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Influence of solution chemistry and surface condition on the critical inhibitor concentration for solutions typical of hot potassium carbonate CO_2 removal plant

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Abstract This research studied the influence of steel surface condition and solution chemistry on the critical inhibitor concentration required for spontaneous passivation of carbon steel in solutions typical of hot potassium carbonate plant (HPC). The inhibitor was added to the solution as V_2O_5. The critical inhibitor concentration depended on solution composition and on the steel surface condition. An inhibitor concentration of 30 g/l may be required to ensure spontaneous passivation under all conditions. The spontaneous passivation of clean polished carbon steel surfaces required a critical inhibitor concentration of 0.5–1.8 g/l. A minimum level of V^{5+} is required for inhibition, so that monitoring the V^{5+} concentration may be crucial to successfully managing corrosion protection in plant.

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Introduction

HPC plant

The Benfield process, used in more than 600 plants worldwide, is based on an aqueous solution of potassium carbonate, vanadate as an anodic inhibitor and typically an amine as an accelerant [1]. (The function of the amine accelerant is explained below). Such hot potassium carbonate (HPC) plant is used to remove unwanted gaseous species, particularly CO_2 and H_2S, from gas streams such as raw natural gas. For example, raw natural gas from central Australia containing typically 20 mol% CO_2 and 20 ppm H_2S [2] is processed to produce sales quality gas with a CO_2 concentration below 2 mol% and a H_2S concentration below 2 ppm. The typical solution concentration, $C_{eqv.wt\%K_2CO_3}$ (expressed as equivalent wt% potassium carbonate), is 27 eqv. wt% K_2CO_3 and is calculated via the following expression:

$$C_{eqv.wt\%K_2CO_3} = C_{K_2CO_3} + 0.691\ C_{KHCO_3} \qquad (1)$$

where $C_{K_2CO_3}$ is the concentration of K_2CO_3 (in wt%) and C_{KHCO_3} is the concentration of $KHCO_3$ (in wt%). A HPC plant comprises a closed circuit, consisting of an absorber vessel, a regenerator vessel and associated connecting pipes, pumps and valves. In the absorber vessel, at a pressure of approximately 70 bar, the upward flowing raw natural gas containing CO_2 and H_2S contacts the down flowing potassium carbonate solution in a counter current flow. Potassium carbonate absorbs CO_2 and is converted to potassium bicarbonate by the following reaction (wherein the amine accelerates the speed of this reaction):

$$K_2CO_3(aq) + H_2O(l) + CO_2(aq) \leftrightarrow 2KHCO_3(aq). \qquad (2)$$

The fraction conversion, F_C, is expressed as,

$$F_C = 1 - (C_{K_2CO_3} / C_{eqv.wt\%K_2CO_3}). \quad (3)$$

$F_C = 0.0$ for pure K_2CO_3 and $F_C = 1.0$ for pure $KHCO_3$. The H_2S in the natural gas is oxidised to thiosulfate and sulfate and the solution may accumulate concentrations of 20 wt% thiosulfate and 1.5 wt% sulfate. Chlorides are also present stemming from the plant make-up water. The measured minimum, maximum and nominal plant chloride concentrations in a typical HPC plant have been reported to be 0.004, 0.08 and 0.015 wt% respectively [3]. The solution exiting the bottom of the absorber vessel is known as the rich solution; it has absorbed CO_2 and has a typical F_C of 0.9. This solution undergoes a pressure reduction as it leaves the absorber and enters the regenerator at close to atmospheric pressure. The CO_2 concentration in solution decreases with decreased partial pressure of CO_2. CO_2 is further stripped from the solution by contact of the solution with steam in the regenerator vessel. The CO_2 is vented to the atmosphere from the top of the regenerator. The regenerated solution, known as the lean solution with a typical $F_C = 0.4$, is recycled back to the top of the absorber vessel. The solution circuit is a closed loop, except for blow down to manage solids loading.

The solutions in the HPC plant are corrosive to the pressure vessel steel due to the high CO_2 concentrations, the highly concentrated solutions, the high temperatures and the high pressures. Consequently, HPC plants have been specified [1, 2, 4] to operate with an anodic inhibitor in order to maintain a protective magnetite passive film on the steel surface. The anodic inhibitor is usually added to the solution as vanadium pentoxide, V_2O_5. It dissolves to form vanadate ions, with the vanadium in its highest oxidation state, the V^{5+} pentavalent state. The reduction of pentavalent vanadium V^{5+} to the lower tetravalent V^{4+} state can passivate the steel surface by anodic oxidation of the iron to magnetite [5]. The concentrations of V^{5+} and V^{4+} are not often measured in plant due to the difficulty in measurement [2].

Corrosion failures in HPC plant have been attributed [5–8] by many operators to localised corrosion caused by passivity breakdown. Passivity breakdown in turn has been attributed [5–8] to inadequate inhibitor concentration at the steel surface (due to poor solution-steel ''wetting'' or poor inhibitor management); the presence of de-passivating ions such as chlorides, thiosulfates and sulfates; erosion due to solution turbulence and high solids loading; mechanical scraping due to loose hardware (e.g., distributor trays) and the erosive effect of froth bubbles imploding on the passivated surface.

Anodic inhibition in HPC plant

It is desired that the carbon steel surfaces passivate spontaneously. An inhibitor concentration below the critical inhibitor concentration required for spontaneous passivation can accelerate corrosion or can create borderline passivity [9]. Both are undesirable for plant integrity. Figure 1a presents schematically the anodic polarisation curve (A) and cathodic polarisation curve (C) for borderline passivity, and Fig. 1b present the curve that would actually be measured. The steel can be either active or passive. Borderline passivity is particularly dangerous as damage to a passive surface can cause an unpredictable shift from the passive to the active state.

This means that for spontaneous passivity the inhibitor concentration should be such that: (1) the inhibitor should provide a potential more noble than the primary passivating potential of the steel and (2) the rate of inhibitor reduction should provide sufficient current to exceed the anodic current density of the active to passive peak to ensure spontaneous passivation.

The specification of anodic inhibition for HPC plants originated from the work of Bienstock and Field [4] who investigated the inhibition of the hot carbonate solutions. Vanadates were found to reduce the corrosion rate of steel to 0.0025 mm/y if present at a concentration of 2,000 ppm. The recommended inhibitor concentration was specified in an original plant HPC manual [2] to be 0.7–0.8 wt% (equivalent to approximately 10 g/l). Leeds [10] also measured the required inhibitor concentration. Leeds [10] measured the critical inhibitor concentration to be between 0.8 and 1.8 g/l and suggested that a concentration of 3 g/l would provide a sufficient safety margin to cover all variations in operating conditions.

However, the original inhibitor study of Bienstock and Field [4] and the subsequent study by Leeds [10] did not investigate the influence of surface state (pitted, creviced, oxidised, scaled). Riggs [11] found that the passivation of a corroded steel surface covered with corrosion product

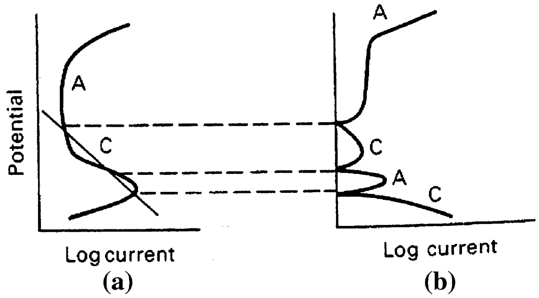


Fig. 1 (**a**) presents schematically the anodic polarisation curve (A) and cathodic polarisation curve (C) for borderline passivity, and (**b**) present the curve that would actually be measured [9]

required an inhibitor concentration greater than that required for a clean steel surface. Similarly, Lunarska and Szypowski [12] investigated the influence of solution chemistry and surface condition. Their study [12] showed that the required inhibitor concentrations ranged from 10 to 35 g/l. This is important for plant operations that passivate large vessels following shutdowns or process trips. Plant operations may not prepare the carbon steel surfaces to the same standard as in laboratory experiments. The carbon steel surfaces may be covered by corrosion products and there may be areas of pitting. Although caustic washing is recommended [13] prior to passivation, some plant operations may not adhere to this recommended practice. Furthermore, the passivation process itself may initially cause corrosion and not spontaneous passivation if the passivation process is commenced by circulating a solution that does not immediately provide adequate inhibition to cause spontaneous passivation throughout the plant.

Aim of research

This study aimed to measure the critical inhibitor concentration required to spontaneously passivate a carbon steel surface exposed to potassium carbonate solutions typical of HPC plant. In particular, the study aimed to clarify the influence of:

- the total carbonate concentration,
- the fraction conversion,
- the presence of aggressive species, including chlorides
- the presence of amines,
- the steel surface condition, and
- the oxidation state of the inhibitor.

The influence of chloride ions is addressed in a separate study [14].

Experimental method

Critical inhibitor concentration

Immersion of a steel surface in an adequately inhibiting solution leads to spontaneous passivation of the steel surface and the free corrosion potential of the steel has a high (positive or noble) value characteristic of passivity [15]. The critical inhibitor concentration necessary to achieve spontaneous passivity can be determined by measuring the steady-state free corrosion potential as a function of inhibitor concentration. A large change in potential in the noble direction occurs at the critical inhibitor concentration [16] as the surface changes from the active state to the passive state. The critical inhibitor concentration was measured in this study using two techniques referred to as static inhibition and dynamic inhibition. These techniques measured the critical inhibitor concentration to spontaneously passivate a polished steel surface and an actively corroding steel surface respectively.

Static inhibition—Clean surface inhibition

The free corrosion potential, E_{corr}, was recorded over a 2 h period for a freshly polished carbon steel sample in a solution containing a nominated amount of the anodic inhibitor, vanadium pentoxide. The linear polarisation resistance (LPR) was measured at the end of the 2 h immersion period. Measurements were repeated with freshly polished steel samples in solutions with increasing inhibitor concentrations until a significant shift in the corrosion potential was measured and the LPR indicated a significant decrease in corrosion rate indicative of passivation. Inhibitor concentrations from 0 to 30 g/l were studied.

Dynamic inhibition—Corroding surface inhibition

The free corrosion potential was measured for a freshly polished steel sample immersed in un-inhibited solution, and a set amount of the anodic inhibitor, vanadium pentoxide, was added at 3 min intervals. Inhibitor concentrations from 0 to 35 g/l were studied. The critical inhibitor concentration was evaluated as that causing an increase in the corrosion potential, from the active to the passive region, as illustrated in Fig. 2. The time interval of 3 min was chosen to represent spontaneous passivation. This dynamic inhibition technique [17, 18] simulated a corroding surface within a HPC plant. This technique caused corrosion during its initial stages when the sample was exposed to an inhibitor concentration below that required for spontaneous passivation. This test therefore measured the critical inhibitor concentration for a corroding surface.

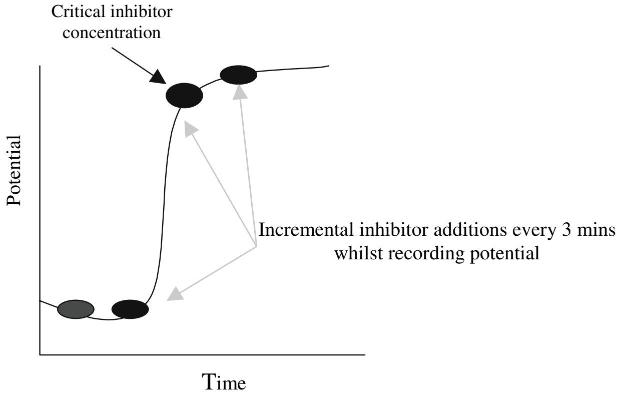


Fig. 2 The dynamic inhibition technique to measure the critical inhibitor concentration [17, 18]

Apparatus

Experiments were carried out in a conventional three-electrode cell consisting of the carbon steel working electrode, a platinum plate counter electrode and a saturated Ag/AgCl reference electrode. A luggin capillary was used to prevent contamination of the test solution with KCl from the reference electrode solution. Potentials were measured with respect to a saturated Ag/AgCl reference electrode and are reported in terms of a standard hydrogen electrode. The capacity of the cell was approximately 1 l. There was negligible change in solution composition and solution pH as the solution volume was large compared with the size of the specimen and as the experiments were of relatively short duration.

Working electrode

For each experiment an ASTM grade A53 carbon steel sample of dimensions 10 mm × 10 mm × 5 mm was polished with successively finer silicon carbide papers from 300 grit to 1,200, washed in acetone in an ultrasonic bath for 2 min and secured by means of a metal screw to the back of the sample onto a glass working electrode holder, which allowed an electrical contact between the to the back of each specimen and the potentiostat. The screw was insulated from the solution by means of an ''o'' ring.

Test solutions

The solutions concentrations are given in Table 1. All solutions were made with reagent grade chemicals and deionised water. All experiments were carried out in solutions that were de-aerated by sparging with CO_2 and at a temperature of 95 °C. The anodic inhibitor was added to the solution as V_2O_5, which dissolved to produce vanadium in the +5 oxidation state.

The rich solution and the lean solution simulated, respectively, concentrations indicative of the rich solution and lean solution in an absorber tower with a total carbonate concentration of 29 eqv. wt% K_2CO_3. The rich + aggressive species solution had chloride, thiosulfate and sulfate concentrations comparable to those found in a typical HPC plant. Two typical amines were studied: diethanolamine, DEA, (branch structured molecule, $HN(CH_2–CH_2–OH)_2$) and piperazine (ring structured molecule, $(CH_2)_4(NH)_2$) [19]. Amines improve solution absorption performance by lowering the solution CO_2 vapour pressure to well below the gas CO_2 vapour pressure. The differential in the respective CO_2 vapour pressures assists with CO_2 absorption from the gas to solution [20]. The amines having greater than 99% purity were obtained from E. Merck. The half strength solution represents a typical start-up potassium-carbonate solution used for plant passivation.

The solutions studied (with the exception of the half strength lean solution) were chosen to give insights into typical HPC plant operation. In contrast, the half strength lean solution was included in order to study such a solution should it be used during plant passivation.

Linear polarisation resistance

The linear polarisation resistance [R_p in Ohms] was evaluated from $R_p = \Delta V/\Delta I$, where ΔV was 40 mV and ΔI was the measured change in current when the working electrode was polarised from E_{corr}—20 mV to E_{corr} + 20 mV at a scan rate of 0.166 mV/s. The applied potential plotted against the current gave a relatively straight line. The corrosion current density, I_{corr} [in A/cm^2], was evaluated using the Stern-Geary equation:

$$I_{corr} = \beta_\alpha \times \beta_c / 2.303 \times R_p(\beta_a + \beta_c),$$

which for $\beta_a = \beta_c$ is:

$$I_{corr} = 0.217/R_p$$

where β_a and β_c are the anodic and the cathodic Tafel constants (in V/decade of current). The corrosion rate, R_c, (in mm/y) was calculated using:

$$R_c = (3.268 \times i_{corr} \times 10^3 \times E) / D$$

Table 1 Solution composition

Solution	F_C	$C_{K_2CO_3}$ (wt%)	C_{KHCO_3} (wt%)	$C_{eqv.wt\%K_2CO_3}$ (wt%)	pH
Rich	1.0	0	42	29	8.5
Rich + aggressive species (0.1 wt% Cl, 10 wt% thiosulfate, 1 wt% SO_4)	1.0	0	42	29	8.5
Rich + 0.5 wt% piperazine	1.0	0	42	29	8.7
Rich + 0.5 wt% DEA	1.0	0	42	29	8.8
Lean	0.46	16	19	29	9.2
Half strength lean	0	13	0	13	10.7

where E is the equivalent weight of the corroding species (Fe) and D is the density of the steel sample (in g/cm^3).

Polarisation curves

Potentiodynamic polarisation curves were measured starting from a significant cathodic current and sweeping in a positive direction to +1,000 mV vs Ag/AgCl at a scan rate of 0.166 mV/s. The curves were measured without anodic inhibitor since its presence distorts the shape of the measured curve [21].

Immersion in Benfield solution

A sample of process solution from a Benfield plant was received with a blue-green colour. The composition of this solution was not analysed; however the Benfield solution has a typical concentration of 27 eqv. wt% K_2CO_3 and may accumulate concentrations of 20 wt% thiosulfate, 1.5 wt% sulfate and 0.08 wt% chloride. The solution colour is determined by the amount and oxidation state of the of the vanadium inhibitor.

This sample was divided into two. One was left at its blue-green colour. The other was aerated for 2 days and its colour changed to yellow, indicating that the vanadium in the V^{4+} state had been oxidised to the V^{5+} state [22]. It was expected that the air exposure would cause negligible change in other aspects of the solution; the solution concentration and the relative amounts of the other solution constituents would remain the same.

Polished ASTM grade A53 carbon steel samples were immersed in these yellow and blue-green solutions at 100 °C for 2 h. The surface appearance of both samples were observed and compared.

Results

Polarisation curves

The polarisation curves are presented in Fig. 3. Table 2 presents the critical parameters for passivation: the primary passivating potential, E_{pp}, the critical current density, i_{crit}, and the passive current density, i_{pass}.

Dynamic inhibition

Figure 4 presents the measurements from the dynamic inhibition technique. For each curve there was a significant increase in potential at the critical inhibitor concentration.

Static inhibition

Figure 5 presents typical curves for the free corrosion potential. Figure 6 presents a summary of the free corrosion potential values, obtained from the 2 h immersion tests. Table 3 presents the corrosion rate as determined from the LPR method. There was a marked decrease in the corrosion rate at the critical inhibitor concentration.

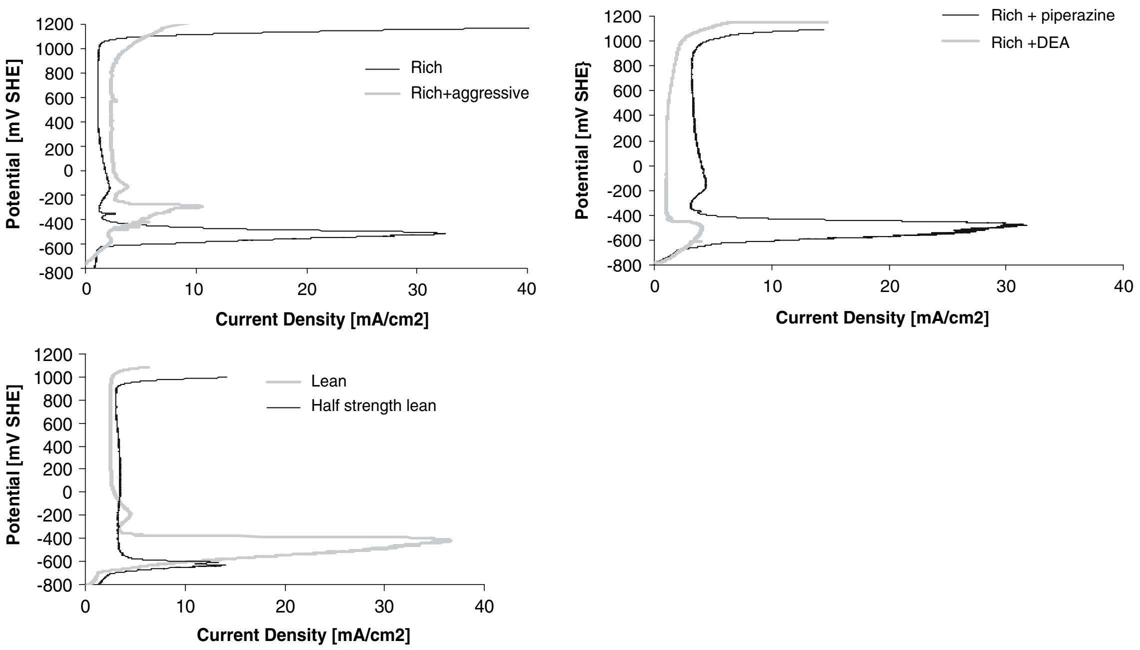


Fig. 3 Polarisation curves for ASTM grade A53 carbon steel in various solutions with CO_2 purging at 95 °C

Table 2 Passivation parameters from the anodic polarisation curves presented in Fig. 3

Solution	E_{pp} (mV SHE)	I_{crit} (mA/cm^2)	I_{pass} (mA/cm^2)
Rich	–518	33	1.1
Rich + Aggressive Species (90 ppm H_2S, 0.1 wt%Cl, 10 wt% S_2O_3, 1 wt% SO_4)	–288	11	2.3
Rich + 0.5 wt% Piperazine	–484	32	3.5
Rich + 0.5 wt% DEA	–463	3.5	1.0
Lean	–411	36	2.5
Half Strength Lean	–415	14	2.5

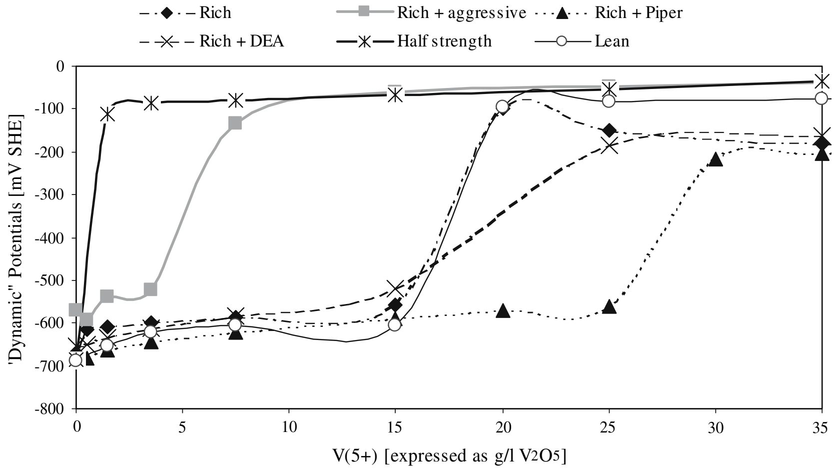


Fig. 4 Dynamic inhibition measurements for ASTM grade A53 carbon steel in solutions at 95 °C purged with CO_2

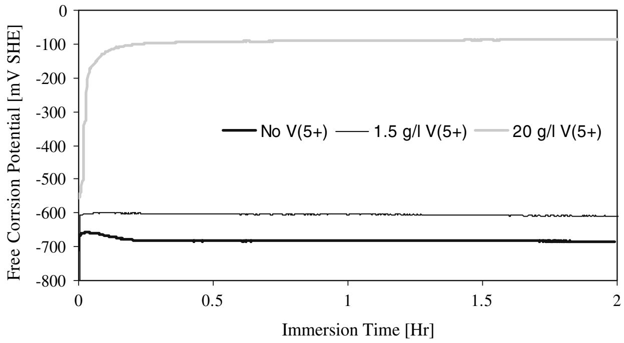


Fig. 5 Static inhibition measurements of the free corrosion potential of ASTM grade A53 carbon steel immersed in the rich solution containing the stated V^{5+} concentration, purged with CO_2 and at 95 °C

Critical inhibitor concentration

Table 4 and Fig. 7 present the critical inhibitor concentrations for spontaneous passivation as determined by the static and dynamic tests.

Immersion in Benfield solution

Immersion of the polished steel sample in the blue-green Benfield solution yielded a corroded surface with a thick, black, poorly-adhering layer which was easy to wipe off, with areas of active shiny corrosion in the form of pits. In contrast, the polished steel surface remained shiny in the yellow solution.

Discussion

Anodic polarisation curves

The polarisation curves, presented in Fig. 3, were similar to those measured in our previous research [14]. The anodic polarisation curves showed that the steel exhibited a wide passive region in all solutions, Table 1. For all the solutions, there was no spontaneous passivity; the steel was in the active state at the free corrosion potential, whereafter there was an increase in current density which occurred until the primary anodic peak at around –411 to –515 mV for most solutions, Table 2. At potentials greater than the primary peak, there was a decrease in current. The critical passivating current density for the majority of solutions was high compared with the current density required to maintain passivity. This was also measured in earlier research, the findings of which support the observation that passivation of carbon steel in hot K_2CO_3–$KHCO_3$ solutions is comparatively difficult due to the high values of the critical passivation current density [15].

Fig. 6 The free corrosion potential for ASTM A53 carbon steel as a function of inhibitor concentration for the static inhibition technique

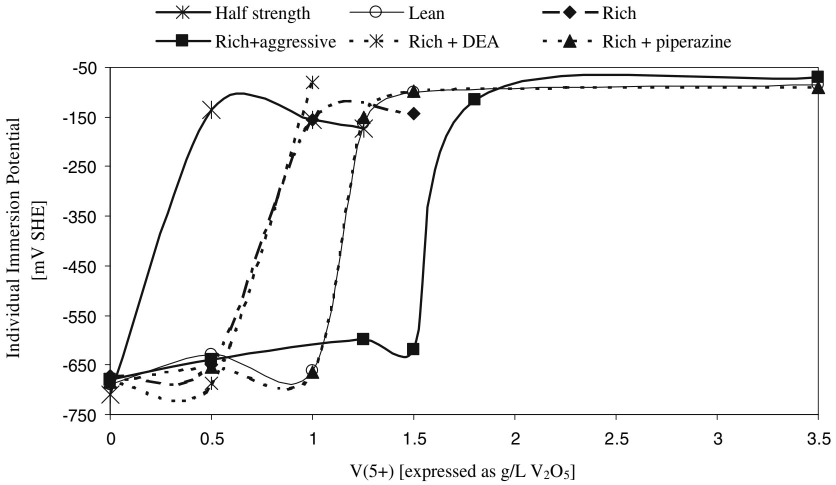


Table 3 Free corrosion potentials and corrosion rates as a function of inhibitor concentration for the various solutions for the static inhibition technique

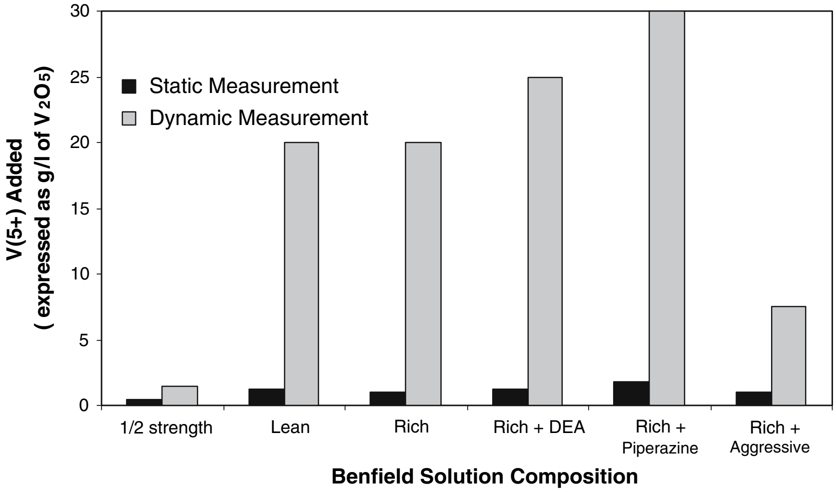
Solution	V^{5+} (g/l)	E_{corr} (mV vs SHE)	Corrosion Rate (mm/yr)
Half Strength	0	–710	0.22
	0.5	–135	0.013
Lean	0	–690	9.0
	1.25	–164	0.065
Rich	0	–671	32
	1.5	–142	1.9
Rich + Aggressive	0	–680	–
	1.8	–115	0.08
Rich + DEA	0	–681	0.3
	1.0	–80	0.028
Rich + Piperazine	0	–664	0.93
	1.25	–130	0.44

Table 4 Critical inhibitor concentration

Solution	Critical V5$^+$ concentration, (g/l)	
	Dynamic inhibition	Static inhibition
Rich	20	1.0
Rich + aggressive species	7.5	1.8
Rich + piperazine	30	1.3
Rich + DEA	25	1.0
Lean	20	1.3
Half strength lean	1.5	0.5

The presence of aggressive species in the rich solution (Table 1) shortened the passive region, as indicated by the increase in the primary passivating potential from –518 to –288 mV, Table 2. The critical current density, i_{crit}, was reduced from 33 (in the absence of aggressive ions) to 11 mA/cm^2 (in the presence of aggressive ions), Fig. 3.

Fig. 7 The critical inhibitor concentration in various carbonate solutions as determined by the static and dynamic inhibition techniques



The presence of DEA decreased the critical passivating current density by approximately 10 times to 3.5 mA/cm^2 in the rich solution + DEA compared with 33 mA/cm^2 in the rich solution (without DEA), Table 2. The other amine, piperazine, did not modify the polarisation curve to any considerable extent but did cause an increase in the passive current density from 1.1 to 3.5 mA/cm^2, Table 2.

The lean solution and the rich solution had comparable total carbonate concentrations. The polarisation curves in these two solutions were similar, Fig. 3. The passivating potential in the lean solution was almost 100 mV more noble that in the rich solution, suggesting bicarbonates have a beneficial influence on passivation.

In the half strength solution the polarisation curve indicated that the critical passivating current density was lower than in the rich and lean solutions. This suggests that passivation was easier in the less concentrated solution.

The following deductions can be made from the anodic polarisation curves:

- A decrease in the total carbonate concentration assisted passivation.
- The presence of bicarbonates assisted passivation; there was a lower critical passivating current density and a lower passivating potential.
- There was a marked difference in passivating influence of the amines DEA and piperazine. DEA assisted passivation in the rich solution.
- The presence of aggressive species shortened the passive region and increased the primary passivating potential. There was a beneficial reduction in the critical current density.

Static and dynamic inhibition

The static and dynamic inhibition techniques, using a polished and a corroding steel surface respectively, indicated that a corroding steel surface required a greater inhibitor concentration to spontaneously passivate. Table 4 and Fig. 7 show that a corroding steel surface required a critical inhibitor concentration of 7.5 to 30 g/l for spontaneous passivation in typical HPC plant solutions (and a much lower critical inhibitor concentration of 1.5 g/l in the half strength lean solution). This critical inhibitor concentration range for the corroding steel specimen was higher than that required by a polished steel surface as determined by the static inhibition tests. The static tests measured the critical inhibitor concentration to be 0.5–1.8 g/l.

The half strength lean solution required the lowest critical inhibitor concentration in both the static and dynamic tests. Furthermore the half strength solution had the most comparable critical inhibitor concentration for both the static and dynamic test indicating that in this dilute carbonate solution, there was little influence of the metal surface condition on the critical inhibitor concentration. This could be related to the low uninhibited corrosion rate of 0.22 mm/y of carbon steel in the half strength solution.

DEA assisted the passivation of carbon steel in the rich solution as deduced from the polarisation curve. Furthermore, the polarisation resistance measurements indicated that the presence of DEA in uninhibited rich solution reduced the corrosion rate of steel from 32 to 0.3 mm/y thus suggesting an inhibiting effect. In contrast, the static inhibitor tests showed that both DEA and piperazine had negligible influence on the critical inhibitor concentration required for spontaneous passivation in the rich solution, whereas the dynamic inhibitor tests showed that both the solutions containing DEA and piperazine required the highest critical inhibitor concentration. The specific chemical mechanisms for these amines is beyond the scope of the present investigation.

DEA is known to oxidise in the presence of an oxidising inhibitor [6], which means that there will be a concomitant decrease in the inhibitor concentration. It is thus possible that the presence of DEA in the plant solution could have increased the inhibitor requirements, the extent of which is unknown, but indicates that certain solution additives may contribute to anodic inhibitor consumption. Therefore, the apparent inhibiting effect of the DEA is offset by its tendency to be oxidised by the inhibitor. Piperazine, unlike DEA, was not observed to have any corrosion inhibiting properties.

The critical inhibitor concentration appeared to be influenced more by the total solution strength rather than the carbonate to bicarbonate ratio. This is deducted from the fact that the rich and lean solutions had comparable critical inhibitor concentrations despite these solutions possessing (a) different carbonate to bicarbonate ratios, and (b) the same total solution strength (29 eqv. wt% K_2CO_3). The half strength lean solution with 13 eqv. wt% K_2CO_3 had the lowest critical inhibitor concentration. This can be attributed to the lower total carbonate concentration, the absence of bicarbonate ions and a higher pH.

A corroding surface exposed to the rich solution required a greater inhibitor concentration than a comparable solution with aggressive species, Table 4. The aggressive species appeared to contribute to establishing a protective film that was analysed (in the present study) by XPS to contain oxides of iron together with sulfur species, either sulfates or sulfides. An important conclusion is that aggressive species in the solution, including a chloride concentration greater than that typical of HPC plant, did not cause an increase in critical inhibitor concentration.

The critical inhibitor concentration determined via the static inhibition technique compared favourably to literature values [4, 10] of between 0.12 and 15 g/l. Similarly, the critical inhibitor concentration determined by the dynamic inhibition technique compared favourably to the literature measurements that active corrosion may require an inhibitor concentration of up 35 g/l in concentrated carbonate–bicarbonate solutions [11, 12, 15]. These critical inhibitor concentrations are greater than current plant inhibitor concentrations [2]. It may be that the current plant inhibitor concentrations may be adequate for clean carbon steel surfaces but may not be adequate for carbon steel that has been corroded.

Immersion in Benfield solution

Immersion of the polished steel sample in the blue-green Benfield solution yielded a corroded surface with a thick, black, poorly-adhering layer which was easy to wipe off, with areas of active shiny corrosion in the form of pits. In contrast, the polished steel surface remained shiny in the yellow solution. Despite both solutions having an identical total vanadium content, the marked difference in corrosion behaviour is attributed to the relative concentrations of V^{5+} and V^{4+}. In particular, these results indicate that there needs to be a sufficient concentration of V^{5+} to have spontaneous passivation. The plant operating manuals [2] specify inhibitor levels in terms of total vanadium and the relative concentrations of V^{5+} and V^{4+} are not specified. This experiment indicated that a minimum level of V^{5+} is required for inhibition, so that monitoring the V^{5+} concentration may be crucial to successfully managing corrosion protection.

Relevance to HPC plant

The critical inhibitor concentration required to achieve spontaneous passivation was influenced by solution chemistry, the presence of amines and aggressive species and the steel surface state.

Corroding surfaces required a critical inhibitor concentration of 7.5–30 g/l of inhibitor for spontaneous passivation in typical HPC plant solutions (and a much lower critical inhibitor concentration of 1.5 g/l in the half strength lean solution).

The spontaneous passivation of a polished carbon steel surface was found to require a critical inhibitor concentration of 0.5–1.8 g/l. Providing the steel surfaces of the absorber tower are cleaned adequately following a plant shutdown, this range of inhibitor concentration is suitable for the start-up passivation procedure.

During operation it may be wise to operate with an inhibitor concentration that is suitable in all solution chemistries and that will spontaneously passivate corroding surfaces. To ensure spontaneous passivation of de-passivated areas, it is suggested that the plant inhibitor concentration be maintained at 30 g/l.

However, if this is concentration not achievable in an HPC plant, it is recommended that plant guidelines include the need to raise the inhibitor concentration (from nominal to 30 g/l) should a process upset have caused de-passivation and active corrosion. Inhibition cannot be relied upon if there is no provision to increasing the inhibitor concentration to re-passivate an actively corroding surface.

A minimum level of V^{5+} is required for inhibition, so that monitoring the V^{5+} concentration may be crucial to successfully managing corrosion protection in plant.

Conclusions

- The spontaneous passivation of a polished carbon steel surface required a critical inhibitor concentration of 0.5–1.8 g/l.
- Corroding surfaces required a critical inhibitor concentration of 7.5–30 g/l of inhibitor for spontaneous passivation in typical HPC plant solutions (and a much lower critical inhibitor concentration of 1.5 g/l in the half strength lean solution).
- Aggressive species in the solution, including a chloride concentration greater than that typical of HPC plant, did not cause an increase in critical inhibitor concentration.
- The half strength lean solution required a low critical inhibitor concentration in the static and dynamic tests, 0.5 and 1.5 g/l respectively.
- A minimum level of V^{5+} is required for inhibition, so that monitoring the V^{5+} concentration may be crucial to successfully managing corrosion protection in plant.

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