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Response of Low Alloy Steels,
Part II: Electrochemical Results**

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**The Effect of Potential
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ABSTRACT

Environmentally assisted cracking (EAC) in low alloy steels was found to be dependent on externally applied potential in low sulfur steels in high temperature water. EAC could be turned on when the specimen was polarized anodically above a critical potential. However, hydrogen additions inhibited the ability of potential to affect EAC. The behavior was related to the formation of hydrogen ions during hydrogen oxidation at the crack mouth. A mechanism based on the formation of hydrogen sulfide at the crack tip and hydrogen ions at the crack mouth is presented to describe the process by which sulfides and hydrogen ions affect the critical sulfide concentration at the crack tip.

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INTRODUCTION

High temperature environmentally assisted cracking (EAC) of low alloy steels in deaerated water is dependent on the concentration of sulfur in the steel.¹ In high sulfur steels, EAC can readily occur, whereas under similar environmental and loading conditions, EAC will not occur in low sulfur steels. Sulfur is present as manganese sulfide inclusions in the steel, which dissolve in high temperature water to form hydrogen sulfide.^{2,3} A necessary condition for EAC to occur is the formation of a critical concentration of hydrogen sulfide at the crack tip.⁴ In high sulfur steels, the generation of hydrogen sulfide from sulfide inclusions is sufficient to overcome the loss of hydrogen sulfide out of the crack by several possible mass transport processes identified in Part 1 of this paper.⁵ However, the rate of loss of sulfides at the crack tip in low sulfur steels is greater than their rate of production, and a critical concentration of hydrogen sulfide cannot be generated to sustain the conditions necessary for EAC.

The addition of oxygen to the environment can cause EAC to become active in steels that do not exhibit this behavior in deaerated environments.^{6,7} The presence of dissolved oxygen (DO_2) results in a significant shift in the steel's open circuit potential (E_{oc}) to more noble potentials. Although the potential at the surface becomes more electropositive, the anoxic conditions at the crack tip remain relatively unperturbed by the oxidizing conditions outside the crack.⁸ Andresen has shown that sulfur anions concentrate at the crack tip in aerated high temperature water, resulting in EAC.⁹ In addition, this work showed that DO_2 does not play a direct chemical role in EAC, but establishes a potential gradient between the crack mouth and tip that will drive anions into the crack.⁹

Atkinson has performed a series of experiments on steels in deaerated water using externally applied potentials to simulate the presence of DO_2 . This work has demonstrated that EAC could be induced in a 0.005% sulfur steel tested in deoxygenated water at 290°C when the specimen was polarized to a potential between -0.25 and 0.02 V_{SHE} .⁷ Recently, Atkinson has postulated that the EAC was dependent on both the concentration of sulfur in the steel and the potential at the steel surface.¹ Specifically, as the concentration of sulfur in the steel increased, the potential necessary to induce EAC would

become more active. Atkinson evaluated the effect of applied potential on steels with a range of sulfur between 0.003 and 0.019%. EAC became active in low sulfur steels tested in high temperature deaerated water when polarized to noble potentials. Furthermore, EAC could be inhibited in steels containing moderate levels of sulfur (0.007%) by cathodically polarizing the specimen 0.2 V more electronegative than E_{oc} .

The work reported on in Part 1 of this paper⁵ was performed on a series of steels with different sulfur concentrations ranging from 0.002 to 0.026% S, and the relationship between applied potential, sulfur concentration, and fatigue crack propagation has been examined. The work reported on in this paper examines the electrochemical response of the steels in hydrogenated and dehydrogenated water (nominal room temperature pH^{RT} of 10.2), and presents a mechanism that describes the EAC response of the steel to applied potential and dissolved hydrogen (DH_2).

EXPERIMENTAL PROCEDURES

The composition of the four steels (A, B, C, D) used in this study are reported in Part 1,⁵ with the mean concentration of sulfur measured at 0.002, 0.011, 0.010 and 0.026 wt.%, respectively. The type and amount of dissolved gas were varied in this study, providing three different conditions for testing. The first was high hydrogen/low oxygen [2.5 to 4.5 ppm hydrogen and <10 ppb oxygen], the second was low hydrogen/low oxygen [<0.3 ppm hydrogen^a and <10 ppb oxygen], and the third was low hydrogen/high oxygen [>2 ppm oxygen]. Testing was performed at either 149°C or 243°C. The method of measuring dissolved gases is reported in Part 1.⁵

The experiments performed in this study involved controlling the potential of the 1T specimen, 1T-CT or 1T-WOL, using a potentiostat. Solution pH^{RT} was nominally 10.2, although this was varied in several experiments to as low as 9.0. All values of pH^{RT} were measured at room temperature. The room temperature conductivity of the test solution,

^a At the start of testing, the lowest level of measureable DH_2 was <0.3 ppm. Later testing under similar conditions using *in situ* monitoring showed the actual DH_2 concentration to be <16 ppb, with levels between 3-7 ppb typically measured.

approximately $48 \mu\text{S cm}^{-1}$, was low and the solution resistance was compensated during applied potential testing. Solution iR correction was periodically performed using a current interrupt technique. The large size and surface area of the fracture mechanics specimens decrease the magnitude of the solution resistance measured in the test, which was typically 120-160 ohms. No attempt was made to mask the specimen to decrease surface area.

The configuration of the electrodes is shown in Figure 1. The specimen itself was electrically isolated from ground and the load train by insulators. The specimen loading pins were insulated using transformation toughened zirconia (TTZ, Mg-stabilized ZrO_2), and the linear variable differential transformer (LVDT) was isolated by a zirconium holder that had been air oxidized. Platinum foil counter electrodes, with a total area approximately equal to the specimen area, were placed on either side of the fracture mechanics specimen. An iron wire was attached to the top of the specimen so that its potential could be monitored and controlled. Flow in the autoclave was very low and the conditions were considered to be quiescent.⁵

Each experiment described in Table 1 was performed in two phases. The first phase involved potentiostatically polarizing the specimen during cycling loading. The potential was adjusted and iR compensated every 15 minutes to ensure that small changes in solution conditions were accounted for in the test. The current was measured during these tests, and the results were reported as an average current during the potential step excluding the initial transient behavior. In many of the measurements, the current was very stable. In those instances where the current density varied significantly, an error bar of one standard deviation has been added. The second phase of the test involved potentiodynamically polarizing the specimen after the potential returned to its pre-potentiostatic polarization measured value.

The reference electrode used in this study was an external $\text{Ag}|\text{AgCl}|0.1 \text{ N KCl}$, which was placed near the back face of the specimen. The salt bridge into the electrode consisted of a PTFE tube filled with the electrolyte zirconia aggregate. The end of the PTFE was sealed with a 70% dense zirconia frit. The potential was referenced back to the standard hydrogen scale.¹⁰ In general, this electrode configuration is very stable and can last for

long periods of time without refreshing the electrolyte. However, the potentiostatic test phase often lasted for months, and on several occasions the reference electrode had drifted during the test. This would be detected at the end of the potentiostatic test if E_{oc} did not return to its pre-potentiostatic value. This drift was found to have occurred on Experiment 1 (see Table 1). The potentials reported in this experiment may not be accurate, although the current did indicate that the specimen was being polarized anodically. In Experiment 9, the reference electrode became erratic during the potentiostatic test phase, and had to be replaced. In all cases, reference electrodes were refreshed or replaced after each experiment sequence.

RESULTS

Table 1 summarizes the results reported in Part 1.⁵ This table shows four important trends: 1) DO_2 drives the surface of the steel to more noble potentials and induces EAC in medium sulfur steels [Experiment 3], 2) an externally applied potential can also induce EAC in low sulfur steels in high temperature water that does not contain DH_2 [Experiments 1, 2, 4 and 5], 3) DH_2 eliminates the ability of an externally applied potential to induce EAC in low sulfur steels [Experiments 7 and 8], and 4) cathodically polarizing very high sulfur steels will not affect EAC, independent of the presence of DH_2 [Experiments 6 and 9]. To more completely understand this behavior, it is necessary to determine the effect that applied potential has on the steel as well as the environment near the specimen.

Anodically polarizing a medium sulfur steel (Heat C, 0.010% S) in an environment that does not contain DH_2 or oxygen with the pH^{RT} adjusted to 9.0 resulted in low corrosion currents and diffusion limited behavior typical of passivated steel. At 149°C, steel forms a magnetite film that passivates the steel and protects it from actively corroding.¹¹ The polarization behavior that arises from steel passivation is shown in Figure 2, with the potentiostatically measured current shown as discrete data points and the potentiodynamic current shown as a continuous curve. At low anodic overpotentials, the scatter in the current density was greater than when the specimens were highly polarized. Subsequent testing reduced the amount of scatter in the current by tuning the current interrupt technique. The onset of EAC occurred when the potential exceeded $-0.4 V_{SHE}$ (see Table

1), indicating that the potential required to activate EAC is between -0.4 and $-0.25 V_{SHE}$. Potentiostatic currents were generally less than the corresponding potentiodynamic measurement, which is typical for a long hold potentiostatic test of a passivated material, where the oxide can continue to grow over time, resulting in a decrease in the measured current relative to the dynamic response.¹²

Performing the same experiment at $243^{\circ}C$ (Heat B, 0.010% S, Experiment 5 in Table 1) resulted in a change in the potential where EAC became active compared to the results measured at $149^{\circ}C$. In this experiment, EAC started between -0.2 and $-0.1 V_{SHE}$, which is in good agreement with the potential reported by Atkinson in tests conducted at $290^{\circ}C$.⁷

The polarization response of the steel changed significantly when DH_2 was added to the environment. A low sulfur steel (Heat A, 0.002%S), which does not normally exhibit EAC behavior in high-temperature, deaerated water; was tested at 149 and $243^{\circ}C$ in hydrogenated and dehydrogenated water (See Table 1). Although EAC became active during anodic polarization at both test temperatures when hydrogen was not present, DH_2 inhibited EAC even at potentials as noble as $0.2 V_{SHE}$. Figure 3 shows the polarization response of the low sulfur steel in water at $149^{\circ}C$ with the pH^{RT} adjusted to 10.2 with low (<0.3 ppm, Experiment 1) and high (2.1 ppm, Experiment 7) concentrations of DH_2 . The E_{oc} of the steel shifts to more active potentials by increasing the concentration of DH_2 . Furthermore, the steel electrode becomes much more electrochemically active, as noted by the shift in the polarization curve to larger currents as a function of the overpotential. The individual points shown in Figure 3 represent the potentiostatic test results. In the case of data from Experiment 1, the potentiostatic currents do not agree with the potentiodynamic results. As mentioned in the experimental section, the reference electrode drifted at some point during this test, and the potential measurements are not correct. However, measured currents did indicate that the specimen was being polarized anodically when EAC became active. In the case of Experiment 7, in which the environment contained hydrogen, the potentiostatic polarization currents are much less than the potentiodynamically measured currents. This behavior was typical of tests performed in hydrogenated water.

Figure 4 shows the results from Experiments 4 (low hydrogen) and 8 (high hydrogen) on the low sulfur steel (Heat A, 0.002% S). The potentiodynamic response in low hydrogen water (pH^{RT} 10.2) shows that increasing the temperature from 149 to 243 °C resulted in an increase in current during anodic polarization. Although DH_2 also increases the measured current, similar to the results found at 149 °C, the difference in polarization response between the low and high hydrogen conditions is not as large as was found at the lower temperature. The potentiostatic response of the steel in dehydrogenated water is in good agreement with the potentiodynamic measurement (Experiment 4). At low overpotentials, where the largest deviation between the two techniques occur, the potentiostatic current is an order of magnitude less than the potentiodynamic response, which could indicate either a significant improvement in the material's passive behavior or a change in the local solution or film chemistry that would shift E_{oc} to more oxidizing potentials so that the effective overpotential is not as large. This effect is diminished at larger overpotentials. In the case of the hydrogenated water (Experiment 8), the potentiostatic polarization currents are always much less than the potentiodynamic response, and slightly less than the potentiostatic currents measured in Experiment 4. This result could indicate that the oxide that forms during anodic polarization in hydrogenated water may better protect the underlying steel.

In the case of anodic polarization of low sulfur steel, Table 1 shows that EAC became active in dehydrogenated water between -0.4 and -0.25 V_{SHE} at 149 °C (pH^{RT} 9.0) and between -0.2 and 0.1 V_{SHE} at 243 °C (pH^{RT} 10.2). The polarization curves shown in Figures 3 and 4 indicate that a current peak exists between -0.25 and -0.15 V_{SHE} at pH^{RT} 10.2 at both temperatures, but was not apparent in tests conducted at pH^{RT} 9.0. This range of potentials for the current peak correlates with the potential where EAC becomes active. To determine the source of the peak, two polarization experiments were run on a medium sulfur steel (Heat B, 0.011% S) at pH^{RT} 9.53 and pH^{RT} 10.25 at 149 °C, and the results are shown in Figure 5. The current peak is related to the oxidation of the additive used to adjust pH. The onset of EAC between -0.4 and -0.25 V_{SHE} in pH^{RT} 9.0 electrolyte, which shows no evidence of a current peak, would indicate that this reaction is not playing a role in the EAC behavior of the steel. Furthermore, lower pH appears to shift the potential for the onset of EAC to more active potentials.

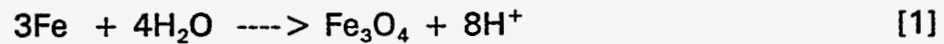
Cathodic polarization was used to reproduce the tests conducted by Atkinson, which showed that cathodically polarizing a 0.007% S steel could affect EAC behavior by decreasing the plateau crack growth rate (da/dN_p) and increasing the threshold stress intensity range (ΔK_{thp}).¹ Two cathodic polarization tests were performed on a high sulfur steel (Heat D, 0.026% S) in low hydrogen (Experiment 6, see Figure 6) and hydrogenated (Experiment 9, see Figure 7) water (pH^{RT} 10.2). In either case, EAC could not be inhibited, even at applied potentials well below water decomposition. This result would indicate that if the potential gradient between the surface and crack tip was the only criteria for controlling EAC, then the difference required to turn off EAC in this steel exceeds potentials that could normally occur in water. Comparison between the potentiostatic data points and potentiodynamic curves show that the static current is lower than the dynamic measurement, similar to the anodic polarization results. In this case, oxide growth due to the externally applied potential cannot account for the difference between the two curves. Rather, the local electrode environment will become more alkaline as hydrogen ions are consumed. The potentiostatic polarization process must alter the surface of the steel so that the cathodic reaction is inhibited in comparison to the surface that exists during a relatively brief potentiodynamic polarization measurement. The discontinuous behavior of the potentiostatic measurements in hydrogenated water (Figure 7) is a result of a reference electrode failure during the test, which had to be replaced.

DISCUSSION

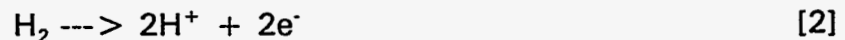
Interaction of DH_2 and Applied Potential

The presence of DH_2 on the polarization behavior of the steel can have several effects. Dissolved hydrogen can affect either the film formation and growth or it can oxidize and contribute to the electrochemical current. In the case of steels, both mechanisms can be expected to be active. Steels passivate by forming a magnetite film and its solubility increases with both DH_2 and pH .¹² If the oxide becomes more soluble, then its ability to protect the underlying steel will decrease.

In the case of steels without reactive dissolved gases in solution, the anodic polarization is dependent on the oxidation of iron to form magnetite.



In this case, oxide growth will be limited by the diffusion of reactive species through the film and the material will exhibit passive behavior, similar to the response shown in Figure 2. As the temperature is increased, the kinetics of film growth will also increase and the measured passive current density will increase. This response was shown in Figures 3 and 4. When DH_2 is added to the environment, the oxidation of hydrogen will become the dominant anodic reaction, since diffusion in the liquid will be much faster than diffusion through the passive film.



This reaction results in the consumption of hydrogen gas in solution and the formation of hydrogen ions at the working electrode. Hence, anodically polarizing steels in water containing DH_2 results in a lower pH near the steel specimen.

The discussion up to this point has focussed on the reactions occurring at the specimen surface, and not on the reactions at the crack tip. The conditions at the crack tip are anoxic and potentials can be much lower than the surface when DO_2 is present.⁸ In deaerated water, the crack tip and surface potentials approach one another. Under open circuit conditions, the potential difference between the crack mouth and tip will be small but measurable, since the environment (pH, ion concentration) between the tip and mouth will be different. Iron metal and manganese sulfide inclusions dissolve to provide ions at the crack tip. The formation of sulfide ions from MnS can be written as:



HS^- can further react with hydrogen ions, which can form from metal hydrolysis, to form hydrogen sulfide. The relative concentration of HS^- and H_2S will depend on the pH of the crack tip.



A number of reactions have been proposed that involve iron reacting with hydrogen sulfide to form $\text{FeS}_2/\text{FeS}^3$ or adsorb on the iron surface to act as a site for proton discharge.¹³ When hydrogen is added to the environment, both the surface and crack tip potentials will be driven near the potential of the hydrogen reaction, because hydrogen will dominate the electrochemistry. Unlike oxygen, it is not readily consumed at the crack mouth and can diffuse to the crack tip. However, the H_2/H^+ reaction will not polarize the steel surface to potentials that are significantly different than the crack tip.

The application of an applied potential will result in driving the reactions at the specimen surface from their equilibrium conditions. However, the crack tip will remain nearly unaffected by the external potential as a result of the large solution resistance in this region.¹ This results in the reactions at the crack tip behaving as though no potential has been applied to the specimen, and the specimen surface being polarized.

EAC Response of Steels

The presence of DH_2 , and its behavior during anodic polarization, plays a key role in the ability to control EAC when the specimen is externally polarized. In the case of steels with less than 0.011 wt.% S, where EAC does not occur spontaneously at E_{oc} , EAC can be induced during anodic polarization only when DH_2 is removed from the environment. If DH_2 is present in the system, anodic polarization of the specimen has no effect on EAC. High sulfur steels containing 0.026% S underwent EAC at open circuit conditions, and this behavior could not be impeded at high cathodic overpotentials either in the presence or absence of DH_2 . Unlike the lower sulfur steels, neither hydrogen nor potential had an effect on EAC.

The mechanism by which DH_2 affects the electrochemistry at the crack mouth must be dependent on the products that are formed at the crack mouth during polarization of the steel. In the case where neither DH_2 nor DO_2 are present (Case 1 in Figure 8), the

potential at the crack tip and on the surface are expected to be similar, and there is no driving force to move ions at open circuit conditions other than electrostatic and diffusion.

The presence of oxygen will result in its reduction at the specimen surface and an increase in the hydroxyl ion concentration in the environment near the steel (Case 2 in Figure 8). Iron at the surface may also oxidize near the local cathode, but this reaction will be diffusion limited and slow (passivation). Anodic reactions occurring at the crack tip will support the cathodic reduction of oxygen at the crack mouth. Under these conditions, the crack tip pH will decrease relative to the bulk due to metal hydrolysis and the presence of sulfide species, which will be predominately H_2S . In regions away from the crack tip, the concentration of OH^- and HS^- will increase. The separation of the local anode and cathode, which is a result of the rapid consumption of DO_2 at the crack mouth, will lead to a potential gradient that can drive anions into the crack tip. Sulfides (H_2S) will form HS^- as they diffuse away from the anoxic conditions at the crack tip toward the surface (crack mouth) where the pH is much higher, and be subsequently driven back into the crack tip due to the potential gradient. This process results in the concentration of sulfides at the crack tip in sufficient quantity to cause EAC.

The application of an external potential to simulate the effect of oxygen also results in the separation of anode and cathode. Similar to the previous case where DO_2 is present, the crack tip pH will decrease (due to metal hydrolysis and the presence of anions) and hydrogen sulfide (H_2S) will predominately form in this region (Case 3 in Figure 8). The migration of H_2S away from the crack tip is not affected by the potential gradient, and can diffuse away from the crack tip until it reaches a region of the crack when the pH is sufficiently high and H_2S is no longer stable. The resulting HS^- that forms is driven back into the crack, stemming the loss of sulfides from the crack tip. In effect, the anodically applied potential acts as a barrier to sulfide loss from the crack, and eventually the concentration of sulfides in the crack reaches a level where EAC can become active.

When DH_2 is present (Case 4 in Figure 8), anodic polarization of the specimen results in oxidation of the hydrogen at the specimen surface to form hydrogen ions (Equation [2]). This reaction will lower the pH near the crack mouth. Similar to the case without DH_2 , H_2S

can diffuse away from the crack tip because it is unaffected by the potential gradient (the change in the reaction at the surface does not alter the surface potential or the driving force on anions into the crack tip). However, the pH at the crack mouth is sufficiently low due to hydrogen oxidation so that H₂S remains stable compared to Case 3; HS⁻ does not form in sufficient quantities to stop the loss of sulfides from the crack tip, and H₂S diffuses out of the crack. The barrier mechanism holding sulfides in the crack is no longer active since H₂S is not affected by the presence of a potential gradient, and the conditions necessary for EAC cannot be established.

In these tests, cathodic polarization had no effect on inhibiting EAC in high sulfur steels, regardless of concentration of DH₂. This result appears to be contradictory to the work by Atkinson, who showed that cathodic polarization of a medium sulfur steel could inhibit EAC.¹ As discussed in Part 1,⁵ Atkinson's experiments were conducted in low-DH₂ water (<70 ppb DH₂). In the case of cathodic polarization, hydrogen oxidation is not possible and the near-electrode pH will not decrease in hydrogenated water. The most likely reaction occurring on the surface of the steel during cathodic polarization is the reduction of water, which would not acidify the local environment. However, the crack tip potential remains relatively invariant to the externally applied potential, and MnS dissolving in this region will still form H₂S and HS⁻. Although HS⁻ will be driven from the crack in the presence of high cathodic overpotentials at the specimen surface, H₂S will not be affected. In addition, for EAC to be affected, the loss of sulfides from the crack must be greater than the production of sulfides due to the dissolution of MnS. In the high sulfur steel used in this study (0.026% S), large potential gradients were not sufficient to overcome the replenishment of sulfides at the crack tip. However, cathodic polarization of steels with lower levels of sulfur, such as the steels used by Atkinson in his study, may result in inhibiting EAC.

Atkinson proposed a predictive model to calculate the effect of sulfur, applied potential, temperature, and loading frequency on the plateau crack growth rate.¹⁴ The "plateau" region is defined as the region where crack growth rates are not strongly dependent on ΔK or \dot{a}_b ; Part 1 for a definition of \dot{a}_b .⁵ The equation that Atkinson developed is as follows:

$$da/dN_p = 1.286 \times 10^{-6} \exp(-1073/RT)f^{-1}[S]^{0.5} + 1.69 \times 10^{-6} \Delta E \text{ (m/cycle)} \quad [5]$$

with R is the universal gas constant (1.987 cal/mol K), f is frequency (Hz), S is the sulfur concentration in weight percent, and ΔE is the difference between E_{oc} and the applied potential. Assuming that the contribution of overpotential is independent of the steel's sulfur concentration, the effect of cathodic polarization on EAC can be predicted for the high sulfur (0.026% S) steel use in this study. Cathodic polarization tests were conducted at 243 °C (516 K) at a frequency 0.002 Hz (see Test Phase 10 of Experiment 6 in Part 1⁵). When these values are input into Equation 5, the result is:

$$da/dN_p = 3.641 \times 10^{-5} + 1.69 \times 10^{-6} \Delta E \text{ (m/cycle)} \quad [6]$$

Equation 6 indicates that the effect of sulfur on the plateau crack growth rate outweighs the contribution of applied potential in the high sulfur steel specimen, and the plateau crack growth rate is relatively insensitive to even large cathodic overpotentials. The maximum cathodic potential applied to the high sulfur steel specimen was $-1.6 V_{SHE}$, resulting in a value for ΔE of $-1.035 V$. Thus, the second term (potential effect) in Equation 6 is a factor of 20 lower than the first term (sulfur effect). This potential difference was not sufficient to affect the crack growth rate.⁵ High concentrations of MnS in the steel will result in high levels of sulfides at the crack tip. Removal of the sulfides in solution will at some point become mass transport limited, and the potential gradient will become less effective at moving sulfide ions away from the crack tip.

A mechanism for EAC that is dependent on developing a critical concentration of sulfides at the crack tip can explain the effect of DH_2 on the EAC behavior of the steel during anodic polarization. The presence of a neutral molecule (H_2S) at the anoxic crack tip, and its conversion at higher pH to HS^- , is critical to establishing the conditions that allow sulfides to build up in the crack in low sulfur steels that are either polarized by oxygen reduction or through the use of an externally applied potential. The quiescent flow conditions typical of the autoclave environment found in this study, and the corresponding EAC behavior of the steel, may change under high flow conditions, where local acidification of the working electrode (specimen surface or crack mouth) would not be allowed to develop.

CONCLUSIONS

Dissolved hydrogen was found to inhibit the conditions necessary for EAC to occur in low sulfur steels imposed during anodic polarization. The mechanism that is proposed in this study involves the effect of applied potential on the local crack mouth chemistry and the stability of hydrogen sulfide anions under these conditions. The model indicates that a critical sulfide concentration at the crack tip is necessary to initiate EAC. This model supports results from this work as well as the data in the literature.

The role of DH_2 on inhibiting EAC is indirect, in that its oxidation lowers the pH at the crack mouth chemistry and results in the stability of H_2S in this region, which is not affected by the potential gradient. Testing in low hydrogen environments using externally applied potentials correctly simulates the conditions present in testing in high oxygen environments. This work clearly establishes that a potential gradient is a necessary condition to drive HS^- to the crack tip, where sulfides can concentrate to develop EAC in low sulfur steels.

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Table 1. Experimental Conditions							
Exp. No.	Heat	Sulfur (wt.%)	Oxygen (ppb)	Hydrogen (ppm)	Temp (°C)	External Polarization	Results
1	A	0.002	^a	<0.33*	149	Anodic	EAC on during anodic polarization ^b
2	C	0.010	^a	<0.33*	149	Anodic	EAC on between -0.4 & -0.25 V _{SHE}
3	C	0.010	8-2000	**	149	N/A	EAC on with O ₂ addition
4	A	0.002	^a	<0.33*	243	Anodic	EAC on between -0.2 & -0.1 V _{SHE}
5	B	0.011	^a	0.008***	243	Anodic	EAC on between -0.2 & -0.1 V _{SHE}
6	D	0.026	^a	0.008***	243	Cathodic	EAC remains active at min potential of -1.6 V _{SHE}
7	A	0.002	^a	2.1 ppm	149	Anodic	No EAC to max potential of -0.25 V _{SHE}
8	A	0.002	^a	2.5 ppm	243	Anodic	No EAC to max potential of 0.2 V _{SHE}
9	D	0.026	^a	4.4 ppm	243	Cathodic	EAC remains active at min potential of -1.125 V _{SHE}

^a Concentration of oxygen measured at 7±3 ppb

^b Reference electrode drifted during test. Current indicated anodic polarization.

* Below detectable limit with ex-situ measurement

** Not measured

*** In-situ thermal conductivity measurement

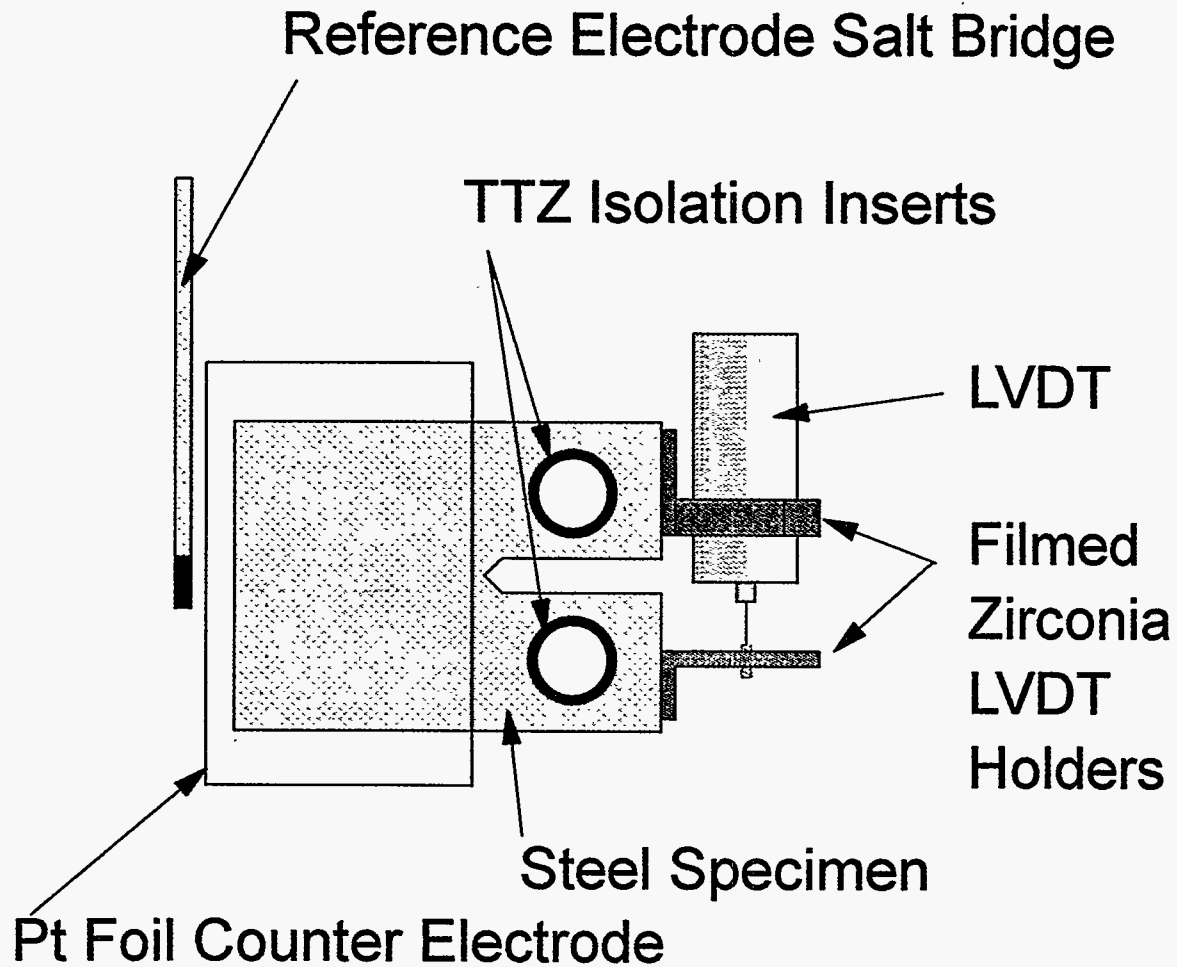


Figure 1. Schematic of the placement of reference electrode, LVDT and Pt counter electrode relative to the Steel specimen. The specimen was electrically isolated using magnesia-stabilized zirconia (TTZ) to isolate the loading fixture and zirconium which had been oxidized (filmed zirconium) to isolate the LVDT.

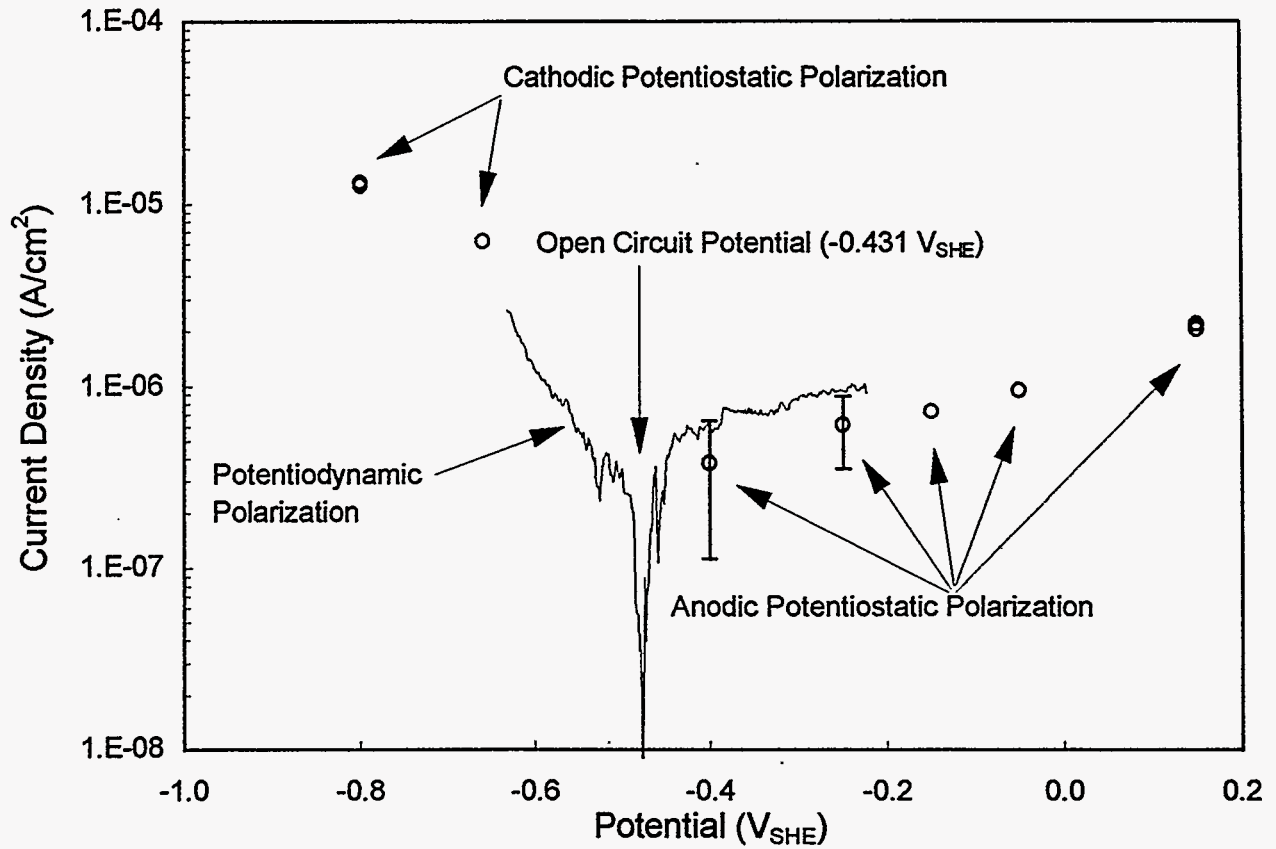


Figure 2. Polarization behavior of a medium sulfur steel (Heat C, 0.010 S) in a low DH₂ environment (Experiment #2, See Table 1).

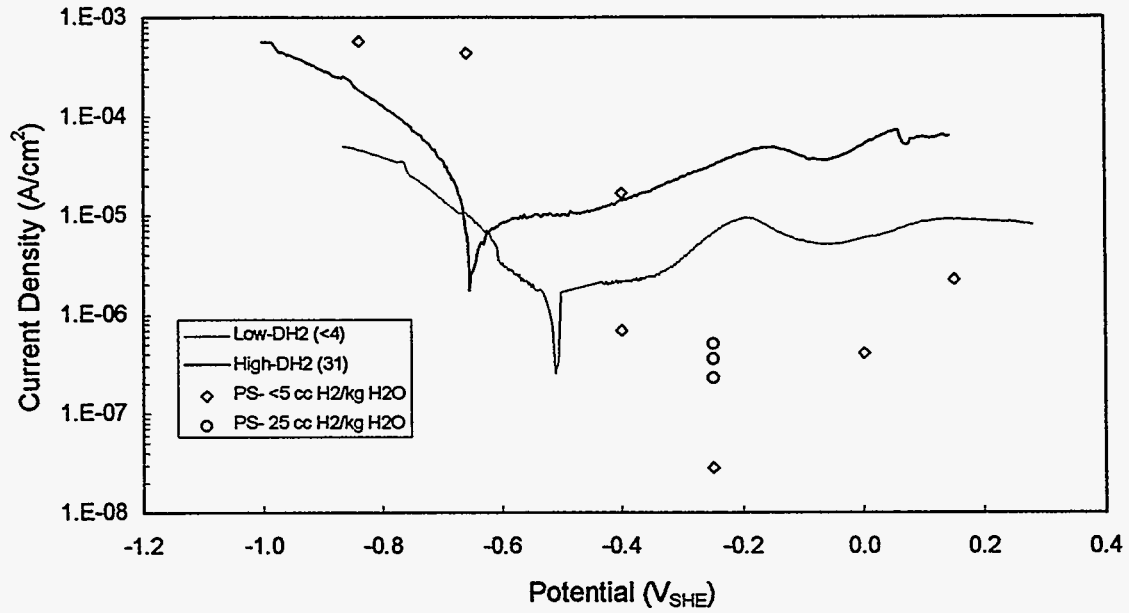


Figure 3. Potentiodynamic polarization behavior of a low sulfur steel (Heat A, 0.002 S) in low-DO₂ water (pH^{RT} 10.2) at 149°C at low-DH₂ (<0.3 ppm, Experiment 1 in Table 1) and high-DH₂ (2.1 ppm, Experiment 7 in Table 1).

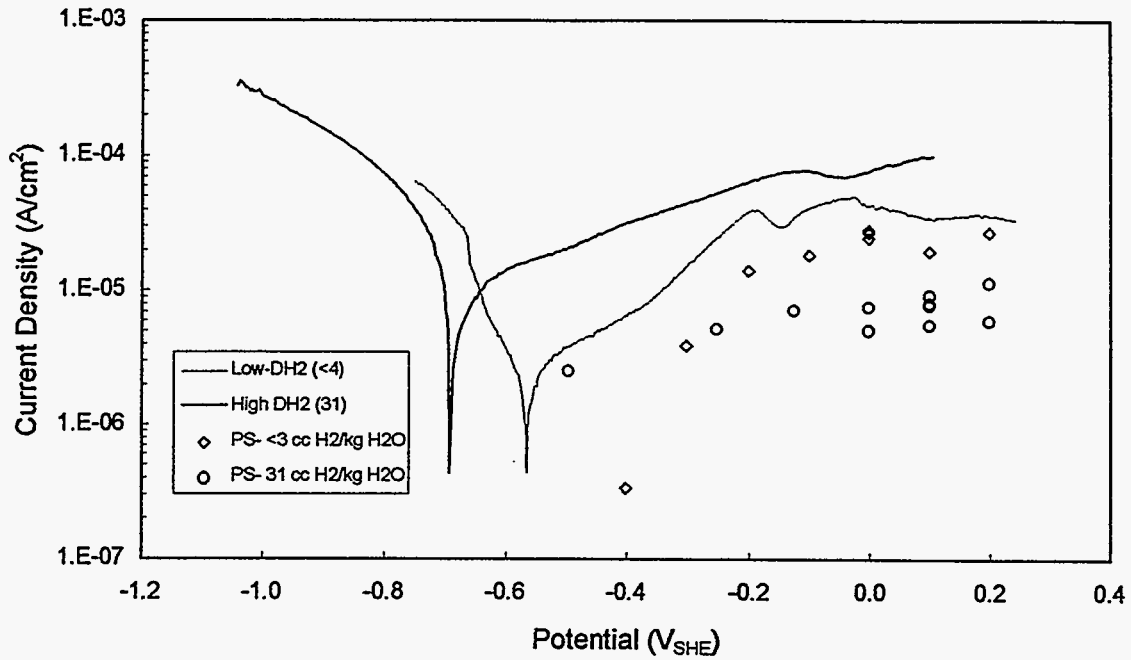


Figure 4. Potentiodynamic polarization behavior of a low sulfur steel (Heat A, 0.002 S) in water (pH^{RT} 10.2) at 243°C at low-DH₂ (<0.3 ppm, Experiment 4 in Table 1) and high-DH₂ (2.5 ppm, Experiment 8 in Table 1).

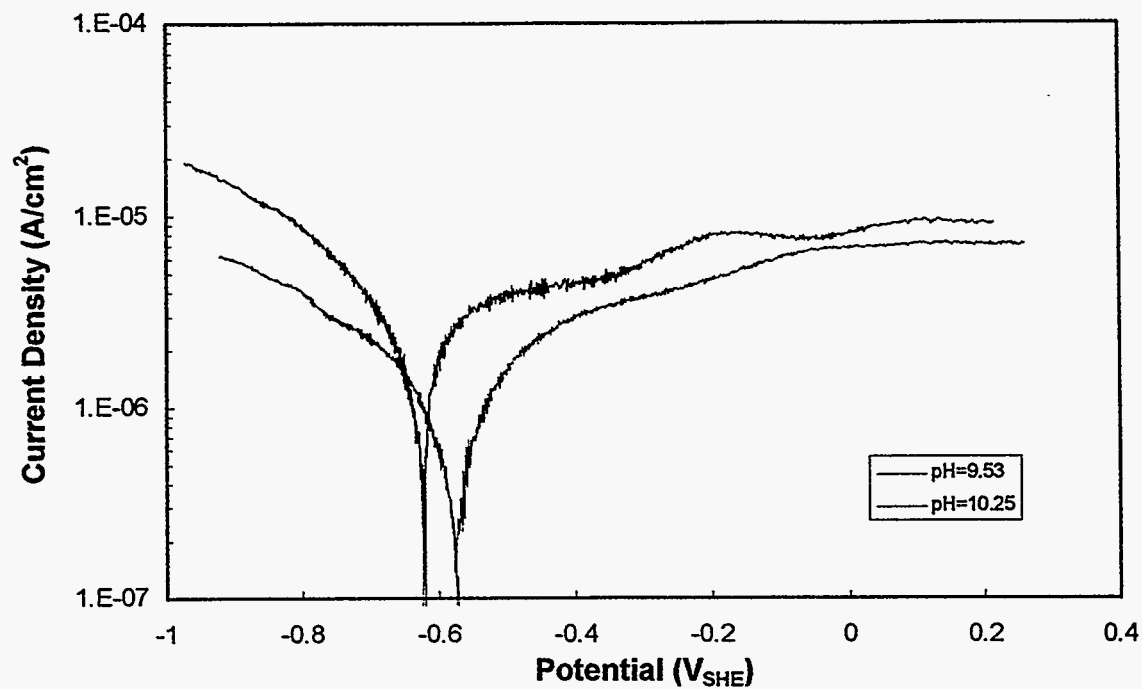


Figure 5. Polarization behavior of a medium sulfur steel specimen (Heat B, 0.011% S) tested at 149°C at two different levels of pH^{RT} in low-DH₂ water.

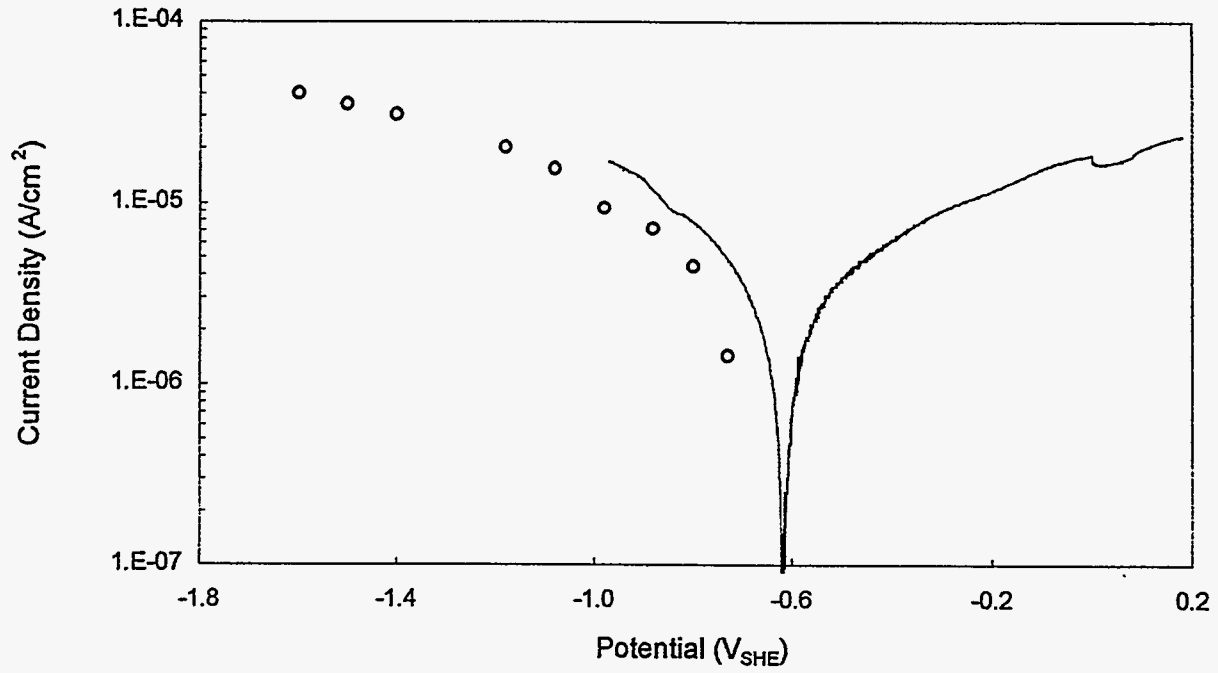


Figure 6. Comparison of potentiostatic and potentiodynamic polarization response of a high sulfur steel (Heat D, 0.026 S) in water (pH^{RT} 10.2) at 243°C with 8 ppb DH₂ (Experiment #6, See Table 1).

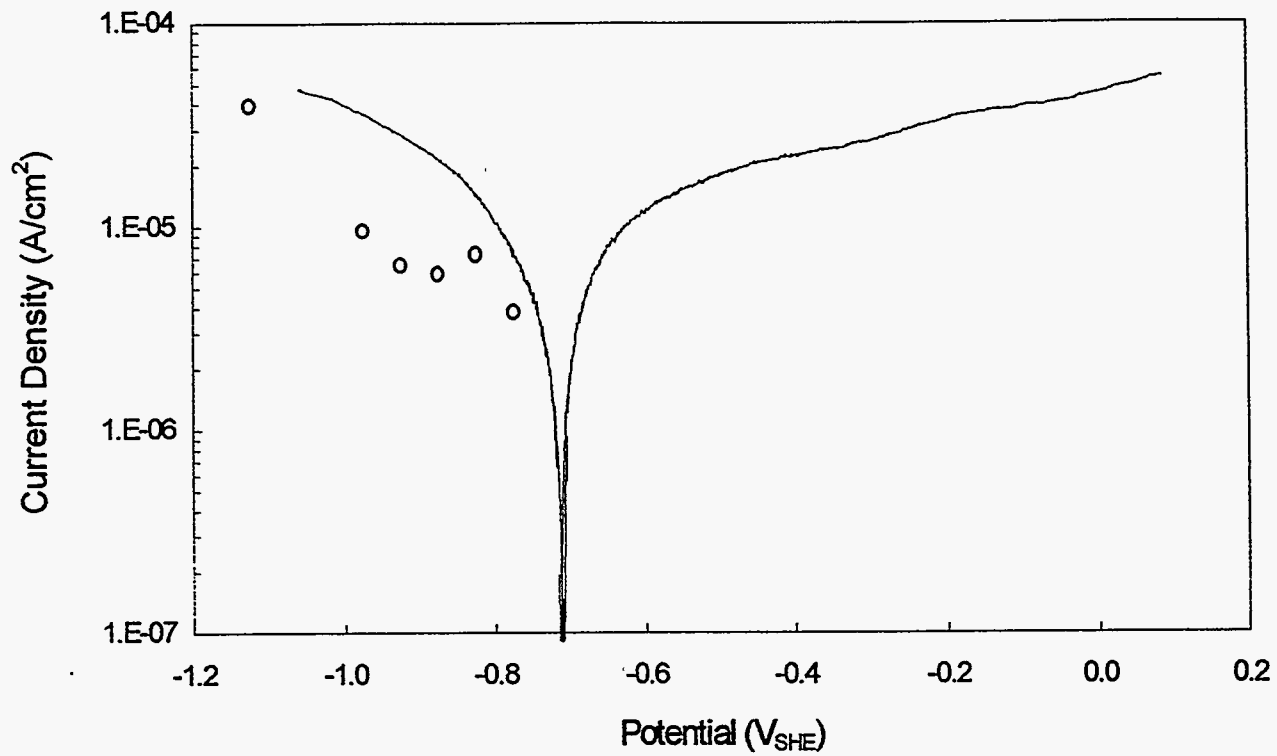


Figure 7. Comparison of potentiostatic and potentiodynamic polarization response of a high sulfur steel (Heat D, 0.026% S) in water (pH^{RT} 10.2) at 243°C with high-DH₂ (4.4 ppm). E_{oc} at the start of the potentiostatic tests was $-0.690 V_{SHE}$, and decreased at the start of the potentiodynamic test to $-0.712 V_{SHE}$ (Experiment #9, See Table 1).

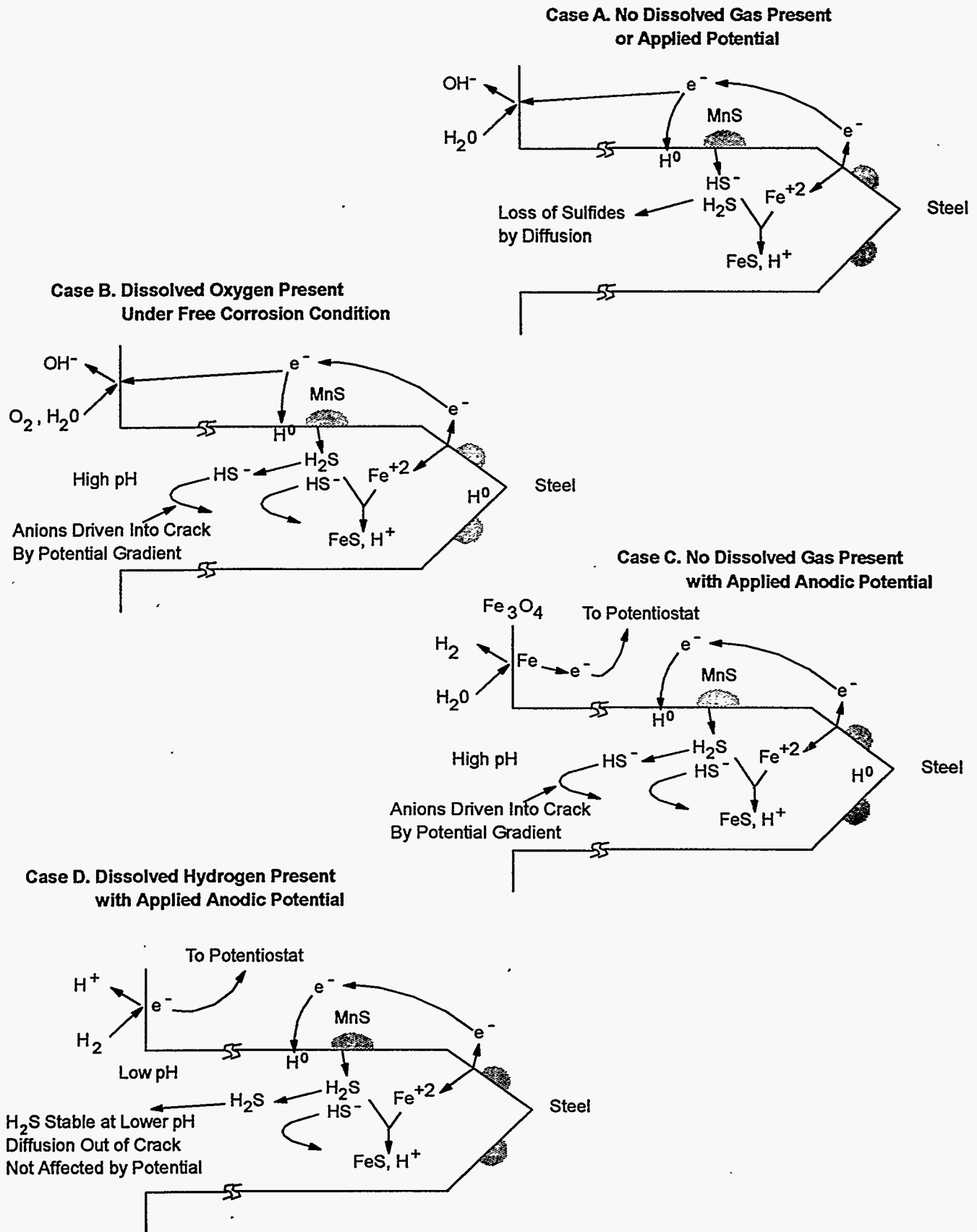


Figure 8 Illustration of the effect of applied potential and reactive dissolved gas on the EAC behavior of low sulfur steels in high temperature water.