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Effect of Chloride Concentration on the Stress Corrosion Cracking (SCC) of CRA Tubulars and Methods to Enhance SCC Resistance in High-Temperature Environments

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Abstract

Recent failures of corrosion resistant alloy (CRA) production tubing and sand control screens due to stress corrosion cracking have been reported. Investigation of these field failures revealed that calcium chloride completion brine or brine containing calcium chloride was a major component in most failures. Consequently, a growing perception is developing that calcium chloride or even calcium chloride/calcium bromide completion brine should not be considered for use in wells completed with high strength CRA tubulars in high-temperature, high-pressure environments. The impact that completion brine, temperature and acid gas have on the SCC of CRA materials in oilfield environments have been presented in several SPE and NACE publications. However, it becomes necessary to further understand the SCC behavior of high strength CRA materials in brines containing calcium chloride and/or calcium bromide, the most widely used, economical completion brines and packer fluids. The question remains: is there a chloride concentration below which high-strength CRA materials can be safely used in high-temperature well completions.

Results for CRA materials tested in calcium chloride, calcium chloride/calcium bromide, and calcium bromide brine for SCC resistance are presented, and the relationship between chloride concentration, type of CRA material, and temperature is discussed. Methods to enhance SCC resistance and minimize the sensitivity of CRA materials to its environment are presented. Practical guidelines for the use of completion brine with CRA metallurgy and chemical treatment is discussed. Results obtained from this study are provided to better design safe, economical completion brine and packer fluids for wells completed with high strength CRA tubulars.

Introduction

The oil and gas industry has successfully used calcium chloride brine, calcium bromide brine, zinc bromide brine and mixtures thereof as well completions and packer fluids for more than 25 years. During this time, brine compositions changed only to prevent crystallization of brine in cold climates and, for some brine, when exposed to high pressure and low temperature (~38F) at the mudline in deepwater environments (Pressure Crystallization Temperature, PCT[1]). Unfortunately, some of the corrosion inhibitors used since the 1980s[2] were found to create severe problems and field failures, especially when used with high-strength chrome tubulars.[3-5] To overcome these problems, new corrosion inhibitor packages have been successfully applied in the field.[6, 7]

Recent failures of high-strength corrosion-resistant alloys (CRAs) involving low-density calcium chloride packer fluids include one failure reported for 95 ksi super 13 chrome [13Cr(2Mo)95] in an 11.0 ppg $CaCl_2$ brine (Resak A-6, Malaysia)[3]. This brine was inhibited with ammonium bisulfite, a morphorline based corrosion inhibitor and glutaraldehyde and used in a well with a bottom-hole temperature of about 300°F. Failure analysis concluded that the presence of oxygen, CO_2 and H_2S in the $CaCl_2$ brine was the most likely cause for cracking. Laboratory evaluations demonstrated that similar SCC susceptibility could occur in $CaCl_2$ brine by lowering pH or not adding an inhibitor package. Similar testing with $CaBr_2$ and NaBr indicated that cracking would not occur. Other failures included high-strength 22 chrome[4] and 25 chrome[5] tubulars, and were discussed at two Corrosion / Stress Cracking Forums organized by El Paso Oil & Gas in January 2002 and September 2003. Significant joint industry projects, such as the “API CRA Testing Program,” have also been funded to better understand the interaction of ‘completion brine-CRA material-and environments.’

While some failures of high-strength chrome tubulars in high-temperature well applications can be attributed to thiocyanate decomposition[8, 9] or oxygen ingress into the annulus space, the role of the $CaCl_2$ packer fluid cannot be overlooked. In order to minimize the potential for chloride-induced SCC, chloride-free brines have been selected for well completions and packer fluids. Of the chloride-free brines, NaBr has lower corrosion rates than $CaBr_2$[2, 10], formate brines decompose and generate hydrogen at high temperature[11], and the extremely high-pH carbonate brines suffer from probable elastomer degradation and formation damage[12]. The utility of buffered sodium bromide brines for high-temperature packer fluid applications has recently been published[6].

In order to more fully understand the failures of high-strength CRAs, massive efforts have been mobilized to identify the controlling factors, determine operational limits for brine-metal combinations, and supply safe brines for brine fluid applications. Previous papers presented an overview of the brine-CRA interactions[7, 13]. This paper is the continuation of an ongoing extensive R&D effort to better understand cracking issues with respect to $CaCl_2$ concentration and presents additional data for discussion.

Experimental

C-Ring coupon specimens were cut from tubular samples of 13Cr(1Mo)110, 13Cr(2Mo)110, 13Cr95, and 13Cr85. The first two numbers identifies the approximate percent chromium (Cr), the number in parentheses identifies the approximate percent of molybdenum (Mo), and the last two or three numbers identify the minimum yield stress for the alloy. When the Mo content is approximately 1 percent, the nickel (Ni) content is approximately 4 percent; when Mo is approximately 2 percent, Ni is approximately 5 percent; and when Mo is not specified, both Ni and Mo are basically low. This presentation of data does not make a distinction amongst respective manufacturers of tubular materials.

Brine fluids used in this investigation were either stock fluids or blends formulated from predetermined mixtures of 11.6 pounds per gallon (ppg) stock $CaCl_2$, 14.2 ppg stock $CaBr_2$ and water. Brine properties, such as pH and density, were measured according to standard API Recommended Practices[1].

Specimens were stressed to 90 or 100% of the actual yield strength of the material utilizing the 0.2% offset calculation as specified by the NACE standard TM0177-96, Method C. Hastelloy® C-276 bolts, isolated from the test specimen by Teflon® tape or glass-filled PEEK insulators, were used to apply the required stress. Immediately after a specimen was stressed, it was immersed into the test brine contained in a Teflon® liner that was inserted into a pressure cell. The test brine was pre-treated with the inhibitor package when used, but was not degassed or purged to remove dissolved oxygen. This procedure was employed to reflect prevailing field operations. The pressure cell was then sealed.

The cell was immediately pressurized with nitrogen, and then depressurized to atmospheric pressure; this procedure was repeated twice more to remove air from the cell headspace (nitrogen pressures were 100 - 300 psi), and finally pressured with nitrogen to at least 200 psi. None of the protocols for tests reported herein required the headspace to contain an acid gas such as CO_2, or CO_2 / H_2S. The instant the target pressure was achieved, the cell valve was immediately shut-in to prevent (minimize) solution of the added gas into the brine. In each case the headspace gas to solution volume was known.

Each cell was heated to the test temperature for 14 to 30 days of heat aging. After aging, each C-ring was rinsed thoroughly with DI-water (de-ionized water), washed with soap and DI-water, rinsed thoroughly with DI-water, dried and examined for SCC under a microscope. If required, the C-ring was first rinsed with DI-water, cleaned with inhibited HCl, rinsed with DI-water and thoroughly neutralized in sodium carbonate DI-water, washed with soap and DI-water, rinsed thoroughly with DI-water, dried and then examined under a microscope for SCC. Results are presented in the tables.

Except for large autoclave tests, each test and C-ring combination was an individual experiment. The master plan guiding this project was designed to define boundaries where cracking tendency begins. As experimental results began to identify a boundary, additional tests would be scheduled. Self-validation is achieved by evaluating each test with its neighbors and closely related tests. When appropriate, exact duplicates would be conducted.

Results and Discussion

Tests with the various metallurgies were conducted in calcium chloride ($CaCl_2$) or calcium chloride/calcium bromide ($CaCl_2$/$CaBr_2$) brine at about 300°F. Each of the brines was either not treated, or treated with a sulfur-free chemical additive(s). Results are presented in table format.

Table 1 provides data for standard 85 ksi 13 chrome tubular materials and the data re-affirms the generally held position that this alloy is not susceptible to SCC. The first brine (# 1) was pure $CaCl_2$ obtained from a typical brine plant operating along the Gulf of Mexico (GOM). Each of the other brines was formulated from a mixture of 11.6 pounds per gallon (ppg) stock $CaCl_2$, 14.2 ppg stock $CaBr_2$ and water, and the chloride ion concentrations ranged from 97 pounds per barrel (ppb) to 30 ppb. As expected, susceptibility of the 13Cr85 is not dependent on chloride ion concentration. Also, the use of a sulfur-free chemical additive(s) (inhibitor) was not necessary; however, inhibitors are generally added to protect the casing string and therefore are always routinely added. As will be evident from the work described herein, addition of certain sulfur-free chemical inhibitors that were used in this investigation appears to have significant benefits for chrome alloyed tubular materials.

Table 1: Calcium Chloride/Calcium Bromide Brines

#	Density ppg	Inhibitor	Temp. °F	Metal	SCC Cracking
1	11.6	no	300	13Cr85	no
2	11.6 [2]	no	300	13Cr85	no
3	11.6	no	300	13Cr85	no
4	11.0	1	250	13Cr85	no

1 - Sulfur-free inhibitor package

2 - Post Test Galvanic Connection to C-276

Data for 95 ksi 13 chrome material is presented in Table 2. One data point obtained from SPE 90188[7] was inserted into this table for obvious reasons. The inserted data was for one 13Cr95 C-ring that had been observed to crack. While the data is listed in Table 2 according to density, it is apparent that density is not the overriding factor in cracking tendency. This view of the data provides only limited information and is not very helpful in understanding the relationship between brine composition and cracking tendencies. To better understand the impact that $CaCl_2$ might have on the cracking tendency of stressed chrome tubular materials, this data is ordered according to chloride ion content in Table 3. The last column contains the chloride ion content in pounds per barrel (ppb). In this and following tables, tests that result in a cracked C-ring are presented in red.

Table 2: Calcium Chloride/Calcium Bromide Brines

#	Density ppg	Inhibitor	Temp. °F	Metal	SCC Cracking
1	12.5	1	300	13Cr95	no
2	12.0	1	300	13Cr95	no
3	12.0	1	300	13Cr95	no
	11.6[2]	no	300	13Cr95	yes
4	11.6	1	300	13Cr95	no
5	11.6	no	300	13Cr95	no
6	11.6	no	300	13Cr95	no
7	11.0	1	250	13Cr95	no
8	11.0	no	150	13Cr95	no
9	11.0[3]	no	150	13Cr95	no
10	10.5	1	150	13Cr95	no

1 - Sulfur-free inhibitor package

2 - Data from SPE 90188

3 - Pure calcium bromide brine

Several observations can be made from the view of the data presented in Table 3. First, it appears that a relatively high chloride ion concentration was required to affect cracking of the 13Cr95 C-ring. When this level was reduced from 116 ppb to 90 ppb (Test #5), no cracking was observed. This was accomplished by substituting bromide ion for chloride ion. In effect, there is an impact of calcium bromide that somehow tends to reduce the ability of calcium chloride to cause cracking of C-rings. Furthermore, cracking was not observed in Test #4 when the sulfur-free inhibitor package was added to the test brine having the same chloride ion content as in the test where a 13Cr95 C-ring was found cracked (116 ppb).

Table 3: Calcium Chloride/Calcium Bromide Based Brines (95 ksi)

#	Density ppg	Inhibitor	Temp. °F	Metal	SCC Cracking	Chloride ppb
	11.6[2]	no	300	13Cr95	yes	116
4	11.6	1	300	13Cr95	no	116
1	12.5	1	300	13Cr95	no	108
5	11.6	no	300	13Cr95	no	90
2	12.0	1	300	13Cr95	no	87
3	12.0	1	300	13Cr95	no	87
10	10.5	1	150	13Cr95	no	77
7	11.0	1	250	13Cr95	no	50
8	11.0	no	150	13Cr95	no	46
6	11.6	no	300	13Cr95	no	30
9	11.0[3]	no	150	13Cr95	no	0

1 - Sulfur-free inhibitor package

2 - Data from SPE 90188

3 - Pure calcium bromide brine

Significantly more cracking was observed for 13Cr(1Mo)110 C-rings exposed to uninhibited $CaCl_2/CaBr_2$ brine containing varying amounts of chloride ion. The data presented in Table 4 indicates that relatively small amounts of chloride ion are tolerated by this material when not inhibited, approximately 30 ppb.

Table 4: Uninhibited Calcium Chloride/Calcium Bromide Brines (110 ksi)

#	Density ppg	Inhibitor[1]	Temp. °F	Metal	SCC Cracking	Chloride ppb
4	11.6	no	300	13Cr(1Mo)110	yes	116
1	13.5	no	300	13Cr(1Mo)110	yes	91
5	11.6	no	300	13Cr(1Mo)110	yes	90
10	10.0[2]	no	300	13Cr(1Mo)110	yes	65
2	13.5	no	300	13Cr(1Mo)110	yes	60
6	11.6	no	300	13Cr(1Mo)110	yes	60
9	10.0	no	300	13Cr(1Mo)110	yes	58
3	13.5	no	300	13Cr(1Mo)110	yes	32
7	11.6	no	300	13Cr(1Mo)110	no	30
8	11.6	no	300	13Cr(1Mo)110	no	0

1 - None

2 - Pure sodium chloride

Similar results were observed for the 13Cr(2Mo)110 material shown in Table 5. For this material, exposure to pure chloride or mixed chloride-bromide brines resulted in cracking of the C-rings. Only pure $CaBr_2$ brine provided a crack-free environment.

Surprisingly, both the 1Mo (Test #10 in Table 4) and 2Mo (Test #3 in Table 5) materials

Table 5: Uninhibited Calcium Chloride/Calcium Bromide Brines (110 ksi)

#	Density ppg	Inhibitor[1]	Temp. °F	Metal	SCC Cracking	Chloride ppb
1	13.5	no	300	13Cr(2Mo)110	yes	91
2	11.6	no	300	13Cr(2Mo)110	yes	90
3	10.0[2]	no	300	13Cr(2Mo)110	yes	65
4	13.5	no	300	13Cr(2Mo)110	yes	60
5	11.6	no	300	13Cr(2Mo)110	yes	60
6	10.0	no	300	13Cr(2Mo)110	yes	58
7	13.5	no	300	13Cr(2Mo)110	yes	32
8	11.6	no	300	13Cr(2Mo)110	yes	30
9	11.6	no	300	13Cr(2Mo)110	no	0

1 - None

2 - Pure sodium chloride

Table 6: Calcium Chloride/Calcium Bromide Based Brines

#	Density ppg	Inhibitor	Temp. °F	Metal	SCC Cracking	Chloride ppb
1	11.6	no	300	13Cr(1Mo)110	yes	116
2	11.6	1	300	13Cr(1Mo)110	no	116
3	13.5	no	300	13Cr(1Mo)110	yes	91
4	11.6	no	300	13Cr(1Mo)110	yes	90
5	10.0[3]	no	300	13Cr(1Mo)110	yes	65
6	11.3	2	225	13Cr(1Mo)110	no	64
7	13.5	no	300	13Cr(1Mo)110	yes	60
8	11.6	no	300	13Cr(1Mo)110	yes	60
9	10.0	no	300	13Cr(1Mo)110	yes	58
10	13.5	no	300	13Cr(1Mo)110	yes	32
11	11.6	no	300	13Cr(1Mo)110	no	30
12	11.6[4]	no	300	13Cr(1Mo)110	no	0

1 - Sulfur-free inhibitor

2 - Sulfur-free inhibitor package

3 - Pure sodium chloride

4 - Pure calcium bromide brine

Table 7: Calcium Chloride/Calcium Bromide Brines (110 ksi)

#	Density ppg	Inhibitor	Temp. °F	Metal	SCC Cracking	Chloride ppb
	11.6[1]	2	300	13Cr(2Mo)110	yes	116
1	12.5	2	300	13Cr(2Mo)110	no	105
2	13.5	no	300	13Cr(2Mo)110	yes	91
3	11.6	no	300	13Cr(2Mo)110	yes	90
4	11.6	3	300	13Cr(2Mo)110	no	90
5	10.0[4]	no	300	13Cr(2Mo)110	yes	65
6	13.5	no	300	13Cr(2Mo)110	yes	60
7	11.6	no	300	13Cr(2Mo)110	yes	60
8	11.6	3	300	13Cr(2Mo)110	no	60
9	10.0	no	300	13Cr(2Mo)110	yes	58
10	13.5	no	300	13Cr(2Mo)110	yes	32
11	11.6	no	300	13Cr(2Mo)110	yes	30
12	11.6[5]	no	300	13Cr(2Mo)110	no	0

1 - Pure $CaCl_2$ - OTC 19210

2 - Sulfur-free inhibitor package

3 - Sulfur-free inhibitor

4 - Pure sodium chloride

5 - Pure calcium bromide brine

were found to crack in the uninhibited pure 10 ppg sodium chloride (NaCl).

Comparative inhibited data are presented in Table 6 for the 1Mo material and in Table 7 for the 2Mo material.

As was observed for the 13Cr95 material, addition of a sulfur-free inhibitor resulted in protection for the exposed C-ring at 300°F in the pure 11.6 ppg $CaCl_2$ brine. Compare Test # 1 and Test #2 in Table 6.

Similar results were obtained for the 2Mo material shown in Table 7. Compare Test #3 with Test #4, and Test #7 with Test #8. In both instances, the addition of sulfur-free inhibitor prevented cracking of the exposed C-ring.

These tests were conducted at 300°F. It should be noted that while the sulfur-free inhibitor package prevented 13Cr(2Mo)110 C-ring cracking when the chloride ion was 105 ppb or less (Table 7), cracking was observed in pure 11.6 ppg $CaCl_2$ brine when inhibited [13] and tested at 300°F.

The systems described above highlight one important concern associated with the sensitivity of certain high-strength tubular materials to uninhibited brine. In most cases where the chrome material is observed to crack in the native brine at 300°F, protection is apparently achieved in the same brine composition inhibited with the sulfur-free inhibitor.

Summary

The fact is that certain tubular materials are resistant to SCC in brine containing relatively high concentrations of $CaCl_2$ while other materials are not, and this was clearly demonstrated herein. By substituting bromide ion for some amount of chloride ion, certain tubular materials became resistant to cracking. In fact, at the high temperature of 300°F, some tubular material was SCC-free only in pure $CaBr_2$.

To some extent, sensitivity to $CaCl_2$ was mitigated when the brine was treated with a sulfur-free inhibitor. This was observed in most cases, with the one exception being for the 13Cr(2Mo)110 exposed to stock 11.6 ppg $CaCl_2$[13].

While this study concentrated on applications at 300°F, temperature is one factor having significant influence[13].

Chloride ion concentration and temperature are not the only factors affecting SCC of oilfield tubular CRA materials that need to be considered. Other factors can significantly impact the SCC of these materials, and these factors must be included in the overall evaluation of "brine–tubular material–environment" matrix. Supplemental data addressing these issues will be presented in a future publication.

Other factors to consider include the relative pH of the brine systems, influence of oxygen incorporated into the brine, brine contamination with acid gases such as CO_2, contamination of brine with oxidants as for example when potable water is used in blend formulations or for brine dilutions, the amount and type of sulfur-free inhibitor package added to brine, and the impact of test duration on test results. Each factor is important and can significantly influence the sensitivity of tubular materials to the brine environment and must be considered in the selection of brine for a given environment.

Conclusions

1. High-Strength CRA tubular materials were shown to be susceptible to SCC in $CaCl_2$ brine at high temperature.

2. The chloride ion concentration has significant impact on the SCC susceptibility of 13 chrome alloys.

3. High-Strength high-alloy CRA tubular materials were found to be more susceptible to SCC in brine containing $CaCl_2$ than lower strength, lower alloy materials.

4. The addition of a sulfur-free inhibitor package mitigated the apparent SCC of most CRA materials at 300°F, but highly alloyed CRA materials with 2% molybdenum remained susceptible to SCC in treated 11.6 ppg $CaCl_2$ brine.

5. Substitution of calcium bromide for calcium chloride tended to reduce the impact of the chloride ion concentration on SCC susceptibility.

6. Calcium bromide brine did not demonstrate SCC of CRA materials as did calcium chloride and sodium chloride brines.

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Metric Conversion Factors

$(^{o}F-32) \times 0.5556 = {}^{o}C$
in × 2.54 = cm
lb × 0.4536 = kg
gal × 3785 = cc
ppg × 119.8264 = kg/m^3
bbl × 0.159 = m^3
psi × 6.895 = kPa