



CORROSION

Brine choice matters

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WHAT IS CORROSION?

The word 'corrosion' originates from the latin word 'corrōdere' which means "to gnaw away". A more scientific definition is "the destruction or deterioration of a material by reaction with its environment". The corrosion types encountered in the oilfield are general corrosion, localised corrosion and hydrogen embrittlement. Within the category of localised corrosion, pitting and stress corrosion cracking are becoming more common with the advent of HTHP drilling and completion.

General corrosion (rust): Occurs slowly. Metal loss is uniform over the exposed surfaces and is often linear with time. Relatively easy to keep under control with corrosion inhibitors, protective coatings and cathodic protection, but can have large economic impact over time.

Localised corrosion: Occurs quickly. Metal loss is concentrated in a small surface area. Creates high risk of unpredictable and rapid failure of metal integrity. Pitting corrosion and stress corrosion cracking (SCC) are most common and frequently occur in well tubulars constructed from so-called corrosion resistant alloys (CRAs). Corrosion inhibitors have little or no effect and can actually initiate corrosion.

Hydrogen embrittlement: A brittle mechanical fracture of high-strength steels caused when atomic hydrogen dissolves in the crystal structure of a metal rather than forming H₂ gas. Occurs in corrosive environments under constant tensile stress, similar to stress corrosion cracking (SCC). The most common form is sulphide stress cracking (SSC), which occurs when stressed metal is exposed to water containing hydrogen sulphide or other sulphur compounds, generally under aerobic conditions. Limited to very high-strength alloys and low temperatures.

High stakes, high risks



General corrosion is relatively easy to control. Localised corrosion is a whole different ball game

Drilling in High Temperature High Pressure environments has turned clear opportunities into real rewards. But when the stakes are high, so are the risks.

If traditional oilfield metals are used under HTHP conditions, corrosion runs rampant. Operators have shown their resourcefulness by using higher-grade metals, such as Corrosion Resistant Alloys (CRAs), and have increased use of brine-based drilling, workover and completion fluids. Paradoxically, increased use has led to a greater risk of potentially catastrophic types of corrosion. Of particular concern are two forms of localised corrosion, namely pitting and stress corrosion cracking (SCC).

New research shows that when CRAs are jointly exposed to a common gas, such as oxygen, carbon dioxide or hydrogen sulphide, and a halide brine, pitting and SCC corrosion are likely to occur. When this happens, costs can be astronomical. The bottom line is this:

CRA + O₂/CO₂/H₂S + halide brine = High risk of localised corrosion

More operators are recognising the 'hidden' costs of using halide brines and are turning to naturally passivating, anti-oxidising formate brines to prevent corrosion. This is paying dividends, as the following equation shows:

CRA + O₂/CO₂/H₂S + formate brine = Insignificant risk of localised corrosion

No CRA failures from formate brines

With over 100 HTHP applications and no CRA failures, formate brines from Cabot Specialty Fluids are ideally suited for challenging drilling, completion, workover and fracing applications. Formate brines have proven their worth in the world's most demanding well environments. At temperatures as high as 216°C (420°F) and pressures up to 1,172 bar (17,000 PSI), corrosive gases, such as carbon dioxide (CO₂), hydrogen sulphide (H₂S) and oxygen (O₂), are commonplace. It's no wonder that high-performance formate brines are replacing high-risk halides as operators' brines-of-choice for extreme wells.



Corrosion protection for over twelve years

No matter how high the temperature or pressure; no matter whether CO₂, O₂ or H₂S are present; no matter which CRA is used, there have been no recorded cases of material failure caused by formate brines in over twelve years' consistent use in drilling, completion or workover applications. The table below provides a selection of field cases where formate brines have proved their worth.

		BP Rhum 3/29a	Shell Shearwater	Marathon Braemar	BP Devenick	Total Elgin/Franklin	Statoil Huldra
No. of wells		3	6	1	1	10	6
Hydrocarbon		Gas condensate	Gas condensate	Gas condensate	Gas condensate	Gas condensate	Gas condensate
Max. temperature	°C	149	182	135	146	204	149
	°F	300	360	275	295	400	300
Completion material	CRA	S13Cr	25Cr	13Cr	13Cr	25Cr	S13Cr
Liner material	CRA	S13Cr	25Cr	22Cr	VM110	P110	S13Cr
Formate brine density	g/cm ³	2.00 – 2.20	2.05 – 2.20	1.80 – 1.85	1.60 – 1.65	2.10 – 2.20	1.85 – 1.95
CO ₂	%	5	3	6.5	3.5	4	4
H ₂ S	ppm	5 – 10	20	2.5	5	20 - 50	10 – 14
Exposure time	days	250	65	7	90	450	45
Application		Perforation Completion Workover	Well Kill CT Workover Perforation	Workover Perforation	Drill Completion	Workover Completion CT / Well Kill Perforation	Drilling Completion / Screens

		Statoil Kvitebjorn	Statoil Kristin	BP High Island A-5	Devon Energy West Cameron 165 A-7, A-8	Devon Energy West Cameron 575 A-3	Walter O&G Mobile Bay 862
No. of wells		7 to date	6 to date	1	1	1	1
Hydrocarbon		Gas condensate	Gas condensate	Gas	Gas condensate	Gas	Gas
Max. temperature	°C	150	171	163	149	163	216
	°F	302	340	325	300	325	420
Completion material	CRA	S13Cr	S13Cr	S13Cr	13Cr	13Cr	G-3
Liner material	CRA	13Cr	S13Cr	S13Cr	13Cr	13Cr	G-3
Formate brine density	g/cm ³	2.00 – 2.06	2.09 – 2.13	2.11	1.03	1.14	2.06
CO ₂	%	2 – 3	3.5	5	3	3	10
H ₂ S	ppm	Max. 10	12 – 17	12	5	5	100
Exposure time	days	57	57	4 (+ 3 yrs packer)	240 and 270	120	16 (+ 325 packer)
Application		Drilling Completion / Screens / Liners	Drilling Completion	Well Kill Completion Packer	Packer	Packer	Well Kill Completion Packer

Corrosion prevention

– why formate brines outperform halide brines

There are significant differences between formate and halide brines in their ability to prevent corrosion. Here's why:

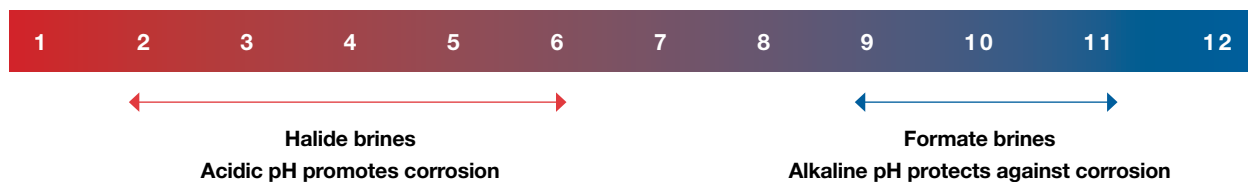
Anti-oxidising properties

Oxidants, such as O_2 , are known to cause corrosion. Formate brines are inherently anti-oxidising, which is demonstrated by their ability to stabilise biopolymers, such as xanthan, at higher temperatures than any other brine.

Naturally protective pH

Formate brines are naturally alkaline (pH 9-11). Most forms of corrosion are promoted at a low pH. For comparison, the pH of a high-density halide brine would normally range from two to six, depending on the type of halide.

pH scale



Compatibility with pH buffer

Influx of CO_2 can cause serious corrosion problems in all brine types. The only effective protection against CO_2 corrosion is the addition of a carbonate/bicarbonate buffer. In formate brines, this buffer not only prevents the pH from dropping, but it promotes the build-up of a passivating iron carbonate layer on the metal surface.

In contrast to formate brines, solutions based on divalent halide brines ($CaCl_2$, $CaBr_2$, $ZnBr_2$) are not compatible with even small amounts of carbonate/bicarbonate buffer. This is due to the precipitation of divalent carbonate salts ($CaCO_3$, $ZnCO_3$). This means that divalent halide brines cannot benefit from the corrosion protection provided by carbonate/bicarbonate buffers.

Scavenges H_2S

An additional benefit of formate brines is their ability to scavenge large amounts of H_2S gas, effectively preventing both stress corrosion cracking (SCC) and sulphide stress cracking (SSC). In an extreme laboratory test, buffered formate brine reduced H_2S levels by 78.4%, from 3,200 ppm to 690 ppm.

With the exception of zinc bromide, halide brines do not scavenge H_2S . This is a clear disadvantage, which makes halides very aggressive towards cracking.

WHAT IS A BUFFER?

A buffer is a solution in which the pH remains reasonably constant when acids or alkalis are added to it, i.e. it buffers against changes in pH. Carbonate/bicarbonate buffers are not compatible with divalent brines, such as calcium and zinc bromide, as they form insoluble calcium carbonate or zinc carbonate.

Corrosive gases and CRAs

– the gamble you take

If the odds for corrosive gases, such as O₂, CO₂ and H₂S, entering the fluid are negligible then the brine's ability to combat corrosion is less important. The problem is, however, that the risk is always there. The question is, how great?

With greater concentration on HTHP drilling, the potential for localised corrosion from corrosive gases is growing. The table below compares halide and formate brines and their propensity to cause corrosion with common gases.

Halide brines vs. formate brines: corrosion susceptibility with common gases

	Halide brines					Formate brines				
	C-steel	13Cr	S13Cr	22Cr	25Cr	C-steel	13Cr	S13Cr	22Cr	25Cr
No gas	● ¹⁾	● ¹⁾	●	●	●	●	●	●	●	●
O₂										
Immediate SCC	–	●	●	●	●	–	●	●	●	●
Long term SCC	–	●	●	●	●	–	● ²⁾	● ²⁾	●	●
Small/medium CO₂, with or without H₂S										
Pitting	●	●	●	●	●	●	●	●	●	●
Immediate SCC	–	●	●	●	●	–	●	●	●	●
Long term SCC	–	●	●	●	●	–	●	●	●	●
General corrosion	●	●	●	●	●	●	●	●	●	●
High CO₂, with or without H₂S										
Pitting	●	●	●	●	●	●	●	●	●	●
Immediate SCC	–	●	●	●	●	–	●	●	●	●
Long term SCC	–	●	●	●	●	–	●	●	●	●
General corrosion	●	●	●	●	●	●	●	●	●	●
S containing additive	–	●	●	●	●	NA	NA	NA	NA	NA

- High susceptibility
- Low susceptibility
- Negligible susceptibility

¹⁾ Dependent on type of halide and use of corrosion inhibitor.

²⁾ Dependent on chloride contamination.

N.B.: Corrosion rates increase with temperature.

HOW ARE CRAS CHOSEN?

Historically, the well engineer selects the tubular metallurgy based on produced fluids and the production conditions in the wellbore. Emphasis is always placed on the potential for H₂S in the production stream. The increased use of CRAs in recent years has raised the costs of tubulars considerably, making it ever more important to maximise life expectancy.

Common CRAs and their properties

Material	Specifi- cation	Cr %	Ni %	Mo %	Strength KPSI	Max. temp. °C	Max. temp. °F
13Cr	L80	13.0	0.4	0.09	80	149	300
S13Cr	LC80-130M	12.92	5.26	0.77	80	177	350
22Cr	EN 1.4462	22	5	3.2	128	232	450
25Cr	EN 1.4410	25.39	6.45	3.92	135	232	450

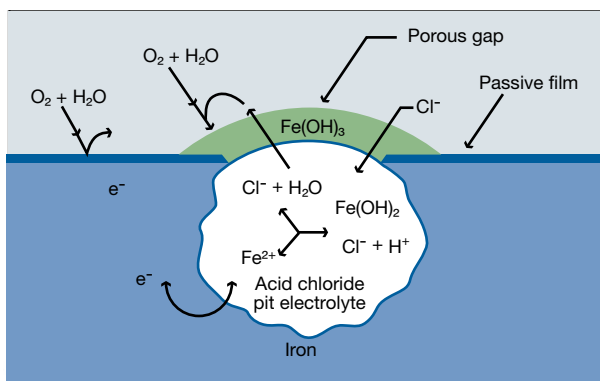
Localised corrosion

– a fight against time

Two of the most common and dangerous forms of localised corrosion seen in the oilfield are pitting and stress corrosion cracking (SCC).

Pitting corrosion – a hole lot of trouble

Pitting corrosion can result in perforation of pipes or equipment and subsequent system failure. It develops from defects in the metal oxide layer (passive film), which provides CRAs with improved corrosion protection. The local corrosion cell created by pitting corrosion propagates into the underlying material and forms narrow but deep pits as illustrated below. Acidification of the aqueous solution trapped in the corroding pit causes self-acceleration of the metal dissolution, resulting in relatively fast corrosion rates and possible perforation of the affected pipe or equipment. In addition to the presence of an oxidising agent, such as oxygen, carbon dioxide or hydrogen sulphide, halide ions, like chlorides or bromides, are usually required for pitting corrosion to develop.



The pitting corrosion mechanism

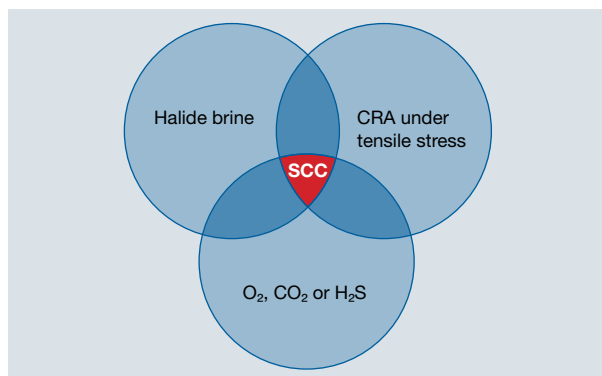


Pitting corrosion attack

SCC - here today, gone tomorrow

The most frightening aspect of stress corrosion cracking (SCC) is the speed of its development. From a small crack to full material failure can happen in a matter of hours. The results can be catastrophic.

SCC develops from local defects in the surface oxide film in areas where pitting corrosion has penetrated the metal surface. The conditions necessary to create SCC are shown in the diagram below.



The combination of three factors cause SCC



Chloride SCC in CRA

The metal dissolution (anode reaction) takes place in the crack tip. This causes the crack to propagate perpendicularly to the tensile stresses in an attempt to relax, or fade out, the stresses. The internal stresses arise from the original steel manufacturing and welding processes or from external loads.

Oxygen

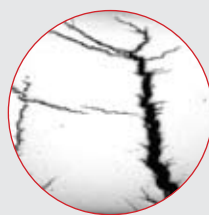
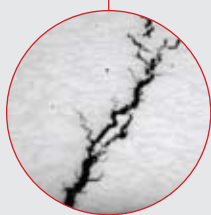
– can you breathe easy?

Dissolved oxygen from the atmosphere is present in all oilfield brines. As halide brines do not enjoy natural protection against this corrosive gas, CRAs weaken and fail through SCC. To prevent this from happening, an oxygen scavenger is normally added. However, this ‘remedy’ is far from dependable and cases where an oxygen scavenger fails or is overwhelmed are relatively frequent. In fact, concentrations of less than 1.0 ppm are all that’s needed to initiate SCC.

In comparison, formate brines contain natural anti-oxidants and prevent SCC without additives of any kind.

Halide brines vs. formate brines: Testing for SCC with oxygen

Calcium bromide				
CRA type	Without added chloride		With 1% added chloride	
	No. of coupons cracked	Time period	No. of coupons cracked	Time period
Super 13Cr	3 out of 3	1 month	3 out of 3	1 month
22Cr	3 out of 3	2 months	3 out of 3	2 months
25Cr	2 out of 3	3 months	2 out of 3	3 months



Latest research uncovers new concerns

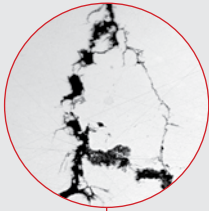
It has long been accepted that chloride brines contaminated with oxygen cause serious SCC problems. However, a research study completed by the Hydro Research Centre Porsgrunn, Norway shows that bromide brines also instigate SCC. In fact, results prove that SCC is already initiated on lower-grade alloyed steel after one month's exposure to bromide brine with minimal or higher levels of chloride contamination (see results on opposite page). It is worth noting that bromide brines, due to their manufacture, always contain chlorides to a lesser or greater degree.

Formate brines, even with a large contamination of chloride, did not cause any SCC during the first month of exposure and limited SCC over the next two months (see results below).

Potassium/cesium formate				
CRA type	Without added chloride		With 1% added chloride	
	No. of coupons cracked	Time period	No. of coupons cracked	Time period
Super 13Cr	0 out of 3 ●	3 months	2 out of 3 with crack initiation ●	3 months
22Cr	0 out of 3 ●	3 months	0 out of 3 ●	3 months
25Cr	0 out of 3 ●	3 months	0 out of 3 ●	3 months



SCC testing on a 1.7 s.g. (14.2 ppg) potassium/cesium formate fluid and a 1.7 s.g. (14.2 ppg) calcium bromide fluid, with O₂ headspace. Temperature of 160°C (320°F). P_{N₂} of 10 bar (145 PSI). P_{O₂} of 0.2 bar (2.9 PSI).

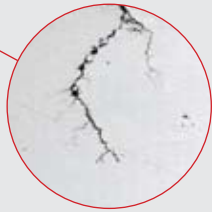


Cracked after seven days

The Hydro study was taken one step further by CAPCIS Ltd. in the UK during a 14-day test of calcium bromide without added chloride. The study establishes that SCC occurs after only seven days in both S13Cr and 22Cr steel. In fact, all three of the S13Cr samples broke in two after 14 days. Based on these results, it is extremely inadvisable to use calcium bromide brine in short-term applications where S13Cr and 22Cr steels are selected.

Short-term SCC test with O ₂ and calcium bromide				
CRA type	No. of coupons cracked	Time period	No. of coupons cracked	Time period
Super 13Cr	1 out of 3	7 days	3 out of 3	14 days
22Cr	3 out of 3 with crack initiation ¹⁾	7 days	3 out of 3	14 days
25Cr	0 out of 3	7 days	0 out of 3	14 days

1) After seven days several suspect areas were found on these samples. These worsened after 14 days. Sectioning showed that cracks were present.



SCC testing on a 1.7 s.g. (14.2 ppg) calcium bromide fluid, with O₂ headspace. Temperature of 160°C (320°F). P_{N₂} of 10 bar (145 PSI), P_{O₂} of 0.2 bar (2.9 PSI).



Nine days

After only nine days, stress corrosion cracking on S13Cr martensitic stainless steel stopped production on Petronas' HTHP Resak A-6 well in Malaysia. Cracks were found on components such as tubing, blast joints, sliding sleeves and the packer mandrel. Analysis suggested that cracking was caused by a combination of the CaCl₂ completion fluid that contained oxygen and CO₂ and H₂S in the well fluid. Laboratory tests in the CaCl₂ brine environment with the same field conditions showed that SCC could be prevented by the use of oxygen scavenger in the brine alone. However, when H₂S and CO₂ were combined with CaCl₂ brine the environment became extremely corrosive and chemical additives could not prevent cracking.

Temperatures varied between 140°C (284°F) and 156°C (313°F), with CO₂ partial pressure of 4.4 to 9.6 MPa (638 to 1,392 PSI) and H₂S partial pressure of 0.0004 to 0.0014 MPa (0.06 to 0.2 PSI).

Ibrahim, et. al.: NACE paper no. 03097

To sum up

The dangerous relationship between oxygen and halide brines is summarised by the following equation. The table then compares halide and formate brines' ability to cause or prevent pitting and SCC.

CRA under tensile stress + O₂ + halide brine = Pitting and SCC

Halide brines

- Halide brines have no anti-oxidising properties.
- Chloride brines contaminated with oxygen have long been known to cause serious pitting corrosion and SCC.
- Bromide brines are now proven to promote SCC, even in the absence of chloride contamination. S13Cr fails in a week and 22Cr shows significant pitting in the same period.

Formate brines

- Formate fluids are strong anti-oxidants.
- Even when formate brines are significantly contaminated with both oxygen and halide ions, no SCC has ever been detected in 22Cr and 25Cr. With such significant contamination, SCC initiation has occurred in S13Cr, although the process is much slower and less aggressive than SCC in halides.

Staying the distance

If it were the Olympics then this would be the marathon and it would be run over some of the toughest country imaginable. In other words, with downhole temperatures in excess of 204°C (400°F) and pressures of 1,105 bar (16,000 PSI), conditions in Total's Elgin wells G1 and G3 couldn't get more extreme.

When Total made the decision to suspend and abandon both wells, it needed to recover its 25Cr Duplex tubing. The tubing had been exposed to cesium formate in both wells, including a 15-month (450-day) period in G3. As recommended by Cabot Specialty Fluids, no corrosion inhibitor or oxygen scavenger were used. Mechanical tests confirmed compliance with the original properties of the tubing material. No localised corrosion was found and it was certified fit for further use in HPHT well conditions.

Furthermore, due to casing cement issues in G3, the well was killed with a combination of SBM and cesium formate. The mechanical tests on the removed tubing compared hydrogen charging on both sections and concluded that, while the 25Cr Duplex tubing was unchanged in the section exposed to cesium formate, the tubing exposed to the SBM showed surprisingly higher levels of hydrogen charging. This proves that formate brines are stable under extreme HTHP conditions and CRAs, immersed in these brines, do not suffer from hydrogen embrittlement.

Carbon dioxide

– eating away your profits

Carbon dioxide is present in most reservoirs and can enter a completion, workover, drilling or suspension fluid over time.

CO₂ corrosion occurs when CO₂ gas combines with water to form carbonic acid (H₂CO₃). Carbonic acid is very corrosive to C-steel and 13Cr steel. The only efficient protection against CO₂ corrosion is a carbonate/bicarbonate pH buffer. While formate brines are highly compatible with buffers, halide brines are incompatible with carbonate/bicarbonate buffers as they form insoluble calcium carbonate or zinc carbonate precipitates.

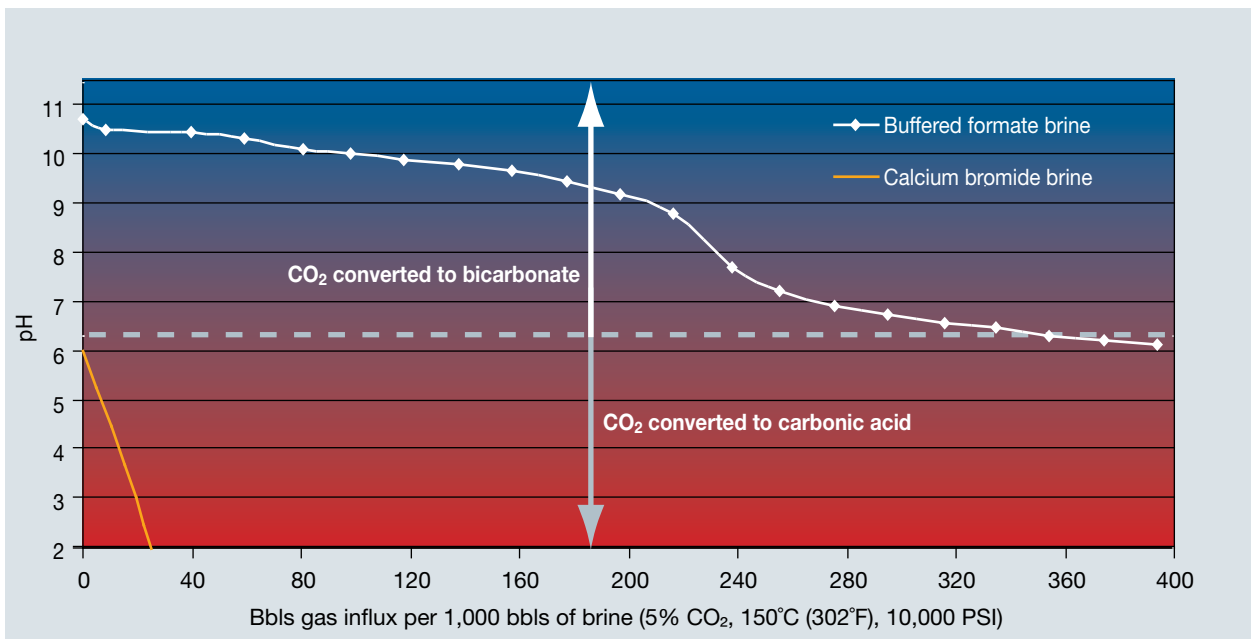
Consequently, when analysing CO₂ corrosion in completion and packer fluids, it is crucial to understand how buffered (formate) and unbuffered (halide) brines compare under all scenarios of CO₂ influx.

When acid gas (CO₂) enters an aqueous completion/packer fluid, the following reactions take place:

1. **CO₂(g) = CO₂(aq)**
2. **CO₂(aq) + H₂O = H₂CO₃(aq)**
3. **H₂CO₃(aq) $\overset{K_a}{\rightleftharpoons}$ HCO₃⁻(aq) + H⁺(aq)**

The value for pK_{a1} in equation three is 6.35. This means that at pH 6.35 equal amounts of bicarbonate (HCO₃²⁻) and carbonic acid (H₂CO₃) exist in solution. In fluids with pH above this level, the dissolved CO₂ is largely converted to non-corrosive bicarbonate, while in fluids with pH below this level, it is largely converted to very corrosive carbonic acid.

Effect of CO₂ gas influx on brine pH



Halide brines vs. formate brines with CO₂ influx

Halide brines

No CO₂ influx

Depending on the brine type or blend, the pH ranges from 1 to 6. Consequently, fluid corrosivity depends on certain factors, e.g. halide type, use of corrosion inhibitors, oxygen scavengers and the initial pH of the brine. Pitting corrosion is frequently seen, particularly in the very acidic zinc bromide brine. At temperatures of 107°C (225°F) and upwards, thiocyanate corrosion inhibitors and other sulphur-containing additives are prone to thermal decomposition and subsequent pitting. In turn, depending on the temperature and material type, SCC or SSC are likely to occur.

Small/medium CO₂ influx

As soon as CO₂ enters the unbuffered halide brine, carbonic acid is created. For each dissolved mole of CO₂, one mole of carbonic acid forms. As carbonic acid is very corrosive, CO₂ corrosion commences immediately. Due to the lack of carbonate/bicarbonate ions in the halide brine, all carbonate required for the formation of the layer comes from the CO₂ gas, slowing the formation process considerably. Consequently, the 'protective' layer that forms is of low quality and pitting corrosion is found in halide brines under these conditions. Small/medium CO₂ influx has the same effect as large CO₂ influx.

Large CO₂ influx

As soon as CO₂ enters the unbuffered halide brine, carbonic acid is created. For each dissolved mole of CO₂, one mole of carbonic acid forms. As carbonic acid is very corrosive, CO₂ corrosion commences immediately and an iron carbonate layer begins to form. Due to the lack of a carbonate/bicarbonate buffer, all carbonate required for the formation of the layer comes from the CO₂ gas, slowing the formation process considerably. Consequently, the 'protective' layer that forms is of low quality and pitting corrosion is found in halide brines under these conditions. Large CO₂ influx has the same effect as small/medium CO₂ influx.

Formate brines

No CO₂ influx

Formate brines remain at the initial pH of 9 to 10 and exhibit lower general corrosion rates than halides. This is due to their favourable pH and anti-oxidising properties. No pitting corrosion has ever been reported in formate brines. The absence of additives, including corrosion inhibitors containing sulphur, eliminates the risk of corrosion caused by thermal decomposition of these materials.

Small/medium CO₂ influx

When carbonic acid forms in formate brines it is absorbed by the buffer and converted to bicarbonate. The amount of carbonic acid that exists in equilibrium with the bicarbonate is insignificant in this high pH range and CO₂ corrosion does not occur. Consequently, corrosion rates remain at an extremely low level.

Large CO₂ influx

If extremely high amounts of CO₂ enter the buffered formate brine, the buffer is eventually overwhelmed, i.e. all carbonate present in the buffer converts to bicarbonate. pH then drops and causes CO₂ corrosion to commence immediately. Although general CO₂ corrosion rates in formate brines can be just as high as in halide brines, pitting and localised corrosion do not occur due to the rapid formation of a high-quality passivating iron carbonate layer. This layer forms quickly as it takes bicarbonate ions from the buffer and provides excellent protection against localised and generalised corrosion.

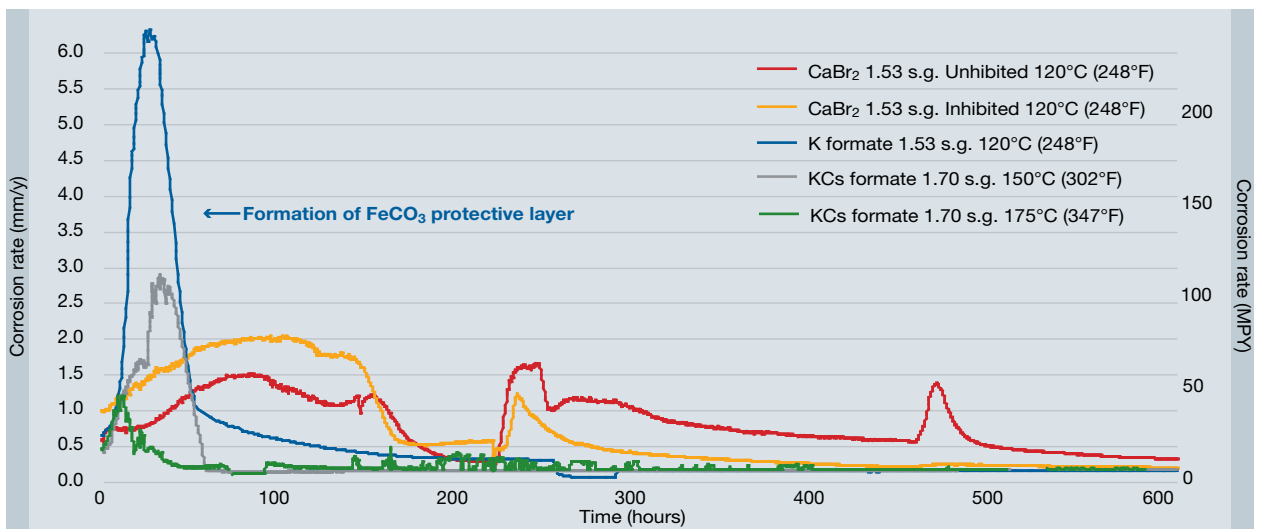
Halides and formates

– the facts speak for themselves

Hydro Research Centre Porsgrunn has completed extensive research into CO₂ corrosion and brines. The key finding of these studies show that buffered formates are superior to halides in building up a protective iron carbonate layer that protects the metals against pitting and general corrosion.

The graph depicts measured CO₂ corrosion rates in various formate and halide fluids as a function of time. The unrealistically high CO₂ level used in the experiment is high enough to overwhelm immediately the pH buffer in the formate brine. As can be seen, the initial corrosion rates during formation of the passivating layer are higher but of much shorter duration in the formate brines than in the bromide brines. This gives a denser, higher-quality passivating layer. The common corrosion inhibitor in the bromide brine used for this test has no effect.

Initial CO₂ corrosion in formates and bromides



Halide brines



C-steel corrosion coupon (1.5 mm thick) exposed to a calcium bromide fluid in the presence of CO₂. The temperature was ramped from 120°C (248°F) up to 180°C (356°F) and down again during the 50-day long exposure. The C-steel coupon experienced severe pitting corrosion and perforated in the calcium bromide brine. A separate test in a calcium bromide fluid with a commonly used corrosion inhibitor gave the same poor performance.

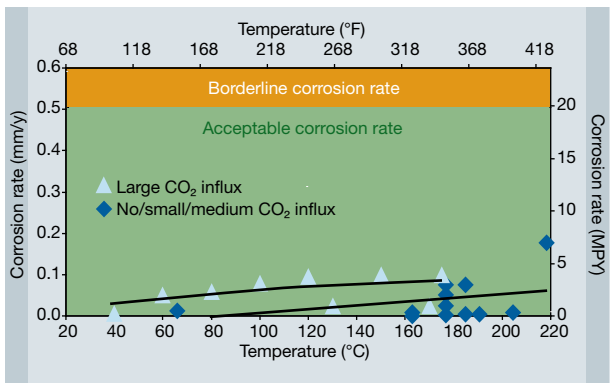
Formate brines



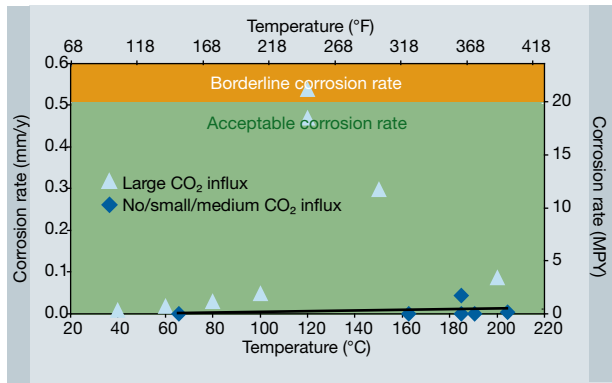
C-steel corrosion coupon (1.5 mm thick) exposed to a potassium formate brine. The CO₂ level used was high enough to immediately overwhelm the pH buffer in the formate brine. Temperature was ramped from 120°C (248°F) up to 180°C (356°F) and down again during the 62-day long exposure. Only limited general corrosion could be seen in the formate fluid.

Graphs show corrosion rates in formate fluids as taken from literature. The rates include a combination of CO₂ influx only and CO₂/H₂S influx. Corrosion rates measured by weight loss of less than 30 days are not included for C-Steel and 13Cr steel. Halide corrosion rates are not plotted as the presence of pitting corrosion makes general corrosion rates meaningless. General corrosion rates in halides, where pitting is not taken into account, are generally higher than in formates. In fact, just low levels of CO₂ influx in halide fluids have comparable corrosion levels to high levels of CO₂ influx in formates. Similar corrosion rates can only be seen in formates and halides with a very large CO₂ influx.

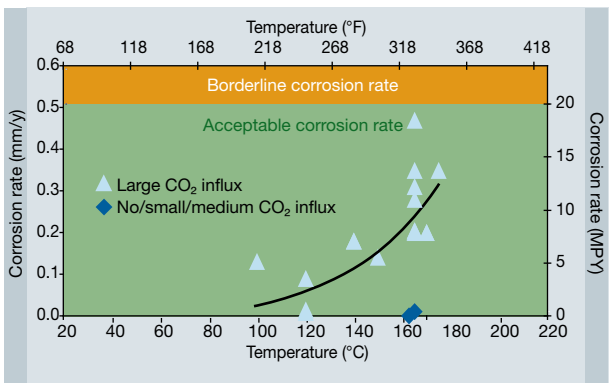
CO₂ corrosion rate of C-steel in formate brines



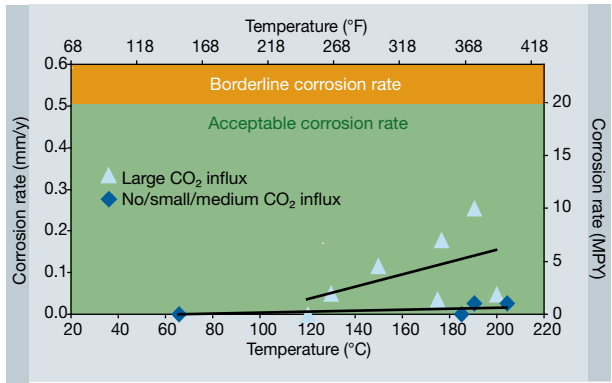
CO₂ corrosion rate of 13Cr in formate brines



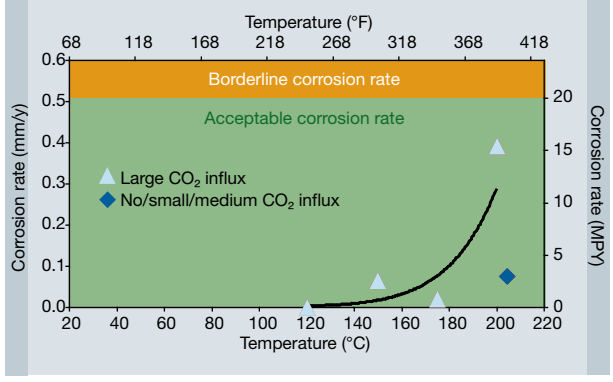
CO₂ corrosion rates of S13Cr in formate brines

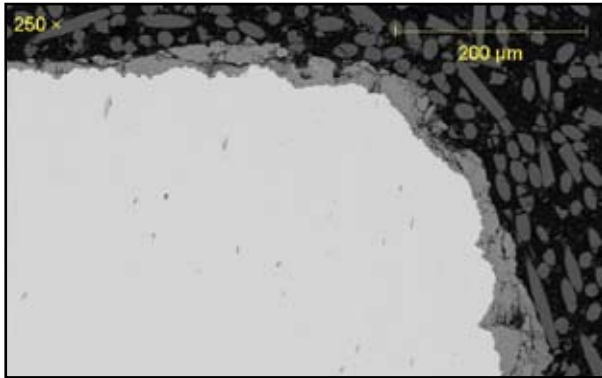


CO₂ corrosion rates of 22Cr in formate brines



CO₂ corrosion rates of 25Cr in formate brines





SEM photo of the protective iron carbonate layer as formed on C-Steel in cesium formate. The CO₂ level used was high enough to immediately overwhelm the pH buffer in the formate brine. A very dense surface film with thicknesses varying from 5 to 20 μm formed in the cesium formate brine.

Halide and formate brines’ performance under CO₂ influx

Halide brines		Formate brines	
No CO ₂ influx	Possible pitting/localised corrosion depending on pH, i.e. brine type	No CO ₂ influx	Insignificant general corrosion
Small CO ₂ influx	CO ₂ corrosion Pitting/localised corrosion	Small CO ₂ influx	No CO ₂ corrosion Insignificant general corrosion
Medium CO ₂ influx	CO ₂ corrosion Pitting/localised corrosion	Medium CO ₂ influx	No CO ₂ corrosion Insignificant general corrosion
Large CO ₂ influx	CO ₂ corrosion Pitting/localised corrosion	Large CO ₂ influx	General CO ₂ corrosion only at high temperatures No pitting/localised corrosion

■ Not advisable to use this brine ■ Proceed with caution ■ Brine safe to use

Pitting leads to SCC

In many SCC incidents, pitting corrosion helps initiate the crack. Formate brines’ and halide brines’ performance against this devastating form of corrosion varies considerably.



Over and out

Erskine is a rich gas condensate field in the North Sea, with a BHT of 177°C (350°F), 965 bar (14,000 PSI) pressure and produced fluids containing 4% CO₂ and 15-30 ppm H₂S. A 25%Cr Duplex stainless steel production tubing was chosen for well W4. When it came to a packer fluid, 1.3 s.g. (11.3 ppg) CaCl₂ was used as the base, with biocide (C₅H₈O₂), oxygen scavenger (NH₄HSO₃) and a thiocyanate corrosion inhibitor (NaCNS) added. After 11 months the production tube failed. A metallurgical investigation concluded that pitting, followed by chloride SCC, was the likely cause of failure, most probably as a result of air O₂ ingress into the annulus during the bleed-off of annular pressure.

Mowat, et.al., SPE67779

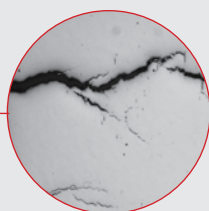
A clear comparison

Research completed at the end of 2005 at the Hydro Research Centre Porsgrunn, clearly compares the effect halide and formate brines have on commonly used metals in the presence of CO₂ without O₂ or H₂S. It confirms field experience by showing that halide brines cause SCC, while formate brines prevent it. What was startling, however, is the speed at which SCC develops on Super 13Cr and Duplex 22Cr. Within a month, SCC had developed on all three coupons for both metals. This shows that there is a risk of SCC even during short-term operations, such as completions and workovers, with halide brines and these common metals.

Halide brines vs. formate brines: Testing for SCC with carbon dioxide

Calcium bromide + 1% Cl ⁻		
CRA type	No. of coupons cracked	Time period
Super 13Cr	3 out of 3	1 month
Duplex 22Cr	3 out of 3	1 month
Duplex 25Cr	2 out of 3 with crack initiation	3 months

Potassium/cesium formate + 1% Cl ⁻		
CRA type	No. of coupons cracked	Time period
Super 13Cr	0 out of 3	3 months
Duplex 22Cr	0 out of 3	3 months
Duplex 25Cr	0 out of 3	3 months



SCC testing on a 1.7 s.g. (14.2 ppg) potassium/cesium formate fluid and a 1.7 s.g. (14.2 ppg) calcium bromide fluid, with CO₂ headspace. Temperature of 160°C (320°F). P_{CO₂} of 10 bar (145 PSI). In this worst-case scenario, with high levels of CO₂ and chloride, the pH buffer in the formate brine was immediately overwhelmed and the pH allowed to drop.

To sum up

The dangerous relationship between carbon dioxide and halide brines is summarised by the following equation. The table then compares halide and formate brines' ability to cause or prevent pitting and SCC.

CRA under tensile stress + CO₂ + halide brine = Pitting and SCC

Calcium bromide + 1% Cl⁻

- When CO₂ enters halide brine, it immediately converts to carbonic acid, creating a corrosive environment. This means that halide brines may cause SCC when exposed to tensile stresses. The speed of SCC depends on material, halide type and temperature. Only a very small amount of CO₂ is required to cause failure.

Potassium/cesium formate + 1% Cl⁻

- No SCC has ever been measured or reported in a formate brine exposed to carbon dioxide. Formate brines provide complete protection against SCC when exposed to CO₂.
- A very significant CO₂ influx, or a long exposure period with a moderate influx, is required for carbonic acid to form due to the unique carbonate/bicarbonate buffer. This prevents any adverse impact on the vast majority of wells with CO₂ influx.
- In extreme laboratory tests when the buffer has been overwhelmed by a massive simulated CO₂ influx over a very long time period, SCC has never been recorded in formate brines, even when saturated with chloride ions. This proves that formate brines protect CRAs against SCC even in very aggressive chloride/CO₂ environments.

Adding to the problem

A 1.32 s.g. (11 ppg) CaCl₂ brine with an oxygen scavenger and sodium thiocyanate high-temperature corrosion inhibitor proved devastating in Shell's Deep Alex gas well in the Gulf of Mexico. A 22Cr Duplex stainless steel production tubing was selected based on temperatures up to 188°C (370°F), pressures of 116MPa (16,800 PSI) and existence of CO₂ and H₂S.

The well produced for one month before the production tubing failed and it was shut in. A closer look showed that multiple joints of the tubing had either failed altogether or contained stress corrosion cracking. A failure analysis and subsequent laboratory programme demonstrated that the problem was caused by environmentally assisted cracking of the 22Cr Duplex. This was proved to be a direct result of H₂S production from decomposition of the sodium thiocyanate corrosion inhibitor and/or ammonium bisulphate oxygen scavenger from the CaCl₂ completion fluid in the annulus.

Mack, et. al., NACE paper no. 02067

Hydrogen sulphide

– a destructive force

Hydrogen sulphide is commonly referred to as ‘rotten egg’ gas and is one of the most destructive gases known to man. Concentrations of 50 ppm cause highly stressed, high-strength steel to fail in a matter of minutes. Small concentrations can reduce drill pipe life by a factor of ten. In fact, only 0.1 ppm greatly reduces failure time of highly stressed, high-strength drill pipe.

H₂S can enter the completion or packer fluid either from the reservoir gas, along with CO₂, or from decomposition of sulphur-containing additives (for example thiocyanate). It causes pitting and stress corrosion cracking (SCC) at high temperatures and sulphide stress cracking (SSC) at low temperatures. Many recent failures in halide brines have been caused by H₂S, which has been formed by decomposition of the commonly used corrosion inhibitor, thiocyanate.

H₂S in halides and formates

Halides

- Sulphur-based additives commonly used. These decompose to form H₂S.
- Lack of pH buffer causes H₂S to react immediately to iron sulphide and atomic hydrogen.

Formates

- No additives means no H₂S from decomposition.
- H₂S influx from the reservoir gas is absorbed by the pH buffer and by the inherent scavenging nature of formates.

Laboratory results show formate brines’ superiority

Both Statoil and Hydro Research Centre Porsgrunn have included H₂S in CO₂ corrosion testing. The CO₂ corrosion results shown earlier are unaffected by the presence of H₂S. Statoil included H₂S in its SCC testing with CO₂ on S13Cr. H₂S did not have any impact on the ability of formate brines to prevent SCC in the presence of H₂S.

Further reading

- Leth-Olsen: CO₂ Corrosion in Bromide and Formate Well-Completion Brines, SPE 95072
- Stevens et. al.: Oilfield Environment-Induced Stress Corrosion Cracking of CRAs in Completion Brines, SPE 90188
- Mack et al.: Stress Corrosion Cracking of a Cold Worked 22Cr Duplex Stainless Steel Production Tubing in High Density Clear Brine CaCl₂ Packer Fluid, NACE 02067
- Ibrahim et al.: Corrosion Behavior of Super 13Cr Martensitic Stainless Steel in Completion Fluids, NACE 03097
- Scoppio et al.: “Corrosion and Environmental Cracking Testing of a High-Density brine for HPHT Field Application”, NACE 04113
- Mowat et al.: Erskine Field HPHT Workover and Tubing Corrosion Failure Investigation, SPE 67779
- Ke and Qu: Thermal Decomposition of Thiocyanate Corrosion Inhibitors: A Potential Problem for Successful Well Completions, SPE 98302
- Downs and Leth-Olsen: Effect of Environmental Contamination of the Susceptibility of Corrosion Resistant Alloys to Stress Corrosion Cracking in High-Density Completion Brines, SPE 100438. To be published May 2006
- API SC13/TG06 Corrosion Resistant Alloy Testing Programme – extensive test programme available for sponsoring companies



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