Mitigation of stress corrosion cracking of carbon steel exposed to CO-CO$_2$-H$_2$O environments through inhibitor addition

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Abstract

Purpose – This investigation aims to find the degree of passivation required to completely inhibit the stress corrosion cracking of carbon steel exposed to CO-CO$_2$-H$_2$O environments.

Design/methodology/approach – A516 pressure vessel steel was exposed to distilled water with 25 per cent CO and 75 per cent CO$_2$ at an overall pressure of 800 kPa with the introduction of potassium bichromate as an additional inhibitor. Slow strain-rate tests were performed to evaluate the steel for sensitivity to cracking. Electrochemical characteristics were investigated in parallel in order to determine the extent of passivation required with the addition of the inhibitor.

Findings – Slow strain-rate tests showed that between 100 and 1,000 ppm potassium bichromate was required to completely mitigate cracking with a significant reduction in passivation current densities.

Research limitations/implications – The chosen inhibitor is not ideal for practical applications as an inhibitor, but gave an indication of the passivation required.

Practical implications – The results showed that the added inhibitor might even cause increased sensitivity to cracking in this environment, with significant passivation required for resistance to cracking.

Originality/value – The degree of passivation required for complete resistance of carbon steel in 25 per cent CO-75 per cent CO$_2$-H$_2$O.

Keywords Inhibitors, Stress corrosion/environmentally assisted cracking

1. Introduction

Stress corrosion cracking of steel in CO-CO$_2$-H$_2$O environments is sensitive to the passivation of the steel through the adsorption of carbon monoxide onto the steel surface (Heusler and Cartledge, 1961). However, the process is also dependent upon the presence of the carbon dioxide to form as a corrosive carbonic acid environment (Schmitt, 1983). These two components, the adsorbing carbon monoxide and the corrosive carbon dioxide, both contribute to the stress corrosion process, the one inhibiting the corrosion process and the other enhancing the corrosion of the carbon steel (Brown *et al.*, 1970; Kowaka and Nagata, 1976).

Stress corrosion cracking can be mitigated by the addition of inhibitors. Berry and Payer (1979) worked on stress corrosion cracking of pipeline steels undertaking screening tests of inhibitors for stress corrosion cracking in a $1N$ Na$_2$CO$_3$ + $1N$ NaHCO$_3$. A whole range of inhibitors were tested at the potential of most severe SCC in the base solution.

Those chemicals found to be effective were tested over a wide potential range to determine if they were true inhibitors or acted by simply shifting the critical potential range for SCC. They found several chromates, potassium silicate, and several phosphates were effective SCC inhibitors. Potassium bichromate inhibited cracking and although chromates are classified as "unsafe" corrosion inhibitors, where insufficient amounts accelerate corrosion, potassium bichromate was tested at low concentrations and no enhanced cracking was seen.

Heaver worked on inhibitors that would specifically enhance the passivity of the steel, but the results were not satisfactory and only at 5,000 ppm was cracking inhibited.

2. Experimental procedure

2.1 Material

The steel used throughout the study was A516 pressure vessel steel, with the composition shown in Table I. The composition was determined by using: Leco Carbon/Sulphur Analysers, 3460 Emission Spectrometer and 8680 + 72RET XRF spectrometers.

Table I The A516 pressure vessel steel composition

Element	Al	B	C	Co	Cr	Cu	V	Mn
wt.%	0.009	0.002	0.217	0.010	0.010	0.010	0.010	1.030
Element	Mo	N_2	Nb	Ni	P	S	Ti	Si
wt.%	0.010	0.007	0.004	0.020	0.009	0.003	0.001	0.290

2.2 Slow strain-rate test

Stress corrosion cracking was evaluated by using the slow strain-rate method according to ISO 7539-7 (ASTM E8), with the initial slow strain-rate being $10^{-6} s^{-1}$. A schematic drawing of the test rig used is shown in Figure 1.

The environment consisted of distilled water saturated with a CO/CO_2 gas mixture. Small-sized specimens proportional to the standard specimen according to ASTM Standard E8 for cylindrical tensile test specimens were used, with a diameter of 4.0 mm and a reduced section length of 22.5 mm, slightly longer than the standard which is at 19.0 mm. This variation on the standard specimen size were used in order to compare with earlier tests that were performed on this slightly longer gauge length. A schematic drawing of the tensile specimen is shown in Figure 2.

2.3 Experimental procedure

The water/gas mixture was prepared in a stainless steel pressure vessel of approximately 160 l. This setup also was used for the other laboratory tests performed during this study. The pressure vessel was filled with distilled water and purged with nitrogen for long enough to ensure that the dissolved oxygen concentration was below 0.1 ppm. Following the nitrogen purge, the test solution was purged with the appropriate gas mixture for approximately 20 min, and thereafter the vessel was sealed and pressurised to the required level. Most of the experiments for the slow strain-rate tests were performed at a pressure of 800 kPa and a gas composition of 25 per cent carbon monoxide and 75 per cent carbon dioxide. The gas mixture was prepared beforehand by a commercial gas company according to the required concentrations.

The prepared solution was transferred to the cell with the slow strain-rate tensile specimen, as shown in Figure 1. The solution was allowed to flow through this unit to ensure that the same conditions were achieved in the environment of the tensile specimen. The temperature was measured with a K-type thermocouple that was introduced into the autoclave with a Swagelock© fitting and the temperature was controlled by a temperature controller that regulated a heating element that was wrapped around the autoclave. The pressure in the slow strain-rate autoclave was measured with a pressure gauge that was also introduced into the autoclave with a 1/8″ stainless steel tube and Swagelock© fitting. Two Viton© seals were used to seal and insulate tensile specimen from the autoclave. The autoclave was manufactured from stainless steel, which would sustain insignificant corrosion with very little contamination. Each tensile specimen was further insulated from the test rig at the pulling rod ends to ensure

Figure 1 A schematic presentation of the tensile specimen in the autoclave that was used for the slow strain-rate test
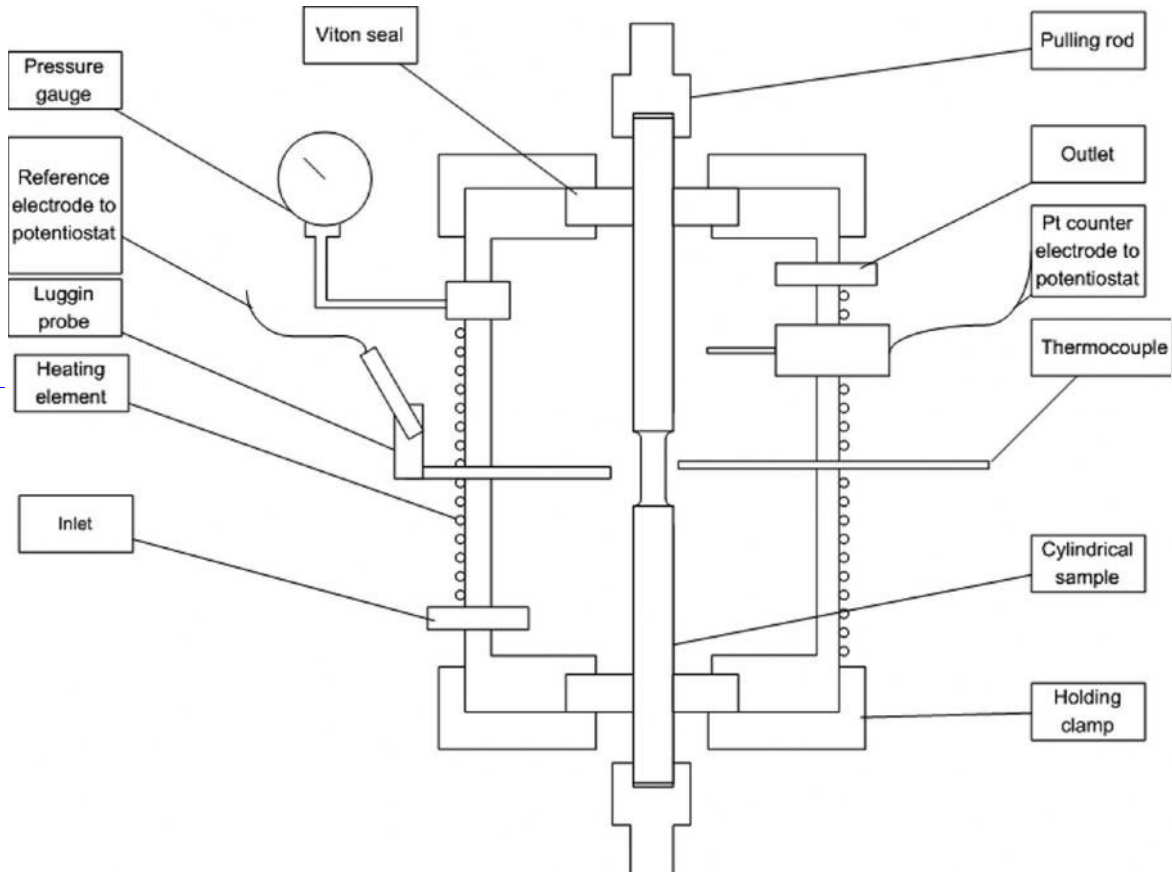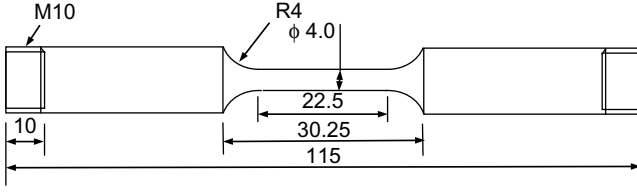
Figure 2 The configuration of the tensile specimen used

that no galvanic cell was formed between the stainless steel autoclave and the carbon steel specimen.

With most of the tests, unless otherwise noted, the specimen was installed in the autoclave, after which the autoclave was filled with the solution and the test was started shortly afterwards. The tensile specimen was slightly pre-stressed to ensure that no time was wasted during the tensioning of the frame and pulling rods, as the strain-rate was low and this would have increased the duration of the test considerably.

The specimen was measured beforehand with a Vernier calliper in terms of its gauge length and original diameter. The accuracy of these measurements was to the nearest 0.1 mm, according to the accuracy of the Vernier calliper. The gauge length measurements were made from shoulder to shoulder on the tensile specimen, which included the radii where no elongation would be expected, but these positions were the best defined and consistent on all the specimens. The original and final diameters were measured, and the final diameter, after the test, was measured by carefully re-joining the two fractured pieces. This measurement was difficult and the accuracy disputable with a definite higher margin of error. Here the lengths of the two fractured sections were measured as l_1 and l_2, therefore l_f, the final length of the specimen was:

$$l_{final} = l_1 + l_2 \qquad (1)$$

The elongation of the specimen was calculated as follows:

$$Elongation = \frac{l_{final} - l_0}{l_0} \times 100 \qquad (2)$$

where l_0 was the original length of the specimen, measured from shoulder to shoulder. The reduction in area was given by:

$$Reduction\ in\ area = \frac{d_0^2 - d_{final}^2}{d_0^2} \times 100 \qquad (3)$$

where d_0 was the original diameter, and d_{final} the final diameter of the gauge length of the sample.

The slow strain-rate test technique was used as a screening test to establish whether any inhibition of cracking occurred or not for varying inhibitor concentrations.

The tests were done in 25 per cent carbon monoxide and 75 per cent carbon dioxide at 800 kPa and 45°C. Distilled water was used and was not de-aerated. This environment was chosen as a sufficiently severe environment for stress corrosion cracking susceptibility, as was seen from previous work (Van der Merwe, 2012).
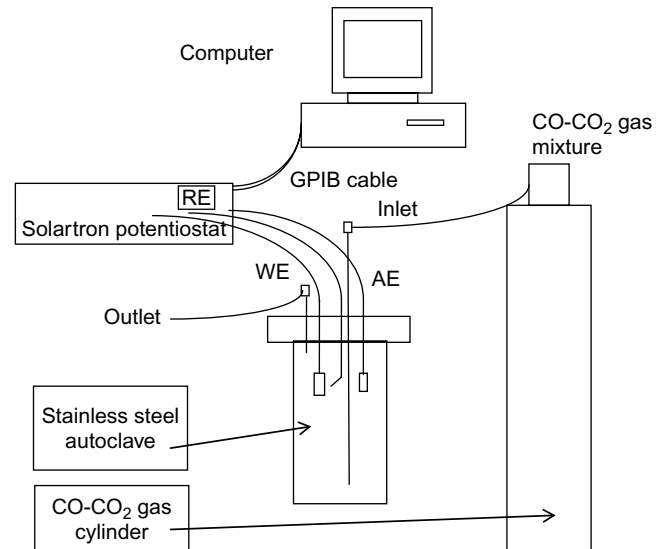
2.4 Potentiodynamic tests
A Solartron instrument was used to undertake the potentiodynamic tests on the steel specimens; the same steel was used as described in Table I. A three electrode system was used: working, auxiliary and reference electrodes. A silver/silver

chloride reference electrode with a Luggin probe was used with a Na_2SO_4 solution as the conducting medium. Figure 3 is a schematic diagram of the entire setup. The working electrode (WE) consisted of a specimen mounted in an epoxy resin, the auxiliary electrode (AE) was in the form of a platinum wire and all of the electrodes introduced into the autoclave through the top lid were properly insulated. The tests were performed inside a Parr© autoclave, which was manufactured from 316L stainless steel, and the solution was contained in a full length glass beaker contained inside the stainless steel autoclave. This beaker almost reached the lid of the autoclave. Temperature was measured with a thermocouple that was positioned close to the WE, and was controlled by immersing the autoclave into a constant temperature water bath. The connections to the autoclave were all Swagelok© fittings, or similar, and the autoclave itself had a Teflon O-ring, which ensured that no leakage was possible.

2.5 Potentiodynamic procedure
A 0.7 M $KClO_4$ solution was used as an electrolyte, to ensure better conductivity than distilled water only without contributing to the cracking process. The electrolyte was de-aerated before it was used to eliminate the influence of dissolved oxygen, therefore simplifying the corrosion reactions. The appropriate gas mixture was bubbled through the electrolyte for 30 min and then was pressurised in an autoclave to establish equilibrium. A steel specimen with an area of 1 cm^2 was used and, for every test, the specimen was ground to a 600 grit finish and dried afterwards. The tests were performed at 0.1 mV/s. The gas composition used comprised 25 per cent carbon monoxide and 75 per cent carbon dioxide. The autoclave was pressurised to 800 kPa and this was maintained for 30 min before testing commenced and the test temperature was 45°C. The holding period from the time that the sample was exposed to the solution, before the test was started, was varied, and a number of holding times were investigated, namely: no holding time, 5 min, 1 and 5 h. The inhibitor concentrations investigated were: 10, 100 and 1,000 ppm. As stress corrosion in the current system is dependent upon the presence of the film, this is a very helpful technique to establish the nature, potential

Figure 3 The experimental setup for the polarisation tests

range and inhibition of the passivation reaction. The use of anodic polarisation curves and related measurements is discussed in ASTM G-5 (ASTM G5-94, 2010).

3. Results

3.1 Inhibitor concentrations
Tests were performed over a range of inhibitor concentrations from 10 to 1,000 ppm potassium bichromate, as shown in Table II. No cracking occurred for the concentrations higher than approximately 300 ppm $K_2Cr_2O_7$, severe cracking occurred for concentrations of lower than 80 ppm, and above 100 ppm the cracking decreased dramatically. These results are shown graphically in Figure 4, indicating the region where inhibition concentration became sufficient to inhibit cracking.

3.2 Polarisation characteristics
The influence of environment on the passivity of the steel was investigated by the use of polarisation characteristics in order to determine if this could give any insight into the cracking process as shown by Brown *et al.* (1970). Thus, the extent of the passive region, as well as any change in the corrosion potential, were investigated with varying concentrations of the appropriate inhibitor.
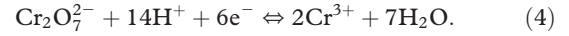
The water was not de-aerated and the same levels of potassium bichromate were used as for the slow strain-rate tests. Additionally $0.007 N$ ClO_4^- was used to lower the solution resistance. A scan rate of $0.1 mV.s^{-1}$ was used. In Figure 5, the polarisation characteristics are shown for a test that was done with no inhibitor added to the water. In the same figure, the polarisation characteristics of samples tested in varying degrees of added inhibitor are shown. It was observed that increased inhibitor concentrations decreased the current density measured for the measured electrochemical potential. However, the corrosion potential that was measured for these tests also increased with increasing inhibitor concentration.

4. Discussion

The inhibitor trials showed a remarkable increase in resistance to stress corrosion cracking, after significant passivation had taken place.

Potassium bichromate was included as a classical passivator which means that the anodic reaction was greatly retarded, but it can also be classified as a mixed inhibitor because the cathodic reaction also was retarded. The reduction of bichromate ions only started at potentials more negative

than -0.6 to $-0.8 V$, rather than at the values that might have been expected on the basis of the oxidation-reduction potential of the reaction:

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \Leftrightarrow 2Cr^{3+} + 7H_2O. \qquad (4)$$

The equilibrium potential of this reaction is $\varphi_{pH=0}^0 = +1.33 V$; however, the reaction proceeded with a large overpotential. The anodic polarisation of steel in a solution containing $0.1 g/l$ of potassium bichromate was more negative than in the initial electrolyte. The rates of dissolution of steel at given potentials, in the range 0.25-0.5 V, increased by two or three orders of magnitude as a result of a preliminary adsorption of potassium bichromate (1.5 g/l or more) and the electrode potential remained in the passive region as the current density was reduced. The effect of the chromates was due to retardation of the rates of both electrochemical reactions, but in particular the anodic reaction. Thus, chromates can be classified electrochemically as inhibitors of the mixed type.

The inhibition process caused two reactions to take place. First, the anodic reaction was inhibited, and second, the electrochemical potential was moved to more positive potentials. It would seem that both of these reactions are necessary for the mitigation process. The passivation observed from these tests was considerable. As the inhibitor concentration was increased by an order of magnitude, the level of the passivated anodic current density also decreased by almost an order of magnitude, to as low as $2 \times 10^{-6} A/cm^2$ for an inhibitor concentration of 1,000 ppm. As seen from the results of the slow strain-rate tests, no stress corrosion cracking was seen with potassium bichromate additions of more than 400 ppm, and it decreased with concentrations above 100 ppm. The necessity for crack inhibition was seen in the difference of these three polarisation characteristics. The polarisation characteristics of the steel that was introduced into the medium and held at the open circuit potential for a specific period showed a definite time dependence in the polarisaion characteristics.

However, from the work of Heaver (1994), Petrotec 1420 was the only inhibitor that mitigated cracking effectively, although at a high concentration of 5,000 ppm, the polarisation characteristics of this inhibitor showed that the corrosion potential was moved nearly 150 mV more positive. Whereas, for the other inhibitors that were tested, they influenced only the passivity of the steel in the solution and not also the corrosion potential. This could have polarised the steel out of the stress corrosion sensitivity region.

The inhibiting properties of chromates consist not so much in a retardation of the reduction of oxygen as in the ability to reduce the rate of the anodic reaction. This passivation reaction was strongly driven to inhibit the corrosion reaction on the surface of the steel, as enhanced by the presence of carbonic acid. However, due to the fact that the chromate ions also acted as an inhibiting agent, the stress corrosion reaction was enhanced when inhibition did not occur completely. Thus, the reaction may even be aggravated in the presence of low concentrations of potassium bichromate, as indicated by polarisation of the anodic curve. In consequence, potassium bichromate was considered to be a dangerous inhibitor.

Table II The results of the slow strain-rate tests performed in 25 per cent CO-75 per cent CO_2-H_2O at 45°C

$K_2Cr_2O_7$ (ppm)	Elongation (%)	Reduction in area (%)
1,000	29	70
100	31	70
87	22	42
73	19	26
60	20	23
30	19	38
10	16	30
200	20	44

Figure 4 The results of slow strain-rate tests that was done at 45°C and 8 ppm O₂ with different potassium bichromate levels

Slow strain-rate test
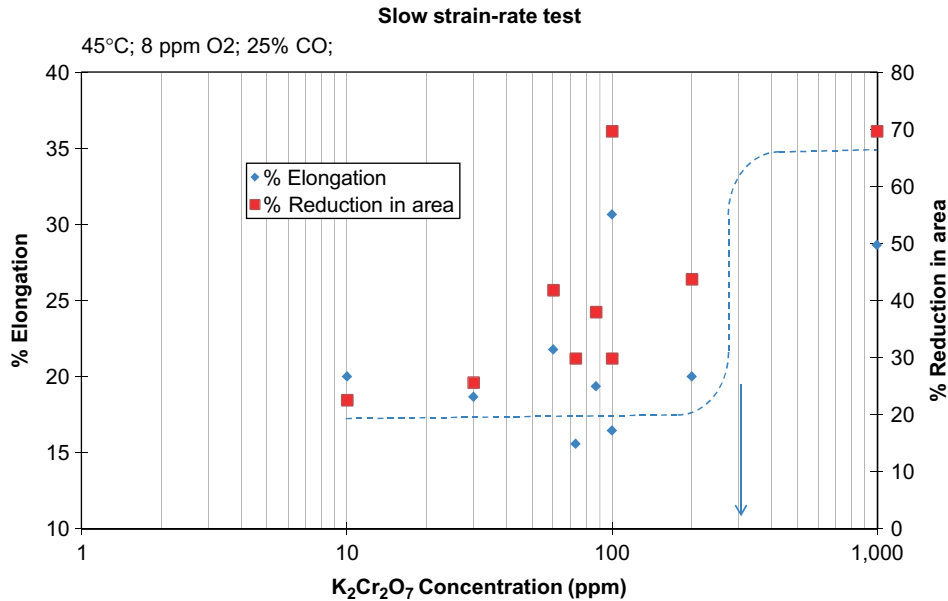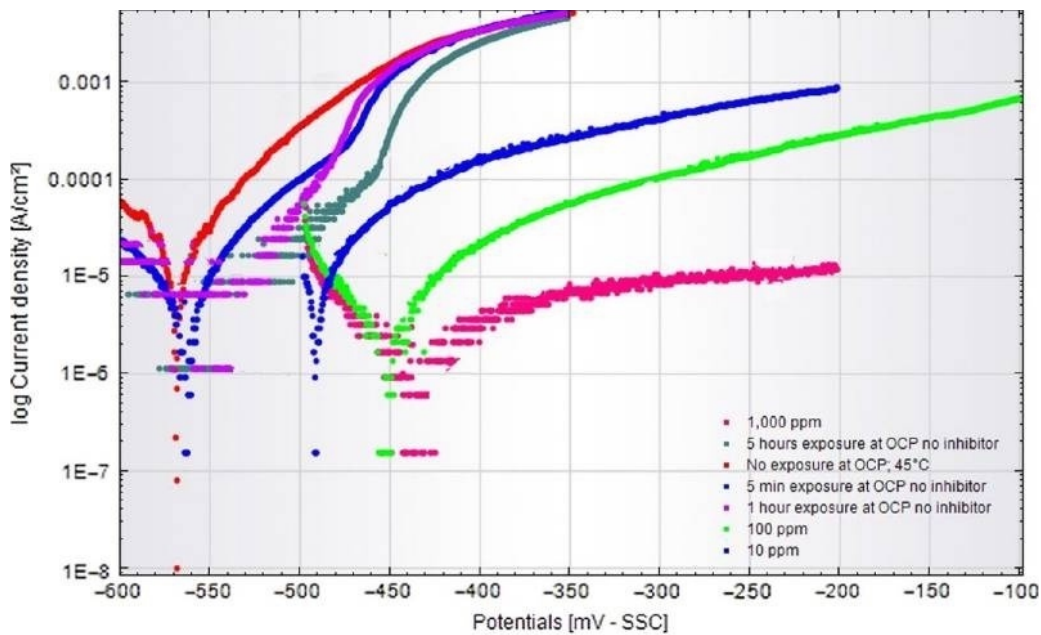
45°C; 8 ppm O2; 25% CO;

Figure 5 The polarization characteristics of a 25 per cent CO gas mixture with varying amounts of inhibitor

Note: The curves without inhibitor indicate the effect of exposure time, and all these tests were performed in a low dissolved oxygen concentration

5. Concluding remarks

- A concentration of more than 200-1,000 ppm potasium bichromate is required to mitigate stress corrosion cracking of carbon steel in wet CO/CO₂ environments.
- The passivation that occurred significantly lowered the passive current density.
- The inhibition of stress corrosion was achieved only after an order of magnitude reduction in the current density of the passive region.

References

ASTM G5-94 (2010), "Standard reference test method for making potentiostatic and potentiodynamic anodic polarization measurements", *Annual Book of ASTM Standards 2010/ASTM International*, Vol. 3.2, ASTM, West Conshohocken, PA, Section 3.

Berry, W.E. and Payer, J.H. (1979), "Internal stress corrosion cracking by aqueous solutions of CO and CO₂", *Sixth Symposium on Line Pipe Research; Pipeline Research Committee of American Gas Association, Houston, TX*, pp. 251-268.

Brown, A., Harrison, J.T. and Wilkins, R. (1970), "Transgranular stress corrosion cracking of ferritic steels", *Corrosion Science*, Vol. 10, p. 547.

Heaver, E.E. (1994), "Stress corrosion cracking of steels in industrial process environments", PhD thesis, University of Pretoria, Pretoria.

Heusler, K.E. and Cartledge, G.H. (1961), "The influence of iodide ions and carbon monoxide on the anodic dissolution of active iron", *Journal of the Electrochemical Society*, Vol. 108 No. 8, pp. 732-740.

Kowaka, M. and Nagata, S. (1976), "Stress corrosion cracking of mild and low alloy steels in CO-CO_2-H_2O environments", *Corrosion*, Vol. 32 No. 10, p. 396.

Schmitt, G. (1983), "Fundamental aspects of CO_2 corrosion", Corrosion '83, Paper 43.

Van der Merwe, J.W. (2012), "Environmental and material influences on the stress corrosion cracking of steel in H_2O-CO-CO_2 solutions", *International Journal of Corrosion*, p. 4.

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