CORROSION MECHANISMS AND MATERIAL PERFORMANCE IN ENVIRONMENTS CONTAINING HYDROGEN SULFIDE AND ELEMENTAL SULFUR

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ABSTRACT

This paper provides an overview of corrosion mechanisms and materials’ performance in environments containing H$_2$S and elemental sulfur (S). Based on this information the factors affecting the service life of materials in highly sour environments are discussed. The source of the data summarised is drawn from the experience of the oil and gas industry in handling sour environments.

KEYWORDS

H$_2$S, sulfur, steel, corrosion resistant alloys

1. PERFORMANCE OF CARBON STEELS IN ENVIRONMENTS CONTAINING H$_2$S AND S

1.1 Protectiveness Of The Sulfide Scale

It is important first to discuss the protectiveness of iron sulfide scales before the role of S is addressed. Iron sulfide scales (also referred to as films) are of great interest from a practical standpoint since protective scales reduce the corrosion rate and in many cases eliminate the need for corrosion inhibitors. However, the protectiveness of corrosion product layers is not easily studied or quantified. Field experience has shown, in areas such as Canada and the Middle East where wells produce oil and gas with H$_2$S but no CO$_2$, that the corrosion product layer can indeed be quite protective even at very high concentrations and partial pressures of H$_2$S. On the contrary, many laboratory investigators have suggested that iron sulfides cannot be protective since many are non-stoichiometric and, therefore, unstable. Not all laboratory studies have evaluated the protectiveness of iron sulfide scales but there have been some efforts in this area.
Smith and Pacheco described the nature of H₂S-controlled corrosion as being typified by discrete pitting attack. Most of the research they reviewed was concerned with high levels of H₂S and there was also elemental S present—a notorious initiator of pitting corrosion. Furthermore, high concentrations of H₂S have been produced in oil and gas fields without pitting so it is not inevitable that localized attack will occur. Other factors such as chlorides, O₂ and CO₂ can increase the likelihood of localized attack.

The role of chlorides in sour systems has not been specifically studied to any real extent but is usually included to some degree in studies aimed at H₂S-CO₂ systems. Sridhar et al. examined the effect of chlorides up to 160,000 ppm on the corrosion rate of steel in H₂S + CO₂ +O₂ and reported very little impact on the average corrosion rate. However, at concentrations greater than 5% (50,000 ppm) chlorides, they observed localized corrosion. No further characterization was made even though this was a crucial observation.

It has been found in field failures of wells, when very high concentrations of chlorides and high concentrations of H₂S are present, that severe pitting can occur. Hamby noted the morphology of the pitting in this type of environment where the H₂S content ranged from 28 to 46% and the CO₂ from 3 to 8%. Figure 1 shows a reproduction of Hamby’s pit morphology and sequence of corrosion products that formed on pitted tubing in these wells. The presence of a thin layer of iron chloride at the bottom of the pit has been found to increase the rate of pit penetration significantly.

Ho-Chung-Qui et al. found the same sequence of corrosion products and severe pitting in flowlines that carried H₂S with water that contained chlorides at 65,000 ppm. There does not appear to be any laboratory studies of H₂S corrosion in very high chloride environments (> 100,000 ppm) which would be of great importance since the acidizing of wells with HCl or the use of brine-water, kill fluids will likely cause the sort of severe pitting noted in Figure 1.

The presence of a thin iron chloride layer at the bottom of pits in H₂S environments has been noted by Kasnick and Engen and the stability of this compound was established by Kesavan and Wilde. FeCl₂ is stable at pH values of 3 or less, confirming the very low pH present at the bottom of these pits.

Oxygen contamination in sour systems is a significant problem from a corrosion standpoint. Mechanistically, there have been numerous studies, all of which generally agree on the reactions that occur. For example, Craig demonstrated that in H₂S saturated solutions at ambient temperature the sulfide that forms is Mackinawite (Fe₃S₄) but with the introduction of oxygen into the test, or by simply exposing the Fe₃S₄ corrosion product to air, it was oxidized to γ-FeO(OH) and then to Fe₂O₃. The S was liberated as either elemental S or a polysulfide. The resulting corrosion rates were not particularly high, 0.19 mm/y, but the time was not sufficient to allow pitting which may be the more likely outcome under these conditions.

While some in the industry understand the oxidation path of iron sulfides, it is remarkable how many researchers mistakenly assume that the presence of iron oxides in their corrosion analysis is a normal product when in fact it signifies that their laboratory procedures were unsatisfactory allowing oxygen entry into the system during testing. This of course nullifies the test results. It is, therefore, extremely important to remove all oxygen in a test system when testing in H₂S and that this complete elimination of oxygen be maintained for the entire test, otherwise the results are meaningless.

Not only does oxygen change the corrosion products in sour systems but it has a significant effect on the corrosion rate. Almost all of the literature on the subject shows a corrosion rate for steel in aerated wet H₂S of less than 1 mm/y and most often about 0.5 mm/y. However, these rates can be misleading, since they are uniform or average corrosion rates, and do not highlight the important fact that oxygen in the system can induce severe localized attack in the form of pitting and HIC. Several important field failures have been caused by this problem. (Hay and Stead, Craig et al.)

Recently Hausler showed that when 800 ppm O₂ (equal to 16 ppb in the water phase) was bled into an H₂S purge gas during corrosion testing of steels the corrosion rate jumped from 0.68 mm/y to 2.8 mm/y. If the oxygen concentration was increased to 2000 ppm in the H₂S stream, the onset of rapid localized corrosion occurred, particularly in the presence of a high concentration of chloride ions.

The effect of oxygen contamination on the corrosion products and their stability is one aspect but oxygen will also lead to changes in the solution chemistry. For example, Crolet, el at indicated that trace amounts of oxygen in a sour system will
produce thiosulfate. This will not be important to the overall corrosivity of the environment but, in the absence of H$_2$S, the role of thiosulfate can be significant to the overall corrosion process.

Furthermore, in the gas phase the following reaction can occur:

$$\text{H}_2\text{S} + \text{O}_2 \rightarrow \text{S} + \text{H}_2\text{O}$$

The generation of S and water can have catastrophic effects on corrosion and hydrogen cracking of steels.

Early laboratory test work (until quite recently) was hampered by the lack of facilities for replenishing gases in the test cell, so reducing corrosion rates are noted as the H$_2$S and CO$_2$ charged in the autoclave was consumed in the reactions. This limits the value of much laboratory test work. Knowing how difficult it is to carry out really well-controlled experiments in H$_2$S systems, with full exclusion of air and sufficient replenishment of gases which are consumed in the corrosion reaction, there is a lot of doubt about the validity of many of the test results quoted. It is expected that tests with once-through, flowing systems, more typical of real service conditions, would show different results. Some examples of these corrosion rates are noted below.

In general the corrosion rates in systems that only contain H$_2$S are relatively low, in the order of 0.5 mm/y or less.

From Shoesmith et al\textsuperscript{12} work at 1 bar H$_2$S the corrosion rate at pH 4 was 0.31 mm/y and at pH 5 was 0.11 mm/y. These results are consistent with more recent work of Cheng et al.\textsuperscript{13} that found the same rates of corrosion at similar pH.

Thomason\textsuperscript{14} found corrosion rates of steel in H$_2$S that never exceeded 0.8 mm/y. Likewise, Lino et al\textsuperscript{15} observed rates of 0.46 mm/y at pH 5.2 and 0.65 mm/y at pH 4.

Shannon and Boggs\textsuperscript{16} did corrosion tests with H$_2$S /N$_2$ mixtures. They noted different scales formed with different concentrations of H$_2$S and a gradual reduction in corrosion rates with time. Corrosion rates increased in going from distilled to chloride-containing water, up to about 1%NaCl. Above this the corrosion rate dropped off and above 6% up to 20%NaCl, the corrosion rate remained steady at about 80% of the distilled water value. The first noted increase in corrosion rates when adding chloride ions may reflect the impact of chloride ions in destabilising the sulfide film. Increasing amounts of chloride ions in solution reduce the solubility of acid gas in solution, effectively reducing the activity of the gas.

Thus, from these examples and other reports, it appears that the literature is quite consistent regarding the corrosion rate of steel in H$_2$S alone (no CO$_2$ or O$_2$): that the rates are generally about 0.5 mm/y or less with some few exceptions up to 1 mm/y. The addition of CO$_2$, however, can significantly affect the corrosion rate.

Consideration of the thermodynamics of carbonate and sulfide scaling (e.g. Smith) leads to the relationship:

$$K_{\text{FeS}/\text{FeCO}_3} = C\left(a_{\text{CO}_2}/a_{\text{H}_2\text{S}}\right)$$

This is the source of the general rule of thumb in the industry that there is a ratio of CO$_2$ :H$_2$S below which the equilibrium scale formed on the surface of steel shifts from being carbonate to sulfide. For example, Rhodes\textsuperscript{17} suggests that a ratio of CO$_2$ :H$_2$S<500:1 should result in sulfide scales forming and he also suggested that the corrosion rate was independent of the flow rate. More recently this 500:1 ratio has been revised downwards. For example Simon-Thomas and Loyless\textsuperscript{18} proposed:
CO$_2$: H$_2$S $>$ 200 $\rightarrow$ CO$_2$ dominated (flow conditions are important in influencing corrosion rates)

CO$_2$: H$_2$S $<$ 200 $\rightarrow$ H$_2$S dominated (flow is much less critical to scale stability and therefore to corrosion rate)

They suggest that the 200 figure may be further revised to 50-100.

They state that the corrosion rate is dominated by CO$_2$, but iron sulfides are very stable and cathodic to steel and can therefore tend to initiate localised corrosion i.e. if there is a little H$_2$S there is a problem of destabilisation of carbonate scales and a risk of pitting with high local corrosion rates (potentially faster than CO$_2$ corrosion rates – driven by the cathodic scale). So, slightly sour systems require careful monitoring. Higher H$_2$S levels result in stable scales and a reduction in corrosion rate as long as the sulfide film can be maintained. This follows normal observations made in the field internationally.

1.2 Corrosion Rate Of Carbon Steel In Presence Of Sulfur

It is recognized that dry solid S does not produce corrosion of carbon steel. It is only when moisture is present that S induces corrosion. Moreover, the pH of the solution and the presence of chlorides are significant contributors to the corrosion of steels in S-containing environments.

Potential – pH diagrams, while useful from a thermodynamic standpoint, are generally for fresh water environments so are not complete without considering the impact of chlorides. Hyne et al. demonstrated that S can be a very potent corroder depending on pH when chlorides are present. Figure 2 shows the effect on corrosion as a function of pH without chlorides and with 1000 ppm chlorides in solution. Figure 3 also indicates the effect of pH and chloride content on the corrosion rate in a S-containing environment.

The corrosion reactions that occur for steel in the presence of wet S are not completely understood and are disputed. The most accepted reaction, according to several investigators, has been published by Macdonald et al.:

$$(x-1)\text{Fe} + S_{y-1} \cdot S^{2-} + 2H^+ \rightarrow (x-1)\text{FeS} + H_2S + S_{y-x}$$

However, this reaction has been criticised by Schmitt since it implies that the cathodic reduction of polysulfide (S$_{x-y}^{2-}$) should occur without direct contact of S with the metal surface which is contradictory to observations.

Boden and Maldonado-Zagal proposed the following:

$$4S + 4H_2O \rightarrow 3 H_2S + H_2SO_4$$

These authors found that the pH dropped to 1.8 when flowers of S were stirred into distilled water. The generation of H$_2$S and sulfuric acid would explain the lower pH and formation of FeS when S is in contact with steel as well as the high corrosion rates. Similar acidification, although stabilising at higher values, was reported by Fang, Young, and Nešić.

While the net result of FeS formation is the same, the difference in corrosion rates between polysulfides and sulfuric acid is substantial. Also, polysulfides lead to localised corrosion, whereas sulfuric acid produces more general corrosion. More work needs to be performed to elucidate this mechanism.
Figure 4 shows the results of work carried out in the absence of oxygen (Kuster et al\textsuperscript{24}). There is a significant increase in corrosion rate from S as the chloride content increases above 0.01 mol/l to a maximum of 15 mm/y. As will be shown later in this report, some field failures have demonstrated pitting corrosion rates in excess of 25mm/y.

1.3 Background to Autocatalytic Mechanism of Corrosion of Steel by Elemental Sulfur

1.3.1 CORROSION TEST WORK

Macdonald, Roberts and Hyne\textsuperscript{20} investigated the corrosion behaviour of carbon steel with wet elemental sulfur on the both aerobic and anaerobic conditions. They measured corrosion rates by the change in resistance of wires made with of mild steel. With time they note that at a pH of 5.79 the change in resistance curves with time tend to be concave upwards, thereby indicating that the rate of corrosion increases with time. This behaviour strongly suggests autocatalysis by a corrosion product. It appears that this autocatalysis mechanism is more severe under anaerobic conditions than under aerobic conditions.

Visual examination of the wires removed at pH 5.79 showed that they were severely etched and uniformly thinned over the entire length in contact with sulfur. Furthermore, the wires were frequently found to have broken at a point of high stress, where the wires were bent through a small radius. This suggested the operation of a stress-related corrosion phenomenon, in agreement with previous observations for the corrosion of iron in systems containing iron sulfides, H\textsubscript{2}S and sulfur.

However in lower pH (1.82) and higher pH (9.10) systems the rate of corrosion is fairly constant or even decreases over the later period beyond 60 days. This sort of behaviour would arise in situations where a non-protective but non-catalytic product is formed, or when the product confers corrosion resistance to the underlying metal.

The general corrosion rate observed in these systems provide good evidence that the corrosion films are protective to some extent i.e. the corrosion reactions result in formation of passive films at the extremes of pH. These results were confirmed by the lack of corrosion products (iron oxides or sulfides) in the sulfur water slurries at the end of the experiment at extreme pH values, whilst there were large amounts of black iron sulfide in the solution of experiments carried out at pH 5.79 in anaerobic condition.

Looking more closely at the pH range 3.88 to 6.14 it can be seen that the rates of corrosion in this range generally increase with time confirming this autocatalytic mechanism. However, there clearly exists an induction period for the onset of catastrophic corrosion, which is dependent upon pH (increasing for pH values above 5) in an anaerobic system. The results carried out with oxygen present show that this reduces the time elapsed before the onset of catastrophic corrosion particularly if the initial pH of the system is low. These relationships suggest that the induction period involves a non-catalytic corrosion process, which is sensitive to oxygen, but one which will, nevertheless, eventually occur under anaerobic conditions. It is also noted that it was only after the induction time that there was formation of black iron sulfide (Mackinawite) and the evolution of H\textsubscript{2}S in the solution.

Tests were made with different sizes of sulfur particles in the suspension. In anaerobic system the induction period was found to be strongly dependent upon particle size, such that smaller particles exhibit the shorter induction times. Also the rate of corrosion is greater with decreasing particle size. It was also noted that if direct contact between the steel and the sulfur was prevented, no increase in the corrosion rate was observed even at a pH of 5.79. This is in general agreement with the observations of many other workers who indicate that intimate contact of the sulfur with the steel is necessary for it to result in corrosion.
1.3.2 MECHANISM

Any mechanism which is proposed to explain the corrosion of mild steel in wet elemental sulfur must account for the following observations.

- An induction time exists before the onset of catastrophic corrosion.
- The induction time decreases with increasing initial pH over the range 3.88 to 5.79.
- The induction time also decreases as the sulfur particle size distribution shifts to smaller values.
- At the onset of catastrophic corrosion both H$_2$S and mackinawite are produced.
- The catastrophic corrosion process is autocatalytic.
- The onset of catastrophic corrosion produces a shift in the corrosion potential to a more positive value.
- Direct contact between steel and sulfur is necessary for catastrophic corrosion to occur (the likelihood of which may be presumed to increase as the sulfur particle size decreases).
- The pH increases with time.

The following reactions are proposed to explain the observed catastrophic corrosion phenomenon:

\[
S_{y-1}\text{S}^2 + 2xH^+ + 2(x-1)e^- \rightarrow xH_2S + S_{y-x} \text{ (cathodic reaction in presence of FeS)}
\]

\[
(x-1)Fe \rightarrow (x-1)Fe^{2+} + 2(x-1)e^- \text{ (anodic)}
\]

\[
(x-1)Fe^{2+} + (x-1)H_2S \rightarrow (x-1)FeS + 2 (x-1)H^+ \text{ (anodic)}
\]

which give the overall corrosion reaction as:

\[
(x-1)Fe + S_{y-1}\text{S}^2 + 2H^+ \rightarrow (x-1)FeS + H_2S + S_{y-x}
\]

An additional cathodic reaction, viz,

\[
H^+ + e^- \rightarrow H_{ads} \rightarrow \frac{1}{2} H_2
\]

presumably also occurs, which accounts for the hydrogen embrittlement of steel in aqueous systems containing hydrogen sulfide.

In the above scheme the species $S_{y-1}\text{S}^2$ is considered to be formed by chemisorption on the surface of a particle of elemental sulfur. It is also possible that the corrosive species involves adsorbed polythionate ions (i.e. $O_3S_xS_ySO_{2x}$), which may be formed by the reaction of elemental sulfur with water. Irrespective of the exact identity of the corrosive species, contact between the steel or steel/FeS and sulfur is therefore necessary for electron exchange to occur, and hence for the reaction to proceed. The above scheme also accounts for the increase in pH and the formation of both H$_2$S and FeS (mackinawite).

The mechanism proposed above also explains the observed autocatalysis, if it is assumed that the overall corrosion process is controlled by the cathodic reaction, and that this reaction is catalysed by Mackinawite. Cathodic catalysis is also consistent with the observed positive shift in the corrosion potential at the onset of catastrophic corrosion. Since the corrosion potential is determined by equality of the partial anodic and cathodic currents, then catalysis of the cathodic process is expected to shift the corrosion potential in the positive direction, from $E_2$ to $E_c$ as observed Figure 5. Catalysis of the anodic reaction would be expected to have the reverse effect.
The mechanism by which iron sulfides (including Mackinawite) catalyse cathodic processes in sulfur containing systems has not been established although it has been attributed to their good electronic conductivity, low over potential for hydrogen evolution, noble electrode potentials and defect structures (Smith and Miller¹).

Furthermore a number of studies have indicated that the composition and protectiveness of iron sulfide scales depends upon the pH of this system, with the least protective (Mackinawite) being formed when the pH of the medium lies between 6.5 and 8.8. Outside of this range, protective scales of pyrrhotite and/or pyrite are apparently formed and the overall corrosion reaction is subject to anodic control (e.g. by ionic diffusion through the sulfide film). This suggests that the induction period may be due to the formation of a protective film on the metal surface which then breaks down at some critical pH value to form non protective Mackinawite. At this point the reaction becomes cathodically controlled, and consequently is subject to cathodic catalysis.

2. PERFORMANCE OF CORROSION RESISTANT ALLOYS IN ENVIRONMENTS CONTAINING H₂S AND S

In considering sour gas production conditions the conservative assumption should be made that there is some chloride ion content in the stream. Even where conditions are gas producing and very little liquid phase is expected, occasional droplets of formation water will be carried in the produced gas and these will generally contain chloride ions.

Thus, for natural gas producing conditions, the selection of corrosion resistant alloys (CRAs) should be made from established limits for stainless steels and nickel alloys. These limits have been made available in publications by Craig²⁶, reviews by Gooch and Gunn²⁷ and as incorporated into Intech Ltd material selection software, “The Electronic Corrosion Engineer” These limits have been used for materials selection for more than 10 years and are continuously checked against published failure data. To date there have been no incidences of failures where materials have been used within these limits and so they can be presented with confidence as a reliable guideline for sour service conditions. As is the case for steels, dry S does not attack stainless steels or nickel-based alloys (CRAs) in the temperature range encountered in oil and gas production.

2.1 Corrosion Of Corrosion Resistant Alloys In The Presence Of Sulfur

The fact that Cr offers protection from corrosion by S is true only in the absence of chlorides. Table 1 shows the effects of chlorides, S and temperature on the pitting of Alloy 825 and Alloy 2550 in an aerated solution (Mahmoud et al.²⁸). The test duration was one month.

<table>
<thead>
<tr>
<th>ALLOY</th>
<th>Temp, °C</th>
<th>NaCl, ppm</th>
<th>S, 1 g/l</th>
<th>Pitting Attack</th>
</tr>
</thead>
<tbody>
<tr>
<td>825, 2550</td>
<td>66</td>
<td>10,000</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>825, 2550</td>
<td>66</td>
<td>10,000</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>825, 2550</td>
<td>66</td>
<td>50,000</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>
ALLOY | Temp, °C | NaCl, ppm | S, 1 g/l | Pitting Attack
---|---|---|---|---
825, 2550 | 66 | 50,000 | Yes | Yes
825 | 93 | 0 | Yes | No
825, 2550 | 93 | 10,000 | No | No
825, 2550 | 93 | 10,000 | Yes | Yes
825, 2550 | 93 | 50,000 | Yes | Yes

Few studies have been performed considering the corrosion of CRAs in S alone without chlorides. This is because the major concern in the petroleum industry has been the great potential for SCC of CRAs in H₂S-S-Cl environments and the need to define those alloys that would be suitable for these environments. A large amount of laboratory evaluation was carried out from the mid 1980s to the mid 1990s evaluating various CRAs in S containing environments primarily because the industry fully expected high pressure high temperature (HPHT) wells in Mobile Bay, Alabama, USA to produce S at some point in their lives. To date, some 15 years after the first well was completed and began producing, none of the numerous wells in that area have ever produced S. Still the output of data was, and is, useful, especially since there are wells around the world that do produce S.

Wilken²⁹ showed the increase in corrosion rate for Alloy 28 and Incoloy 925 compared to steel in a sour gas environment containing various concentrations of S, both as a liquid and a solid, Figure 6. There was no significant difference between the different states of S and the resulting corrosion rate. The corrosion rates of the CRAs was less than 0.1 mm/y when S was present as a solid and less than 0.2 mm/y when it was present as a liquid even at 30 g/l S. The test environment was 10 bar H₂S, 10 bar CO₂ and 80 bar N₂. The test duration was 120 hrs. It is unclear what the chloride content was, but, probably 5% NaCl.

Ikeda et al.³⁰ observed a similar relationship for the corrosion rate of SM 2550 to the S content in a 25% NaCl solution at 177°C with 1 MPa H₂S and 1 MPa CO₂ (Figure 7).

There has been a tendency for the industry to use 1 g/l S additions when testing CRAs based on the limiting solubility of S in solution according to the work of Eills³¹ as shown in Figure 8. However, as can be seen in Figure 5 there was a very significant increase in the corrosion rate for all alloys above the 1 g/l S industry standard (note logarithmic corrosion rate scale). Thus testing with 1g/l S may give unrealistically low corrosion rate values from what may be experienced in practice.

Since the melting point of Sₙ, the most common allotrope, is 112.8°C to 114.6°C, corrosion testing for down-hole applications covers the range of phases from solid to liquid to gas, which requires careful attention to the method of adding S to the test environment to ensure S participates in the corrosion tests. As indicated by the preceding discussion, S has the greatest impact on corrosion of alloys when it is in intimate contact with the alloy surface. Thus considerable effort has been expended in configuring test cells to guarantee contact of the S with the surface. In some cases this has been achieved by placing a cup that holds the liquid S around the slow strain rate specimens (Martin et al.³⁵).

2.2 Stress Corrosion Cracking Of Corrosion Resistant Alloys In The Presence Of Sulfur

It has been found that not only does S cause serious pitting attack of many CRAs but that it also leads to stress corrosion cracking (SCC).
2.2.1 Nickel Alloys. Figure 9 shows the increasing corrosion rate, localized attack and, ultimately, SCC of Alloy 825 in the presence of S as a function of chloride content at 250°C. The more corrosion resistant Alloy 625 did not crack but did pit in this environment (Miyasaka et al. 33).

Similar results were found by Chaung et al. 34 who showed cracking of Alloy 825 with 1000 ppm S, at 149°C, with 25% NaCl. Tests by Craig et al. 35 in 1991 showed that Alloy 825 could pass a SSRT but in less severe conditions (100 ppm S, 5% NaCl in an environment of 62 bar H₂S and 107 bar CO₂ at a temperature of 218°C). Craig specifically noted that samples were fine-grained and had no twinning and were also resistant to pitting, crevice corrosion and C-ring tests at the same conditions.

Extensive testing by Martin et al. 32 using SSRT techniques confirm the deleterious effect of temperature and chloride content on the SCC of nickel based alloys exposed to S, Figure 10. The alloys tested were Hastelloy G50 (UNS N06950), Hastelloy G3 (UNS N06985) and SM2550 (UNS N06255). The method of adding S, by filling a cup attached to the SSRT specimen, makes quantifying the S content of the environment impossible. However, the data in Figure 10 are expected to be quite conservative and as such present a good means to select CRAs for S bearing environments.

Craig 36 also presented data on the effect of chlorides and S content on the corrosion rate of Alloy 825 and cracking of Alloy G3 (see Tables 2 and 3).

### TABLE 2
CORROSION RATE OF UNSTRESSED SAMPLES OF ALLOY 825 IN SOUR ENVIRONMENTS AFTER 30 DAYS

<table>
<thead>
<tr>
<th>H₂S (psi)</th>
<th>CO₂ (psi)</th>
<th>Temp (°C)</th>
<th>S(g/l)</th>
<th>Cl (ppm)</th>
<th>Corr Rate (mm/y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>195</td>
<td>335</td>
<td>121</td>
<td>10</td>
<td>1,500</td>
<td>0</td>
</tr>
<tr>
<td>195</td>
<td>335</td>
<td>121</td>
<td>10</td>
<td>50,000</td>
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<tr>
<td>360</td>
<td>600</td>
<td>149</td>
<td>10</td>
<td>1,500</td>
<td>0</td>
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<tr>
<td>360</td>
<td>600</td>
<td>149</td>
<td>10</td>
<td>50,000</td>
<td>0</td>
</tr>
<tr>
<td>360</td>
<td>600</td>
<td>177</td>
<td>10</td>
<td>1,500</td>
<td>0</td>
</tr>
</tbody>
</table>

### TABLE 3
SSRT RESULTS FOR ALLOY G-3 IN 1100 psi H₂S, 1900 psi CO₂ AND DEAERATED NaCl AT THE CONCENTRATIONS AND TEMPERATURES SHOWN.

<table>
<thead>
<tr>
<th>Temp (°F)/Cl(ppm)</th>
<th>S(g/l)</th>
<th>% Tf Ratio</th>
<th>% RA Ratio</th>
<th>Secondary Cracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>375 / 10,000</td>
<td>1.2</td>
<td>1.03</td>
<td>1.04</td>
<td>None/None</td>
</tr>
<tr>
<td>425 / 10,000</td>
<td>1.2</td>
<td>0.92</td>
<td>0.95</td>
<td>None/None</td>
</tr>
<tr>
<td>425 / 100,000</td>
<td>10.0</td>
<td>0.81</td>
<td>0.90</td>
<td>None/None</td>
</tr>
<tr>
<td>425 / 150,000</td>
<td>10.0</td>
<td>0.13</td>
<td>0.09</td>
<td>Yes/Yes</td>
</tr>
</tbody>
</table>

Cracking was observed in Alloy G3 only at the highest temperature and concentration of chloride ions and elemental S. Because of the good resistance to SCC at high temperatures in S containing environments with moderate chlorides, G3 type alloys have been widely used in Mobile Bay and other areas of the world where S production has been considered a risk, with great success.

Using SSRT, Wilhelm 37 determined that Alloy 825 and Alloy G were acceptable in a sour solution (27.6 bar H₂S) with 1 g/l S up to 204°C when the chloride content was 90,500 ppm. Hibner and Tassen 38 demonstrated that Alloy 825 failed at 177°C when 0.5% acetic acid was also present with elemental S and the chloride content was raised to 165,000 ppm.
Figure 11 shows one scheme for ranking CRAs in a sour environment containing 1 g/l S with 0.5% acetic acid and 25% NaCl (Special Metals\textsuperscript{39}).

Thus it can be seen that in the presence of chlorides and S there is a limiting temperature for each alloy that is largely related to the Mo content. Even Alloy C276 has a limit of about 275ºC. This is a much higher temperature limit than found by Vaughn and Greer\textsuperscript{40} under the same conditions. These latter authors set the limit for C276 as 177ºC. However, Craig et al\textsuperscript{35} did not observe SCC of C276 when tested to 210ºC. Regardless of the exact limit, there does appear to be a limit for the nickel based alloys. However, the titanium alloys offer the potential for much higher resistance to SCC in the presence of chlorides and S at temperatures above 210ºC.

2.2.2. Titanium Alloys. Considerable work has been carried out by RMI Titanium, and some limited work by Sumitomo, regarding the suitability of Ti alloys for environments containing H\textsubscript{2}S and S. For high-strength, down-hole tubulars and components, the beta alloys, such as Beta C and Beta III, were initially considered but, more recently, the alpha beta alloys such as Ti-6Al-4V-Ru, Ti-3Al-2.5V-Ru and Ti-6Al-2Sn-4Zr-6Mo have been tested since they are less expensive, are heat-treatable and have better SCC resistance than do the beta alloys. In the same environment as for the C276 above (1g/l S with 25%NaCl and acetic acid) the Ti alloys were completely resistant to SCC and localized corrosion up to 260ºC. In the absence of S and with lower chlorides they are resistant up to 330ºC.

Therefore, the Ti alloys represent the next higher level of resistance to corrosion and cracking in S with chlorides above the nickel-based alloys.

3. THE PRACTICAL APPLICATION OF STEELS AND CRAS

3.1 Fields That Produce H\textsubscript{2}S With No Sulfur

This section addresses selection of materials for oil and gas wells that contain H\textsubscript{2}S with no S and H\textsubscript{2}S with CO\textsubscript{2} at levels low enough that the CO\textsubscript{2}/H\textsubscript{2}S<200 resulting in sulfide scale formation dominating – but this does not necessarily mean that stable sulfide scales will be present if other conditions (pH, chloride…etc.) are unfavourable. Both laboratory and field experience reviewed in this paper indicate that sulfide film breakdown may result in pitting attack with potential for extremely rapid failure. Thus the forms of corrosion control in sour systems are primarily targeted at maintaining stable filming conditions and preventing pit initiation.

Across a wide pH range and a considerable variation in H\textsubscript{2}S concentration (partial pressure) the predominant corrosion product that will form on steels is Mackinawite(Fe\textsubscript{1+x}(S), that may or may not be protective but will generally not produce a high corrosion rate. At temperatures above about 100ºC, Pyrrhotite forms (sometimes with a thin cover of Pyrite) and is very protective. However, high chlorides can interfere with the protective nature of Mackinawite and Pyrrhotite and induce localized pitting.

The combined action of H\textsubscript{2}S and CO\textsubscript{2} can influence the composition, stability and protective nature of the corrosion product scale.

The formation of iron sulfide corrosion product is known to form a sulfide scale on the surface which can be very protective and persistent and can, therefore, significantly reduce the corrosion rate relative to systems without H\textsubscript{2}S present. When corrosion does take place it tends to be localised, with the surrounding sulfide scale acting as a large cathode area. This can give very high corrosion rates.

Many of the discrepancies in field experience and the reported influence of H\textsubscript{2}S in the literature are probably due to the cathodic nature of iron sulfide scales with respect to the steel substrate. Hence, if the scale cracks or spalls when it reaches a critical thickness, high rates of pitting can ensue due to local galvanic effects.
Another factor that can also have a similar effect in causing local scale breakdown is the physical removal of iron sulfide corrosion product by mechanical means. The localised removal of sulfide scale would cause a direct galvanic effect with the exposed steel substrate acting as an anode to the surrounding cathodic scale. The resulting high rates of localised attack could continue for considerable periods thereafter due to the difficulty in redeveloping protective scale at these locations.

A further potential source of corrosion may be the ingress of oxygen. Traces of oxygen in systems containing H₂S may be sufficient to oxidise the H₂S and result in free S, which is highly aggressive, and will lead to serious pitting attack as well as HIC or SOHIC in flowlines.

Carbon steel will be the main material of consideration for equipment as long as there is confidence that initiation of pitting corrosion can be prevented or is unlikely to occur (i.e. low chlorides and moderate pH). It is assumed that once pitting corrosion commences, the rate of attack is too quick for it to be detected and controlled before perforation of the steel has taken place. Thus the whole approach to considering carbon steel shifts from one of trying to estimate a corrosion rate, to one of evaluating the risk of pit initiation.

Factors which influence pit initiation in a sulfide–filmed surface:

- High ratio of CO₂:H₂S, i.e. CO₂ : H₂S >200
- Chloride ion concentrations in excess of 50,000 ppm.
- Pre-corrosion of surface of steel, particularly prior exposure to chloride containing fluids like completion brines or hydrochloric acid from acidising treatment.
- Low pH conditions e.g. from acidising returns.
- Lack of inhibition or low frequency batch inhibition.
- Erosive flow
- Oxygen ingress through air entrained in injected chemicals or from mechanical operations.
- Damage directly to sulfide layer by inspection equipment

Consideration of the factors listed above may make it immediately clear that the risks involved in using carbon steel may be rather high, in which case there may be an immediate preference for choosing a CRA material. Other situations may be less clear-cut and there may be scope for using carbon steel with operational procedures carefully controlled to prevent sulfide film breakdown.

The risk of pit initiation is important to address, but the consequence of such a pit and likely leak also have to be addressed.

When the decision is taken to select a CRA for sour oilfield environments, the choice can generally be made between Alloy 825 and Alloy 625. Both have been used as cladding or lining in flowlines and vessels or as solid piping in facilities.

### 3.2 Fields That Produce H₂S With Sulfur

One of the most difficult problems when S is expected in the produced fluids is accurately to predict its occurrence. If S does not appear but was predicted, the cost of completions can be extraordinarily expensive when lesser alloys would have sufficed. On the other hand, if S occurs unexpectedly, failure can be rapid.

S prediction is still very difficult and not accurate. Alberta Sulfur Research (ASR) has been active in this area for many years and is considered one of the leaders in S precipitation modelling. One of the important factors concerning whether S precipitates is if hydrocarbon condensate is present in the well or not. Field experience has demonstrated that S often precipitates when the production was dry gas and no liquid hydrocarbons were present.
Once it is determined, or suspected, that S will be produced and the phase in which the S will be present is known the following are recommended.

All the considerations of the previous section apply, but in addition there is the question to address whether the S will actually be in contact with the steel surface. If it is, it can be assumed that perforation of the wall will be rather rapid (Bich and Goerz of Shell Canada quote one case with corrosion rate as high as 30 mm/y). It should also be considered that there is a greater sensitivity towards the presence of chloride ions, so when there are expected to be chloride ions in excess of about 5,000 ppm, combined with elemental S production, there should be careful consideration of the preference for CRA material selection. Similarly, the presence of liquid hydrocarbon may be considered beneficial in helping to take and keep S in solution. Systems which do not produce liquid hydrocarbon, but do have elemental S, should be considered particularly aggressive.

4. CONCLUSIONS

Although there are considerable data in the literature concerning corrosion from H$_2$S and S (and the same is true for field experience), there is essentially no accepted set of guidelines for the selection of materials in these environments. To date most oil companies have based materials selection in these environments solely on their own field experience around the world or that of other operators. As seen in the details of the above report, there are many factors that determine the corrosion rate of steels and CRAs in H$_2$S and S bearing environments. In fact so many factors that simply basing materials selection decisions on experience can easily lead to the wrong choices and in some cases, premature failure.

Generally speaking the issue of material choice and corrosion control approach is strongly influenced by the consideration of the factors that will enhance the stability of the sulfide film, or will tend to destabilise it and encourage pit initiation. The evaluation of all of the influencing factors, based on the review of the literature and best practice from many operators, gives a good basis for evaluation of new producing conditions with aggressive environments.

It is considered that it is possible to handle aggressive, high H$_2$S and S –containing environments safely and with expectation of long service life if care is given to the materials selection at the beginning of a project.
REFERENCES


17. Rhodes P.R., “Corrosion Mechanism of Carbon Steel in Aqueous H2S Solutions”, The Electrochemical Society, Inc, held in Las Vegas, Nevada, Fall 1976


Figure 1 – Corrosion product layers inside the pits including a thin FeCl$_2$ layer.

Figure 2 – Corrosion rate of steel (mpy) in S as a function of pH and chloride content. (Hyne et al.). Corrosion rate in mm/y is mpy figure divided by 39.37.
Figure 3 – Corrosion rate of steel in a S–containing environment as a function of pH and chloride content of the fluid. (Hyne et al.).

Figure 4 – Effect of chloride concentration on corrosion of steel in solution of S/NaCl at room temperature (Kuster et al.).
Figure 5 - Schematic current/potential curves for cathodic catalysis (a) and anodic catalysis (b)
Figure 6- Corrosion rate of three alloys in a sour environment containing S at two different temperatures. Note that the vertical line denotes the transition from gaseous to solid/liquid sulfur.
Figure 7- Effect of S on Corrosion Rate of SM 2550

Figure 8 – Effect of temperature on the solubility of S in water.
Figure 9 – Effect of NaCl concentration on the corrosion and cracking of alloys 825 and 625 in an environment containing S.

Figure 10 – SCC resistance of Alloy G50 (UNS N06950), Alloy 2550 (UNS N06255) and Alloy G3 (UNS N06985) as a function of chloride content in an environment containing S.
Figure 11- Suitable alloys for service in environments containing S as a function of alloy composition and temperature.