$\rm H_2S$ MULTIPHASE FLOW LOOP: $\rm CO_2$ CORROSION IN THE PRESENCE OF TRACE AMOUNTS OF HYDROGEN SULFIDE

A thesis presented to

the faculty of the

Fritz J. and Dolores H. Russ

College of Engineering and Technology

of

Ohio University

In partial pulfillment of the requirements for the degree Master of Science

> Bruce N. Brown November 2004

This thesis entitled

H₂S MULTIPHASE FLOW LOOP: CO₂ CORROSION IN THE PRESENCE OF TRACE AMOUNTS OF HYDROGEN SULFIDE

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BROWN, BRUCE N. M.S. November 2004. Interpersonal Communication

H₂S MULTIPHASE FLOW LOOP: CO₂ CORROSION IN THE PRESENCE OF TRACE AMOUNTS OF HYDROGEN SULFIDE (122p.)

Director of Thesis: Srdjan Nesic

An experimental series was conducted to measure the effect of low concentrations of H_2S (3, 15, 100 ppm) under "non-film forming conditions" for iron carbonate at pH 4 in a CO₂ saturated environment on the corrosion rates of UNS C1018 and X65 carbon steels at two temperatures (60°C and 80°C). These experiments in the Hydrogen Sulfide Multiphase Flow Loop provide the first example of the effect of H_2S concentration on corrosion rates measured concurrently in single phase and multiphase flow in a CO₂ saturated environment. At 60°C and 80°C, any addition of H₂S retarded the corrosion rate in both single phase and multiphase flow conditions over a 96-hour exposure period as compared to the corrosion rate measured under the same partial pressure of CO₂ without the presence of H₂S. At pH 4, films of 5 to $10\mu m$ were produced over 96 hours for UNS C1018 flush-mounted coupons in a system with a 100ppm concentration of H_2S in the gas phase. Electron dispersion spectroscopy of the films provides proof of an iron sulfide (FeS) film. Thinner films were developed under conditions of 3ppm and 15ppm H₂S concentrations, but film thickness was not as easily quantified by scanning electron microscopy. Overall, higher corrosion rates consistently occurred in multiphase flow when compared to those measured under single phase conditions. Pitting corrosion was observed at 80°C for both 3ppm and 15ppm H_2S concentrations. System validation tests on the Hydrogen Sulfide Flow Loop system prior to this experimentation show repeatability and good comparison to another flow system under the same operating conditions without the presence of H_2S .

APPROVED:

Srdjan Nesic Professor of Chemical Engineering

DEDICATION

То

my wonderful wife, Debi,

who has supported my endeavors since 1981,

and

to our two children,

Lindsay and Garret,

who have enriched my life everyday since they came into this world.

ACKNOWLEDGEMENTS

The Masters Degree in Chemical engineering represents a major achievement in my lifetime and I would like to show gratitude to those who have truly provided me guidance along the way. From 1994 to 1996, I worked as a research technician for Dr. Mamdouh Salama. Dr. Salama encouraged me to continue my education during my employment and was instrumental in contacting Dr. Paul Jepson of the Institute of Corrosion and Multiphase Technology to recommend me for a position that would ultimately benefit my entire family. On top of the benefits my new career has offered my family, I would also like to thank Dr. Paul Jepson for pushing me to the best of my abilities during my undergraduate work. In the period between my undergraduate and graduate studies, Dr. Chuck Alexander, interim Director of the Institute for Corrosion and Multiphase Technology and former President of IEEE, helped me to understand the need to complete a graduate program of study, and helped me to improve my orator abilities. His wonderfully positive outlook of life on a daily basis was an encouragement I will always remember; anyone who knows him will wholeheartedly agree. I would not have even begun my graduate degree program without having a knowledgeable advisor in my field of study. With his appointment as the Director of the Institute for Corrosion and Multiphase Technology in 2002, Dr. Srdjan Nesic fulfilled that need. His guidance helped me to achieve a Masters Degree and has put me in a position to interact with well known researchers in the field of CO_2/H_2S corrosion. I sincerely want to thank Srdjan for the respect he has given me as a researcher and for the future opportunities available to me from having the chance to work with a world renowned expert in the field of corrosion. Thank you all.

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INTRODUCTION

The simultaneous presence of CO_2 and H_2S in produced fluids makes for a very aggressive environment that can lead to severe corrosion of mild steel. There are a limited number of studies that cover this area, particularly when compared to the extensive literature available about corrosion in a CO_2 saturated environment. H_2S -related corrosion is a topic of great concern due to the increased safety awareness necessary when dealing with this insidious gas. Pipeline failures in service conditions containing trace amounts of H_2S have led to the need for more knowledge to characterize its relation to the corrosion process. Srinivasan and Kane⁵ stated that " H_2S related corrosion has not been studied extensively in the laboratory due to the difficulty of working with H_2S , but the need for understanding CO_2/H_2S corrosion has grown with the advent of deeper and more corrosive production systems."

Information from laboratory experimentation provides correlations between empirical corrosion rate data and the specific conditions of exposure. These correlations are then used in corrosion prediction software that can help an engineer to design and monitor industrial production pipeline life expectancies. Various corrosion rate prediction models are currently used in industry and some even use a constant factor correlation for the addition of small amounts of H₂S in a CO₂ rich environment. The experimental studies¹⁻⁴ that have been published in the open literature on the subject of corrosion in a CO₂/H₂S environment have been limited to autoclaves and glass cells. These types of research apparatus provide results now used for corrosion models, but are small in total volume and not capable of producing multiphase flow regimes similar to industrial pipeline conditions.

The experimental parameters used in the current study will investigate the effect of trace amounts of H_2S on CO_2 corrosion of mild steel in single phase (liquid) and twophase (liquid & gas) flow. The range of experimental parameters are chosen to eliminate the precipitation of iron sulfide (FeS) and iron carbonate (FeCO₃) films while mapping the effects of trace amounts of H_2S on the corrosion rate of a general purpose carbon steel. Parameter variation includes three concentration additions of H_2S , in two types of flow, at two different temperatures, with a constant pH and constant partial pressure of CO_2 . The range of H_2S concentrations studied constitutes a "small" or "trace" amount of H_2S in the gas phase of less than 100 ppm.

The "H₂S Multiphase Flow Loop" at Ohio University was used for experimentation. The 10 cm I.D. Hastelloy C-276 flow loop was constructed in order to fulfill an informational gap in multiphase slug flow corrosion research. Since hydrogen sulfide at low concentrations has been shown to decelerate a CO_2 corrosion rate in small scale testing, the current focus on the H₂S system is find out if these conclusions are repeatable in a large scale flow loop.

Previous studies in a CO_2 saturated environment have shown that, under multiphase flow conditions, particularly in slug flow, a significant increase of the CO_2 corrosion rate is obtained as compared to corrosion rates under single phase flow conditions.⁸ There have been no similar studies performed for the CO_2/H_2S corrosion environment. The "H₂S Multiphase Flow Loop" at Ohio University was constructed in order to fulfill this informational gap. Since hydrogen sulfide at low concentrations has been shown to have a synergistic effect on the CO_2 corrosion rate in small scale testing, the current focus on the H₂S system is to find out if these conclusions are repeatable in a large scale flow loop.

LITERATURE REVIEW

H₂S and CO₂ are known as "acid gases." The behavior of the solubility of carbon dioxide is very similar to that of hydrogen sulfide; both form weak acids in water. At low pressure, the solubility of both hydrogen sulfide and carbon dioxide can be estimated using Henry's law. The difference in the aqueous phase gases is that aqueous carbon dioxide must undergo a hydration reaction to form carbonic acid before dissociation while aqueous hydrogen sulfide is acidic and will directly dissociate into solution. This means that for equivalent gas phase concentrations in a gas-liquid system, hydrogen sulfide will reduce the pH more than carbon dioxide. The accepted equilibrium reaction equations are in Appendix A.

Previous research by Ikeda, et al,¹ has shown that a low concentration of H_2S (<30 ppm) in a CO₂ saturated water solution accelerated the corrosion rate significantly in comparison to corrosion in a similar CO₂ environment without H_2S . Corrosion rates were determined by coupon weight loss from a closed autoclave tester. They assume that, at low partial pressures of H_2S in a CO₂ environment, the co-existence of H_2S

simply accelerates the corrosion reaction and increases the corrosion rate in the temperature region less than 100°C. Above 100°C, a protective FeCO₃ film begins to occur. This "H₂S effect" seems to vanish at H₂S concentrations greater than 30 ppm or temperatures greater than 80°C when a protective film forms.^{1,2} From this research, the current study will focus on trace amounts of H₂S at gas phase concentrations of 3, 15, and 100 ppm.

In a study² by the Institute for Energy Technology (IFE), it was suggested that the effect of H₂S could be significant only in the low pH range (<pH 5); an important factor not discussed in other studies. Kvarekval² studied 1 and 5 mbar partial pressure of H₂S in a 1 bar CO₂ saturated environment (1,000 ppm and 5,000 ppm H₂S) and proposed that H₂S accelerates hydrogen evolution by acting as a catalyst. In 1 m/s single phase flow at 25°C, corrosion rates calculated from linear polarization resistance measurements at pH 4 were consistently higher than those measured without H₂S in a similar "pure" CO₂ environment. At pH values between 5.5 and 7, he found the effect of H₂S on corrosion rate to be ambiguous. From this research, a pH of 4 was chosen to study the effect of H₂S in a non-iron carbonate film forming environment.

Valdes, et al³, found an effect similar to Ikeda, et al,¹ at 3.1 MPa (450 psi) CO_2 and low concentrations of H₂S in the range of 0 to 40 ppm in the gas phase. These experiments show the increase in corrosion rate at temperatures closer to 50°C.

Perdomo, et al⁴, measured corrosion rate as a function of CO_2 partial pressure at 38°C (100°F) at four different H₂S partial pressures, from under 20 ppm to over 200 ppm. These experiments also reported the same phenomena of low partial pressures of H₂S acting as a catalyst for corrosion that occurred throughout the range of 50 to 500 kPa CO_2 .

In general, the reasons behind an " H_2S effect" on CO_2 corrosion are not entirely understood. It has been speculated that adsorbed sulfide species and/or sulfide films accelerate the corrosion rate of mild steel through a catalytic or a galvanic effect.³ All of the previously conducted studies have largely ignored the effect of flow with the exception of Kvarekval² who conducted experiments at room temperature and low pressure.

Current laboratory research associated with sour gas has been mainly conducted in autoclaves because of the ability to reproduce the wellhead temperature and pressure conditions; some even have circulatory pumps to achieve better mass transfer in the corrosion process. Srinivansan⁵ describes an autoclave system developed to simulate fluid flow induced corrosion in CO₂/H₂S systems. This small-scale system provides an adequate environment for reproducing the corrosive constituents and wall shear stress effects, but lacks the size for development of certain flow regimes. Studies such as those by Pargeter⁶ have provided information on maximum permissible hardness levels for welded steels at risk of sulfide stress corrosion cracking, but researchers did have some concerns that the 16:1 solution volume to sample surface area was small and resulted in a higher contamination of the aqueous environment by corrosion products that would be much higher than is seen in a production environment.

When hydrogen sulfide is present in low concentrations in a CO₂ dominated system, the iron sulfide (FeS) film interferes with the formation of the carbonate scale

(FeCO₃), but is considered to have a protective effect at about 60°C under film forming conditions.¹¹ This is of interest because the iron sulfide film would seem to be more easily removed from the pipe wall than the iron carbonate scale. Under turbulent conditions (i.e. slug flow), removal of the "protective" scale will lead to an increased corrosion rate.

In two-phase liquid-gas flow, the flow regime will transition from a stratified pattern to an intermittent pattern with an increase in gas velocity. This intermittent pattern is called slug flow. In stratified flow, gas and liquid move in a layered, non-turbulent flow. With an increase in superficial gas velocity, waves are created on the flowing liquid surface. By further increasing superficial gas velocity, slug flow begins when a wave reaches the top of the pipe and then becomes accelerated in relation to the volumetric gas flow rate. Slug flow is intermittent and highly turbulent. A much greater increase in superficial gas velocity will produce annular flow, which is a less turbulent flow regime where fluids are forced to the pipe wall and the inner core of flow is a fast moving gas. All of the multiphase corrosion testing is done in turbulent flow defined as "slug flow."

Calculations for flow regime determination were taken from correlations made by Wilkens.¹⁹ Wilkens modeled the transition from stratified flow to slug flow in liquid gas systems and determined film Froude numbers for different gas velocities at specific liquid velocities under 0.27, 0.45, and 0.79MPa partial pressures of CO₂ in 100% ASTM seawater. Film Froude number is a non-dimensional ratio of inertial effects to gravitational effects. The strength or turbulence in slug flow is directly related to the Froude number.

Vuppu¹² measured corrosion rates in slug flow and concluded that the corrosion rate increases with an increase in the temperature up to the 60°C scaling temperature. Above this temperature, the corrosion rate decreases with an increase in temperature. Vijay¹³ has shown that the corrosion rate increases with increasing Froude number at a given temperature and gas density. His study also found that corrosion films on coupons exposed to slug flow conditions were thinner than those produced in similar conditions in a full pipe flow pattern. Vijay postulated that stripping of the corrosion products on the metal surface was due to higher levels of shear and turbulence. Jepson and Bhongale¹⁴ provided corrosion rate data points for CO₂ partial pressures of 0.27, 0.45, and 0.79MPa at Froude 6 for a temperature range of 40 to 90°C in 100% seawater. All three data sets provide valuable information for understanding the influence of turbulence and water chemistry on measured corrosion rates, but each study used the same high-pressure horizontal multiphase flow system that maintained a stationary slug over the test surface. Stationary slug conditions provide a continual highly turbulent zone for placement of corrosion measurement devices, but may skew the desired results by producing an unrealistic pipeline environment. The hydrogen sulfide system uses a closed circulatory system that maintains repetitious conditions of moving slug flow over two different test sections. Gas and liquid phases are separated after the second test section and re-mixed in specific superficial velocities based upon volumetric flow rates of three pumps. The continual separation and re-mixing of measured flows in a closed system provide the desired flow regime in a very stable environment.

The study of CO_2/H_2S corrosion under multiphase conditions of water and gas mixtures is still a relatively new field. Multiphase flow pattern reproduction in a controlled

environment provides researchers with an opportunity to study corrosion and corrosion control mechanisms. Jepson and Taylor⁷ found that, in order to mimic the flow mechanisms observed in large diameter pipelines, test facility pipelines should be above 7.5 cm in diameter. The advantage of large diameter pipelines is the ability to produce flow regimes which are similar to that of pipelines in field operations. Slug flow is a flow regime phenomenon that is studied extensively due to the turbulence developed at the slug front. Under various multiphase conditions, the slug flow regime has been shown enhance the corrosion damage to pipelines^{8,9}. High velocity slugs are very turbulent with the existence of pulses of entrained bubbles in the mixing zone behind the front of the slug. These pulses of bubbles impact the pipe wall and accelerate the mass transfer of species, leading to increased corrosion rates¹⁰.

SPECIAL CONSIDERATIONS

System Specifications

The hydrogen sulfide system is located in an isolated environmental chamber. The 150 m² room houses two progressive cavity pumps, one positive displacement gear pump, an alloy C-276 clad mixing and separations tank, and over 50 m of alloy C-276 Schedule 40 pipe. Important features of the system include two test sections for insertion of corrosion and system parameter measurement devices, two different size liquid feed pipelines for a more accurate measurement of flow rates over a larger range of flows, and a gas combustion system located outside the building.

The H₂S system has a 1950 liter (515 gallon) total capacity and a 1130 liter (300 gallon) liquid capacity. With a maximum pressure limit of 7.9MPa (1000 psig), the system is designed to accommodate partial pressures of N₂, CO₂, H₂S, and/or methane through a gas-mixing panel. De-ionized water, brines, or oils are added directly to the tank through a 2.54 cm (1 inch) valve at the base of the tank at ambient temperature and pressure before purging and heating occur. Two 4.5kW immersion heaters, inserted into alloy C-276 sleeves filled with heat transfer fluid, control the system temperature through a thermocouple feedback from the tank to a controller mounted outside the room.

The progressive cavity pumps used are considered to be positive displacement pumps, so that volumetric flow is directly related to the pump rpm. The 50 Hp progressive cavity pump transfers the liquids from the tank through either a 5 cm I.D. pipe or a 10 cm I.D. pipe. The volumetric flow rate for each line has been measured using an ultrasonic flow meter and calibrated to the motor rpm. The 150 Hp progressive cavity pump is used as the gas circulatory pump. The gas pump requires liquid lubrication during operation, so a positive displacement gear pump provides a small percentage of the calculated volumetric flow to maintain lubrication. Gas volumetric flow, used to calculate the superficial gas velocity, V_{sg} , is equivalent to the space not occupied by liquid. The volume of liquid from the gas pump discharge is added to the liquid pump discharge to determine the superficial liquid velocity, V_{sl} . All pumps and electrical equipment in the room are explosion proof. The system schematic diagram is shown in Figure 1.



Figure 1. Schematic diagram of Multiphase flow loop (P&ID).

All controls for the system are located together in an operator area outside the environmental chamber in order to be able to monitor the system operation from a safe location.

Hazardous Gas

The special consideration for this set of experiments is the use of pure hydrogen sulfide gas. Since high concentrations of H_2S can easily cause fatalities, safety devices and safety training were of the utmost importance. According to the Occupational Safety and Health Administration (OSHA), a worker can be exposed to gas phase concentrations of hydrogen sulfide up to 10 ppm for 8 hours per day, 7 days per week, for 30 years with no ill health effects. Corrosion studies in an H_2S/CO_2 environment could involve hydrogen sulfide concentrations in the gas phase of the system above the 100 ppm value that is reported by the OSHA to be "immediately dangerous to life and health" (IDLH) and exposures to gas phase concentrations of H_2S above 500 ppm can be fatal.

The room housing the Hydrogen Sulfide System has had several safety reviews and safety procedures are strictly followed. The lecture bottle of pure H_2S in an enclosed cabinet with an internal H_2S fixed sensor and four more fixed sensors are located throughout the room to monitor for unwanted leaks. If a leak of H_2S occurs while the researcher is in the room, escape is the number one priority. A researcher in the room will wear a personal H_2S sensor for immediate visual and audio notification of H_2S concentrations encountered greater than 10 ppm. An alarm and ventilation system is connected to the fixed sensors and is designed to automatically operate and notify the researcher if concentrations of H_2S greater than 10 ppm are detected by any of the five sensors. With a total of five exit doors, the operator is always within 30 feet (10 m) of an exit at all times. All five doors are opened easily from inside the test cell, but require a building master key to unlock them from the outside. During times when the operator must enter the test cell, a "buddy" will be stationed in visual contact at all times with an unlocked door between them. The "buddy" is also someone trained in the hazards of hydrogen sulfide. A positive pressure, self-contained breathing apparatus (SCBA) is available for the "buddy" for entry into the room if a major incident should occur that requires rescue. During a release of gas where rescue is not required, the H₂S System can be shut down from outside the room and ventilation of the room occurs through a combustion system until safe entry is possible at levels below 10 ppm H₂S.

The two main Hydrogen Sulfide System operators are required to attend an H_2S instruction program that follows the ANSI Z390.1 – 1995 Hydrogen Sulfide Training Standard every three years. This OSHA training course provides the operators with the knowledge required for teaching others how to work safely in the field with and around hydrogen sulfide. Since the initial training, they have taught a certified course on hydrogen sulfide safety biannually to students and oilfield workers in Ohio.

RESEARCH OBJECTIVES

To establish the effects of low concentrations of H_2S in a CO_2 rich environment on corrosion of mild steel under single phase flow and slug flow regimes. These series of tests were conducted to determine corrosion rates of mild steel based upon no iron carbonate precipitation film formation in a pH 4 solution with exposures to gas phase concentrations of H_2S in a CO_2 saturated environment at 7.9 bar (100psig). Films formed during exposure to these conditions are thought to be produced by solid state film growth since the water chemistry is prohibitive for precipitation of iron carbonate or iron sulfide films.

EXPERIMENTAL PROCEDURE

The experimental set-up and operation of the multiphase flow loop has previously been described¹⁷ with the exception of a single phase test section that was added to allow WL (weight loss), ER (electrical resistance), and LPR (linear polarization resistance) monitoring in full pipe flow. Three probe locations were added to the system in single phase flow allowing for seven (7) simultaneous corrosion rate measurement devices to be used. Two probe locations are available at each of the multiphase test sections; all probe locations are on the bottom of the pipeline.

The system has a 300-gallon (1150 L) liquid capacity and is designed to accommodate partial pressures of N_2 , CO_2 , H_2S , and/or methane up to a total pressure of 7.0 MPa (1000 psig). De-ionized water, brines, or oils are added to the tank through a valve at the base of the tank and two 4.5kW immersion heaters inserted into alloy C-276 sleeves filled with heat transfer fluid maintain the system temperature. A thermocouple mounted on the exterior of the tank is used by the temperature controller to achieve the desired test temperature. Another thermocouple is located at the 6 o'clock position in the multiphase flow stream for confirmation of desired test section temperature. After the necessary liquid(s) and salts have been added to the tank, the system is to be purged of oxygen by full system operation under slug flow and addition of carbon dioxide. Operating temperature will also be set during this time. Once the system is deoxygenated and up to temperature, the test environment (partial pressures and temperature) is set by addition of the gases. The mass of hydrogen sulfide needed is calculated by mass and added through a 10 cc/min mass flow meter. The final concentration of H_2S is measured directly from a sampling tube off the gas phase of the system by use of a hand-held pump and colormetric tubes. A fume hood extension is located opposite the operator during this measurement to draw any gases released away from the operator. The operator wears personal gear such as a H_2S gas detector and an H₂S escape mask during this operation. Once system conditions are stable, probes and coupons will be loaded under pressure through glands for minimal release of system gases or fluids. The operator then monitors all system operations and corrosion rates from the operator area outside the environmental chamber.

Corrosion Monitoring Probes

Weight loss (WL), electrical resistance (ER), and linear polarization resistance (LPR) flush mount probe elements were inserted in specific locations and the order remained constant throughout the testing procedure. Elements tested in single-phase flow (in order of the direction of flow) were WL, ER, and LPR. Elements tested in the upstream multiphase flow section were WL and LPR. Elements tested in the downstream multiphase flow were WL and ER.

Weight loss coupons are 1.14 cm (0.45") diameter, 0.3175 cm (0.125") thick with a slight bevel on the reverse edge for press-fit, flush mounted in a nylon holder. Four coupons will fit in the nylon holder that is attached to a holding rod with a flat head stainless steel screw. Each coupon is labeled with a number and orientation mark on the back prior to being polished on the front to a 600-grit finish, weighed to the nearest ten-thousandth (0.0001) of a gram, and mounted in the holder according to coupon number and orientation. A mark on the holder is used to maintain orientation of coupons with respect to flow direction and coupons are mounted in numerical order in a clockwise direction. Each coupon is mounted in the holder so that the orientation mark can be used to determine the coupons' orientation to flow after the experiment is completed. The press-fit, flush mount design of the coupons allows for the top surface area of 1.03 cm² (0.159 sq. in.) to be exposed to system conditions. Design drawings for the nylon holder, holding rod, and WL coupon are in Appendix A. Weight loss corrosion rate is determined by measuring the coupon's mass lost over the time of exposure and converting to thickness lost per year. Conversion from grams lost to millimeters per year corrosion rate is done by using the density of generic UNS C1018 carbon steel, the assumption of general corrosion, and a time conversion. The assumption of "general corrosion" is that even layers of material are removed from a cylindrical shape at 0.103cm³ of material volume per millimeter of coupon thickness; the 3rd factor in the equation:

$$\frac{grams_lost}{hrs_of_exp\,osure} \bullet \frac{cm^3}{7.85g} \bullet \frac{mm}{0.103cm^3} \bullet \frac{8760hrs}{yr} \equiv \frac{mm}{yr}$$
(1)

Electrical resistance (ER) probes are flush-mount, modular style probes with a 10 mil thickness ("FL10") made by Metal Samples[®]. The corroding material for these probes is UNS C1010 carbon steel. Within each ER probe is also a non-corroding element used as a reference for temperature compensation. A "dial box" is used to measure the relative amount of material remaining on the working thickness as compared to the reference element on a scale from 0 to 1000. ER probe use also assumes general corrosion rate measurement with the measurement "span" of a probe equivalent to $\frac{1}{2}$ of the corroding material thickness. The change in the dial box reading (ΔDR) with time is used to calculate the corrosion rate according to:

$$\frac{\Delta DR_units}{hrs_exposure} \bullet \frac{5_mil_span}{1000_span_units} \bullet \frac{8760hrs}{yr} \bullet \frac{mm}{40mil} \equiv \frac{mm}{yr}$$
(2)

The linear polarization (LPR) probes are also made by Metal Samples[®] and are designed in a "concentric ring" style. A diagram of this probe is shown in Figure 2. The dark band in between each electrode surface is a non-conductive epoxy.



Figure 2. Metal Samples[®] Concentric Ring LPR Modular Probe Head

Linear polarization measurements are made using a Gamry[®] computer-operated potentiostat that can make small perturbations (+/- 5 mV) in the corrosion potential and

determine the corrosion rate with little effect on the corroding surface. Measurements of polarization resistance are repeated once every half hour. Polarization resistance is defined as the slope of the polarization curve at the origin when a change in potential $(\Delta \varepsilon)$ is measured for a change in applied current (Δi_{app}) .

$$R_{p} = \left[\frac{\Delta\varepsilon}{\Delta i_{app}}\right]_{\varepsilon \to 0} = \frac{B}{i_{corr}}$$
(3)

The "B" value is the proportionality constant, relating corrosion rate to the polarization resistance, where B is defined as:

$$B = \frac{\beta_a \beta_c}{2.3(\beta_a + \beta_c)} \tag{4}$$

The Tafel constants used to determine the B value for these experiments were defined as: $\beta_a = 40 \text{ mV/decade}$, $\beta_c = 120 \text{ mV/decade}$.

Testing Procedure

Testing began with validation of the system by comparing results between two large scale flow loops and three theoretical calculations to prove the legitimacy of data collected. Experimentation began by looking at the effect of velocity on corrosion rate during a 4 hour exposure to system conditions; 24 hour experiments at a mid-range liquid flow rate of 1.0 m/s would be used for additional corrosion information with weight loss coupons. Pumps and pipes of the Hydrogen Sulfide system are similar in size to those found in field production pipelines between the surface drilling operation and the storage or refining facilities. The range of liquid velocities used therefore reflects those found in field operations. Annular flow occurs when gas velocities are greater than 10 m/s, so 3 m/s gas velocity was chosen to provide a volumetric gas flow rate for stratified or wavy flow at 0.2 and 0.5 m/s V_{sl} and slug flow for V_{sl} greater than or equal to 1.0 m/s.

All of the experimental parameters used in the study of corrosion in the presence of trace amounts of H_2S are shown in Table 1. This range of experimental parameters was chosen to limit the precipitation of iron sulfide (FeS) and iron carbonate (FeCO₃) precipitation while mapping the effects of trace amounts of H_2S on the corrosion rate. The partial pressure of CO₂ used ensures that the water chemistry remains stable during experimentation and is similar to those found in field production conditions.

Linear polarization probes, electrical resistance probes, and weight loss coupons were used to monitor corrosion rates. Corrosion rate results from each method are compared and, along with surface analysis of the WL coupons, provide information toward the mapping of the H_2S effect over the area of interest.

LPR and ER measurement readings were taken manually each half hour when an operator was present. Data collection overnight was done only for LPR, which had the only automated measurement system available, and only for multiphase, since only one automated corrosion-measurement technique was available.

Table 1. Test Matrix

Parameter	<u>Conditions</u>	
CO ₂ partial pressure	0.79MPa (7.9 bar)	
Solution	100% synthetic sea water, pH4	
	C1018 and X-65 weight loss (WL)	
Corrosion Rate Measurement	Electrical Resistance (ER)	
	Linear Polarization Resistance (LPR)	
H ₂ S / CO ₂ ratio (mass basis in the gas phase)	0, 3, 15, and 100 ppm	
Dissolved Oxygen	< 20 ppb	
Dissolved Iron	As measured (< 20 ppm)	
Single phase flow	V _{sl} = 0.2, 0.5, 1.0, 1.5, and 2.0 m/s	
Multiphase flow	V_{sg} = 3 m/s V_{sl} = 0.2, 0.5, 1.0, 1.5, and 2.0 m/s	
Temperature	60°C, 80°C	
Test Time	4 , 24, & 96 hrs	

The single phase flow will be at a liquid velocity of 1.0 m/s while the multiphase flow will be at 3.0 m/s superficial gas velocity and 1.0 m/s superficial liquid velocity to produce slug flow.

It was noted that other researchers have used a variety of methods to report the H_2S concentrations used in their research, so a comparison of H_2S concentrations used in this research as "ppm H_2S by mass" to equivalent partial pressures of CO_2 and H_2S and CO_2/H_2S ratios is shown in Table 2.

Table 2. Comparison of H_2S/CO_2 mass ratio to CO_2/H_2S ratio.

H₂S ppm	pCO₂ (MPa)	pH₂S (Pa)	CO ₂ /H ₂ S ratio
3	0.79	2	3 x 10⁵
15	0.79	12	6 x 10 ⁴
100	0.79	79	1 x 10 ⁴

To relate these ratios to others from the literature, a graphic from Pots¹⁸, redrawn to scale in Figure 3 with 100ppm and 500ppm H_2S concentrations drawn in, shows the ratios used in this experiment are considered to be in the CO_2 "sweet" corrosion regime as defined in his model.


Figure 3. Corrosion regimes in CO_2/H_2S corrosion as defined in the literature¹⁸.

As coupons and probes were removed from the system after each test, the surface of each was rinsed with isopropyl alcohol to remove water. All coupons were allowed to dry, weighed with the film, and stored in a desiccator. WL coupons to be used for weight loss were rubbed with a clean cotton cloth using isopropyl alcohol as a cleaning agent. WL coupons to be used for scanning electron microscopy (SEM) analysis remained in isopropyl storage until removal for examination; WL coupons for surface edge analysis were mounted in clear epoxy, cut, polished, and gold coated prior to SEM.

RESULTS AND DISCUSSION

Testing without Hydrogen Sulfide

Validation of Testing System.

Table 3.	Sinale	phase	test	matrix
10010 01	en gie	p11000		

Parameters	Conditions
Liquid Phase	D.I. Water (1% NaCl)
Temperature	40°C ±1°C
CO ₂ Partial Pressure	4.4 bar
Total Pressure	4.5 bar (50 psig)
Superficial Liquid Velocity (V _{sl})	1 m/s
Superficial Gas Velocity (V _{sg})	0 m/s (full pipe flow)
рН	4
Dissolved Oxygen	< 20 ppb
Dissolved Iron	As measured (< 20 ppm)

To begin the series of experiments, a working comparison between two operational flow loops was performed to validate the corrosion rate data collection on the Hydrogen Sulfide system to another previously documented large diameter multiphase flow loop. The "High Pressure" system, a 316SS, 10 cm diameter flow loop system, was chosen for the validation test.

Publicly available corrosion rate prediction models^{20,21,23} were used to calculate corrosion rates expected to be measured by the flow loop systems when provided with the test matrix parameters as shown in Table 3.

Corrosion Rate Prediction Model	Corrosion Rate (mm/yr)
Dugstad, Videm and Lunde ²⁰	13.5
de Waard, Lotz, Dugstad ²¹	13.2
Jepson, Stitzel, Kang, and Gopal ²³	11.7

Table 4. Predicted corrosion rate calculations for single phase corrosion rate validation experiment.

By rearranging Equation 1, the expected weight loss by corrosion coupons during a 24 hour exposure can be calculated. By predicted corrosion rates, an expected loss of 25 to 30 mg can be expected, or about 1% of the total 2.5 gram WL sample weight. This also minimizes the possible error of balance measurements (\pm 0.5 mg accuracy used to weigh the samples) to less than 2%.

Corrosion rate data was collected for ER, LPR, and WL for each system over a 24 hour time period. The results collected from the single phase validation test, displayed in Figure 4, show a very good correlation between the two systems in each of the three test methods.

Data sets are integrated with time for the ER and LPR and averaged for WL. ER and LPR have multiple data points that show a higher corrosion rate at the beginning of the experiment and diminish with time. For the WL corrosion rate, the average corrosion rate value is shown for three coupons and the error bars represent the maximum and minimum of those values. The error bars show the maximum and minimum of each respective single corrosion rate data set for each method.



Figure 4. Corrosion rate vs. method of corrosion measurement for two large scale systems. ($pCO_2 = 0.45MPa$, pH=3.9, $T=40^{\circ}C$, 24 hours).

Testing with Hydrogen Sulfide

The Effect of Velocity

The first set of experiments measures corrosion rate in five different liquid velocities at three different concentrations of H_2S under a fixed partial pressure of CO_2 . Each set of experiments at one concentration of H_2S consists of one 24-hr experiment and four 4-hr experiments that cover a range of superficial liquid velocities from 0.2 to 2.0 m/s. The first six test parameters listed in Table 1 were used in both single phase flow and multiphase flow experiments; these parameters were chosen from the indicative studies of previous research.^{1,2,3,4} Both single-phase flow and multiphase flow experiments were run simultaneously in different sections of the test loop.

Publicly available corrosion rate prediction models^{20,21,23} were again used to calculate corrosion rates expected to be measured at 60°C and 7.7 bar partial pressure of CO₂, assuming no effect of H₂S on the corrosion rate. The predicted corrosion rates, shown in

Table **5**, are approximately 80% higher than those calculated for the validation experiments due to the effect of higher temperature and higher partial pressure of CO_2 .

Corrosion Rate Prediction Model	Corrosion Rate (mm/yr)
Dugstad, Videm and Lunde ²⁰	20.2
de Waard, Lotz, Dugstad ²¹	24.6
Jepson, Stitzel, Kang, and Gopal ²³	27.5

Table 5. Predicted corrosion rate calculations for 60° C, pCO₂ = 7.7 bar experiment.

Under "non-filming forming conditions" at pH 4, a steady state corrosion rate is expected to be obtained within 4 hours by LPR and ER measurements. The 24-hr experiment, at the mid-range superficial velocity of $V_{sl} = 1.0$ m/s, would utilize WL coupons, LPR, and ER to measure the corrosion rate since WL coupons would require more time to lose enough mass to minimize weight comparison error. The 4-hour tests at superficial liquid velocities of 0.2, 0.5, 1.5, and 2.0 m/s would utilize only LPR and ER because of their quicker measurement response time.



Figure 5. Corrosion rate integrated over 4 hours vs. velocity for ER in single phase flow. $(pCO_2 = 0.79MPa, 60^{\circ}C, 4hr.)$

Figure 5 and Figure 6 show the relationship of corrosion rate to a change in flow velocity for ER measurements. During the four hours of exposure to system conditions, the overall trend for ER probe corrosion rate measurements at 0 ppm H_2S and 3 ppm H_2S show an increase in corrosion rate with an increase in flow velocity in both single phase and multiphase flow. The effect of an increase in flow rate on corrosion rate is an expected result due to the increase in mass transfer away from the surface of the corroding material with the increase in turbulence.



Figure 6. Corrosion rate integrated over 4 hours vs. velocity for ER in multiphase flow. (Vsg = 3.0 m/s, pCO₂ = 0.79MPa, 60° C, 4hr.)

But in single phase and multiphase cases, the addition of 100 ppm H_2S suppressed the corrosion rate. The LPR corrosion rate data shown in Figure 7 and Figure 8 do not show the effect of flow velocity on corrosion rate, but repeat the effect that 100 ppm H_2S added to the system suppressed the corrosion rate.



Figure 7. Corrosion rate integrated over 4 hours vs. velocity for LPR in single phase flow. (pCO₂ = 0.79MPa, 60° C, 4 hr.)

This is an indication that a stable film of FeS is formed very quickly on the surface of the corroding material to limit the corrosion rate within the first few hours of exposure to system conditions with 100 ppm of H_2S .



Figure 8. Corrosion rate integrated over 4 hours vs. velocity for LPR in multiphase flow. (Vsg = 3.0 m/s, pCO₂ = 0.79MPa, 60° C, 4 hr.)

Figure 9 and Figure 10 show the change in corrosion rate as a function of time for each of the 24-hr experiments at V_{sl} = 1.0 m/s as measured by LPR. Note the higher corrosion rate measured during exposure to 3 ppm H₂S in multiphase flow.



Figure 9. Corrosion rate vs. time by LPR in multiphase flow. (pCO₂ = 0.79MPa, pH=4.0, Vsg = 3.0 m/s, V_{sl} = 1 m/s, T= 60° C, 24 hr.)

This increase in corrosion rate at 3 ppm H_2S was first thought to mimic previous research by lkeda, et al,¹ that, at low partial pressures of H_2S in a CO₂ environment, the co-existence of H_2S accelerates the corrosion reaction. But if the theory was correct, this phenomenon would also have been reflected in corrosion rate measurements in single phase flow as shown in Figure 10. But the corrosion rate measured under single phase flow in the exact same system conditions did not reflect the same phenomenon. In single phase flow, any addition of H_2S below 100 ppm lowered the general corrosion rate measured as compared to measurements done in just a CO₂ saturated environment.



Figure 10. Corrosion rate vs. time by continuous LPR in single phase flow. (pCO₂ = 0.79MPa, pH=4.0, V_{sl} = 1 m/s, T=60°C, 24 hr.)

Without the repetition of the accelerated corrosion rate in both single phase flow and multiphase flow, a more in depth look at the measured corrosion rates is necessary. To compare the corrosion rates calculated from 4-hr experiments and 24-hr experiments, data from the 24-hr experiments were analyzed and categorized to provide the calculated values shown in Table 6.

H ₂ S / CO ₂ Ratio	Single Phase / Multiphase	4 hr integrated value	24 hr integrated value	24 hr final corrosion rate	4 hr integrated value	24 hr integrated value	24 hr final corrosion rate
ppm H₂S	SP / MP	ER (mm/yr)	ER (mm/yr)	ER (mm/yr)	LPR (mm/yr)	LPR (mm/yr)	LPR (mm/yr)
0	SP	15.9	13.3	12.5	12.8	7.3	7.9
3	SP	3.4	3.9	3.9	5.9	5.8	3.3
15	SP	7.0	6.6	6.7	1.2	1.0	0.9
100	SP	2.0	1.7	1.6	3.3	2.0	1.2
0	MP	17.4	12.8	13.7	7.3	6.1	6.6
3	MP	11.3	12.0	11.8	19.7	15.1	10.8
15	MP	2.8	1.7	1.4	3.7	3.6	3.6
100	MP	2.4	4.9	5.4	3.6	2.7	1.9

Table 6. Empirical Corrosion Rate Comparison using data from 24 hour experiments. $(pCO_2 = 0.79MPa, pH=4.0, T=60^{\circ}C, 24 hr.)$

As expected in most cases, the corrosion rate during the first 4 hours of exposure is higher than the stabilized corrosion rate 20 hours later. To compare ER and LPR corrosion rate values directly with WL corrosion rate values, the 24-hour integrated corrosion rate values were used. To compare ER and LPR across different liquid velocities, the 4-hour integrated corrosion rate data were used. Although corrosion rate does decrease almost 30% in each case from the 4-hour integrated value to the 24-hour final stabilized corrosion rate, the trends established in each data set are similar.

When corrosion rates for LPR, WL, and ER in multiphase flow are grouped together for the 24 hour exposure time, as in Figure 11, the corrosion rate at the concentration of 3ppm H_2S is viewed as the highest measured value for WL and LPR in comparison to those measured at any other concentration of H_2S in the system.



Figure 11. Corrosion rate vs. H_2S concentration for LPR, WL, and ER. (pCO₂ = 0.79MPa, pH = 4.0, V_{sq} = 3.0 m/s, and V_{sl} = 1.0 m/s, 60°C, 24 hr.)

Error bars depicted in Figure 11 through Figure 17 are only shown on weight loss corrosion rates values because more than one calculated value was used for each test. All other corrosion rate measurements (ER, LPR) are integrated by time over 24 hours, providing only one value for direct comparison to WL. The error bars in Figure 11 for the WL coupon corrosion rate measurements represent the minimum and maximum general corrosion rates determined for those coupons and show an overlapping region around 17 mm/yr. Therefore, we are left with only LPR data in multiphase flow to provide evidence of an accelerated corrosion rate due to trace amounts of H₂S. When corrosion rates for LPR, WL, and ER in single phase flow are grouped together for the 24 hour exposure time, as in Figure 12, the exact same system conditions did not reflect the same phenomenon.



Figure 12. Corrosion rate vs. H_2S concentration for LPR, WL, and ER. (pCO₂ = 0.79MPa, pH = 4.0, and V_{sl} = 1.0 m/s, 60°C, 24 hr.)

Figure 13, Figure 14, and Figure 15 compare corrosion rate measurements for each of the specific corrosion rate measurement methods in multiphase and single-phase flow. Both the LPR and WL coupons seem to be in agreement with the H_2S effect seen, but the ER probe gives consistent readings for the 0 and 3 ppm concentrations.



Figure 13. Corrosion rate vs. H_2S concentration for LPR in multiphase and single phase flow. (pCO₂ = 0.79MPa, pH = 4.0, 60°C, V_{sg} = 3.0 m/s, and V_{sl} = 1.0 m/s.)



Figure 14. Corrosion rate vs. H₂S concentration for WL in multiphase and single phase flow. (pCO₂ = 0.79MPa, pH = 4.0, and V_{sg} = 3.0 m/s, V_{sl} = 1.0 m/s.)



Figure 15. Corrosion rate vs. H_2S concentration for ER in multiphase and single-phase flow. (pCO₂ = 0.79MPa, pH = 4.0, and V_{sg} = 3.0 m/s, V_{sl} = 1.0 m/s.)

Figure 16 and Figure 17 show the comparison of WL corrosion rate measurements for coupons made of C1018 and X-65 exposed to H_2S/CO_2 ratios of 0, 3, and 100 ppm in single phase and multiphase flow, respectively.



Figure 16. Corrosion rate vs. H_2S concentration for C1018 and X-65 materials in multiphase flow. (pCO₂ = 0.79MPa, pH = 4.0, V_{sg} = 3.0 m/s, and V_{sl} = 1.0 m/s.)



Figure 17. Corrosion rate vs. H_2S concentration for C1018 and X-65 materials in single phase flow. (pCO₂ = 0.79MPa, pH = 4.0, and V_{sl} = 1.0 m/s.)

Upon discovery that the concentrations of hydrogen sulfide used in the series would form a surface film under these conditions, scanning electron microscopy (SEM) and electron dispersion spectroscopy (EDS) analysis were done for the WL coupons exposed to 100ppm concentration of H_2S . An SEM of a surface defect on C1018 coupon is shown in Figure 18.



Figure 18. SEM of damaged film after coupon removal from 24 hour experiment, multiphase flow. (V_{sg} = 3.0 m/s, V_{sl} = 1.0 m/s, pCO₂ = 0.79MPa, 60°C, 100% ASTM seawater, 100ppm H₂S.)

In association with the retardation of the corrosion rate by exposure to 100ppm H_2S , analysis of the surface by SEM and EDS provide proof of a thin surface film resistant to corrosion. In "APPENDIX B: H_2S Corrosion Mechanism," reaction scenarios

for the corrosion of iron exposed to aqueous hydrogen sulfide rate are provided for two different authors. Both authors expect the formation of a mackinawite film, developed as a solid state reaction on the surface of the corroding iron. Mackinawite films can be extremely thin, but are characterized by the presence of sulfides. EDS analysis of the surface area shown in Figure 18 produced the EDS spectrum in Figure 19.



Figure 19. EDS of visual area shown in SEM photo Figure 18.

Cross-sectional SEM analysis of coupons exposed to single phase flow (Figure 20. a, b, c) and multiphase flow (Figure 21. a, b, c) at 100ppm H₂S for 24 hours show a minimal film deposit does exist, but in each case are less than 2μ m in thickness. In each set of photos, the upper portion is the epoxy and the lower portion is C1018 carbon steel. In Figure 20a., the white line at the interface between the epoxy and C1018 is a cross-sectional view of the corrosion retarding layer seen previously in Figure 18.



Figure 20. SEM of coupons exposed to 24 hours of 100 ppm H_2S environment. 1018 carbon steel, single phase flow. (24hrs, 0.79MPa CO₂, 100ppm H_2S , V_{sl} = 1 m/s, 60°C)



Figure 21. SEM of coupons exposed to 24 hours of 100 ppm H₂S environment. X-65 Carbon Steel, Multiphase flow. (V_{sg} = 3.0 m/s, pCO₂ = 0.79MPa, 60°C.)

By lowering the SEM magnification in Figure 20b. and Figure 20c., it can be seen that the film is uniform and consistent across the surface of the coupon. In Figure 21a,

b, and c, the interface between the epoxy and the metal surface also has a distinct highlight, suggesting a deposition or growth layer on the coupon surface.

The assumption gained from the comparison of film thickness in single phase flow to multiphase flow is that the rate of film growth is less in multiphase flow due to the increased turbulence and bubble impact on the surface during film growth.

Changing the Exposure Time

Questions arose about the films that developed during the short exposure times of the coupons and probes to the system conditions. At pH 4, the dissolution rate of carbonate films is much greater than the precipitation rate, so no carbonate films can be expected to form. But an obvious film, which caused the retardation of the corrosion rate over a short period of time, did occur. With the knowledge that the concentrations of hydrogen sulfide used in the series would form a surface film under these conditions, test length was increased in steps to determine an appropriate corrosion probe exposure time.

Coupon exposure to a system with 100ppm H_2S produced $2\mu m$ films over a 24 hour period that were obvious on the surface and measurable in cross sectional analysis, but the retardation of the corrosion rate also occurred at 15 ppm of H_2S , yet the film was not obvious or visible to the naked eye. Because the effect of 100 ppm H_2S on corrosion rate is dramatically seen within the first few hours of coupon exposure to

system conditions, an increase in test exposure time was necessary to better observe this phenomena. Subsequent testing was conducted to compare film growth and corrosion rates developed over a longer period of time with the same system conditions. Experiments were conducted for 4 hrs, 24 hrs, 72 hrs, and 96 hours under conditions of 0.79MPa CO₂, 100ppm H₂S, V_{sl} = 1.0 m/s, and Vsg = 3.0 m/s at 60°C. The variation in the slope of the corrosion rate vs. time and the thickness of the developed corrosion layer were investigated to determine a testing time adequate enough to produce comparable results.

Each corrosion coupon (LPR, ER) tends to follow a general scheme of corrosion rate measurement values as given in Figure 22 with slight alterations in peak height and length. Most corrosion values attained a stable corrosion rate within 24 hours.



Figure 22. Generic pattern for a change in corrosion rate with time.

After 24 hours exposure to system conditions, the change in corrosion rate per hour (Δ (mm/yr)/hour) as measured by LPR is less than 10%. After 45 hours this same change is less than 1% in each case and diminishes over time.

Figure 23 shows the comparison of LPR data for three experiments, displaying both single phase (SP) and multiphase (MP) results for 6 experimental results. Similar results were obtained for electrical resistance and show that the system has developed a constant corrosion rate after less than 24 hours of exposure. This observation of a constant corrosion rate developed prior to 24 hours exposure time proves the validity of the previous test series for comparison of the corrosion rate at the end of 24 hours. Calculations of weight loss corrosion will be much lower due to the fact that the largest part of the general corrosion happens within the first 20 hours of exposure to system conditions.



Figure 23. Comparison of the "rate of change" of the corrosion rates for linear polarization probes under conditions of 0.79MPa, 60°C, and 100ppm H_2S in single phase (SP) and multiphase (MP) flow from 6 experiments.

Product film thickness has been a more difficult comparison to achieve due to the fragile nature of the films produced. From a 24-hour exposure time in a system with 100ppm H_2S in the gas phase, a film of sub-micron proportions is visible as a thin white line as previously shown in Figure 20b.

By lengthening the exposure time to 72 hours, a more substantial product layer is produced. A similar film was measured on both C1018 and X-65 steels from a 72 hour exposure to a 0.79MPa CO₂, 100ppm H₂S, V_{sl} = 1.0 m/s, and V_{sg} = 3.0 m/s at 60°C environment. This measurable 10µm corrosion product layer is shown in Figure 24.



Figure 24. Corrosion product film on C1018 steel coupon exposed to multiphase flow conditions. (72hrs, 0.79MPa CO₂, 100ppm H₂S, V_{sg} = 3 m/s, V_{sl} = 1 m/s, 60°C)

Further testing completed at 96 hours shows growth of the corrosion film under the same conditions with an approximate 10µm corrosion product thickness as shown in Figure 25 and Figure 26 for single phase and multiphase flow, respectively. The surfaces of these exposed coupons have been analyzed with EDS and show the existence of sulfides on the coupon surface.



Figure 25. Corrosion product film on C1018 steel coupon exposed to single phase flow conditions. (96hrs, 0.79MPa CO₂, 100ppm H₂S, V_{sl} = 1 m/s, 60°C)



Figure 26. Corrosion product film on C1018 steel coupon exposed to multiphase flow conditions. (96hrs, 0.79MPa CO₂, 100ppm H₂S, V_{sg} = 3 m/s, V_{sl} = 1 m/s, 60°C)

From this testing, it was concluded that a 96 hour exposure time has produced a measurable corrosion product film for the 100ppm concentration of H₂S under conditions of 0.79MPa CO₂, 100ppm H₂S, V_{sg} = 3 m/s, V_{sl} = 1 m/s, 60°C. The 96-hour exposure was used subsequently in all further experimentation.

Tests at Two Temperatures

Each series of experiments at 60°C and 80°C began with the system at steadystate conditions with pH and H₂S concentration set before insertion of corrosion monitoring probes. Steady-state includes a CO₂ saturated environment at 7.9 bar (100psig) total pressure with reproducible flow rates in single-phase flow (V_{sl} = 1 m/s) and multiphase flow (V_{sg}=3 m/s, V_{sl}= 1 m/s), oxygen concentration measured at or below 10ppb, and ferrous ion concentration less than 10ppm. The multiphase flow regime was a slug flow, approximately Froude 6, with a slug frequency of 15/min. The experiments at 100ppm concentration of H₂S were conducted before the 3ppm and 15ppm tests at each temperature with the temperatures alternated at each concentration.

Twelve weight loss coupons were used in each experiment and the general corrosion rate for each determined by the amount of mass lost during exposure to system conditions. Comparison of the difference between maximum and minimum weight loss within each experiment shows repeatability when this range is small

compared to the general corrosion rate calculated from the weight loss. For each test, 4 coupons are in the single-phase test section and 8 coupons are in the multiphase test section.

Interest in pitting and localized corrosion can also be quantified by metallurgical microscopic measurement of depth and density of corrosion locations. The pit/localized corrosion depth was measured for each coupon and the maximum penetration rate was used to calculate a localized corrosion rate value for each set of coupons. The concentration of localized corrosion or pit density is also an important factor to consider.

Testing at 60°C

Initial corrosion rates at 60°C were expected (as previously tested) to show an effect of an increase in corrosion rate over a 4 hour period of time and were observed to show repeatability error of less than 30%. Figure 27 and Figure 28 show the relationship of corrosion rate to concentration of H_2S for the first four hours of experimentation and reflect previous experimental data with an increase in LPR measured corrosion rate in multiphase flow at 3ppm H_2S over that with no H_2S present. No WL coupons were removed at the 4-hour interval for the 96-hour test.



Figure 27. Measured corrosion over the first four hours of exposure to system conditions; multiphase flow. (0.79 MPa CO₂, 60° C, V_{sg} = 3.0m/s, V_{sl} = 1.0m/s, gas phase ppm concentration of H₂S)



Figure 28. Measured corrosion rate over the first four hours of exposure to system conditions; single phase flow. (0.79 MPa CO₂, 60°C, V_{sg} = 3.0m/s, V_{sl} = 1.0m/s, gas phase ppm concentration of H₂S)

After exposure for 96 hours, all measured corrosion rate values for coupons decreased to $1.6 \text{ mm/yr} \pm 1.0 \text{ mm/yr}$ as seen in Figure 29. The cause for this retardation in the corrosion rate is due to the film that is forming on the face of the coupon. Non-corroding surfaces on probes (ie. stainless steels, epoxy, or nylon surfaces) removed from the system do not show any visible film layer suggesting that the film formed was via a solid-state chemical reaction, probably mackinawite, and not by a precipitation reaction.



Figure 29. General corrosion rate based on 96 hours of exposure to system conditions. Average and standard deviation shown. (0.79 MPa CO₂, 60°C, V_{sg} = 3.0m/s, V_{sl} = 1.0m/s, gas phase ppm concentration of H₂S)

To study the types of films obtained, scanning electron microscopy (SEM), electron dispersion spectroscopy (EDS), x-ray diffraction (XRD), and auger electron spectroscopy (AES or ESCA) were tested for their abilities to confirm the composition of the film. Of the methods used, SEM and EDS were the most useful. XRD and AES provided similar information, but neither had the ability to analyze selective locations.

Films obtained at 100ppm H₂S, 60°C

In order to compare films, a surface SEM and a cross-sectional SEM from coupons of the same test and location were produced. Figure 30 shows the surface of a C1018 coupon exposed to a system with 100ppm H_2S in the gas phase at 60EC for 96 hours. The film is as expected with an approximate thickness of 10µm as shown previously in the cross sectional SEM of Figure 25.



Figure 30. Surface of C1018 coupon after 96 hours of exposure to system conditions; single phase flow. (0.79 MPa CO₂, 60°C, V_{sl} = 1.0m/s, 100ppm gas phase concentration of H₂S)

The interesting features in Figure 30 are the circular failures of the film. This is a widespread anomaly on this surface. One explanation could be the release of CO_2 from under the film upon removal of the coupon from the operating conditions and the sudden release of the pressure. This explanation is valid because an EDS did not show sulfides in the holes, but sulfides were measured on the surface film. With such a fast growing solid state film, it would be impossible to have discontinuities of the film occur within the system without exposing new surface to hydrogen sulfide and generating an iron sulfide surface film.

The film would have to be porous to allow some mass transfer of corrosion products, yet well attached to the surface to show explosive failures from

decompression. The cleaned surface, shown in Figure 31, shows circular corrosion initiation locations indicative of CO_2 corrosion and a noted deeper pit location.



Figure 31. Metallurgical microscopic picture of C1018 coupon surface after 96 hours exposure to system conditions; single-phase flow. (0.79 MPa CO₂, 60°C, V_{sl} = 1.0m/s, 100ppm gas phase concentration of H₂S) Arrow shows pit location.

The cross sectional SEM in Figure 25 shows the thickness of the scale of about $10\mu m$ which was tight enough to trap a dissolved gas layer and limited the corrosion rate to 1.37 mm/yr.

In the same experiment, but under multiphase conditions, Figure 32 shows a much thinner and weaker film that has fragmented on the surface of the coupon.



Figure 32. Surface of C1018 coupon after 96 hours of exposure to system conditions; multiphase flow. (0.79 MPa CO₂, 60°C, V_{sg} = 3.0m/s, V_{sl} = 1.0m/s, 100ppm gas phase concentration of H₂S)

The corrosion rate for this coupon was 2.35 mm/yr, so the film provided some corrosion protection as compared to non-filming corrosion conditions without the presence of H_2S . The cross section in Figure 33 provides some insight to the actual thickness of the film. From the photo, the film measures ~3.3µm and has lifted from the surface of the coupon; this probably occurred from the coupon removal and storage process to keep the coupon from oxidizing. Since no localized corrosion was evident in this case, it can be deduced that the film fully covered the surface under the operational conditions. The film would also be defined as very porous because of the corrosion rate of more than 2 mm/yr proves that diffusion mass transfer of ferrous ions was occurring through the film, undermining the film and leaving a gap between the corrosion product layer and the metal surface.


Figure 33. Cross section of C1018 coupon after 96 hours of exposure to system conditions; multiphase flow. (0.79 MPa CO₂, 60°C, V_{sg} = 3.0m/s, V_{sl} = 1.0m/s, 100ppm gas phase concentration of H₂S)

From similar conditions of multiphase flow at 60°C, Figure 34 and Figure 35 show the same relationship for X-65 carbon steel. The film fractured with approximately the same fracture pattern as the film on the C1018 coupon in Figure 32, but more of the film remains attached and the cross-section of Figure 35 shows a 2.2μ m film layer that is also loosely attached to the coupon surface. The corrosion rate for WL of X-65 in this condition was 1.34 mm/yr.



Figure 34. Surface of X-65 coupon after 96 hours of exposure to system conditions; multiphase flow. (0.79 MPa CO₂, 60°C, V_{sg} = 3.0m/s, V_{sl} = 1.0m/s, 100ppm gas phase concentration of H₂S)



Figure 35. Cross section of X-65 coupon after 96 hours of exposure to system conditions; multiphase flow. (0.79 MPa CO₂, 60°C, V_{sg} = 3.0m/s, V_{sl} = 1.0m/s, 100ppm gas phase concentration of H₂S)

Films obtained at 15ppm H₂S, 60℃

A much different surface film is observed when the system has a 15ppm gas concentration of H_2S . A layer is observed, but has not totally covered the surface of the coupon.



Figure 36. Surface of C1018 coupon after 96 hours of exposure to system conditions; single-phase flow. (0.79 MPa CO₂, 60°C, V_{sl} = 1.0m/s, 15ppm gas phase concentration of H₂S)



Figure 37. Surface of C1018 coupon after 96 hours of exposure to system conditions; single-phase flow. (0.79 MPa CO₂, 60°C, V_{sl} = 1.0m/s, 15ppm gas phase concentration of H₂S)

This is intriguing, because the corrosion rate of WL coupons exposed in this experiment were only 0.33 mm/yr; suggesting a very thin protective film has formed. Figure 36 is a higher magnification view of the same surface to compare with the cross section in Figure 37. A surface film in this SEM photograph is barely visible on this cross section and measures $<1\mu$ m.

To relate SEM photographs to what could be seen visually, some metallurgical microscope pictures were taken. Figure 38 is an SEM of a C1018 coupon exposed to a 60°C system with 15ppm H₂S in the gas phase and Figure 39 is the same coupon photographed under a 20X magnification with the metallurgical microscope. The bright metal in the cracks supports the previous assumption that the film formed under system conditions cracks when dried for analysis. The circular pattern in the film that has formed on the surface is characteristic of general CO₂ corrosion, but with a corrosion rate of only 0.52 mm/yr for multiphase WL coupons under these conditions another factor of corrosion retardation must be influencing the behavior of the films.



Figure 38. Surface of C1018 coupon after 96 hours of exposure to system conditions; multiphase flow. (0.79 MPa CO₂, 60°C, V_{sl} = 1.0m/s, 15ppm gas phase concentration of H₂S)



Figure 39. Surface metallurgical microscope photograph of C1018 coupon after 96 hours of exposure to system conditions; multiphase flow. (#91, 20x mag, 0.79 MPa CO_2 , 60°C, V_{sl} = 1.0m/s, 15ppm gas phase concentration of H₂S)

EDS analysis of the two possible surfaces in Figure 38 shows a high iron content in the cracks visible in both figures and a sulfur content in the film. From the EDS spectrum, the cracks (Figure 40a.) show no sulfur content within the cracks and a very high iron content, supporting the fact that this happened after removal from the system. From the EDS spectrum for the films (Figure 40b.), it can be seen that the iron peaks and sulfur peaks are equivalent suggesting an iron sulfide film (FeS) with various salts from the brine used showing up in the other peaks.



Figure 40. EDS (a.) of the dark crack in Figure 38 shows only iron peaks on the spectrum, while the EDS (b.) of the film on surface shows equivalent peaks for iron and sulfur detected in the film.

Probes removed from the system after exposure show the differences in the formed films. At 60°C, films formed at 15ppm H₂S were tightly held, but would crack with drying. Figure 41 shows an LPR probe and a set of WL coupons immediately after removal from system conditions and rinsed with isopropyl alcohol. Notice the cleanliness of the stainless steel on the LPR and of the nylon on the WL. This is indicative that no precipitate formed and deposited on the probe.



Figure 41. Photograph of LPR probe (left) and weight loss C1018 coupons (right) after 96 hours of exposure to system conditions; multiphase flow. (0.79 MPa CO_2 , 60°C, V_{sl} = 1.0m/s, 15ppm gas phase concentration of H₂S)

Films obtained at 3ppm H₂S, 60°C

A quick and direct comparison of the films can be made visually by looking at probes removed from the system conditions at 3ppm H_2S in Figure 42 for WL and ER to films produced under 15ppm H_2S shown in Figure 41. Films from 3ppm H_2S experiments at 60°C were very fragile upon removal from system conditions. Adherent films exposed to conditions of 3ppm H_2S were shown to have a very small "granular" structure as compared to the higher concentrations.



Figure 42. Photograph of ER probe (left) and weight loss C1018 coupons (right) after 96 hours of exposure to system conditions; multiphase flow. (0.79 MPa CO₂, 60°C, V_{sl} = 1.0m/s, 3ppm gas phase concentration of H₂S)

Figure 43 and Figure 44 show the films at the same SEM magnification as previous photographs. These films are very thin, because drying does not produce cracking in a similar way as in 15ppm or 100ppm experiments. Corrosion rates from WL were 0.16 mm/yr for single phase and 2.24 mm/yr for multiphase exposures of 96 hours at 3ppm.



Figure 43. Surface of C1018 coupon after 96 hours of exposure to system conditions; single phase flow. (0.79 MPa CO₂, 60°C, V_{sl} = 1.0m/s, 3ppm gas phase concentration of H₂S)



Figure 44. Surface of C1018 coupon after 96 hours of exposure to system conditions; multiphase flow. (0.79 MPa CO₂, 60° C, V_{sl} = 1.0m/s, 3ppm gas phase concentration of H₂S)

Figure 45 and Figure 46 show the average weight loss corrosion rate calculated for single-phase and multiphase flow exposures at 60°C with the range between maximum and minimum added as an error bar to provide the comparison. The number coupons measured are provided next to each bar in the chart.



Figure 45. Measured corrosion rate deviation at 60° C, 96-hr in single-phase for each H₂S concentration tested. Average corrosion rate and variance by weight loss for the number of coupons shown above the values.



Figure 46. Measured corrosion rate deviation at 60°C, 96-hr in multiphase for each H2S concentration tested. Average corrosion rate and variance by weight loss for the number of coupons shown above the values.



Figure 47. Maximum localized/pitting corrosion and general corrosion for C1018 weight loss coupons. (0.79 MPa CO₂, 60° C, pH 4, Vsg = 3.0m/s, V_{sl} = 1.0m/s)

Figure 47 shows the relationship between corrosion rate and localized corrosion rate for each concentration of H_2S tested in single-phase and multiphase flows for 60°C.

Testing at 80°C

A test was also completed at a higher temperature to observe the effects of increasing reaction kinetics.

Figure 48 shows the corrosion rates measured by LPR and ER after the first four hours of exposure to multiphase flow conditions at 80°C. The trend is a steady decrease of corrosion rate for an increase in concentration of H₂S. Even in single phase conditions, the corrosion rates after 4 hours shown in Figure 49 decrease (as measured by LPR) for increasing concentrations of H₂S, while the ER probe gives erratic results.



Figure 48. Measured corrosion rate over the first four hours of exposure to system conditions; multiphase flow. (0.79 MPa CO_2 , 80°C, Vsg = 3.0m/s, V_{sl} = 1.0m/s, gas phase ppm concentration of H₂S)



Figure 49. Measured corrosion rate over the first four hours of exposure to system conditions; single-phase flow. (0.79 MPa CO₂, 80°C, V_{sg} = 3.0m/s, V_{sl} = 1.0m/s, gas phase ppm concentration of H₂S)



Figure 50. Stabilized corrosion rate after 96 hours of exposure to system conditions. (0.79 MPa CO₂, 80°C, V_{sg} = 3.0m/s, V_{sl} = 1.0m/s, gas phase ppm concentration of H₂S)

After 96 hours of exposure to the system conditions, Figure 50 shows that the corrosion rates for all methods of measurement have decreased to 1.4 ± 0.8 mm/yr. In every case, the corrosion rate values for MP are greater than for SP as reflected in the comparison of WL coupon corrosion rates shown in Figure 51.



Figure 51. Corrosion rate determined for weight loss coupons after 96 hours of exposure to system conditions. (0.79 MPa CO_2 , 80°C, V_{sg} = 3.0m/s, V_{sl} = 1.0m/s, gas phase ppm concentration of H_2S)

Films obtained at 100ppm H₂S, 80°C

The surface film developed at 100ppm H_2S , pictured in SEM Figure 52, shows a solid surface film, even after removal from system conditions and drying for analysis. One surface defect (Figure 53) was noticed on the coupon face that measured ~1 mm in length in the flow direction by ~0.5 mm wide.



Figure 52. Surface of C1018 coupon after 96 hours of exposure to system conditions; multiphase flow. (0.79 MPa CO₂, 80°C, V_{sg} = 3.0m/s, V_{sl} = 1.0m/s, 100ppm gas phase concentration of H₂S)



Figure 53. Surface defect of C1018 coupon after 96 hours of exposure to system conditions; multiphase flow. (0.79 MPa CO₂, 80°C, V_{sg} = 3.0m/s, V_{sl} = 1.0m/s, 100ppm gas phase concentration of H₂S)

Films obtained at 15ppm H₂S, 80°C

Surface films at 80°C seemed to be tightly bound, Figure 54, as compared to the films at 60°C, but pitting under the films is much more prevalent to the point of being considered a high general corrosion rate rather than localized corrosion.



Figure 54. Corrosion product covered surface of C1018 coupon after 96 hours of exposure to system conditions; multiphase flow. (0.79 MPa CO₂, 80°C, pH 4, V_{sg} = 3.0m/s, V_{sl} = 1.0m/s, 15ppm gas phase concentration of H₂S)

Figure 55 shows a cross section with two locations of pitting corrosion about 50μ m in depth. Pit growth occurs when a porous cap of the corrosion product layer provides a sheltered area that minimizes mass transport between the pit interior and the bulk solution. Cathodic reduction of hydrogen sulfide (Equation 18, Appendix B) on the exterior of the pit location consumes electrons helping to sustain the anodic polarization

of the pit interior. The visible thin film scattered above the pitted area shows a very strong detection of iron and sulfide on EDS.



Figure 55. Cross section of C1018 coupon after 96 hours of exposure to system conditions; multiphase flow. (0.79 MPa CO₂, 80°C, V_{sg} = 3.0m/s, V_{sl} = 1.0m/s, 15ppm gas phase concentration of H₂S)

Pitting corrosion is sustained when the area surrounding the pit location provides the cathodic reduction capability to support the pit anode. Therefore, pits do not normally occur in close proximity due to the cathodic protection provided in a large area surrounding the pit location. In the case where we see widespread "pit" locations, equivalent growing "pits" join together for a high general corrosion rate with no localized events.

In this discussion, weight loss corrosion rates are based on total material lost in the corrosion process and pitting corrosion rates are calculated from maximum microscopy depth measurements with the understanding that they may represent the same corrosion rate value.

Films obtained at 3ppm H₂S, 80°C

Some pitting was also seen under thin films in single-phase flow, Figure 56, and multiphase flow, Figure 58, for WL coupons exposed to 3ppm H_2S conditions. For the single-phase flow WL coupon in Figure 57, the corrosion rate was measured as 1.15 mm/yr and for the multiphase flow WL coupon in Figure 59 the corrosion rate was measured at 2.70 mm/yr.



Figure 56. Corrosion product covered surface of C1018 coupon after 96 hours of exposure to system conditions; single phase flow. (0.79 MPa CO_2 , 80°C, pH 4, V_{sl} = 1.0m/s, 3ppm gas phase concentration of H₂S)



Figure 57. Corrosion under the cleaned surface of C1018 coupon after 96 hours of exposure to system conditions; single phase flow. (0.79 MPa CO_2 , 80°C, V_{sl} = 1.0m/s, 3ppm gas phase concentration of H_2S)

Figure 58, Figure 59, and Figure 60 show the surface of a C1018 coupon that has been exposed to 3ppm H₂S in the gas phase at 80°C for 96 hours. The surface of the coupon in Figure 58 shows salt blooms or salt crystal growth that would occur as saltwater, trapped in the surface of the coupon, evaporates slowly and wicks upward. This is seen in field conditions and is usually indicative of pitting corrosion. Figure 59 clearly shows the numerous pitting locations by SEM that were later measured with a metallurgical microscope. Cross sectional analysis in Figure 60 shows a pit of 30 to 40 μ m in depth and the associated salt bloom in the epoxy above the metal surface.



Figure 58. Corrosion product covered surface of C1018 coupon after 96 hours of exposure to system conditions; multiphase flow. (0.79 MPa CO₂, 80°C, pH 4, Vsg = 3.0m/s, V_{sl} = 1.0m/s, 3ppm gas phase concentration of H₂S)



Figure 59. Corrosion under the cleaned surface of C1018 coupon after 96 hours of exposure to system conditions; multiphase flow. (0.79 MPa CO₂, 80°C, Vsg = 3.0 m/s, V_{sl} = 1.0m/s, 3ppm gas phase concentration of H₂S)



Figure 60. Cross section of C1018 coupon after 96 hours of exposure to system conditions; multiphase flow. (0.79 MPa CO_2 , 80°C, V_{sg} = 3.0 m/s, V_{sl} = 1.0m/s, 3ppm gas phase concentration of H_2S)

Figure 61 and Figure 62 provide show the average weight loss corrosion rate calculated for single-phase and multiphase flow exposures at 80°C with the range between maximum and minimum added as an error bar to provide the comparison. The number coupons measured are provided next to each bar in the chart.



Figure 61. Measured corrosion rate deviation at 80° C, 96-hr in single-phase for each H₂S concentration tested. Average corrosion rate and variance by weight loss for the number of coupons shown above the values.



Figure 62. Measured corrosion rate deviation at 80° C, 96-hr in single-phase for each H₂S concentration tested. Average corrosion rate and variance by weight loss for the number of coupons shown above the values.

Figure 63 shows the relationship between corrosion rate and localized corrosion rate for each concentration of H_2S tested in single-phase and multiphase flows for 80°C.



Figure 63. Maximum localized/pitting corrosion and general corrosion for C1018 weight loss coupons. (0.79 MPa CO₂, 80°C, pH 4, V_{sg} = 3.0m/s, and/or V_{sl} = 1.0m/s)

Corrosion rate comparisons of 60°C and 80°C

Figure 64 through Figure 66 provide comparison of the general corrosion rates of

C1018 weight loss coupons measured in relation to the H₂S concentration exposure.



Figure 64. Corrosion rate comparison at 100ppm H_2S for single WL coupon measurements (0.79 MPa CO₂, V_{sg} = 3.0 m/s, V_{sl} = 1.0m/s, SP – single-phase, MP - multiphase).



Figure 65. Corrosion rate comparison at 15ppm H_2S for single WL coupon measurements (0.79 MPa CO₂, V_{sg} = 3.0 m/s, V_{sl} = 1.0m/s, SP – single-phase, MP - multiphase).



Figure 66. Corrosion rate comparison at 3ppm H_2S for single WL coupon measurements (0.79 MPa CO₂, V_{sg} = 3.0 m/s, V_{sl} = 1.0m/s, SP – single-phase, MP - multiphase).

In all three concentrations of H_2S , it can be seen that coupons exposed to multiphase flow (striped bars) consistently have a higher corrosion rate than those exposed to single phase flow conditions (solid bars). This should also be considered as a direct relationship to film thickness shown in previous observations of thinner films forming under multiphase flow conditions. At 100ppm H_2S in Figure 64 the highest corrosion rate was also associated with the thickest film (10µm), which means the film is porous and non-protective. At 15ppm H_2S in Figure 65, the corrosion rates associated with an increase the concentration of H_2S were retarded in relation to "sweet" corrosion. But the pitting that occurred at 80°C, 15ppm H_2S , shows here as an increase in the general corrosion rate of the coupon. Also at 3ppm H_2S , the increased general corrosion rates shown in Figure 66 are because of pitting type corrosion.

Figure 67 shows the relationship of the pit density to the H_2S concentration of the system during coupon exposure for each temperature and flow regime. Note the relationship of increased pit density to an increase in temperature and an increase from single phase to multiphase conditions in almost every case.

Compilation of the localized/pitting data for 60° C and 80° C is given in Figure 68 as a direct comparison to the pit density observation. Note that even the maximum corrosion rate obtained by addition of the general corrosion rate to the maximum pitting rate still shows retardation in the corrosion rate from addition of H₂S shown in Figure 29 and Figure 50. Note the relationship of increased pit density to an increase in temperature and an increase from single phase to multiphase conditions in almost every case.

Figure 67 shows the relationship of the pit density to the H_2S concentration of the system during coupon exposure for each temperature and flow regime.

Localized corrosion attack across the range of pit density as given in Figure 67 can be shown by a visual comparison of coupon morphology for a sample exposed to 60°C, 100ppm H₂S in single-phase flow, to that of a sample exposed to 80°C, 3ppm H₂S in multiphase flow. For this comparison, a surface SEM, surface metallurgical microscopy, and cross-sectional SEM from coupons of the same test and location were produced.



Figure 67. Observed qualitative pit density for C1018 weight loss coupons after 96-hr exposure. (0.79 MPa CO₂, pH 4, V_{sg} = 3.0m/s, and/or V_{sl} = 1.0m/s)



Figure 68. Maximum localized/pitting and general corrosion rates for C1018 weight loss coupons. (0.79 MPa CO₂, pH 4, V_{sg} = 3.0m/s, and/or V_{sl} = 1.0m/s, 96-hr)

Corrosion rate modeling

Adding trace amounts of H_2S to a CO_2 saturated environment has been shown to have a retarding effect on the corrosion rate when compared to corrosion rates obtained in a "pure" CO_2 environment. Figure 69 shows the effect of increasing the H_2S concentration on corrosion rate at 60°C for both single phase and multiphase flow and Figure 70 shows the effect of increasing the H_2S concentration on corrosion rate at 80°C for both single phase and multiphase flow.



Figure 69. Corrosion rate trends for LPR data at 60°C in the Hydrogen Sulfide Multiphase Loop. Error \pm 1.0 mm/yr from Figure 29. (96hrs, 0.79MPa CO₂, V_{sg} = 3 m/s, V_{sl} = 1 m/s, pH 4)



Figure 70. Corrosion rate trends for LPR data at 80°C in the Hydrogen Sulfide Multiphase Loop. Error \pm 0.8 mm/yr from Figure 50 (96hrs, 0.79MPa CO₂, V_{sg} = 3 m/s, V_{sl} = 1 m/s, pH 4)

Lee²⁸ measured corrosion rates of a rotating cylinder electrode in a glass cell at ambient temperature and atmospheric pressure with the same concentrations of H_2S in a CO₂ saturated system. These measurements, shown in Figure 71, reflect a similar trend to data collected in the Hydrogen Sulfide system despite changes in temperature and total pressure.



Figure 71. Effect of H₂S gaseous concentration on the final stabilized corrosion rate (measured by LPR) of carbon steel X65 in pH 5 saturated CO₂ solution, water + 3% NaCl, p = 1 bar, $t = 20^{\circ}$ C, $\omega = 1000$ rpm

A plot of the normalized corrosion rate trend from the three experiments at 20°C, 60°C, and 80°C in single phase flow versus concentration of H_2S shows a very close relationship for gas phase concentrations up to 100 ppm H_2S and the stabilized corrosion rate after 96 hours of exposure as seen in Figure 72.



Figure 72. Normalized corrosion rate trends of single phase LPR data for 20° C, 60° C, and 80° C.

According to literature (APPENDIX B: H2S Corrosion Mechanism), a solid state reaction occurs on the surface of the metal exposed to a system with trace amounts of H_2S and a mackinawite film forms. The limiting step in this process according to Shoesmith is adsorption of HS⁻. As there is a clear relationship between the retardation of the general corrosion rate and the concentration of H_2S , one can conclude that it is related to the surface coverage by sulfide species and can be described by a adsorption isotherm.

Considering that the total rate of the corrosion reaction $(i_{corr})_{\theta}$ is equivalent to the sum of the corrosion reaction at uncovered locations $(i_{corr})_{\theta=0}$ plus the corrosion reaction at covered locations $(i_{corr})_{\theta=1}$,:

$$(i_{corr})_{\theta} = (1 - \theta)(i_{corr})_{\theta=0} + \theta(i_{corr})_{\theta=1}$$
(5)

As measured, $(i_{corr})_{\theta=0} >> (i_{corr})_{\theta=1}$, so that the measured corrosion rate $(i_{corr})_{\theta}$ can be directly related to the coverage of the surface (θ) :

$$\theta = 1 - \left[\frac{(i_{corr})_{\theta}}{(i_{corr})_{\theta=0}}\right]$$
(6)

In the simplest model of chemisorption, every adsorption site is equivalent and only monolayer adsorption occurs with no interactions between molecules at adjacent sites. If chemisorption of hydrogen sulfide provides the surface coverage with no interaction between adsorbed species, a classical isotherm, such as the Langmuir isotherm for a homogeneous flat surface, can be used to determine the adsorption factors.

$$\theta = \frac{K_i c_i}{1 + K_i c_i} \tag{7}$$

where θ is the monolayer surface coverage,

 K_i is an equilibrium constant, and

 c_i is the concentration.

The Langmuir isotherm assumes independence and equivalence of the adsorption sites. The Freundlich isotherm is also a classical isotherm for a heterogeneous flat surface and corresponds to an exponential distribution of heats of adsorption,

$$\theta = K_i c_i^{m_i} \tag{8}$$

where m_i is a positive number and generally not an integer,

 K_i is an equilibrium constant.

The Radke-Prausnitz isotherm combines both the Langmuir isotherm and the Freundlich equation, but reduces to the Langjuir isotherm for m=1.

$$\theta = \frac{K_i p_i}{\left(1 + K_i p_i\right)^m} \tag{9}$$

Using the three different isotherms, parameters were adjusted to calculate the surface coverage and minimize the variance between the data and the curve fit. As shown in Figure 73, all three are within the error limitations set by the data, with variances of 0.055, 0.052, and 0.053 respectively for the Langmuir, Freundlich, and Radke-Prausnitz isotherms.

Parameter values at this point in time are speculative, but can be improved with further study. Assuming that corrosion would only occur on unoccupied surface sites and therefore be in direct relation to the corrosion rate, a normalized corrosion rate curve based upon the Freundlich isotherm resembles the solid line in Figure 74 and fits very well with experimental data.



Figure 73. Calculated isotherms in comparison to empirical data for surface coverage comparison.



Figure 74. Classical Freundlich isotherm for heterogenous adsorbents over a wide range of concentrations.
CONCLUSIONS

- The study of CO₂/H₂S corrosion under multiphase conditions of water and gas mixtures is a relatively new field. These experiments in the Hydrogen Sulfide Multiphase Flow Loop provide the first example of the effect of H₂S concentration on corrosion rates measured concurrently in single phase and multiphase flow in a CO₂ saturated environment..
- 2. The phenomenon of the CO₂ corrosion rate acceleration was thought to be seen during the first few hours of exposure at low H₂S concentration, 60°C, 0.79MPa (100 psig), and 3ppm H₂S in multiphase flow. Corrosion rate measurements by linear polarization and weight loss of C1018 and X-65 steels show this phenomenon of increased corrosion rate in multiphase flow, but not in single-phase flow. This phenomenon is best attributed to fluctuations in corrosion rate measurements during short term exposures since it was not seen as exposure times were increased. Therefore this series of experiments reverses the findings of Ikeda, et al, 1984 for long term studies in H₂S/CO₂ environments.
- 3. The addition of trace amounts of H₂S to a CO₂ saturated system retarded the general corrosion rate over the 96-hour experimental time. As the concentration of H₂S was increased above 10 ppm the corrosion rate significantly decreased for all tests as compared to pure CO₂ corrosion.

- Three adsorption isotherms were was used to prove that the H₂S mechanistic theory of corrosion through adsorption and surface reaction in a CO₂ saturated system is valid.
- 5. Turbulence under multiphase flow conditions was seen to reduce the film thickness produced as compared to films produced under single phase flow at the same environmental conditions. A slightly higher corrosion rate was also observed in multiphase flow as compared to single phase flow.

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APPENDIX A: Distribution of Species for an H₂S/CO₂ System

Vapor-liquid equilibrium reactions for carbon dioxide and hydrogen sulfide are described as:

$$CO_{2(g)} \leftrightarrow CO_{2(aq)}$$
 (10)

$$H_2 S_{(g)} \leftrightarrow H_2 S_{(aq)} \tag{11}$$

Henry's law is used to calculate the composition of vapor-liquid equilibrium:

$$x_{CO_2} H_{CO_2} = P_{CO_2}$$
(12)

$$x_{H_2S}H_{H_2S} = P_{H_2S}$$
(13)

Where x_{CO_2} and x_{H_2S} are the mol fractions of carbon dioxide and hydrogen sulfide in solution and H is the Henry's constant. P_{CO_2} and P_{H_2S} are the partial pressures of carbon dioxide and hydrogen sulfide.

Because there are no reactions between carbon dioxide and hydrogen sulfide, the composition of the solution can be determined through a sequence of chemical reactions. As carbon dioxide gas dissolves in water, aqueous carbon dioxide, $CO_{2(aq)}$, is hydrated to form carbonic acid.

$$CO_{2(aq)} + H_2O_{(aq)} \xleftarrow{Khyd}{} H_2CO_{3(aq)}$$
 (14)

The carbonic acid dissociates to release a hydrogen ion and a bicarbonate ion in solution.

$$H_2CO_{3(aq)} \longleftrightarrow^{K_{ca}} H_{(aq)}^+ + HCO_{3(aq)}^-$$
(15)

The bicarbonate ion also dissociates to release another hydrogen ion and a carbonate ion.

$$HCO_{3(aq)}^{-} \longleftrightarrow H_{(aq)}^{+} + CO_{3(aq)}^{2-}$$
(16)

After hydrogen sulfide dissolves in water, it does not need to hydrate with water to form an acid in order to dissociate hydrogen ions. Since it is acidic, hydrogen sulfide dissociates to bisulfide (HS⁻) and sulfide (S²⁻) species in a series of dissociation reactions in solution.

$$H_2S_{(aq)} \longleftrightarrow^{K_1} H_{(aq)}^+ + HS_{(aq)}^-$$
(17)

$$HS_{(aq)}^{-} \longleftrightarrow H_{(aq)}^{+} + S_{(aq)}^{2-}$$
(18)

Since these processes occur in water, all are in dynamic equilibrium with H_2O , H^+ , and OH^- ions.

$$H_2 O_{(aq)} \longleftrightarrow^{K_W} H_{(aq)}^+ + O H_{(aq)}^-$$
(19)

The distribution of species is dependent upon the partial pressures of carbon dioxide and hydrogen sulfide of a known system, the temperature of the system, and the pH. Concentrations of each species can be determined by solving the corresponding equilibrium reactions above.

APPENDIX B: H₂S Corrosion Mechanism

Two authors have provided scenarios for the corrosion of iron exposed to aqueous hydrogen sulfide. Shoesmith's²⁵ proposal is based upon studies of corrosion products' morphology and phase identity while Smith²⁶ used thermodynamic calculations to predict when a mackinawite film will form. Both consider the reaction to be a solid state reaction, occurring on the metal surface while FeS is undersaturated in solution.

Shoesmith, et al, ²⁵ proposed a sequential chemisorption reaction,

$$Fe + H_2S + H_2O \rightarrow FeSH_{ads}^{-} + H_3O^+$$
⁽²⁰⁾

an anodic discharge reaction,

$$FeSH_{ads}^{-} \rightarrow FeSH_{ads}^{+} + 2e^{-}$$
 (21)

and cathodic reaction

$$2H_2S + 2e^- \rightarrow H_2 + 2HS^- \tag{22}$$

for the corrosion reaction of carbon steel in an environment with dissolved H_2S . Following the anodic discharge reaction, the $FeSH_{ads}^+$ species can then be directly incorporated into a growing layer of mackinawite (FeS_{1-x}) film.

$$FeSH_{ads}^{+} \rightarrow FeS_{1-x} + xSH^{-} + (1-x)H^{+}$$
(23)

If the adsorbed species, FeSH_{ads}^+ , is hydrolyzed to yield ferrous ions at the electrode surface,

$$FeSH_{ads}^{+} + H_3O^+ \to Fe^{2+} + H_2S + H_2O$$
 (24)

local supersaturation can occur at the surface leading to nucleation and growth of iron sulfides: mackinawite, cubic ferrous sulfide, or troilite.

Smith²⁶ proposed a set of surface reactions for the mackinawite corrosion mechanism.

Hydrogen sulfide is adsorbed from the solution to the metal surface.

$$Fe + H_2 S_{(aq)} \to Fe + H_2 S_{(adsorbed)}$$
⁽²⁵⁾

Adsorbed hydrogen sulfide dissociates.

$$Fe + H_2 S_{(adsorbed)} \rightarrow Fe + HS_{(adsorbed)}^- + H_{(adsorbed)}^+$$
(26)

The bisulfide ion combines with the iron on the surface.

$$Fe + HS_{(adsorbed)}^{-} + H_{(adsorbed)}^{+} \rightarrow FeHS_{(adsorbed)}^{-} + H_{(adsorbed)}^{+}$$
 (27)

Charge transfer to lower chemical potential produces hydrogen on the surface.

$$FeHS_{(adsorbed)}^{-} + H_{(adsorbed)}^{+} \rightarrow FeHS_{(adsorbed)}^{+} + H_{(adsorbed)} + e^{-}$$
(28)

$$FeSH^{+}_{(adsorbed)} + H_{(adsorbed)} + e^{-} \rightarrow FeS_{(adsorbed)} + 2H_{(adsorbed)}$$
(29)

Mackinawite is formed from amorphous FeS by Tayor's²⁷ pairing reaction:

$$2nFeS_{(adsorbed)} \to nFe_2S_2 \to FeS_{(mackinawite)}$$
(30)

In both cases, iron is consumed in a similar corrosion process.

The H₂S corrosion process can lead to blistering and/or stress corrosion cracking of pipelines. Strongly chemisorbed dissolved sulfur species, H₂S and HS⁻, will replace the weakly adsorbed H₂O molecules on most transition metals.²⁴ Therefore, the population of species (FeSH⁺, FeS_{1-x}, xSH⁻, and FeS) on the surface acts as an inhibitor for H⁺ recombination and protons (H⁺) will migrate into the metal lattice if allowed to remain on the surface. These protons will combine with other protons within the metal lattice can cause blistering or stress corrosion cracking of higher strength steels.

APPENDIX C: Design Drawings for Weight Loss Coupons and Holder



All measurements are +/-0.005"

Figure 75. Dimensions for nylon pressfit coupon holder.



Figure 76. Design drawing for carbon steel weight loss coupon.



This piece is made of 300 series stainless steel and requires a 1.5" to 2" length of 1/2-20 stainless steel all thread and a 5/8" O.D. rod, 28" to 30" in length, that is threaded to accept the 1/2-20 all thread.

Figure 77. Design drawing for holding rod end.