COMPATIBILITIES AND INTERACTIONS

SECTION B4
COMPATIBILITY WITH OILFIELD FLUIDS

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B4.1 Introduction

Monovalent formate brines used as well construction fluids are very soluble in water and form brines of high density. These brines do not contain divalent ions, although some divalent carbonate ions are normally introduced as buffer.

The compatibility of formate brines with other oilfield fluids is important for knowing when a spacer fluid is needed, the design of spacer fluids, and how to handle formate brines contaminated with other fluids.

B4.2 Compatibility with other formate brines

All monovalent formate brines used in the oilfield are very soluble in water, and because lighter density brines are cheaper than higher density brines, formates are normally blended together. Normally, cesium formate is blended with potassium formate and potassium formate is blended with sodium formate. Sodium formate can also be blended with cesium formate, but as sodium formate is saturated at a much lower density than potassium formate, this blend requires more cesium formate than a cesium / potassium formate blend of the same density, and is therefore not as cost effective.

Any contamination of formate brine with another formate brine does not cause any compatibility problems, and no precipitation occurs. However, any contamination of higher-density formate brine with lower-density formate brine lowers brine density and more brine or powder of the heavier kind is needed to bring the density back up again.

Potassium formate brine (weighted with solids or unweighted) is commonly used as spacer fluid when higher-density formate fluid containing cesium is used.

B4.3 Compatibility with halide brines

Halide brines are regularly used as completion and packer fluids. Two types of halide brines are used in the oilfield: monovalent halide brines (sodium chloride, potassium chloride, and sodium bromide) and divalent halide brines (calcium chloride, calcium bromide, zinc bromide, and their blends). Although some combinations of formate and halide brines do not form precipitates when blended, care should be taken as large amounts of halide ions can promote localized corrosion, such as pitting and stress corrosion cracking. High levels of halide-ion contamination can also affect the fluid's TCT (true crystallization temperature) and thereby have an adverse effect on fluid density.

B4.3.1 Monovalent halide brines

All three monovalent halide brines are relatively compatible with formate brines. Combinations that could potentially precipitate are shown in Table 1 for ambient temperature and Table 2 for 70°C / 158°F (Cabot, 2008a). As can be seen, sodium formate is fully compatible with all monovalent halide brines, while cesium formate is compatible with *NaCl, KCl* and, at higher temperatures, *NaBr*. Potassium formate forms precipitates when in contact with all monovalent halide brines, except with very low contamination levels (<10%vol) at certain temperatures. These tests are completed with unbuffered formate brines with the exception of cesium formate, where a small amount of buffer is added. Contamination of buffered formate brines with monovalent halide brines does not have any adverse effect on the carbonate / bicarbonate buffer. Although precipitate can form at the interface between these two brines, for example during a well displacement operation, these solids are very water soluble and soluble in both the original formate and halide brines. Crystallization is therefore just a temporary interface phenomenon.

B4.3.2 Divalent halide brines

As divalent formate brines are less soluble than monovalent halide brines, divalent formate precipitates when formate brines come in contact with divalent halide brines or their blends. Precipitates are calcium formate and zinc formate. Other precipitates could be potassium or cesium bromide, but these are more soluble than the divalent formate salts. Table 1 and Table 2 give some indication of the degree of precipitation expected when unbuffered formate brines are contaminated by divalent halide brines at ambient temperature and 70°C / 158°F respectively (Cabot, 2008a). Although precipitate can form at the interface between these two brines, for example during well displacement, these solids are moderately water soluble and should, to some extent (depending on the amount of crystals and brine volume), dissolve in both the original formate and halide brines.

If formate brines with a carbonate / bicarbonate pH buffer are contaminated by divalent halide brine, it is important to notice that the buffer will always precipitate out as calcium or zinc carbonate. If a buffered formate brine undergoes such contamination, new carbonate / bicarbonate buffer needs to be added until all divalent ions precipitate out and the desired buffer concentration is re-established.

Table 1 Compatibility between concentrated formate brines and concentrated halide brines at ambient temperature (20 – 25°C / 68 – 77°F). The brines used for testing are: *NaFo* 1.30 g/cm³ / 10.85 lb/gal, *KFo* 1.56 g/cm³ / 13.02 lb/gal, *CsFo* 2.20 g/cm³ / 18.36 lb/gal, *KCl* 1.16 g/cm³ / 9.68 lb/gal, *NaCl* 1.20 g/cm³ / 10.01 lb/gal, *NaBr* 1.53 g/cm³ / 12.77 lb/gal, $CaCl_2$ 1.39 g/cm³ / 11.60 lb/gal, $CaBr_2$ 1.71 g/cm³ / 14.27 lb/gal, and $ZnBr_2$ 2.30 g/cm³ / 19.19 lb/gal. The table shows the amount of precipitate formed.

Brine blend Ambient temp.	Formate-to-halide blend ratio (vol/vol)				
	90:10	75:25	50:50	25:75	10:90
NaFo + NaCl	None	None	None	None	None
NaFo + KCl	None	None	None	None	None
NaFo + NaBr	None	None	None	None	None
NaFo + $CaCl_2$	Light	Medium	Heavy	Medium	Light
NaFo + $CaBr_2$	Light	Medium	Heavy	Medium	Light
NaFo + $ZnBr_2$	None	Light	Medium	Light	None
KFo + NaCl	Trace	Light	Medium	Light	Trace
KFo + KCl	Trace	Light	Medium	Light	Trace
KFo + NaBr	Trace	Medium	Heavy	Medium	None
KFo + $CaCl_2$	Light	Medium	Heavy	Medium	Light
KFo + $CaBr_2$	Medium	Heavy	Heavy	Heavy	Light
KFo + $ZnBr_2$	Medium	Heavy	Heavy	Heavy	Medium
CsFo + NaCl	None	None	None	None	None
CsFo + KCl	None	None	None	None	None
CsFo + NaBr	Trace	Medium	Medium	Light	None
CsFo + $CaCl_2$	Light	Medium	Medium	Medium	Trace
CsFo + $CaBr_2$	Medium	Heavy	Heavy	Heavy	Medium
CsFo + $ZnBr_2$	Medium	Heavy	Heavy	Heavy	Medium

Table 2 Compatibility between concentrated formate brines and concentrated halide brines at 70°C / 158°F. The brines used for testing are: *NaFo* 1.30 g/cm³ / 10.85 lb/gal, *KFo* 1.56 g/cm³ / 13.02 lb/gal, *CsFo* 2.20 g/cm³ / 18.36 lb/gal, *KCl* 1.16 g/cm³ / 9.68 lb/gal, *NaCl* 1.20 g/cm³ / 10.01 lb/gal, *NaBr* 1.53 g/cm³ / 12.77 lb/gal, $CaCl_2$ 1.39 g/cm³ / 11.60 lb/gal, $CaBr_2$ 1.71 g/cm³ / 14.27 lb/gal, and $ZnBr_2$ 2.30 g/cm³ / 19.19 lb/gal.

Brine blend 70°C / 158°F	Formate-to-halide blend ratio (vol/vol)				
	90:10	75:25	50:50	25:75	10:90
NaFo + NaCl	None	None	None	None	None
NaFo + KCl	None	None	None	None	None
NaFo + NaBr	None	None	None	None	None
NaFo + $CaCl_2$	Light	Medium	Heavy	Medium	Light
NaFo + $CaBr_2$	Light	Medium	Heavy	Medium	Light
NaFo + $ZnBr_2$	None	Light	Medium	None	None
KFo + NaCl	Trace	Light	Medium	Light	None
KFo + KCl	Trace	Light	Medium	Light	None
KFo + NaBr	Trace	Medium	Heavy	None	None
KFo + $CaCl_2$	Light	Medium	Heavy	Medium	Light
KFo + $CaBr_2$	Medium	Heavy	Heavy	Heavy	Light
KFo + $ZnBr_2$	Medium	Heavy	Heavy	Heavy	None
CsFo + NaCl	None	None	None	None	None
CsFo + KCl	None	None	None	None	None
CsFo + NaBr	None	Medium	None	None	None
CsFo + $CaCl_2$	Light	Medium	Medium	Medium	Trace
CsFo + $CaBr_2$	Medium	Heavy	Heavy	Heavy	Medium
CsFo + $ZnBr_2$	Medium	Heavy	Heavy	Heavy	Medium

B4.4 Compatibility with seawater

The three oilfield formate brines – sodium, potassium, and cesium – are all compatible with seawater at ambient and high temperatures (Cabot 2008b, 2009b). Consequently, no precipitate forms when these brines are contaminated by seawater in realistic quantities. At lower temperature (seabed temperature), a very small amount of potassium sulfate might form if concentrated potassium formate is contaminated with seawater at a certain ratio (about 10 – 25% (vol/vol) seawater). Table 3 shows results of compatibility testing seawater and concentrated potassium formate. As sodium and cesium sulfate are significantly more soluble than potassium sulfate, and sodium and cesium formate brines are less concentrated on a molar basis, no sulfate precipitation is expected in these two brines.

For field use, formate brines are normally buffered with sodium or potassium carbonate and bicarbonate. If buffered formate brine is contaminated with seawater, the buffer components immediately precipitate out with the divalent ions of seawater. Where a buffered formate brine has been contaminated with seawater, new carbonate / bicarbonate buffer should be added until all divalent ions precipitate out and the desired buffer concentration is re-established.

B4.5 Compatibility with base oil

Formate brines are not surface active and normally do not contain any surface-active additives. Therefore, when formate brine is in contact with oil, emulsification is unlikely to occur. Displacements between formate brines and base oils might therefore not require any spacer fluid.

B4.6 Compatibility with oil- and synthetic-based muds

Contact between formate brines and oil- or synthetic-based muds should be avoided as these muds contain emulsifiers. Consequently, emulsification can easily occur.

B4.7 Compatibility with water-based drilling fluids

Formate brines are believed to be compatible with most water-based drilling fluids. As any halide brine-based drilling fluid is normally based on monovalent halide brines, no precipitation problems are expected when these fluids contact each other. Divalent halide brines are very rarely used for drilling fluids, but if such a fluid comes in contact with formate brine, divalent formate salts can precipitate.

Traditional water-based drilling fluids are normally weighted with barite. As both potassium formate and carbonate pH buffer can react with barite (see Section B12), such contamination should be avoided if at all possible. Formate brines could also have an adverse effect on clouding glycols commonly used in some water-based shale drilling fluids. When such a clouding glycol is added to a formate brine its cloud point is lowered and it clouds out (phase separates) at a much lower temperature than when it would cloud out in water, or a less concentrated brine.

B4.8 Compatibility with methanol

Formate brines and methanol are fully miscible, and no precipitation occurs at any blending ratio (Cabot, 2009a).

B4.9 Compatibility with glycol

The compatibility between concentrated potassium and cesium formate brines and four commonly used glycols has been tested (Cabot, 2009a). The glycols tested were monoethylene glycol (*MEG*), diethylene glycol (*DEG*), triethylene glycol (*TEG*), and polyethylene glycol (*PEG*). The fluids were blended at different proportions and held for some hours at ambient temperature and 70°C / 158°F. No major reactions were experienced, but some slight hazing or minor crystallization was observed at and around 50 / 50 volume blend with some of the formate / glycol combinations. The results are summarized in Table 4. Further information regarding compatibility of formate brines with non-aqueous solvents, such as glycol, is found in Section B14 Solubility in Non-Aqueous Solvents.

References

Cabot (2008a). "Compatibility between formate and halide brines", Report no. LR-268, Cabot Operations & Technical Support Laboratory Aberdeen, September 2008.

Cabot (2008b). "Compatibility between formate brines and seawater", Report no. LR-261, Cabot Operations & Technical Support Laboratory Aberdeen, December 2008.

Cabot (2009a). "Formate Brine Compatibility with Glycols and Methanol", Report no. LR-281, Cabot Operations & Technical Support Laboratory Aberdeen, February 2009.

Cabot (2009b). "Seawater contamination", Report no. LR-305, Cabot Operations & Technical Support Laboratory Aberdeen, March 2009.

Table 3 Compatibility between a 75% potassium formate brine (1.57 g/cm³ / 13.10 lb/gal) and seawater at different temperatures. The potassium formate brine used for testing was free of buffer. The slight precipitate formed at 10 and 25% seawater is potassium sulfate.

Temperature	Potassium formate-to-seawater blend ratio (vol/vol)								
	99 : 1	98 : 2	95 : 5	97 : 3	90 : 10	75 : 25	50 : 50	25 : 75	10 : 90
5°C / 41°F	-	-	-	-	Slight prec.	Slight prec.	-	-	-
Ambient	-	-	-	-	-	-	-	-	-
70°C / 158°F	-	-	-	-	-	-	-	-	-

Table 4 Compatibility between concentrated potassium and cesium formate brines and four different glycols (*MEG*, *DEG*, *TEG*, and *PEG*) after one hour's exposure at ambient temperature and 70°C / 158°F. The brines used for testing are: potassium formate 1.56 g/cm³ / 13.02 lb/gal and cesium formate 2.20 g/cm³ / 18.36 lb/gal.

Brine	Temp.	Formate-to-glycol blend ratio (vol/vol)				
		90 : 10	75 : 25	50 : 50	25 : 75	10 : 90
KFo + MEG	Ambient	-	Slight haze	Haze	Slight haze	-
	70°C / 158°F	-	-	-	-	-
KFo + DEG	Ambient	-	-	-	-	-
	70°C / 158°F	-	-	Slight yellow	Slight yellow	Yellow
KFo + TEG	Ambient	-	-	Precipitation	-	-
	70°C / 158°F	-	-	-	-	-
KFo + PEG	Ambient	Haze	Haze	Haze	Slight haze	Slight haze
	70°C / 158°F	Precipitation	Precipitation	Haze	-	-
CsFo + MEG	Ambient	Stratification	Stratification	Stratification	Stratification	Stratification
	70°C / 158°F	-	-	Very slight haze	Very slight haze	-
CsFo + DEG	Ambient	Stratification	Stratification	Stratification	Stratification	Stratification
	70°C / 158°F	-	-	-	-	-
CsFo + TEG	Ambient	Stratification	Stratification	Very slight haze, stratification	Haze, stratification	Very slight haze, stratification
	70°C / 158°F	Yellow	Yellow	Haze, yellow	Haze, yellow	Yellow
CsFo + PEG	Ambient	-	-	Slight haze	Slight haze	-
	70°C / 158°F	-	-	Haze, yellow	Haze	-