



COMPATIBILITIES AND INTERACTIONS

SECTION B1

COMPATIBILITY WITH GASES

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B1.1 Introduction

Influx of gases is one of the main causes of corrosion failures in completion and packer fluids. The most destructive gases are carbon dioxide (CO_2) and hydrogen sulfide (H_2S), which can leak into the wellbore along with other reservoir gases, and oxygen (O_2) that enter the fluid during circulation at the surface or, in the case of packer fluids, during annular pressure bleed-off operations.

Oxygen and H_2S scavengers are commonly used in halide brines to try and eliminate the problems caused by these gases. Unfortunately, scavengers do deplete during use, and the addition of these scavengers is likely to contribute to deferral rather than removal of the problem.

B1.2 CO_2 compatibility

Carbon dioxide, CO_2 , is a stable oxide of carbon composed of two double-bonded oxygen atoms. Due to its weak bi-polar nature, CO_2 is highly soluble in water, with which it reacts to form carbonic acid.

The consequences of CO_2 leakage into a halide-based completion fluid can be catastrophic for the integrity of sub-surface equipment and tubulars. Both pitting and stress corrosion cracking (SCC) can occur in CRAs that have been exposed to CO_2 and halide brines.

Buffered formate brines are very different from halide brines in the way they respond to a CO_2 influx. The difference is largely due to the influence of the carbonate / bicarbonate pH buffer.

B1.2.1 Buffered formate brines protect against CO_2 acidification

Formate brines used in field applications are buffered by the addition of potassium or sodium carbonate and potassium or sodium bicarbonate. Typical recommended levels are 17 to 34 kg/m³ / 6 to 12 lb/bbl of carbonate or a blend of carbonate and bicarbonate (see Part A of the manual). The main purpose of this buffer is to provide an alkaline pH and to prevent the pH from fluctuating as a consequence of acid or base influxes into the brine.

A buffered solution is defined as a solution that resists a change in its pH when hydrogen ions (H^+) or hydroxide ions (OH^-) are added. The ability to resist changes in pH comes about by the buffer's ability to consume hydrogen ions (H^+) and / or hydroxide ions (OH^-).

The carbonate / bicarbonate buffer system provides strong buffering at two different pH levels:

- Higher buffer level at pH = 10.2



where $pK_{a_2} = 10.2$

At pH = 10.2 (pK_{a_2}) the buffered solution contains the same amount of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-).

- Lower buffer level at pH = 6.35

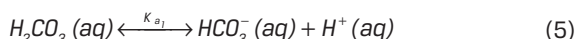
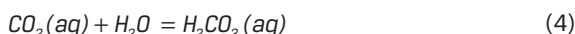


where $pK_{a_1} = 6.35$

At pH = 6.35 (pK_{a_1}) the buffered solution contains the same amount of bicarbonate (HCO_3^-) and carbonic acid (H_2CO_3).

The exact levels of pK_{a_1} and pK_{a_2} will vary somewhat with brine concentration, temperature, and pressure.

The acidification that takes place in completion brines when carbon dioxide gas (CO_2) enters into the wellbore can be described by the following equations:



Depending on pH in the brine system, dissolved CO_2 remains in the brine as either carbonic acid (H_2CO_3) or bicarbonate (HCO_3^-) according to equation 5. As more CO_2 gas enters into the brine, the equilibrium gradually moves to the left and a larger portion exists as carbonic acid. This makes the pH drop, and allows unbuffered brines to acidify.

Figure 1 demonstrates how three different brine systems react to a CO_2 influx:

- Conventional divalent halide brines** are incompatible with carbonate-based pH buffers due to the precipitation of divalent carbonate salts ($CaCO_3$, $ZnCO_3$) that inevitably occurs when these two classes of chemicals are mixed together. These divalent brines have a naturally low pH (2 – 6), and an influx of CO_2 may cause a further drop in pH. The CO_2 will largely be converted to carbonic acid, which is very corrosive.

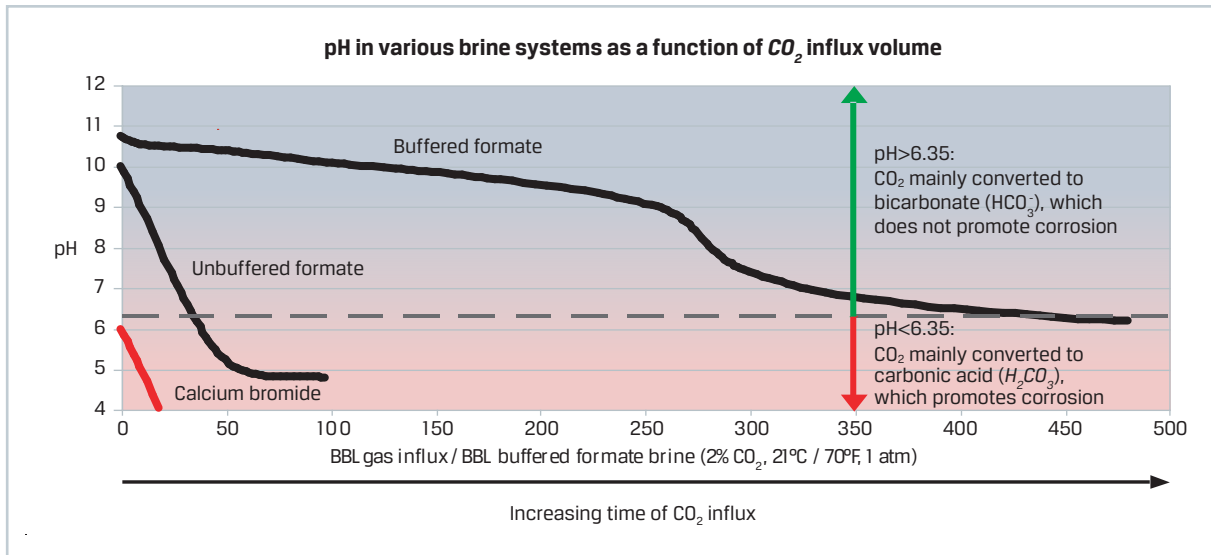


Figure 1 pH as a function of CO_2 influx in a typical halide brine, an unbuffered formate brine, and a buffered formate brine.

- **Buffered formate brines** are capable of absorbing large amounts of CO_2 . Unless the influx is unusually large, the brine maintains a pH (at around the upper buffer level), which is high enough to prevent carbonic acid being present in the fluid. With a large influx of CO_2 , pH drops down to the lower buffer level (pH = 6.35) where it stabilizes. Measurements of pH in formate brines exposed to various amounts of CO_2 have confirmed that pH never drops below 6 – 6.5. This pH is still close to neutral, meaning that this brine system can not be 'acidified' to any great extent by exposure to any amount of CO_2 .
- **Unbuffered formate brines:** The pH of these brine systems behave very much like halide brines when exposed to CO_2 gas. However, they do have a higher initial pH, and the pH drop is limited as formate brine is a buffer in itself (pKa = 3.75). The use of unbuffered formate brines is not recommended.

In order for the pH to drop below this second buffer level of 6.0 – 6.5, an acid needs to be added that is stronger than the acid formed, i.e. carbonic acid. As any CO_2 gas influx into the buffered solution dissolves and converts to carbonic acid, a CO_2 influx is therefore incapable of pulling the pH much below this second buffer level.

To summarize for buffered formate brines:

- For **small and medium size influxes of CO_2** , the buffer fully absorbs the gas influx, and pH remains high, i.e. above 8.
- Only for **very large influxes of CO_2** , does the pH drop to 6 – 6.5 and some carbonic acid exists in equilibrium with bicarbonate. The pH never drops below this level.

There are no scavengers for this gas that are compatible with conventional high-density halide brines, which puts formate brines in a unique position over traditional halide brines in any well application where CO_2 is a potential threat.

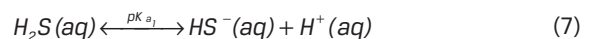
B1.3 H_2S compatibility

Hydrogen sulfide, chemically the sulfur analog of water, is deadly poisonous. Concentrations above 600 ppm can be fatal in three to five minutes. Hydrogen sulfide is also the most corrosive gas encountered in the oilfield. Concentrations of 50 ppm causes highly stressed, high-strength steel to fail in only minutes. Small concentrations of H_2S in drilling fluids can reduce drill pipe life by a factor of ten.

H_2S can enter the completion or packer fluid either from the reservoir (along with CO_2) or from decomposition of sulfur containing additives used as corrosion inhibitors in halide brines, for example thiocyanates. A number of recent failures of sub-surface well equipment in halide brines have been caused by H_2S formed from the thermal decomposition of sulfur-based corrosion inhibitors [1][2].

B1.3.1 How formates scavenge H_2S

H_2S is a very weak acid with pKa₁ of about 7. When introduced into an aqueous solution, the following equilibrium is created:



Therefore, in an alkaline aqueous solution, the dissolved H_2S gas will largely exist as bisulfide (HS^-).

Fortunately, formate brines used as completion fluids are heavily buffered with soluble carbonate. This buffer acts like an H_2S scavenger by converting any H_2S that is solubilized in the brine phase to HS^- . In buffered formate brines at pH 9.5 – 10.5, the majority of any H_2S gas influx is converted to bisulfide ions unless the influx brings with it a large volume of CO_2 that makes brine pH drop.

As an additional benefit, formate brines do not require corrosion inhibitors of any kind, which negates a potent man-made source of hydrogen sulfide.

B1.3.2 H_2S scavengers in formates

The carbonate / bicarbonate buffer that is added to formate brines when they are used as well construction fluids provides useful protection against H_2S corrosion. The alkaline pH helps to push the chemical equilibrium (Equation 7) towards the less harmful bisulfide (HS^-). Additionally, in the alkaline pH range, the large amount of alkali metal ions (Na^+ , K^+ , Cs^+) present in the formate brine helps to scavenge the bisulfide through the following reaction:



where $M = Na, K, \text{ or } Cs$.

The capacity of the carbonate / bicarbonate buffer is enormous (as demonstrated in Figure 1), and large amounts of acid gas can be converted to HCO_3^- and HS^- before the pH starts dropping. However, if the carbonate portion of the buffer is overwhelmed, its scavenging effect is lost and H_2S gas comes back out of solution. It is unlikely that the buffer will be overwhelmed during field use, but to reduce the risk associated with this, an H_2S scavenger could be added.

The inclusion of H_2S scavengers has additional benefits over the use of buffer alone as scavengers tie up sulfide long term rather than just changing the equilibrium. Furthermore, use of an additional H_2S scavenger also removes bisulfide from formate brine.

Adding an H_2S scavenger to buffered formate brine therefore provides double protection against this very harmful gas.

A zinc-free, iron-based H_2S scavenger, Ironite Sponge[®], has been tested in formate brines, and is shown to have some positive effects in scavenging H_2S . However, Ironite Sponge[®] is a solid, which limits its application in clear completion brines.

Another iron-based scavenger, compatible with high concentration formate brines, is iron gluconate [3], a $Fe(II)$ complex, which is water-soluble at high pH. In addition to being solids free, this scavenger has the added benefit of reacting very rapidly on a quantitative basis with sulfide. Three pounds per barrel of iron gluconate has been tested in buffered 2.2 g/cm³ / 18.3 lb/gal cesium formate brine (pH = 11). The added scavenger was shown to be compatible with the brine; it dissolved completely within five minutes without any change in pH.

A third iron-based scavenger that may be compatible with formate brines is iron oxalate. Compatibility testing still needs to be carried out with this scavenger.

Another group of zinc-free H_2S scavengers, which is expected to be compatible with formates are the electrophilic organic inhibitors that bind up sulfur in an organic form. These have the advantage that they do not form any solids when reacting with H_2S .

B1.4 O_2 compatibility

Dissolved oxygen from the atmosphere is present in all oilfield brines. Oxygen is a strong oxidizing agent, which means that it is reduced in redox reactions according to:



The strong oxidizing properties of oxygen makes this gas corrosive to materials and commonly used organic additives.

Concentrated formate brines have beneficial properties that protect against damage caused by oxygen:

1. Low solubility of oxygen in formate brines:

The solubility of oxygen in low-salinity aqueous solutions at surface temperature and pressure is about 9 ppm. Solubility decreases in high-salinity formate brines and at elevated temperatures [4], as shown in Figure 2.

2. Formate brines are antioxidants:

Formate is an anti-oxidant and free radical scavenger. As these are properties of the formate ion itself, which are present in massive quantities in high-density formate brines, they will never be depleted. The product of this oxygen scavenging is bicarbonate.

Halide brines have no anti-oxidant properties. Therefore if oxygen is not removed from halide-based drilling and completion fluids, the soluble oxygen can cause serious problems with metals, elastomers, plastics,

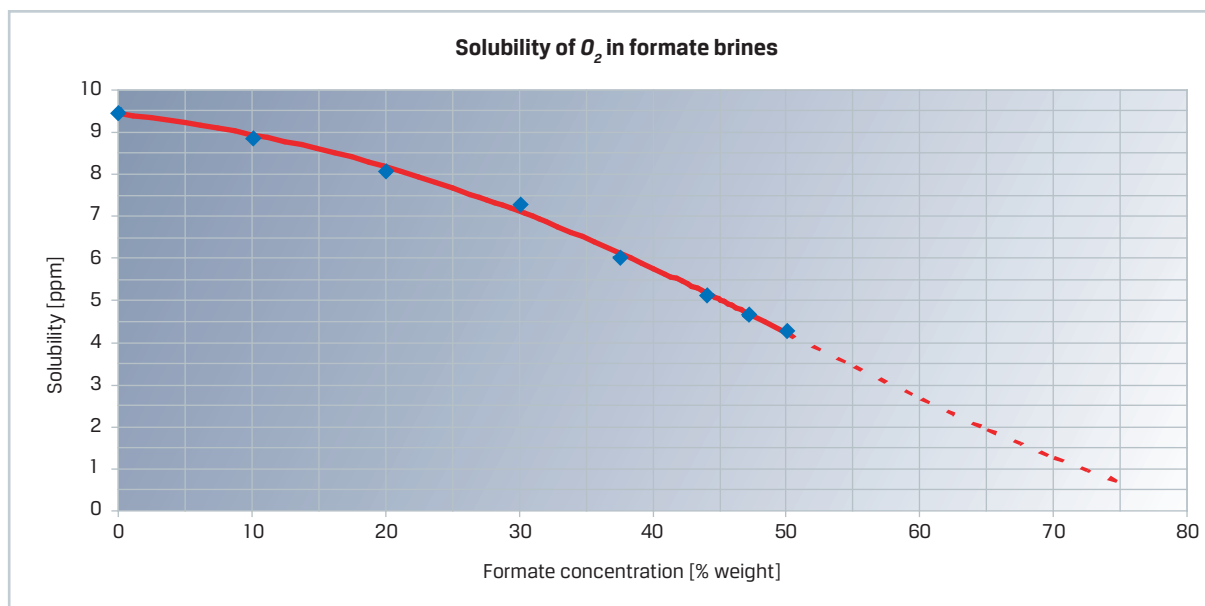


Figure 2 Solubility of oxygen in potassium formate at 21°C / 70°F.

and additives. For this reason, it is essential to add an oxygen scavenger to halide brines. These scavengers are generally quite effective until they become depleted (consumed) or degraded, at which point further contamination with oxygen could cause a problem. A recent well tubular failure [5] was caused by oxygen (air) ingress into a $CaCl_2$ packer fluid during an annular pressure bleed-off operation. In this instance, the oxygen scavenger present in the brine was apparently unable to cope with the new influx of oxygen.

B1.4.1 Use of O_2 scavengers in formate brines

Due to their strong antioxidizing properties, it has never been thought necessary to scavenge soluble oxygen from concentrated formate brines. Furthermore, it isn't normal practice to add oxygen scavengers to formate brines prior to field use.

There are, however, some indications that the addition of fast-reacting antioxidants and oxygen scavengers to high-concentration formate brines can contribute to further polymer stabilization at high temperatures [6].

Low-density formate brines, containing more water than formate, may not offer the same protection against oxygen as high-density brines, and will likely benefit from the addition of an oxygen scavenger.

Sodium ascorbate and sodium erythorbate have been proposed as effective oxygen scavengers in formate brines.

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