTPA-K) raised the $BaSO_4$ solubility in unbuffered potassium 75 wt% formate from 7,500 mg/L to 122,000 mg/L. The new understanding of dissolution and precipitation mechanisms gained in this study can be helpful in the future when designing scale dissolvers and filter-cake breakers.

Table 1 Measured soluble barium and sulfate concentration in potassium formate brines at different concentrations after exposure to excess $BaSO_4$ powder at various temperatures for various amounts of time. The buffered brines contain about 5 lb/bbl of dissolved carbonate and bicarbonate.

Brine type	Buffer	Exposure temperature		Exposure time	Ba^{2+}	SO_4^{2-}
		°C	°F		[mg/L]	[mg/L]
KFo, 30 wt%, 1.19 g/cm ³	Unbuffered	100	212	16 hours	154	151
KFo, 40 wt%, 1.26 g/cm ³	Unbuffered	100	212	16 hours	204	195
KFo, 50 wt%, 1.34 g/cm ³	Unbuffered	100	212	16 hours	432	287
KFo, 55 wt%, 1.38 g/cm ³	Unbuffered	100	212	16 hours	567	266
KFo, 60 wt%, 1.43 g/cm ³	Unbuffered	100	212	16 hours	782	173
KFo, 65 wt%, 1.47 g/cm ³	Unbuffered	100	212	16 hours	988	100
KFo, 75 wt%, 1.57 g/cm ³	Unbuffered	100	212	16 hours	3,471	227
	Buffered	100	212	16 hours	64	67
	Buffered	150	302	16 hours	133	76
	Buffered	200	392	16 hours	231	61
	Buffered	100	212	6.7 days	81	80
	Buffered	150	302	6.7 days	328	111
	Buffered	Ambient	Ambient	1 week	65	81
	Buffered	Ambient	Ambient	2 weeks	93	52
	Buffered	Ambient	Ambient	3 weeks	107	36

Table 2 Measured soluble barium and sulfate concentration in cesium formate brines at different concentrations after exposure to excess $BaSO_4$ powder at various temperatures for various amounts of time. The buffered brines contain about 5 lb/bbl of dissolved carbonate and bicarbonate.

Brine type	Buffer	Exposure temperature		Exposure time	Ba^{2+}	SO_4^{2-}
		°C	°F		[mg/L]	[mg/L]
CsFo, 40 wt%, 2.20 g/cm ³	Unbuffered	100	212	16 hours	64	185
CsFo, 60 wt%, 1.71 g/cm ³	Unbuffered	100	212	16 hours	144	238
CsFo, 80 wt%, 2.20 g/cm ³	Unbuffered	100	212	16 hours	340	325
	Buffered	100	212	16 hours	6	24
	Buffered	150	302	16 hours	5	1,330
	Buffered	200	392	16 hours	No data	No data
	Buffered	100	212	6.7 days	1	1,041
	Buffered	150	302	6.7 days	12	1,205
	Buffered	Ambient	Ambient	1 week	0	651
	Buffered	Ambient	Ambient	2 weeks	0	1,048
	Buffered	Ambient	Ambient	3 weeks	1	1,042

Table 3 Measured soluble barium and sulfate concentration in various blends of cesium and potassium formate brines after exposure to excess $BaSO_4$ powder at various temperatures for various amounts of time. The buffered brines contain about 5 lb/bbl of dissolved carbonate and bicarbonate.

Brine type	Buffer	Exposure temperature		Exposure time	Ba^{2+}	SO_4^{2-}
		°C	°F		[mg/L]	[mg/L]
CsFo (25 vol%) / KFo (75 vol%)	Unbuffered	100	212	16 hours	1,181	137
	Buffered	100	212	16 hours	31	72
	Buffered	150	302	16 hours	64	90
	Buffered	200	392	16 hours	150	79
	Buffered	100	212	6.7 days	38	98
	Buffered	150	302	6.7 days	86	101
	Buffered	Ambient	Ambient	1 week	50	80
	Buffered	Ambient	Ambient	2 weeks	47	57
	Buffered	Ambient	Ambient	3 weeks	38	29
CsFo (50 vol%) / KFo (50 vol%)	Unbuffered	100	212	16 hours	451	171
	Buffered	100	212	16 hours	17	111
	Buffered	150	302	16 hours	35	130
	Buffered	200	392	16 hours	89	96
	Buffered	100	212	6.7 days	19	121
	Buffered	150	302	6.7 days	70	140
	Buffered	Ambient	Ambient	1 week	28	103
	Buffered	Ambient	Ambient	2 weeks	31	57
	Buffered	Ambient	Ambient	3 weeks	24	36
CsFo (75 vol%) / KFo (25 vol%)	Unbuffered	100	212	16 hours	102	-
	Buffered	100	212	16 hours	9	141
	Buffered	150	302	16 hours	29	190
	Buffered	200	392	16 hours	53	201
	Buffered	100	212	6.7 days	7	274
	Buffered	150	302	6.7 days	45	203
	Buffered	Ambient	Ambient	1 week	13	247
	Buffered	Ambient	Ambient	2 weeks	15	140
	Buffered	Ambient	Ambient	3 weeks	6	106

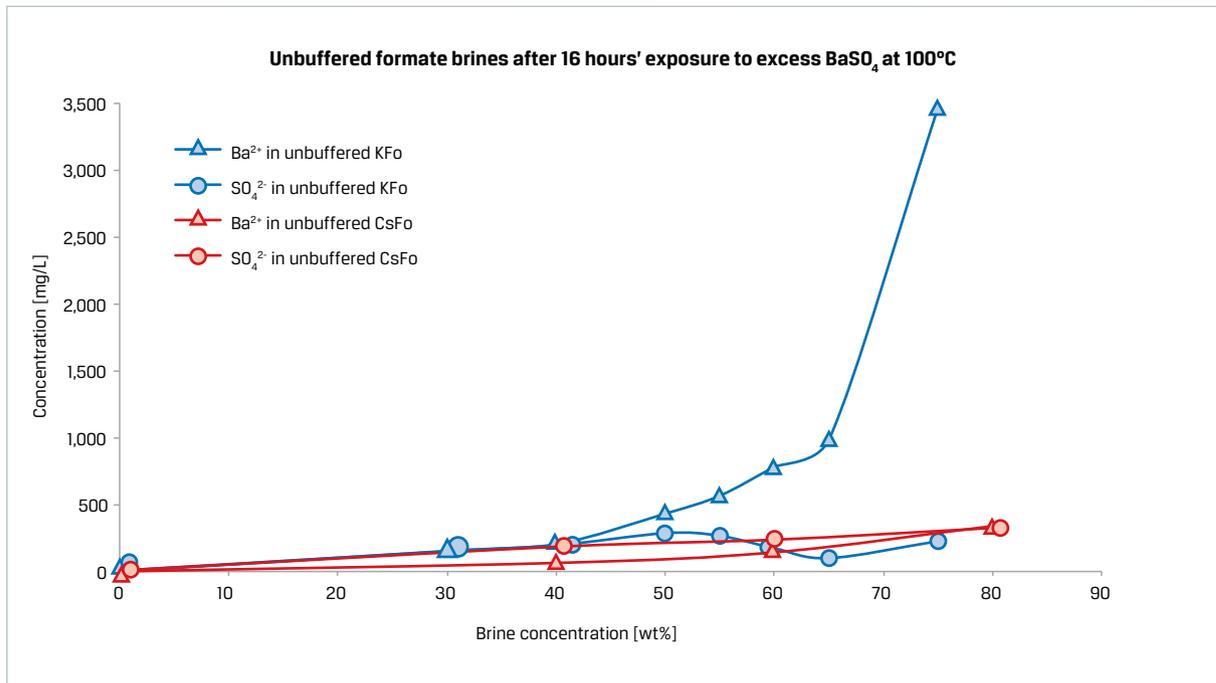


Figure 1 Measured soluble barium and sulfate concentration after exposure of unbuffered potassium and cesium formate brines to excess barium sulfate for 16 hours at 100°C / 212°F.

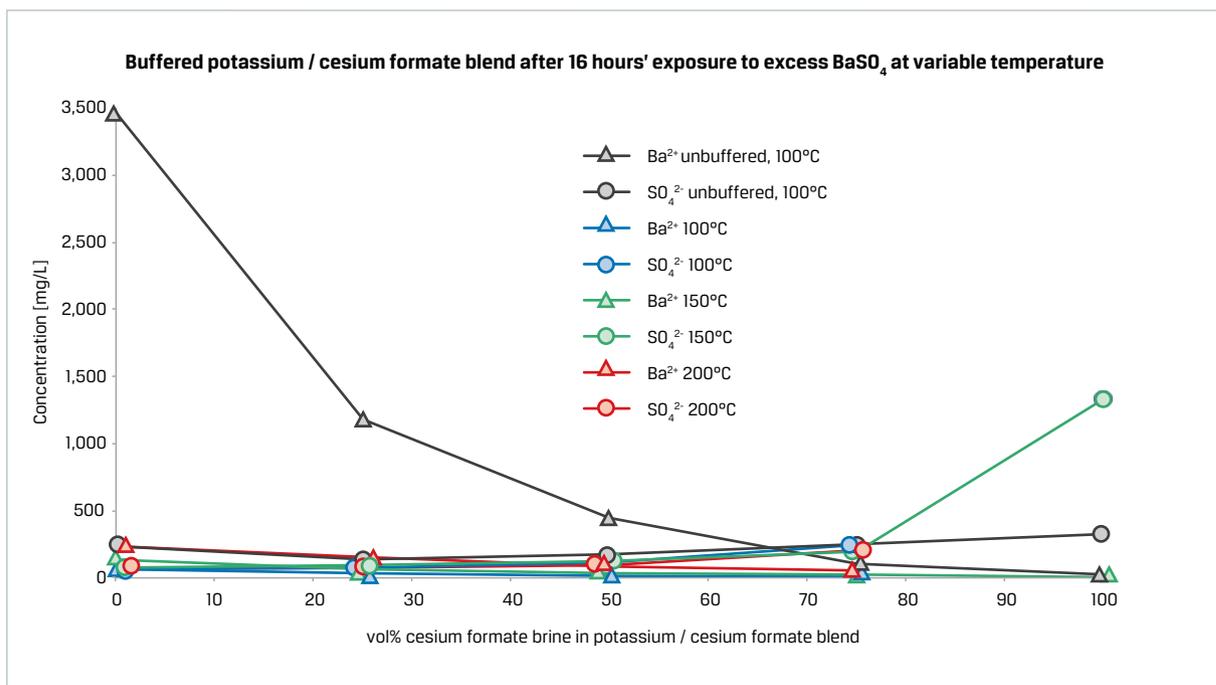


Figure 2 Measured soluble barium and sulfate concentrations after exposure of buffered and unbuffered blends of potassium and cesium formate brines to an excess amount of barium sulfate for 16 hours at variable temperature. The measured concentrations are plotted as a function of increased cesium-to-potassium volume ratio.

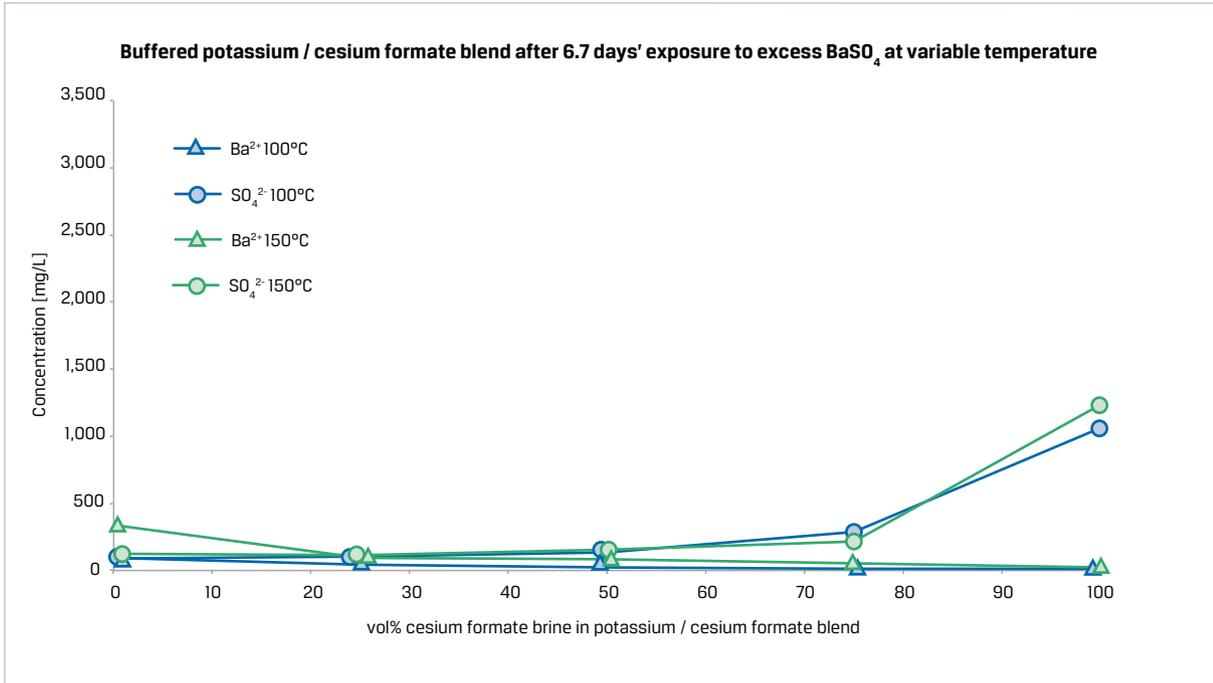


Figure 3 Measured soluble barium and sulfate concentrations after exposure of buffered blends of potassium and cesium formate brines to excess barium sulfate for 6.7 days at 100°C / 212°F and 150°C / 302°F.

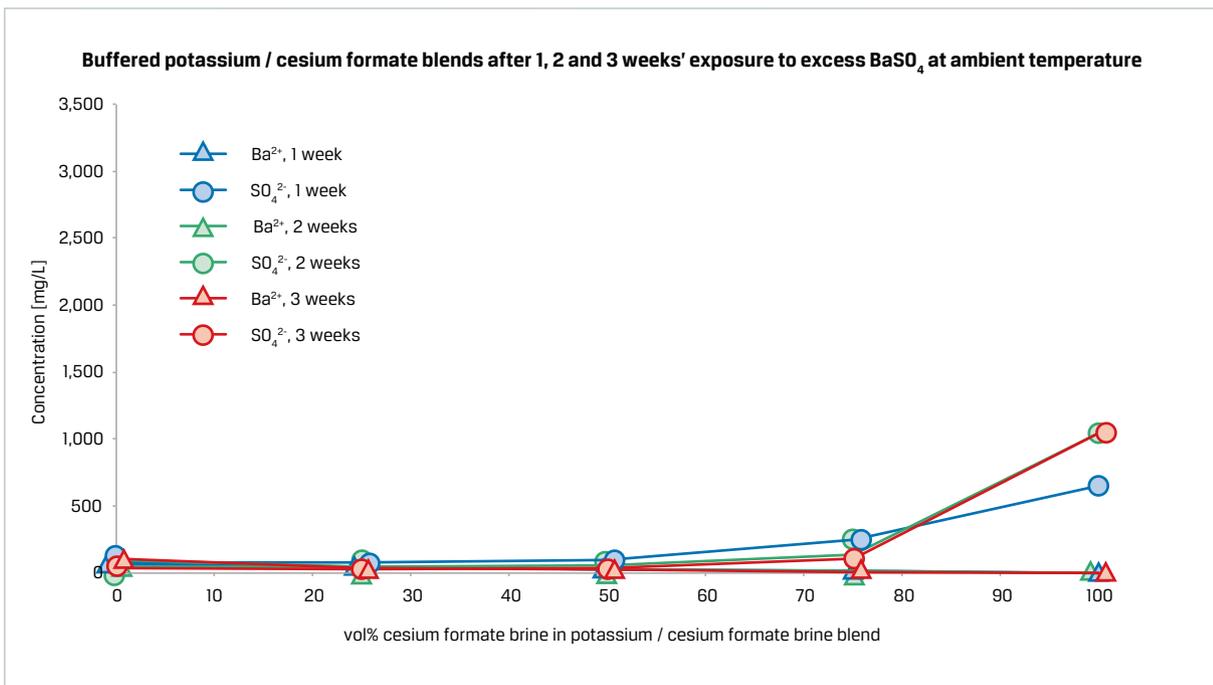


Figure 4 Measured barium and sulfate concentrations after exposure of buffered blends of potassium and cesium formate brines to excess barium sulfate for one, two, and three weeks at ambient temperature.

B12.3 Dissolution of shales in formate brines

Some dissolution data are available for certain common shales in concentrated sodium, potassium, and cesium formate brines (Howard et al., 1996). The shales tested were sodium montmorillonite $[(Na, Ca)_{0.33}(Al, Mg)_2Si_4O_{10}(OH)_2 \cdot n(H_2O)]$, Kaolinite $[Al_2Si_2O_5(OH)_4]$, and Manco shale.

The extent of solubilization was estimated by measuring levels of soluble Al and Si in the brine phase after 16-hour contact of the brine with shale at 85°C / 185°F. The results of the soluble Al and Si analyses shown in Table 4 indicate that few shales are dissolved or leached by formate brines.

B12.4 Dissolution of silicates in formate brines

Dissolution data for quartz and amorphous silicate (glass) in concentrated formate brines and water are shown in Table 5. Apart from slightly elevated levels of silicate dissolved from amorphous silica by cesium formate there is little practical difference between water and formate brines.

Table 4 Measured concentrations of Al³⁺ and Si⁴⁺ in concentrated sodium formate (46 wt% = 1.33 g/cm³ / 11.1 lb/gal), potassium formate (75 wt% = 1.57 g/cm³ / 13.1 lb/gal), and cesium formate (82 wt% = 2.26 g/cm³ / 18.9 lb/gal) brines after exposure to common shales for 16 hours at 85°C / 185°F.

Clay	Concentrations of Al ³⁺ and Si ⁴⁺ [mg/L]					
	Al ³⁺	Si ⁴⁺	Al ³⁺	Si ⁴⁺	Al ³⁺	Si ⁴⁺
Montmorillonite	45.0	45.0	4.0	77.0	4.0	8.5
Kaolinite	7.5	8.0	1.0	7.0	8.5	8.5
Manco shale	4.0	7.0	4.0	5.0	-	4.0

Table 5 Measured concentrations of Si⁴⁺ in concentrated sodium formate (46 wt% = 1.33 g/cm³ / 11.1 lb/gal), potassium formate (75 wt% = 1.57 g/cm³ / 13.1 lb/gal), and cesium formate (82 wt% = 2.26 g/cm³ / 18.9 lb/gal) brines after 16 hours' exposure to 85°C / 185°F.

Silicate	Concentration of Si ⁴⁺ [mg/L]				
	pH	Water	NaFo	KFo	CsFo
Quartz	8	21	10	14	18
	10	25	27	28	17
	12	82	170	58	17
Amorphous silicate (glass)	8	165	120	440	755
	10	200	120	440	755
	12	235	115	435	730

B12.5 Solubility of galena, hematite, and ilmenite in formate brines

Galena (PbS), ilmenite (TiO₂ FeO), and hematite (Fe₂O₃) are all insoluble in formate brines. Measurements show solubilities of less than <10 ppm, which is at the detection limit of the instrument (ICP).

B12.6 Solubility of calcium carbonate in formate brines

Calcium carbonate is the most commonly used bridging material in formate fluids. Its solubility in formate brines is dependent on pH. At the alkaline pH of commercial formate brines used in the field, solubility of calcium carbonate is negligible. This is particularly true of formate brines buffered with carbonate / bicarbonate.

References

- Howard, S.K. (1995). "Formate Brines for Drilling and Completion: State of the Art", SPE 30498.
- Howard, S.K., Houben, R.J.H., Oort, E. van, and Francis, P.A. (1996). "Report # SIEP 96-5091 Formate drilling and completion fluids - technical manual", Shell International Exploration and Production.
- Monin, C. (1999). "A Thermodynamic Model for the Solubility of Barite and Celestite in Electrolyte Solutions and Seawater to 200°C and to 1 kbar", Chemical Geology 153 (1999) 187-209.
- Neuman, E. W. (1933). "Solubility relations of barium sulfate in aqueous solutions of strong electrolytes", J. Am. Chem. Soc., 55 (1933) 879-884.
- Silva, J.M. (2012). "Produced Water Pretreatment for Water Recovery and Salt Production", RPSEA report 08122-36, 2012.
- Templeton, C. (1960). "Solubility of Barium Sulfate in Sodium Chloride Solutions from 25° to 95°C.", Journal of Chemical and Engineering Data, 5 (1960) 514-516.
- Wat, R, Wennberg, K., Holden, R., Hustad, B., Heath, S., Archibald, M., Singdahlsen, K. (2008). "The Challenges Associated With Performing and Combining Scale Dissolver and Squeeze Treatments in Kristin - A Subsea HP/HT Gas Condensate Field", SPE 114079, 2008.