

Study of Sweet Corrosion in Horizontal Multiphase, Carbon Steel Pipelines

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ABSTRACT

Sweet corrosion in carbon steel pipelines carrying oilwater mixtures has long been a problem in the oil industry. A study to determine the corrosion rates and the type of deposits formed on the pipe surface under such multiphase flow conditions is described. Experiment are performed in a 10.16cm ID flow loop. Full pipe flow and slug flow conditions and the effect of a few inhibitors is studied. Temperatures upto 60C and several pressures, flow rates, oil-water fractions are studied. It is observed that non protective iron carbonate scales are formed below 60C. Iron carbide skeleton which emerges from the carbon steel is detected. Corrosion rates increase with an increase in temperature and carbon dioxide partial pressure and liquid flow rates. With an increase in oil/water fraction, corrosion rates increase upto 60% oil, for the conditions studied. Iron carbonate crystal deposition increases with temperature and pressure. Evidence of bubble collapse and localized corrosion is observed under slug flow conditions.

Keywords : carbon dioxide, carbon steel, corrosion, multiphase, iron carbonate, full pipe flow, slug flow, inhibitors, bubble impact.

INTRODUCTION

Corrosion related problems in oil-gas production and processing operations result in millions of dollars each year in down time, lost production and damaged pipelines. With the use of enhanced oil recovery techniques, carbon dioxide corrosion in oil-water pipelines has become common causing much concern in transportation of these multiphase fluids over long distances from remote wells to separation sites. The use of corrosion inhibitors, surfactants and drag reducing agents to reduce the corrosion has met only with partial success. The effectiveness of these corrosion reducing agents depends on the flow regimes existing in the pipeline.

Several workers have studied carbon dioxide corrosion in carbon steel pipelines. However most of the studies were carried out in single phase systems using deionized water, or brine solutions saturated with STUDY OF SWEET CORROSION IN HORIZONTAL, MULTIPHASE CARBON STEEL PIPELINES

carbon dioxide. Almost all the previous studies were conducted in rotating cylinder electrode equipment and in autoclaves. Recently some research was conducted in small diameter, single and two phase horizontal pipelines. However the flow mechanisms in small diameter pipelines, i.e. less than 5 cm can be different from those existing in 10 cm and larger diameter pipes. The effects of different flow regimes such as stratified, plug flow and slug flow have not been addressed. Hence, any extrapolation of results from single/two phase small diameter pipelines to multiphase larger diameter ones can lead to grave errors in prediction of corrosion rates.

Green, Johnson and Choi¹ have shown the significant effect of the different flow regimes on corrosion rates. In slug flow, the instantaneous corrosion values obtained when a slug passes were at least two orders of magnitude larger than those existing under stratified flow conditions.

Many investigators have studied the chemistry of carbon dioxide corrosion in water and have determined iron carbonate as the main corrosion product. Videm and Dugstad^{2,3} have reported from their flow loop studies that the corrosion takes place without an iron carbonate corrosion film if the Fe²⁺ ions in the water are in the solubility range and the corrosion rates increase with carbon dioxide partial pressure. Possibility of flow induced mesa attack was indicated in waters saturated with FeCO₃ under turbulent flow conditions when film formation is prevented locally.

Ikeda et al.⁴ divide the mechanisms of carbon dioxide corrosion into 3 types on the basis of temperature. They reported that, at low temperatures (below 60C), ferrous carbonate does not adhere to the metal surface. At temperatures below 30C, the hydrolysis of carbon dioxide seems to be the rate determining step but above 30C, the carbon dioxide diffusion is the controlling factor.

Xia, Chou and Szklarska⁵ reported from their studies with brine solution in an electrolytic cell that iron bicarbonate formed at room temperatures in the initial phases of corrosion. This then changed to iron carbonate. Pitting corrosion was observed at circular sites where small gas bubbles had been present and attached to the steel surface. These sites had a diameter of approximately 0.05 mm.

Studies by De Waard, Lotz and Milliams^{6,7,8}, Mishra, Olson, Al-Hassan and Salama⁹, and other researchers lead to the conclusion that iron carbonate scale formation (dissolution) depend on various parameters such as temperature, pH, CO_2 partial pressure, brine content, material composition, flow velocity and flow regimes. The corrosion rate may itself depend, in addition to the above factors, on the heat treatment and surface preparation of the material.

Lunde and Nesic¹⁰ performed interesting work in two phase (water and carbon dioxide) corrosion. They have reported from their studies in a flow loop that the corrosion rates increase with an increase in temperature, partial pressure and flow velocities. At very high temperatures, the corrosion rates were found to decrease due to the formation of protective carbonate scales. Iron carbide was detected which comes from the carbon steel.

Similar studies by Kanwar and Jepson¹¹ in a 10 cm diameter flow loop has made some valuable contribution to the study of multiphase corrosion. They considered the effect of the addition of a third oil phase and measured the corrosion rates at various oil/water fractions with 2 different oils, carbon dioxide partial pressures and liquid flow rates at a constant temperature of 40C. Using the resulting corrosior rates, a predictive model was formulated using the wall shear stress and partial pressure of carbor dioxide.

It is clear however that irrespective of the exact mechanisms involved, the formation of iron carbonate films is a major controlling factor that influence the final corrosion rates observed. This study observes the change in the corrosion deposit formed with the introduction of the oil phase at different system. conditions. Experiments are performed in a stainless steel flow loop under full pipe flow and, slug flow conditions with and without corrosion inhibitors. Several temperatures, pressures, oil-water fractions and flow rates are studied.

EXPERIMENTAL SETUP AND PROCEDURE

The experiments are performed in a 316 stainless steel flow loop shown in Figure 1. The system is designed to withstand a maximum pressure of 10 MPa. The tank has a capacity of 1.15 m³. Two heaters connected to a thermostatic controller maintain the desired temperature in the system. The fluid is pumped by a 5 kW stainless steel pump to a 7.62cm ID pipe where the flowrate is measured. It then passes into a 10 m long, 10.16 cm ID pipeline. The test section within the 10 m pipeline is outlined in Figure 2. Electrical resistance (ER), linear polarization resistance (LPR) probes and coupons are placed at positions C and E to determine the corrosion rates. It was found that the LPR probes did not perform well at high oil concentrations. Its use was limited to oil concentrations up to 20%. All the probes are flush mounted with the pipe wall. The pressure drops, wall shear stress were also be measured at points P and S respectively. These results are not discussed here.

The fluids used are ASTM standard sea water and Conoco LVT200 oil, for the liquids and carbon dioxide for the gas. The oil has a density of 825 kg/m³ and a viscosity of 2cp at 40C and is similar to a light condensate oil. The system is filled with the desired oil-water composition and is then deoxygenated by purging the system with carbon dioxide gas. Regular checks are made for the oxygen content in the liquid using the CHEMets dissolved oxygen testing kits. The procedure is continued till the oxygen level falls below 30 ppb. The system is then pressurized with carbon dioxide to the desired value. The iron level in the system is maintained below 10ppm and is checked through out the time of the experimental run. If the iron level increases then the salt water in the system is discarded and filled with fresh salt water.

Circular coupons, 12 mm in diameter and 3.5 mm thick, made of hot rolled 1018 carbon steel are used. Before using the coupons they are cleaned according to the ASTM standard pretreating procedure. Four coupons are mounted in a teflon coupon holder shown in Figure 3 and inserted into the test section at the bottom of the pipe. After each experimental run, the coupons are carefully removed from the holder and cleaned delicately with deionized water and acetone and dried and stored in a desiccator. The coupons are coated with a thin gold film and examined using a scanning electron microscope (SEM). For studying the metal surface beneath the corrosion products, ASTM standard post test cleaning procedure for dissolving the corrosion deposits is used. The coupons are treated for 15-20 min at 20-25C in a solution made by adding 20gms Sb₂O₃ and 50gms SnCl₂ in 1000ml of HCl and stirring continuously. The coupons are then washed in deionized water and cleaned in the ultrasonic cleaner to remove loosely held corrosion products. They are then cleaned with deionized water and acetone and dried and studied under a SEM. A clean uncorroded coupon is always placed as a basis along with the other corroded coupons to observe if any damage is done to the coupon metal because of chemical cleaning. To identify the corrosion products formed on the coupons, Auger spectroscopy and X-ray photoelectron spectroscopy (XPS) examinations were performed at the Materials Research Laboratory at the University of Illinois.

Temperatures of 40C and 60C, carbon dioxide partial pressures of 0.27 MPa and 0.79 MPa, and liquid velocities of 0.28 m/s and 1 m/s are used for full pipe flow conditions at water cuts of 0%, 20%, 40%, 60%, 80%, and 100%. Slug flow studies have been carried at a temperature of 40C and at liquid velocities corresponding to Froude numbers of 6, 9 and 12. A limited study on the use of corrosion inhibitors was also carried out at a carbon dioxide partial pressure of 0.136 MPa.

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RESULTS AND DISCUSSIONS

Equilibrium corrosion rates measured by the ER probe are plotted at various pressures and flow rates. Figure 4 shows the graph of corrosion rate vs oil composition. These results show that the corrosion rate increases slightly as the oil fraction increases and then decreases rapidly to a negligible value below 40% water cuts. Samples taken from the flow show the presence of a water layer at the bottom of the pipe up to 40% water cut. Below this, oil seems to be the continuous phase adjacent to the pipe wall.

The corrosion rates increased with carbon dioxide partial pressure, liquid velocity, and temperature. These corrosion rates are much higher than those predicted by the De Waard and Lotz⁸ equation for the similar conditions.

From optical observations, it is found that for all the conditions studied, the coupon surfaces were covered with a black/grey deposit.

No distinctive trend was observed in the corrosion deposit formed on the coupon surface with a change in flow rate from 0.28 m/s to 1 m/s for the conditions studied. All the results described below are at a liquid velocity of 1 m/s.

The results from the XPS studies identified the corrosion deposits formed under the experimental conditions.

Initially, XPS tests on siderite and precipitated $FeCO_3$ samples were performed to provide the standards for the corrosion compounds present on the coupons.

It is observed that $FeCO_3$ is the major product of these corrosion films. Auger studies have indicated the presence of significant amounts of Fe, C, O, some Cl and traces of Si, N in their scans. When an EDAX was performed on these films, traces of Ca, Mg, Si, Cr were found along with relatively larger amounts of S, Cl and Mn and a large iron peak. The presence of these compounds in the corrosion deposit come from components in the salt water and has a substantial effect on the characteristics of the layer of corrosion products.

The corrosion deposits at all the conditions are very loosely held to the metal and are easily removed by the sharp edge of a paper, indicating the absence of any adherent protective corrosion layer. The corrosion rates are significant and do not change substantially with time.

From the SEM studies, the effects of oil/water fractions, temperature, pressures and fluid velocities on corrosion has been determined for full pipe flow conditions.

Uniform corrosion is generally observed in full pipe flow. This is shown in Figure 5 which is for 100% saltwater at 40C and 0.136 MPa at a magnification of 97. Here, it can be seen that the corrosion deposit is in the form of a layer of relatively constant thickness with many long cracks in it. This layer seems to be porous in nature and can easily be removed.

XPS studies indicate the presence of iron carbonate, iron carbide, and the constituents present in the saltwater mentioned earlier. Higher magnifications show that the iron carbonate is in the form of small crystals embedded in the porous material. The carbide comes from the metal itself. This is shown in Figure 6 which is a photograph of the corroded coupon metal surface after the corrosion deposit is removed by chemical treatment. It is observed that the soft α iron(ferrite structure) in the metal had corroded leaving behind the hard pearlite skeleton containing ferrite and cementite in a lamellar fashion. There is a possibility that the cementite skeleton may help in anchoring the loose carbonate films.

Similar deposits were found at the different pressures and temperatures for salt water. As the oil composition is increased up to 60%, the crystals of iron carbonate become much larger but there are fewer of them. This is illustrated in Figure 7 which is for 60% oil, at 40C and 0.79 MPa. The crystals are

still embedded in a porous layer. The porosity increased with increasing oil concentration. Above 60% oil, the coupon surfaces become almost devoid of any kind of corrosion deposits. This is shown in Figure 8 for oil only at 40C and 0.79 Mpa.

The effect of increasing temperature from 40C to 60C is illustrated in Figures 7 and 9. For 60% oil, as the temperature is increased, the coupon surface is covered by a layer of iron carbonate crystals. The crystals are loosely spread and do not appear to form a dense film. Cracks are present in the carbonate layer. On top of the crystals is a smooth, crumbly crust which can be easily broken away.

For 20% oil concentrations, the iron carbonate crystals are smaller and are again embedded in the porous corrosion deposit. This tends to become more crusty with an increase in temperature.

The effect of increasing carbon dioxide partial pressure is shown in Figures 10, 11 and 12. Figures 10 and 11 are for 20% oil at 60C and 0.27 and 0.79 MPa respectively. It can be seen that, at the lower pressure, the iron carbonate is present in a smooth, porous layer with several deep cracks in it. For the higher pressure, the porous layer becomes coarser with more carbonate crystals present. For 60% oil at 60C, a comparison of Figures 9 and 12 shows that, at the lower pressure, the corrosion product consisted of small iron carbonate crystals deposited in the form of circular pools while in the other areas the crusty layer similar to the one present in Figure 9 is found. Increasing pressure increases the extent of crystal formation.

Slug flows were examined at Froude numbers of 6 and 9. These correspond to slugs moving at approximately 3 and 4.5 m/s respectively.

At 20% oil fractions, there are no large iron carbonate crystals deposited on the coupon surface. However the coupons were covered with a loose corrosion product similar to those found in full pipe flow conditions. This is illustrated in Figure 13. The deposit on the coupon at Froude number 6, for 20% oil at 40C and 0.27 MPa was very thin and uniformly deposited and had cracks in it. A large number of small flakes were present which may be due to the turbulence in the slug flow. This can break up the corrosion layer. Similar deposits were found at Froude number of 9 at both 0.27 and 0.45 MPa. At Froude 6 and 0.79 MPa, there were present a large number of islands of sodium chloride crystals in between the general corrosion deposit. The sodium chloride islands formed may lead to localized corrosion. The coupon surface showed a great number of small pits when the corrosion deposit is removed by chemical treatment. Though the entire coupon surface was uniformly corroded, such pits were observed at Froude 6 and 9, indicating the presence of localized corrosion. This is shown in Figure 14.

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When a drag reducing agent was used in slug flow studies, signs of severe, flow induced corrosion was noticed. At 60% oil, at a Froude number of 12, a large number of circular craters were noticed. These are shown in Figure 15. The adsorbed drag reducing agent and the corrosion deposit in these areas were ripped off. This is attributable to gas bubbles, that are entrained at the slug front, being forced to impinge on the bottom of the pipe in the mixing zone of the slug. These bubbles can collapse producing a cavitation type phenomenon. The pressure wave released has great strength and is sufficient to remove the corrosion products from the pipe wall at the point of impact. The corrosion deposit around these "impact points" is similar to that without any drag reducing agent present but is very thin. In these impact areas there is bare metal which leads to further corrosion.

The impact regions have a diameters between 0.1mm to 0.2mm. These are about twice as large as those reported by Xia et al^5 . This is due to the non-stagnant nature of the flow here.

At lower Froude numbers, the impact effect was more widely spread but less severe in tearing off the deposits.

The effect of corrosion inhibitors was then studied. Several inhibitors that were used exhibited signs of bubble impact points at the high Froude numbers. When the coupons were examined, it is found that a very thin film of the inhibitor is deposited on top of iron carbonate crystals. However, bubble impact points are observed throughout the coupon face and evidence of breakdown of the inhibitor film can be seen. This is evident in Figure 16. There were still high levels of corrosion in these areas and showed a lack of effectiveness under these conditions.

CONCLUSIONS

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For the conditions studied, the corrosion rates are found to increase with an increase in liquid velocity, temperature and pressure for oil/water fractions up to 60% oil. Above 60% oil, the corrosion rate decreases rapidly and is negligible at higher oil fractions.

Iron carbonate is the main corrosion product. No protective carbonate films are formed for the conditions tested. Non-adherent, porous deposits with cracks in them are present. Significant equilibrium corrosion rates are reported.

The soft ferrite phase in the steel is corroded leaving the cementite skeleton behind which helps in anchoring the loose corrosion films.

Uniform surface corrosion is observed in full pipe flow conditions. However with slug flow conditions considerable localized corrosion is observed at higher partial pressures and Froude numbers.

Bubble collapse phenomena is found with slug flow when the inhibitors/drag reducing agents are present. Circular impact regions of diameter 0.1 mm - 0.2 mm are noted. These impacts can tear holes in the inhibitor film making that inhibitor very ineffective. Corrosion is observed in these areas.

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Figure. 5 Corrosion products for 100% Salt water at 40C and 0.136 MPa, Full pipe flow.



Figure. 6 - Carbon steel coupon after corrosion deposit removal. White area is the cementite skeleton left over after ferrite is corroded.



Figure. 7 - Larger carbonate crystals embedded in a porous layer at conditions of 60% oil, at 40C and 0.79 MPa.

 $(x_{i+1}, \dots, x_{i+1}) \in \mathbb{R}^n$



Figure. 8 - Surface with very less corrosion product for Oil only conditions at 40C, 0.79 MPa.



Figure. 9 - Iron carbonate crystals loosely distributed and covered by a crust with large cracks for 60% oil, at 40C and 0.79 MPa.



Figure. 10 - Corrsoion products for 20% oil at 60C and 0.27 MPa.



Figure. 11 - Corrosion deposits for 20% oil at 60C and 0.79 MPa.



Figure. 12 - Circular pools of Iron carbonate crystals deposited on top of a porous corrosion deposit for 60% oil at 60C and 0.27 MPa.



Figure. 13 - Deposit is broken into small flakes by the turbulence for Slug flow at Froude No. 6 for 20% oil at 40C and 0.45 MPa.



Figure. 15 - Circular bubble impact points in the corrosion deposit at a Froude No. 12 for 60% oil with 50 ppm drag reducing agent at 40C and 0.136 MPa.



Figure. 14 - Severe local corrosion for slug flow at a Froude No. 9 for 20% oil at 40C and 0 .27 MPa.



Figure. 16 - Regions of local corrosion in the bubble impact points on the inhibited surface at a Froude No. 11 for 60% oil with 50 ppm inhibitor, at 40C and 0.136 MPa.