CORROSION, STRESS CORROSION CRACKING, AND
ELECTROCHEMISTRY OF THE IRON AND NICKEL BASE
ALLOYS IN CAUSTIC ENVIRONMENTS

MASTER

Final Report

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Abstract

The electrochemical behavior of high purity (99.95% - 99.99%) iron in 0.6M NaCl and 1.0M Na₂SO₄ containing hydrogen sulfide (50 ppm to 34000 ppm) has been investigated by the electrochemical techniques of cyclic voltammetry, chronoamperometry, and slow scan rate polarization. The purpose of this research was to obtain kinetics data of the dissolution of iron in these solutions containing H₂S. The results have indicated that iron does undergo passivation in sulfate solutions containing H₂S. Corrosion rates for iron in sulfate solutions with H₂S are highly dependent on H₂S concentration, but the corrosion rate of iron in unbuffered 0.60M NaCl with H₂S depends on solution pH and H₂S concentration. Apparently, the dominant mechanism of iron dissolution depends on the presence of Cl⁻, the concentration of H₂S and solution pH. Polarization studies of iron in 4.0 pH-buffered 0.60M NaCl indicate that the anodic Tafel current densities can be described as

$$i_a = nF[H_2S]^{0.25} \theta_{Fe} \exp[\alpha F(\phi - \phi_{eq})/RT]_{pH, Cl^-, E}$$

where ϕ_{eq} is approximately -716mV(SCE).

The slow strain rate test was used to evaluate the effect of electrode potential on the susceptibility of 2-1/4Cr, Mo steel to stress corrosion cracking in boiling 50% NaOH solution. Susceptibility decreased and general corrosion increased with increasing potentials. Failures contained a combination of ductile and brittle fracture. Time-to-failure was longest for controlled potentials of -700 and -600mV (Hg/HgO reference) in the -1100 to -400mV range used in this study.

PART I

Electrochemical Behavior of High Purity Iron in Weakly Acidic, Aqueous Solutions of Sodium Chloride, Sodium Sulfate and Hydrogen Sulfide

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INTRODUCTION

The electrochemical behavior of high purity (99.95% - 99.99%) iron in 0.60M NaCl and 1.0M Na₂SO₄ containing hydrogen sulfide (50 ppm to 3400 ppm) has been investigated by the electrochemical techniques of cyclic voltammetry, chronoamperometry and slow scan rate polarization. The purpose of this research was to obtain kinetics data of the dissolution of iron in these solutions containing H₂S. A wide range of solution pH values was encountered during these studies (3.90 pH to 8.0 pH) which resulted from the amount of H₂S dissolved in the unbuffered test solutions. The kinetics of iron dissolution were also studied by using a 4.0 pH-buffered 0.60M NaCl solution with various H₂S concentrations.

EXPERIMENTAL

Test Specimens. The high purity iron specimen was purchased in the form of a 1/4-inch diameter, 6.5-inch long rod from the Materials Research Corporation. The iron rod was electron beam melted material and cold fabricated to size under clean room conditions by MRC. The determination of impurities was accomplished by mass spectrographic, Leco Method (gases) and conductometric (carbon) methods at MRC. The chemical analysis of this iron is as follows: less than 1 ppm H; 12 ppm C; 10 ppm N; 60 ppm O; 1.6 ppm Na; 0.87 ppm Mg; 0.70 ppm P; 2.6 ppm S; 0.80 ppm Cl; 1.80 ppm K; 0.80 ppm Ca; 1.40 ppm Ti; 1.60 ppm Cr; 0.60 ppm Cu; and 1.90 ppm Zn. The iron rod was cut into 11-millimeter lengths for test specimens.

The working electrode design was very simple because it consisted of a machined Teflon holder, the iron pellet and a connecting rod encased in a Teflon tube. Electrical contact between the connecting rod and the iron pellet was accomplished by turning the threaded metal rod into the threaded iron pellet.

The Teflon holder was $3/4$ -inch in diameter and $1/2$ -inch in thickness. The opening in the front face of the holder was slightly smaller in diameter than the $1/4$ -inch diameter pellet. In order to assemble the electrode, the Teflon holder was immersed in boiling water for at least thirty minutes. The holder was quickly removed and the iron pellet carefully (but quickly) inserted into the hot Teflon. The insertion of the pellet was made much easier when the holder had expanded slightly after being heated in the water. After the holder had cooled, the pellet was firmly in place and could not be turned inside the holder. Teflon tape was wrapped around the Teflon threads of the connecting rod in order to assure a water-tight seal between the rod and the holder. The connecting rod was not turned into the pellet very tightly in order to prevent mechanical distortion of the Teflon holder by the pellet. Assembled in this manner, the working electrode holder never suffered leakage of test solution between the holder and the pellet.

The iron surface was mechanically polished to a "mirror finish" in the following manner. The corroded or new iron surface was given a quick grinding on the 180 grit belt polisher in order to remove adherent corrosion products and any pits in the metal surface. Then the surface was hand-polished under running tap water with the following series of silicon carbide papers: 240 grit, 400 grit and 600 grit.

A mirror finish on the iron surface could be achieved by polishing with the 600 grit paper (with running tap water) taped on a rotating polishing wheel. The term "mirror finish" is highly subjective in its application here and is intended to mean an iron surface which has the fewest number of 600 grit polishing lines and can offer a mirror-like reflection of an object without any evidence of image distortion. A fresh iron surface was prepared for every electrochemical experiment.

Apparatus. A dual function Princeton Applied Research potentiostat/galvanostat (Model 173) was used to control the potential between the working and reference electrodes (potentiostat mode). The PAR universal programmer (Model 175) was useful for providing a wide range of potential sweep rates. The PAR instruments were used for all chronoamperometry experiments, most of the slow scan rate experiments and for cyclic voltammetry experiments which required scan rates greater than 50mV/s. A Wenking potentiostat (Model 68TS3) and Erwin Halstrup motorpotentiometer (Model MP 165) were used for approximately six of the slow scan rate experiments and for all cyclic voltammetry experiments which involved scan rates less than 50mV/s. The current responses to the potential stimuli were recorded on a Hewlett-Packard strip chart recorder (dual pen, Model 7132A).

The surface of the iron specimen was not studied by scanning electron microscopy (SEM) or Auger electron spectroscopy (AES) techniques. The condition of the surface immediately at the completion of an experiment was observed by using a Vickers microscope (400X magnification). The measurement of solution pH was accomplished with a Corning Scientific Instruments pH meter (Model 12). Several samples of the working

electrode solution were withdrawn during the course of a chronoamperometry experiment and these were analyzed by atomic absorption spectrophotometry. A Perkin-Elmer Atomic Absorption Spectrophotometer (HGA furnace, Model 360) was used to determine the concentration of iron in these samples. The source of radiation for analysis of iron was the Perkin-Elmer iron hollow cathode lamp (Intensitron Model). The sample solutions from several of the chronoamperometry experiments were analyzed for the presence of polysulfide ions by using a Bausch and Lomb Spectronic 21 Spectrophotometer (Model 21 D-V). Finally, various concentrations of aqueous H_2S were obtained by mixing hydrogen sulfide gas (Matheson, 99.95% purity) and the prepurified argon (Ar) and passing this gas mixture to the working electrode and counter electrode compartments (see Figure 1). The gas mixtures were produced by a Matheson gas proportioner (Model 7352T).

A schematic presentation of the polarization cell and ancillary equipment is provided in Figure 1. The entire cell was constructed of Pyrex glass. Connections between the gas proportioner (4) and the working electrode (12) and counter electrode (13) compartments consisted of 1/4-inch diameter glass tubing and shrinkable Teflon tubing joined the glass tube sections in locations which required a small degree of bending. Flexible tygon tubing was used for directing Ar gas to the gas proportioner and to the deaeration reservoir (15). The entire cell could be disassembled for easy cleaning after each experiment.

The electrode compartments were open to the atmosphere via gas washers and solutions of 0.1M $FeCl_3$ (not shown in Figure 1). The gas washers consisted of Pyrex cannisters filled with Wilson's brand

Figure 1: Schematic of the polarization cell and ancillary equipment.

Key to the Arrangement of Equipment in Figure 1

- 1 Potentiostat
- 2 Function generator
- 3 Strip chart recorder
- 4 Gas proportioner
- 5 Hydrogen sulfide cylinder
- 6 Prepurified argon cylinder
- 7 Magnetic stirrer
- 8 Stir bar (38 mm)
- 9 Glass frit (dense)
- 10 Working electrode (Fe mounted in Teflon holder)
- 11 Counter electrode (Pt sheet, 37.5 mm X 21.5 mm)
- 12 Working electrode compartment
- 13 Counter electrode compartment
- 14 Luggin probe
- 15 One-liter deaeration reservoir
- 16 Gas sparger with porous glass frit
- 17 Outlet to atmosphere
- 18 Right side of reference cell (test solution)
- 19 Left side of reference cell (saturated KCl solution)
- 20 Ground glass stopcock wetted with KCl solution
- 21 Reference electrode (saturated KCl calomel electrode)
- 22 Plastic tube used to transfer test solution from (12) to (18)
- 23 Plastic and glass tubing used to transfer deaerated solution from (15) to (12) and (13)
- 24 Removable ground glass caps to compartments (12) and (13)
- 25 Plastic tubing connected to the gas washers; gas washers are not shown

"Sodasorb" (soda lime). This specially-manufactured absorbent took up the excess H_2S that passed out of the electrode compartments. Residual H_2S gas that managed to pass through the gas washers reacted with the FeCl_3 solution.

The reference electrode compartment (19) was always filled with a saturated KCl solution. The reference electrode was housed in a small glass reservoir (19) and connected to the Luggin capillary (14) via the test solution in (18) and the KCl-wetted glass stopcock (20). The opening of the Luggin probe was always positioned 0.75 mm to 1 mm from the center of the iron surface.

The schematic of the polarization cell (Figure 1) does not provide any indication of the cell dimensions. The most important dimensions are as follows: (1) volume of each electrode compartment is approximately 400 mls; (2) distance from the WE to the CE is 165 mm; (3) magnetic stir bar (8) is 38 mm in length; (4) inner diameter of the compartments (12) and (13) is 64 mm; (5) length of the compartments (12) and (13) (without the glass cap (24)) is 165 mm; (6) total length of the glass cap-compartment combination is 191 mm; and (7) length of the connecting glass frit-midsection (9) is 51 mm.

Solutions. The aqueous environments which were studied included deaerated double distilled water, 0.5M Na_2SO_4 , 1.0M Na_2SO_4 , unbuffered 0.60M NaCl, pH-buffered 1.0M Na_2SO_4 and pH-buffered 0.60M NaCl. The buffer solutions were prepared according to instructions in the CRC Handbook of Chemistry and Physics¹ (4.0 - 5.9 pH $\text{KHC}_8\text{H}_4\text{O}_4$ buffers).

All of the solutions were sparged with high purity Ar gas for 1.5 to 2 hours before being transferred to the electrode compartments.

After a solution had been transferred to the WE and CE compartments, the H_2S -Ar mixture (or simply pure H_2S or pure Ar) was directed into both compartments. The gas mixture was passed into the solutions throughout the entire experiment. The 610 tube and 603 tube in the gas proportioner were calibrated for hydrogen sulfide gas and prepurified argon gas (at 25°C), respectively. However, these two calibration plots for the tubes were used only as guides to produce mixtures of an approximate, desired H_2S concentration. Because the solubility of H_2S in aqueous solutions is heavily dependent on temperature,² electrolyte concentration and solution pH, the precise H_2S concentration for each experiment was determined by an iodometric titration technique. This technique has been explained elsewhere.³ The gas mixture was passed through the electrode compartments for approximately forty minutes and during this time the solutions required for the iodometric titration were prepared. After the titration had been completed, the electrical connections between the polarization cell and the potentiostat were made and then the experiment was begun.

At the completion of an experiment, the electrical connections to the potentiostat were undone, solutions were drained from both compartments and the entire cell was disassembled for cleaning. The solutions containing H_2S gas were neutralized with an excess quantity of lump ferric chloride before they were discarded at the laboratory sink. The glassware was always cleaned with soapy water, rinsed very well with tap water and finally rinsed with a spray of double distilled water.

Procedure. Before the experimental techniques are described, a few remarks about the experimental conditions encountered for all of these techniques should be listed. The experiment solutions were always prepared

with double distilled demineralized water and analytical reagent grade chemicals. Solutions were always deaerated with prepurified (99.99%) argon before the electrochemical experiment was begun. The experiments were performed at ambient temperatures ($25^{\circ}\text{C} \pm 3^{\circ}\text{C}$) and atmospheric pressure. The solution in the working electrode compartment was always stirred very well (but no turbulent stirring) in order that the kinetics of charge-transfer at the iron electrode could be studied. Solutions containing various concentrations of H_2S were always analyzed by an iodometric titration just before beginning the experiment. There was no attempt made to adjust the observed electrode potentials for iR drop by any of the methods listed by Britz.⁴ All current densities are based on the geometrical area of the iron electrode (0.318 cm^2) and all electrode potentials have been reported on the basis of the saturated KCl calomel reference electrode. These potentials can be converted to the standard hydrogen electrode scale by adding 241.5mV.

This section will briefly describe the techniques that were followed during the course of the electrochemical experiments. The slow scan rate voltammetry experiments were conducted at several scan rates (mainly 1500 mV/hr and 1800 mV/hr) and, except for the first polarization experiment, all of these scans were begun at least 400 to 500 mV below the measured rest potential E_r . The range of potentials covered by a scan was usually from -1200mV to -200mV or 0mV. A cathodic current was applied to the WE at this starting potential for approximately 10-15 minutes before beginning the scan. The presence of ferrous and ferric ions in the WE compartment was checked by two spot tests for these ions at the end of each scan.³ Also, the solution pH at the start and pH at

the finish were measured and recorded.

The cyclic voltammetry experiments were performed only with iron in 0.5M Na_2SO_4 solutions (plus various concentrations of H_2S) and 3.5% NaCl solution (no H_2S). The forward (anodic) scan was reversed (i.e., a back or return scan) when the passive current region was just entered. Since no passivation currents were observed for iron in 3.5% NaCl solutions, the forward scan was reversed when the current had just exceeded 500mA. The solution pH at the start and at the finish were recorded and spot tests were used at the completion of the experiment.³ The scans were always started at the measured rest potentials. No cathodic current pretreatment was used prior to the start of the scan. A wide range of scan rates was used (0.42 mV/s to 500 mV/s) and up to 50 continuous cycles were recorded.

The chronoamperometry experiments were performed only with pH-buffered 0.60M NaCl solutions and pH-buffered 1.0M Na_2SO_4 solutions. The iron electrode was initially held at a potential approximately 50 to 100mV more negative than the measured rest potential for 10 minutes. Then the applied external potential (from the PAR universal programmer) was turned off and a new potential difference was imposed on the iron electrode by the PAR potentiostat. The current decay was measured as a function of time and, during the course of the experiment, 5-ml samples of the WE solution were withdrawn for later determination of iron. The pH of these sample solutions were also measured and recorded. During several of the chronoamperometry experiments, the absorbance of the samples was measured with a spectrometer (wavelength = 368 nm) in order to monitor the build-up of polysulfide ions with time. According to Teder⁵,

absorption due to polysulfides is expected at this wavelength. For these spectroscopic measurements, the absorbance of each sample was referred to the deaerated solution (no H_2S). The chronoamperometry experiments usually were conducted for a period of 6 to 7 hours.

The concentration of iron in each aliquot was determined by atomic absorption spectroscopy (AAS). The spectrophotometer that was used for this study employed an HGA graphite furnace assembly. This unit was advantageous for this research because solutions containing small, solid particles of iron sulfide could be analyzed during the high-temperature atomization step just as easily as solutions containing only dissolved iron.

Calibration curves of absorbance versus iron concentration as ppm Fe were prepared each time the spectrophotometer was operated. The dilutions for various iron concentrations were prepared from a 1000 ppm ferric chloride solution (atomic absorption spectroscopy standard) and triple distilled water. Finally, the operating conditions of the graphite furnace were as follows: (1) wavelength = 248.3 nm; (2) drying time = 30 sec. and solution drying temperature = $105^{\circ}C$; (3) char time = 30 sec. and char temperature = $1100^{\circ}C$; (4) atomization time = 7 sec. and atomization temperature = $2700^{\circ}C$; (5) volume of sample injected into the graphite furnace tube was 25 microliters; and (6) the (Ar) gas-flow interrupt technique was used during the sample atomization cycle. A good description of this spectrophotometer and its operation is offered in the Perkin-Elmer manual.⁶

RESULTS

The primary objective of the cyclic voltammetry experiments was to observe the electrochemical behavior of iron in the range of potentials beyond the anodic Tafel region as a function of scan rate, H_2S concentration and presence of Cl^- ion. A detailed examination of the passive films produced by these scans was not pursued in this research project and the data that have been obtained from the strip chart recordings³ will not be analyzed by a method used by Shoesmith, et al.⁷ for describing the behavior of iron oxide-sulfide film formation.

A series of one cycle scans for iron in 0.5M Na_2SO_4 with various H_2S concentrations is presented in Figure 2 to Figure 6. The peak potential (E_p) and peak current density (i_p) refer to the first major peak in the active region prior to passivation of the iron electrode. The back scan in Figure 2b indicates a very small anodic current in the active region. Figures 3 to 6 show that increasing H_2S concentrations tend to cause an increase in the anodic currents for potentials more positive than E_p . The forward scan for iron in 0.5M Na_2SO_4 saturated with H_2S indicates a broad region of numerous sharp peaks until the electrode finally reaches a passivation potential. Note that the values of E_p are not appreciably affected by the concentration of H_2S and that the active regions cover the same range of potentials regardless of H_2S concentration. Finally, there does seem to be a small degree of hysteresis between the currents of the forward scan and the back scan.

The forward and back scans for iron in 3.5% NaCl (no H_2S) are presented in Figure 7. There is no passive potential or peak current. However, a current "spike" can be seen in the forward anodic scan at

Figure 2a: Forward anodic cyclic voltammetry scan of Fe in 0.5M Na_2SO_4 , 0ppm H_2S . Scan rate is 5.56 mV/s.

Figure 2b: Back anodic cyclic voltammetry scan of Fe in 0.5M Na_2SO_4 , 0ppm H_2S . Scan rate is 5.56 mV/s.

Figure 3a: Forward anodic cyclic voltammetry scan of Fe in 0.5M Na_2SO_4 containing 85 ppm H_2S . Scan rate is 5.56 mV/s.

Figure 3b: Back anodic cyclic voltammetry scan of Fe in 0.5M Na_2SO_4 containing 85 ppm H_2S . Scan rate is 5.56 mV/s.

Figure 4a: Forward anodic cyclic voltammetry scan of Fe in 0.5M Na_2SO_4 containing 1100 ppm H_2S . Scan rate is 5.56 mV/s.

Figure 4b: Back anodic cyclic voltammetry scan of Fe in 0.5M Na_2SO_4 containing 1100 ppm H_2S . Scan rate is 5.56 mV/s.

Figure 5a: Forward anodic cyclic voltammetry scan of Fe in 0.5M Na_2SO_4 containing 1400 ppm H_2S . Scan rate is 5.56 mV/s.

Figure 5b: Back anodic cyclic voltammetry scan of Fe in 0.5M Na_2SO_4 containing 1400 ppm H_2S . Scan rate is 5.56 mV/s.

Figure 6a: Forward anodic cyclic voltammetry scan of Fe in 0.5M Na_2SO_4 containing 3100 ppm H_2S . Scan rate is 5.56 mV/s.

Figure 6b: Back anodic cyclic voltammetry scan of Fe in 0.5M Na_2SO_4 containing 3100 ppm H_2S . Scan rate is 5.56 mV/s.

Figure 7a: Forward anodic cyclic voltammetry scan of Fe in 3.5% NaCl, 0 ppm H_2S . Scan rate is 5.56 mV/s.

Figure 7b: Back anodic cyclic voltammetry scan of Fe in 3.5% NaCl, 0 ppm H_2S . Scan rate is 5.56 mV/s.

approximately 393mV (SCE). This small peak was present for all scan rates except the very rapid rates of 100 mV/s and 500 mV/s.

The electrochemical behavior of iron in four different aqueous environments was investigated by the slow scan rate potentiodynamic technique. The four environments are deaerated double distilled water, 1.0M Na_2SO_4 , unbuffered 0.60M NaCl and 4.0 - 4.1 pH-buffered 0.60M NaCl. The original plan for this research project was concerned with obtaining corrosion rate data for iron in only the deaerated double distilled water and unbuffered 0.60M NaCl, but later in the research work the sodium sulfate solution and the pH-buffered sodium chloride solution were added. The system Fe/1.0M Na_2SO_4 + various H_2S concentrations was investigated in order to obtain well-defined anodic and cathodic Tafel regions and to observe the values of the Tafel slopes when the solution iR drop is very small. The system Fe/4.0 pH-buffered 0.60M NaCl + various H_2S concentrations was studied for two reasons: (1) to observe the trend in corrosion rates as a function of H_2S concentration for constant pH and (2) to evaluate the electrochemical reaction order $n_{+\text{H}_2\text{S}}$.

$$\left(\frac{\partial \log(i_a)}{\partial \log C_{\text{H}_2\text{S}}} \right)_{E, \text{pH}, \text{Cl}^-}$$

The polarization curves that were drawn for all of the slow scan rate potentiodynamic experiments will not be presented in this report.³ A graphical summary of the anodic Tafel regions and cathodic Tafel regions for all of the aqueous solutions mentioned above is offered in this report as Figures 8, 9, 10 and 11. The values of the anodic Tafel slope (b_a), cathodic Tafel slope (b_c), corrosion current density (i_{corr}) and corrosion potential (E_{corr}) are presented in Tables 1, 2, 3 and 4 for these aqueous environments.

Figure 8: The anodic and cathodic Tafel regions taken from the polarization curves for iron in deaerated double distilled water, plus various H_2S concentrations. Anodic Tafel regions are at the left half of the graph; cathodic Tafel regions are at the right half of the graph.

H ₂ S Conc., ppm	pH	<u>E_{corr},</u> <u>mV(SCE)</u>	<u>i_{corr},</u> <u>mA/cm²</u>	<u>E_r,</u> <u>mV(SCE)</u>	<u>b_a,</u> <u>mV</u>	<u>b_c,</u> <u>mV</u>	Anodic Tafel Region, mV(SCE)	Cathodic Tafel Region, mV(SCE)	Scan Rate, mV/hr
3426	3.78	-751.8	8.3x10 ⁻²	NR	298	343	-636 to -575	NA	1500
1891	4.18	-748.6	4.1x10 ⁻²	NR	349	409	-600 to -580	-960 to -900	1500
1119	4.44	-771.2	2.85x10 ⁻²	NR	354	383	-630 to -580	-950 to -900	1500
279	4.60	-768.4	1.8x10 ⁻²	-774	201	226	-696 to -648	-888 to -840	1800
170	4.83	-811.0	1.76x10 ⁻²	-782	461	538	-624 to -552	-1104 to -976	720
55	5.12	-817.1	1.6x10 ⁻²	-847	296	376	-705 to -635	-990 to -950	1119.4
0	7.00	-895.3	9.5x10 ⁻⁴	-779	113	79	-864 to -844	-946 to -922	720

Table 1: Summary of the kinetics data for the dissolution of iron in double distilled deaerated water with various concentrations of H₂S. NR = not reported. NA = not available from the polarization curve.

Figure 9: The anodic and cathodic Tafel regions taken from the polarization curves for iron in 1.0M Na₂SO₄ with various H₂S concentrations. Anodic Tafel regions are at the left side of the graph; cathodic Tafel regions are at the right side of the graph.

H ₂ S Conc., ppm	pH	E _{corr} , mV(SCE)	i _{corr} , mA/cm ²	E _r , mV(SCE)	b _a , mV	b _c , mV	Anodic Tafel Region, mV(SCE)	Cathodic Tafel Region, mV(SCE)	Scan Rate, mV/hr
2926	4.74	-718.0	7.7x10 ⁻²	-735	54	191	-670 to -620	-1000 to -800	1500
1274	5.14	-727.5	2.95x10 ⁻²	-744	50	130	-690 to -612	-800 to -768	1500
1047	5.32	-737.5	2.8x10 ⁻²	-749	46	125	-708 to -678	-786 to -774	1500
148	6.10	-801.2	1.75x10 ⁻²	-777	66	185	-624 to -576	NA	720
124	6.43	-789.4	1.73x10 ⁻²	-787	62	274	-708 to -624	-1008 to -936	1800
77	6.84	-787.8	1.7x10 ⁻²	-793	68	518	-648 to -576	-1092 to -984	1800
0	7.99	-811.2	7.0x10 ⁻³	-793	117	158	-744 to -696	-1104 to -984	1800

Table 2: Summary of the kinetics data for the dissolution of iron in 1.0M Na₂SO₄ with various concentrations of H₂S. NA = not available from the polarization curve.

Figure 10: The anodic and cathodic Tafel regions taken from the polarization curves for iron in unbuffered 0.60M NaCl with various H₂S concentrations. Anodic Tafel regions are at the left side of the graph; cathodic Tafel regions are at the right side of the graph. The arrow for the anodic Tafel region (0 ppm H₂S) indicates that the upper limit of this region lies beyond -530mV.

H ₂ S Conc., mM	pH	<u>E_{corr},</u> mV(SCE)	<u>i_{corr},</u> mA/cm ²	<u>E_r,</u> mV(SCE)	<u>b_a,</u> mV	<u>b_c,</u> mV	Anodic Tafel Region, mV(SCE)	Cathodic Tafel Region, mV(SCE)	Scan Rate, mV/hr
3218	4.00	-733.9	6.6x10 ⁻²	-734	55	116	-696 to -648	-888 to -860	1800
915	4.29	-744.4	7.1x10 ⁻²	-748	51	181	-708 to -678	-984 to -912	1800
358	4.53	-748.2	9.6x10 ⁻²	-757	64	261	-660 to -624	-1056 to -978	1800
175	4.80	-739.7	1.39x10 ⁻¹	-764	69	338	-642 to -612	-1014 to -960	1800
140	5.05	-763.0	1.5x10 ⁻¹	-774	89	798	-596 to -564	-1206 to -1080	1800
99	5.25	-776.6	1.67x10 ⁻¹	-786	91	NA	-570 to -546	NA	1800
0	5.91	-832.9	1.82x10 ⁻¹	-777	227	NA	-552 to -336	NA	1800

Table 3: Summary of kinetics data for the dissolution of iron in unbuffered 0.60M NaCl with various concentrations of H₂S. NA = not available from the polarization curve.

Figure 11: The anodic and cathodic Tafel regions taken from the polarization curves for iron in 4.0 - 4.1 pH-buffered 0.60M NaCl with various H_2S concentrations. Anodic Tafel regions are at the left side of the graph; cathodic Tafel regions are at the right side of the graph.

<u>H₂S</u> <u>Conc.,</u> <u>ppm</u>	<u>pH</u>	<u>E_{corr},</u> <u>mV(SCE)</u>	<u>i_{corr},</u> <u>mA/cm²</u>	<u>E_r,</u> <u>mV(SCE)</u>	<u>b_a,</u> <u>mV</u>	<u>b_c,</u> <u>mV</u>	<u>Anodic</u> <u>Tafel</u> <u>Region,</u> <u>mV(SCE)</u>	<u>Cathodic</u> <u>Tafel</u> <u>Region,</u> <u>mV(SCE)</u>	<u>Scan</u> <u>Rate,</u> <u>mV/hr</u>
3260	4.04	-722.0	2.9x10 ⁻¹	-726	69	207	-636 to -588	-1008 to -900	1800
515	4.05	-714.0	2.1x10 ⁻¹	-724	69	195	-624 to -552	-1008 to -888	1800
215	4.06	-709.6	1.5x10 ⁻¹	-721	63	181	-612 to -588	-960 to -864	1800
146	4.08	-710.9	1.3x10 ⁻¹	-721	61	162	-642 to -594	-888 to -828	1800
78	4.08	-712.9	1.16x10 ⁻¹	-724	61	170	-606 to -588	-918 to -840	1800
0	4.01	-622.0	3.2x10 ⁻²	-627	37	141	-594 to -564	-690 to -660	1800

Table 4: Summary of the kinetics data for the dissolution of iron in 4.0 - 4.1 pH-buffered 0.60M NaCl with various concentrations of H₂S.

The anodic Tafel slopes for iron in 1.0M Na_2SO_4 range from 54 mV to 68 mV regardless of the H_2S concentration, but b_c becomes very large (-518 mV) as the H_2S concentration decreases. Values of b_a and b_c are larger than expected for iron in 1.0M Na_2SO_4 without H_2S . A notable feature of the anodic and cathodic Tafel regions in Figure 9 is that they extend over at least 5/10 order of magnitude of current density. Also, the anodic Tafel regions for iron in 1.0M Na_2SO_4 with H_2S occupy a more narrow range of potentials compared to the Tafel lines in Figure 8.

The polarization curves for iron in pH-buffered 0.60M NaCl with H_2S show that the anodic and cathodic Tafel regions are well-defined³. There are two notable features of these Tafel regions as presented in Figure 11. First, the cathodic Tafel region for 0 ppm H_2S and very low H_2S concentrations could be located easily in contrast to the curves pertaining to iron in unbuffered 0.60M NaCl. Second, with the exception of 0 ppm H_2S , the cathodic Tafel regions in Figure 11 were closely-spaced over a narrow range of potentials and this trend was not observed for any of the unbuffered solutions.

The corrosion rate data presented in Tables 1, 2, 3 and 4 are shown in graphical form in Figure 12. The corrosion rate data for iron in 1.0M Na_2SO_4 and deaerated double distilled water show good agreement because both solutions can be represented by one curve. The corrosion current densities for pH-buffered 0.60M NaCl appear to be represented best by a straight line and its slope is +0.256. If the anodic Tafel regions in Figure 11 are examined closely, it can be seen that one potential (-594 mV) lies in all of these regions. Hence, the values of i_a at $E_{\text{SCE}} = -594$ mV can be obtained from the polarization curves for iron

Figure 12: Summary of the corrosion current densities for iron in 1.0M sodium sulfate, unbuffered 0.60M sodium chloride, 4.0 - 4.1 pH-buffered 0.60M sodium chloride and deaerated double distilled water.

in 4.0 - 4.1 pH-buffered 0.60M NaCl.³ This set of data has been plotted in Figure 13. Therefore, i_a appears to vary linearly with H_2S concentration and the slope of this line is +0.233.

The corrosion rate data for iron in these four solutions have been summarized in Table 5 in terms of the units mils per year (mpy) and millimeters per year (mmpy). The values of mpy and mmpy were calculated from the formula

$$\text{corrosion rate} = Kai/nD$$

where K = a constant depending on the units of corrosion rate (i.e., 0.129 for mpy and 0.00327 for mmpy)

a = atomic weight of iron = 55.8 g/mol

i = current density in microamps/cm²

n = number of electrons lost during the oxidation = 2

D = density of iron = 7.86 g/cm³.

It must be emphasized that the oxidation of H_2S to sulfur ($H_2S \rightarrow 2H^+ + 2e + S^0$) is negligible or non-existent at E_{corr} . Hence, the simultaneous reduction and oxidation reactions at E_{corr} would be $2H^+ + 2e \rightarrow H_2$ and $Fe \rightarrow Fe^{2+} + 2e$.

The chronoamperometry experiments were designed to yield data about the dissolution rates of iron in pH-buffered aqueous solutions of Na_2SO_4 and NaCl with various H_2S concentrations. The electrochemical behavior of iron at one applied potential within the anodic Tafel region was studied by recording the current decay as a function of time and by analyzing WE solution samples for total iron concentration by AAS.

During the course of this research work, sixteen different chronoamperometry experiments were performed. Only one of these experiments utilized an unbuffered 0.60M NaCl (0 ppm H_2S) solution. Because the

Figure 13: Plot of i_a (at $E_{SCE} = -594mV$) versus H_2S concentration for obtaining the electrochemical reaction order n_{+H_2S} .

<u>Solution</u>	<u>H₂S Conc., ppm</u>	<u>mpy</u>	<u>mmpy</u>
1	3426	38.0	0.963
1	1891	18.8	0.476
1	1119	13.1	0.331
1	279	8.2	0.209
1	170	8.1	0.204
1	55	7.3	0.186
1	0	0.4	0.011
2	2926	35.3	0.894
2	1274	13.5	0.342
2	1047	12.8	0.325
2	148	8.0	0.203
2	124	7.9	0.201
2	77	7.8	0.197
2	0	3.2	0.081
3	3218	30.2	0.766
3	915	32.5	0.824
3	358	44.0	1.114
3	175	63.6	1.613
3	140	68.7	1.741
3	99	76.5	1.938
3	0	83.3	2.113
4	3260	132.8	3.366
4	515	96.2	2.438
4	215	68.7	1.741
4	146	59.5	1.509
4	78	53.1	1.346
4	0	14.7	0.371

Table 5: Summary of the corrosion rates for iron in the following solutions: 1 = deaerated double distilled water; 2 = 1.0M Na₂SO₄; 3 = unbuffered 0.60M NaCl; and 4 = 4.0 - 4.1 pH-buffered 0.60M NaCl. "mpy" is mils per year and "mmpy" is millimeters per year.

solution pH changed from 5.65 at the start to 3.80 at the finish, all subsequent experiments utilized the potassium hydrogen phthalate buffers. The most meaningful chronoamperometry experiments that will be mentioned in this report involved 4.0 - 4.1 pH-buffered NaCl with various H_2S concentrations ($E_{SCE} = -594$ mV). The applied potential for these experiments was determined from the polarization curves of iron in 4.0 pH-buffered 0.60M NaCl.³ The current decay curves are presented as Figure 14 and these curves illustrate that the current densities for times greater than 1 second are virtually independent of H_2S concentration. For times greater than 300 seconds, the currents for iron in 0.60M NaCl (0 ppm H_2S) are about one-half the currents for iron in NaCl solutions with H_2S . The iron concentration-time data for these four experiments are presented in Figure 15. A least squares analysis was performed on the iron concentration-time data and the resulting lines of slope +1 were drawn. It is quite obvious that the dissolution rate of iron in pH-buffered NaCl solution is independent of H_2S concentration. This finding also supports the conclusion from previous chronoamperometry experiments that iron dissolution rates depended primarily on electrode potential rather than on H_2S concentration (at constant pH).³

The electrochemical reaction order n_{+H_2S} can be evaluated by calculating the $\partial \log(dC/dt) / \partial \log C_{H_2S}$ for the condition of constant potential, constant Cl^- concentration and constant pH. The plot of $\log[d(C)/d(t)]$ versus H_2S concentration is presented as Figure 16. The very small and negative slope (-0.0225) strongly indicates that the kinetics of iron dissolution in 4.0 pH-buffered 0.60M NaCl are independent of H_2S concentration. Hence, the electrochemical reaction order n_{+H_2S} is virtually

Figure 14: Current density - time profiles for iron in pH-buffered 0.60M NaCl (4.0 - 4.1 pH) containing various concentrations of H_2S . Applied potential for all experiments is -594 mV (SCE).

Figure 15: Iron concentration - time profiles for iron in pH-buffered 0.60M NaCl (4.0 - 4.1 pH) containing various concentrations of H_2S . Applied potential for all experiments is -594mV (SCE).

Figure 16: Evaluation of the electrochemical reaction order $n_{H_2S} = \frac{\partial \log(dC/dt)}{\partial \log C_{H_2S}}$ at E, Cl^-, pH . The y-axis is labelled "log(dC/dt)" and the x-axis is labelled "concentration of H_2S (ppm)."

zero for iron dissolution in the anodic Tafel region. This result does not agree with the evaluation of $n_{\text{H}_2\text{S}} = +0.233$ from Figure 13.

Finally, the data pertaining to solution analyses for polysulfide ions by visible spectroscopy have not been reported because the absorbance values for all environments except one were very close to zero.³ This result is in good agreement with the work of Teder⁵ because his solubility plot for polysulfide ions in aqueous sulfur solutions predicts a very low polysulfide ion concentration in weakly acid solutions. Only the experiment of iron in 5.20 pH-buffered 1.0M Na_2SO_4 with 2503 ppm H_2S produced absorbances only slightly less than 0.2 after six hours.³ However, an absorbance of 0.20 is still very low. Therefore, if any sulfur had been electrochemically-deposited on the iron electrode during the course of an experiment, it seems likely that virtually no polysulfide ions were in equilibrium with the sulfur for these weakly acidic solutions.

The iron surface was not analyzed by scanning electron microscopy or by Auger electron spectroscopy during this research work. A few words about the corrosion products and iron surface appearance that were observed during these experiments would be in order. First, the polarization experiments and the cyclic voltammetry experiments always produced a mixture of ferrous and ferric ions. By noting the intensity of the color formed during the spot tests for Fe^{2+} and Fe^{3+} , it was concluded that the ferrous ions were always the dominant of the two species.

The cyclic voltammetry experiments produced a variety of surface corrosion products and tarnishes depending upon the H_2S concentration

and whether NaCl was present. Often, the iron electrode had a loose outer scale that was black in color and a gray (or dark gray) tarnish on the metal substrate when H_2S was present in 0.5M Na_2SO_4 . Sometimes white deposits were located near the electrode edge; perhaps these products were elemental sulfur. Iron in Na_2SO_4 solutions (no H_2S) generally possessed a gray tarnish after one cycle, but a black removable film could be produced by ten or twenty cycles at medium scan rates (i.e., 20,000 mV/hr). Cycling experiments with sodium chloride solutions (no H_2S) always produced numerous cone-shaped pits. The metal surface was never tarnished but, instead, possessed a lustrous appearance.

Polarization experiments (slow scan rates) produced virtually the same type of corroded surface that was noted for the cyclic voltammetry experiments. Iron in 1.0M Na_2SO_4 with H_2S always possessed a light tarnish after thirty minutes at E_p , but a black, loose corrosion product formed after thirty minutes at E_p when the solution was deaerated water with H_2S . The polarization experiments with iron in unbuffered 0.60M NaCl and various H_2S concentrations did produce numerous white deposits in the vicinity of the surface pits, but no white deposits were noted for iron in pH-buffered 0.60M NaCl. Numerous white and yellow-white deposits were noted for the experiments involving iron in 1.0M Na_2SO_4 with various H_2S concentrations.

The chronoamperometry experiments for iron in 1.0M Na_2SO_4 with H_2S and 0.60M NaCl with H_2S also produced white deposits. Significant pitting in sulfate solutions with H_2S was noted, but no pits were observed when H_2S was not present in the sulfate solutions. The pitting by sodium chloride solutions was not very extensive in these experiments

and most pits were shallow. A black corrosion product (probably mackinawite) usually covered a portion of the electrode surface and this product could be removed easily. The chronoamperometry experiments at -594 mV (SCE) (Figures 14 and 15) always produced a loose, black corrosion product and the extent of electrode coverage decreased with smaller H_2S concentrations. Also, the iron surfaces in the experiments at -594 mV always possessed numerous white deposits at the surface or just inside the pits.

DISCUSSION

The cyclic voltammetry experiments clearly indicate that iron can be passivated by an oxide-sulfur film in weakly acidic sodium sulfate solutions containing various H_2S concentrations. Furthermore, the constancy of the peak current density (i_p) and rest potential with scan number indicate that these films are very effective at passivating the iron surface in the pH range of 4.6 to 8.0. This result was not observed by Shoesmith, et al.⁷ for iron in alkaline solutions. They found that the peak current continued to rise with each cycle when HS^- ion was not present, but passivation and steady peak currents could be attained with HS^- ion in alkaline solutions.

The corrosion potentials that have been recorded in Tables 1, 2, 3 and 4 are in good agreement with the steady-state E_{corr} values observed by Ewing⁸ and the values derived from slow scan polarization experiments by Hart⁹ and Essock.¹⁰ The corrosion potentials show a decrease for pH-buffered 0.60M NaCl solutions with H_2S and this same trend has been reported by Kawashima, et al.¹¹ for iron in more acidic H_2S solutions. The corrosion potentials for iron in those¹¹ acidic

H_2S solutions were 30mV to 160mV more positive than the values listed in Table 4. The corrosion potentials for iron in 1.0M Na_2SO_4 , deaerated water and unbuffered 0.60M NaCl increase with H_2S concentration and this trend probably reflects the combined importance which solution pH and H_2S concentration share in determining the corrosion behavior of iron.

The corrosion potentials for iron in pH-buffered 0.60M NaCl with H_2S suggest that the anodic and cathodic electrode reactions might be polarized due to the presence of H_2S . Figure 11 indicates that the anodic reaction is not polarized, but all of the cathodic Tafel regions are displaced to lower potentials when H_2S is present. Also, the current densities for the cathodic Tafel regions in Figure 11 do not show a significant dependence on H_2S concentration. These observations are contrary to the data in Figures 8, 9 and 10 which show that the anodic Tafel regions and/or the cathodic Tafel regions are shifted closer to the equilibrium potential for higher H_2S concentrations. Bartonicek¹² has noted that H_2S in acidic solutions will cause the depolarization of the hydrogen evolution reaction and the iron dissolution reaction. Perhaps the depolarization trends in Figures 8, 9 and 10 are the result of lower pH values for those solutions with increasing H_2S concentration. However, a weakly acidic solution of constant pH (Figure 11) provides a much different chemical environment at the electrical double layer for hydrogen ion reduction. Hence, perhaps the direct reduction of H_2S as proposed by Bartonicek¹² is stifled in weakly acidic solutions by a larger OH^- concentration. Bartonicek¹² has also mentioned that the catalytic influence of H_2S decreases as the concentration of hydroxide ions increases.

The corrosion rates of iron in Table 5 are in reasonably good agreement with the results by several researchers.^{8,12,13} However, the corrosion currents for iron in 0.60M NaCl (0 ppm H₂S) appear to be somewhat lower than that reported by Nelson.¹³ He states that the corrosion rate for cast iron in 10% NaCl solution from weight loss measurements is less than 0.020 inches per year while this research work yields a corrosion rate of 3.2 mpy for 3.4% NaCl solution. Perhaps this discrepancy is due to two different experimental techniques, incorrect anodic Tafel line extrapolation in this work, or a complex corrosion behavior by cast iron in NaCl solutions which prevents direct correlation of corrosion rates with NaCl concentration. In any case, it is easy to conclude from Table 5 that solutions of sodium sulfate or sodium chloride which contain any concentration of H₂S are very corrosive to high purity iron.

A few statements about the chronoamperometry experiments involving iron in 4.0 pH-buffered 0.60M NaCl with various H₂S concentrations might explain the apparent contradictory values for the electrochemical reaction order $n_{\text{H}_2\text{S}}$. According to the results of Figures 12 and 13, the electrochemical reaction order for H₂S is approximately +0.25, but the chronoamperometry data in Figure 15 indicate that the concentration of iron in solution was independent of H₂S concentration. All of the lines in Figure 15 have a slope of +1.0 which indicates that the dissolution of iron is first-order with respect to time. However, when the electrochemical reaction order $n_{\text{H}_2\text{S}}$ is determined from a plot of $\log(dC/dt)$ versus H₂S concentration (Figure 16), the slope is very close to zero. Apparently, the iron concentrations in Figure 15 are determined

by the dissolution rate of mackinawite, the initial corrosion product. In other words, the rate of release of iron ions from the working electrode depends upon the dissolution rate of mackinawite and this rate seems to be independent of H_2S concentration. Tewari and Campbell¹⁴ have stated the same conclusion about the corrosion of carbon steel in aqueous H_2S solutions at $25^\circ C$: The dissolution rate is controlled by a chemical reaction between mackinawite and the H_2S solution and by the transport of the complexed iron corrosion product from the interface to the bulk solution. Incidentally, the anodic current densities in Figure 14 also indicate that the electrochemical dissolution of iron is governed strongly by the mackinawite film for times greater than 0.5 seconds.

These chronoamperometry results are in complete disagreement with the electrochemical reaction order n_{+H_2S} that was determined from Figures 12 and 13. Perhaps a simplistic explanation of these two values for n_{+H_2S} can be offered as follows. The electrochemical reaction order $n_{+H_2S} = +0.25$ indicates that the initial dissolution of iron by H_2S , HS^- and Cl^- is dependent on hydrogen sulfide concentration. However, after the iron corrosion product (mackinawite) forms, it does not merely diffuse away from the electrode toward the bulk solution. Instead, the mackinawite that is produced at different sites on the electrode can serve as tiny nuclei for the formation of a mackinawite (poreous) film product. Consequently, the kinetics of iron (i.e., solid electrode) dissolution appear to be impeded by the dissolution rate of the mackinawite film product. To summarize, the corrosion behavior of iron in aqueous chloride solutions containing H_2S appears to be dependent upon two different chemical

species: (1) For very short-term corrosion at a potential in the anodic Tafel region, the dissolution of iron depends on H_2S concentration and (2) for long-term corrosion at a potential in the anodic Tafel region, the dissolution of iron is governed by the dissolution rate of mackinawite.

An expression that relates the anodic current density to electrode potential can be written on the basis of the polarization experiments of iron in 4.0 pH-buffered 0.60M NaCl with various H_2S concentrations.³ The surface coverage of iron by H_2S or the reaction intermediate product $FeSH^+$ has not been determined in this work and so these parameters are identified by the symbol theta. Therefore:

$$i_a = nF[H_2S]^{0.25} \theta_{Fe} \exp \left[\frac{eF(\phi - \phi_{eq})}{RT} \right]_{pH, Cl^-, E}$$

where ϕ_{eq} is approximately -716mV (SCE).

CONCLUSIONS

The electrochemical behavior of a stationary iron electrode in well-stirred aqueous solutions containing H_2S , Cl^- and SO_4^{2-} has been studied by the techniques of cyclic voltammetry, slow scan rate voltammetry and chronoamperometry. The cyclic voltammetry experiments have indicated that high purity iron is readily passivated in solutions containing hydrogen sulfide and sulfate ion by an oxide-sulfur film and than no passivation is observed for iron in chloride solutions. Passivation is attained only after the electrodeposition of sulfur (at a range of potentials more positive than potentials at which iron is oxidized) has been completed.

The slow scan rate polarization experiments and chronoamperometry experiments have been useful to determine corrosion rates of iron in

aqueous solutions containing H_2S , Cl^- and SO_4^{2-} and can provide some insight to the mechanism of iron dissolution in these solutions. It has been shown very clearly in section 6.2 of the Master's thesis³ that the determination of corrosion rates by an electrochemical technique requires the researcher to be aware of the possible mechanisms which may describe iron dissolution. An awareness of the possible iron dissolution mechanisms is required because two Tafel regions can be observed during the anodic scan and either one can be extrapolated to E_{corr} to yield a value of i_{corr} . Consequently, the chronoamperometry experiments are valuable for indicating which iron dissolution mechanism is applicable to the anodic Tafel region that defines i_{corr} . The chronoamperometry experiments can indicate the predominance of one mechanism because they are conducted with respect to time.

Finally, the corrosion behavior of iron in neutral and weakly acidic solutions containing H_2S and Cl^- is studied best by using pH-buffered solutions. There is ample evidence in section V of the Master's thesis³ which shows that the pH at the electrode surface is not identical to the bulk solution pH in the absence of a buffer. Therefore, the kinetics of iron dissolution are effectively altered when the local pH is permitted to change drastically to lower values. In any event, pH-buffered solutions are required when performing the chronoamperometry experiments and so the polarization experiments must utilize the same electrolyte in order that the interpretation of results from these two techniques can be facilitated.

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PART II
Stress Corrosion Cracking Susceptibility of
2-1/4Cr-1Mo Steel in Boiling 50% NaOH

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INTRODUCTION

The general objective of this task is to investigate the stress corrosion cracking (SCC) susceptibility of molybdenum containing ferritic steels (Fe-Cr-Mo) in boiling 50% NaOH solution. In the present study, the stress corrosion cracking susceptibility of 2-1/4Cr-1Mo steel has been investigated for an environment of 50% NaOH (approximately 17.5N NaOH) at 138°C. Stress corrosion cracking tests were performed at anodic and cathodic controlled potentials in order to simulate the oxidizing and the reducing environments. The slow strain rate technique was used for the stress corrosion cracking tests.

EXPERIMENTAL

Test specimens. A description of the tensile test specimen and the preparation of the gage surface before an experiment are provided in another study¹ that utilized this same alloy. The only variations from the procedure in reference (1) are: (1) the tensile rods were machined to a 0.265 cm diameter in the gage section (compared with 0.25 cm in reference 1) and (2) the gage section was 1.45 cm in length at the center of the 23 cm rod (compared with 1.25 cm in reference 1).

Solutions. The test environment was only boiling 50% NaOH solution (138°C). A tensile specimen was also tested in air at 25°C and this was used as a reference for all other specimens.

Apparatus. A description of the slow strain rate machine, the electrolytic cell with its connections and the potentiostat have been presented in reference (1). The slow strain rate machine is powered by

a 1/8th h.p., 1800 rpm, single-phase electric motor geared to produce nominal strain rates of 10^{-7} s^{-1} , 10^{-6} s^{-1} , and 10^{-5} s^{-1} . All tests in this report used the middle range in a specimen with 1.45 cm gage length. Hence, for a crosshead speed of $2.9 \times 10^{-6} \text{ cm/s}$, the strain rate was calculated as $2.07 \times 10^{-6} \text{ s}^{-1}$.

Unlike the procedure in reference (1), a mercury-mercury oxide (Hg/HgO) internal reference electrode was used in this work for reporting the electrode potentials. The electrode potentials in this work can be converted to the standard hydrogen electrode scale by adding 461.5 mV. A description of the Hg/HgO reference electrode is presented in reference (2).

Procedure. After a specimen was mounted in the electrolytic cell on the straining machine, the cell was filled with hot test solution (about 50°C) and degassed with prepurified argon. While the solution was heated to its boiling temperature (138°C), a cathodic current was passed through the cell by the potentiostat. A potential was applied and the slack on the specimen was removed before beginning the slow strain rate experiment. Fractured specimens were removed from the cell and examined under a scanning electron microscope (SEM).

The slow scan rate potentiodynamic experiments for the Cr-Mo steel in boiling 50% NaOH utilized a cylindrical steel specimen that was turned onto a Teflon-encased metal rod.² The metal rod provided electrical contact between the steel specimen and the potentiostat. The scans were begun at -1300 mV (Hg/HgO electrode) and ended at 0 mV (Hg/HgO electrode), and a scan rate of 25 mV/min. was used for these experiments.

The time versus load curve was used to calculate the ultimate tensile

strength (UTS), true fracture stress and reduction in cross-sectional area by using the cross-sectional area at the fracture tip. These results were then compared with those obtained in the inert (air) environment.

RESULTS

The results of the slow scan rate potentiodynamic experiments can be illustrated by the polarization curve in Figure 17. This steel does exhibit an active-to-passive electrochemical behavior as indicated by the single current peak at approximately -850 mV. The passive currents in Figure 17 are large (about 0.4 mA), but the presence of this passive region indicates that a surface film does exist at potentials more positive than -850 mV.

In total, nineteen specimens were tested on the slow strain rate machine. The ratios of reduction in area, UTS, and the fracture stress at the test condition in the environment to their respective values in air are shown in Table 6. The types of failure observed under the different test conditions could be classified into three general types: ductile failure, brittle failure and corrosion failure. None of these failure modes could be described by only one surface appearance. The fractographic studies revealed that intergranular attack, transgranular cracking and/or repassivation of the metal accompanied each of the three failure modes.

DISCUSSION

The data in Table 6 illustrate that the stress corrosion behavior of 2-1/4Cr-1Mo steel in boiling 50% NaOH is highly dependent on the electrode potential. The fractographic studies revealed that brittle fracture

Figure 17: Polarization curve for 2-1/4Cr-1Mo steel in 50% NaOH at 138°C.

Table 6: Comparative mechanical properties for 2-1/4Cr-1Mo steel in boiling 50% NaOH at different potentials.

#	Pot. mV	Time hrs	UTS Ksi	Fracture Ksi	RA %	Ratio of...Environment/Air			
						UTS	Fract.	Time	RA
17	-1100	29.90	66.105	52.188	40.35	.888	1.084	.756	.49
5	- 912	5.50	29.828	.548	95.00	.400	.011	.139	1.17
6	- 912	7.50	37.950	---	95.71	.509	---	.189	1.18
18	- 912	7.25	68.886	11.597	93.02	.925	.241	.183	1.15
19*	- 912	6.20	65.505	42.110	46.22	.879	.565	.157	.57
7	- 825	22.50	60.306	41.750	39.10	.804	.867	.569	.48
11	- 800	29.25	63.875	44.650	61.20	.856	.927	.740	.73
16	- 750	27.40	64.365	30.153	42.98	.864	.626	.693	.53
17	- 700	30.50	56.827	36.183	63.90	.763	.751	.772	.79
12	- 700	21.83	62.046	41.750	57.00	.836	.867	.555	.70
13	- 600	27.60	61.002	38.851	70.80	.819	.807	.698	.87
15	- 600	30.90	63.875	40.590	59.58	.856	.843	.782	.74
8	- 400	23.25	63.875	33.052	63.50	.836	.867	.588	.78
14	Air	39.50	74.455	48.129	80.80	1.000	1.000	1.000	1.00

Note : Potential mV with respect to Hg/HgO electrode
 # is the symbol of the specimen
 * higher strain rate 10^{-5} s^{-1}

was the dominant mode of failure for electrode potentials between -825 mV and -600 mV (Hg/HgO electrode). At potentials more positive than -600 mV (Hg/HgO electrode), film formation readily occurs and the stress corrosion mechanism is controlled by metal dissolution.

CONCLUSIONS

The 2-1/4Cr-1Mo steel is susceptible to stress corrosion cracking in boiling 50% NaOH. The degree of susceptibility is controlled by electrode potential: SCC susceptibility decreases and general corrosion increases at more positive potentials. The time-to-failure was longest for the controlled potentials of -700 mV and -600 mV (Hg/HgO electrode). These specimen failures were a combination of ductile and brittle fractures for these controlled potentials.

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- ²Soendjasmono, B.N. M.Sc. Thesis, Ohio State University, 1979.

PUBLICATIONS

In addition to five previous reports to the sponsor (C00-2421-01 through C00-2424-05) the following papers, articles, theses and dissertations have been presented on the work of this contract.

Papers Presented and/or Published

"Effects of Temperature, Alloy Composition, and Solution Concentrations on the Anodic and Cathodic Polarization Behavior of Fe-Cr-Ni Alloys in Caustic Solution," A.K. Agrawal, M.F. Long, and R.W. Staehle in HIGH TEMPERATURE HIGH PRESSURE ELECTROCHEMISTRY IN AQUEOUS SOLUTIONS, Conference Proceedings, NACE (1976).

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"Stress Corrosion Cracking and Anodic Behavior of Type 304 Stainless Steel during Straining in Boiling 20N NaOH Solution," Y.S. Park, J.R. Galvele, A.K. Agrawal and R.W. Staehle. Abstract No.34, Electrochemical Society Meeting, Washington, D.C. 1976

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