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PRECIPITATION AND KINETICS OF FERROUS CARBONATE IN SIMULATED BRINE SOLUTION AND ITS IMPACT ON CO_2 CORROSION OF STEEL

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ABSTRACT
The aim of present study was to study the stability of iron carbonate films formed on the surface of low alloy carbon steel used in pipeline applications in brine solution. All the tests were carried out in a stirred autoclave at various temperatures and low partial pressure of CO_2*. Usually, American Petroleum Institute (API) specification steels are used for carrying the crude oil and gas from the offshore to refining platforms and ultimately to the customers through pipeline routes. Developed and modified alloy steel of API grade such as API X-52, API X-56, API X-60 and L-80 are used in this study that are rapidly using in petroleum industries to transport the oil and gas. The first three grade of steel are used for transportation while L-80 grade is used for tubing and drilling the wells for recovery of oil and gas from offshore. The comparative study of their susceptibility of corrosion in severe corrosive condition has been made by measuring the corrosion rate of steel using weight loss method in simulated 3.5% NaCl test solution. The fluid velocity of simulated brine solution was maintained at a rate of 1.5 m/s for each test. The exposed samples were characterized by using Scanning Electron Microscope and X-ray diffraction techniques.*

KEY WORDS: *API grade steel, Partial pressure of carbon dioxide, Autoclave, Brine solution*

I. INTRODUCTION

The CO_2 corrosion of carbon steel is one of the most important problems in the petrochemical industries since 1940, because of their localized attack and severe corrosion [1-3]. These steels have wide application in just about every sphere of oil and gas industries and it requires critically assessment of corrosion severity to ensure safe utilization of these steels. An increased number of offshore developments are based on transporting the unprocessed or partially processed multiphase well streams from wells to onshore processing platforms and from there to ultimate consumers. In such circumstances carbon dioxide often present in the fluids and is known for its high corrosion potential when dissolved in water. These aspects are responsible to adequately assess the integrity of the steels used in the oil and gas industry for production and transport equipment. Many parameters are involved in the process and even small differences in chemical composition between one steel and another can strongly influence scale formation during CO_2 corrosion [4]. Scale formation and salt accumulation are another analogous rigorous problem for the operation of multiphase pipelines [4-5]. Usually, well fluids and other products are transported through pipelines in the oil and gas industry and these fluids contain aqueous phases which are considered to be inherently corrosive. CO_2 is a gas that reacts with water to form carbonic acid which lowers the pH of the solution and thus responsible for increased corrosion rate. Despite, of its many studies frequent questions are still raised regarding the mechanism of CO_2 corrosion responsible for its occurrence. Many developed corrosion resistant alloys such as 13% Cr steel and duplex stainless steel are used for the downhole drilling and also for short flow lines [7-9]. But for long distance and large diameter pipelines, carbon steels are the only economically feasible alternatives [9]. However, these steels are susceptible to corrosion in both either

CO_2 and H_2S or combination of these two. The susceptibility of their corrosion depends on various parameters such as temperature, CO_2 partial pressure, H_2S concentration, pH, oxygen solubility, chloride concentration, flow rate and characteristics of the materials [1-3]. The presence of acidic gas like CO_2, H_2S and free water can cause severe corrosion problem in the oil and gas industries [5]. The small change in one of these parameters can change the corrosion rate drastically due to change in the properties of the layers of corrosion products that accumulates on the steel surface. The selection of materials that transport oil and gas is not always made with sufficient emphasis on corrosion resistance, but rather on good mechanical properties, ease of fabrication and low cost. Due to the material loss rates resulting from internal corrosion, it becomes necessary to thoroughly characterize the behavior of these high strength steels used for oil and gas pipelines. Many authors emphasized on the importance of the evaluation of the specific nature of the film formed under a given set of conditions, as these conditions can affect the type of film formed on the steel [10]. In general, the precipitation of an iron carbonate film on the steel surface significantly affects the rate of corrosion. The corrosion rate may increase or decrease depends on the nature of the film that forms on the metal surface. Usually the carbonate film reduces the corrosion rate however in some certain cases it can contribute to localized corrosion due to its non-uniform nature [11]. Also, the corrosion rate is closely dependent on a series of parameters such as temperature, pressure, pH and steel composition. Nesic et. al proposed a theoretical model of carbon dioxide corrosion in which the main focus was on the factors which influence $FeCO_3$ film formation [6]. They suggested that corrosion rates are not, in fact, closely associated simply with the thickness of the protective film, but rather with its degree of coverage and homogeneity on the metal surface. These films can partially or completely cover the metal surface and consequently block only a portion of the exposed metal or, in some cases, it can homogeneously cover the entire surface of steel. By covering entire surface it can prevent the further corrosion due to restrict in further dissolution. The voids and holes may form at the underneath of corrosion films that interface with the metal. The rate of void formation is important for determining the type of film that formed on the metal surface. The protectiveness of film depends on many factors such as film density, degree of protectiveness, porosity, and thickness. With the aid of their model, they also confirmed that high levels of pH, temperature, partial pressure of CO_2 and Fe^{2+} concentration associated with a low formation rate of the above mentioned voids can favour the formation of a protective iron carbonate film [10-12].

II. MECHANISM AND KINETICS OF CO_2 CORROSION

Iron carbonate is the main corrosion product in carbon dioxide corrosion is also known as sweet corrosion since 1940 and it is considered as one of the most important problems in the oil and gas industry due to its presence in the well fluids [10-11]. The iron carbonate scale formed on the metal surface may be protective or non protective depends on the conditions at which they are formed and influenced by many factors such as the concentration of ions present in the solution, pH, temperature, pressure and velocity of the solution. The formation of protective films of iron carbonate called siderite is possible when the concentration of bicarbonate ions increases rather than carbonic acid. Since carbon dioxide dissolve in water and form carbonic acid which is mild acidic in nature and corrosive. Among the most popular mechanisms postulated for this type of corrosion are proposed by De Waard and Milliams, Schmitt and Rothmann and George and Nesic et. all which involve carbonic acid and bicarbonate ions formation during dissolution of CO_2 in water [1-6]. Both chemical and electrochemical reactions are important factors in CO_2 corrosion and one of the most common chemical reactions that occur in the system is as follows;

$$CO_{2\,(g)} + H_2O \leftrightharpoons CO_{2\,(dissolved)} \qquad (1)$$

$$CO_{2\,(dissolved)} + H_2O \rightleftarrows H_2CO_3 \qquad (2)$$

This is followed by the carbonic acid dissociation:

$$H_2CO_3 \leftrightarrows H^+ + HCO_3 \qquad (3)$$

$$HCO_3 \leftrightarrows H^+ + CO_3^{2-} \qquad (4)$$

On the surface of the steel, the electrochemical reactions which occur include an anodic reaction and three cathodic reactions. The anodic reaction is:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (5)$$

The following cathodic reactions takes place are as follows;

$$2H^+ + 2e^- \rightarrow H_2 \qquad (6)$$

$$2H_2CO_3 + 2e^- \rightarrow H_2 + 2HCO_3^- \qquad (7)$$

$$2HCO_3^- + 2e^- \rightarrow H_2 + 2CO_3^{2-} \qquad (8)$$

In CO_2 corrosion of carbon steel, when the concentrations of Fe^{2+} and CO_3^{2-} ions exceed the solubility limit, they can precipitate to form solid iron carbonate film according to the reaction as below;

$Fe^{2+} + CO_3^{2-} = FeCO_3$ (s) (9)

The properties of these films depend on precipitated iron carbonate ($FeCO_3$) film called siderite on the metal surface. It may act either in a protective or non-protective manner, depending on the specific conditions under which it forms. At $pH < 7$, the carbonate ion (CO_3^{2-}) is a minority species, and the direct reduction of bicarbonate ions (HCO_3^-) is an important factor in the formation of the $FeCO_3$ films on the steel surface. The $FeCO_3$ forms by the following equation:

$Fe^{2+} + HCO_3^- = FeCO_3 + H^+$ (10)

The overall reaction can be expressed as:

$$CO_2 + H_2O + Fe \rightleftarrows FeCO_3 + H_2 \qquad (11)$$

Thus dissolved CO_2 have the tendency to form carbonic acid (H_2CO_3) in the solution which increases the cathodic reaction kinetics by dissociation to bicarbonate and hydrogen ions. Under stagnant condition, dissolved ferrous ions combine with the H_2CO_3 to form ferrous carbonate ($FeCO_3$). However under flow condition some part of the iron carbonate dissolved and thus the reaction rate become faster due to removal of corrosion scale from the metal surface. De Waard and Milliams developed a semiempirical correlation between corrosion rate and CO_2 partial pressure. This relationship later simplified in the form of a nomogram and given as below;

$\text{Log C.R. (mm/y)} = 5.8 - 1780/T + 0.67 \text{ Log } (pCO_2)$ (12)

The above equation provide a conservative estimate of corrosion rate under flowing condition because it does not account for the effect of non-ideality of the gas phase and scale formation. In equation 4, the hydrogen ion is produced through the bicarbonate ions near the surface rather than direct H_2CO_3. In this sense, the carbonic acid acts as catalysts for the evolution of hydrogen. The high concentration of H_2CO_3 or its precursor CO_2 relative to H^+ ion in the bulk solution increases the rate of overall mass transfer and depolarized the cathodic reaction. The ability of carbonic acid to sustain high cathodic reduction rate at relatively high pH indirectly aids the anodic reaction as per equation (5), which is faster at higher pH. Also, the value of pH has the tendency to both either increase or decrease the CO_2

based corrosion. The determination of pH is a function of partial pressure of mild acidic gas, concentration of bicarbonate ions and temperature. Practically, the contribution of mild carbonic acid (H_2CO_3) and temperature in pH determination is another way of representing effective level of partial pressure of carbon dioxide (CO_2) in the solution. As the solution pH decreases the localized attack involved in the steel surface. The temperature of the solution has a significance influence on the CO_2 corrosion. An Arrehenius type of relationship has been reported as below;

$$\text{Log}(I_{corr}) = 7.58-10,700/2.303\ RT \qquad (13)$$

The temperature effect on film formation has been summarized by Burke in 1984 and reported that below 60°C the corrosion product formed on the metal surface is mainly consists of siderite and magnetite which is non-protective in nature. However, at higher temperature range (80-120°C) this scale becomes dense in association with Fe_2O_3 and Fe_3O_4 and protects the metal for further degradation.

III. EXPERIMENTAL

The materials used in the current study were obtained in pipe form. The as-received materials were cut into the rectangular specimen of dimension 20 mm x 12 mm x 2.5 mm with a center hole of diameter 1.5 mm at the top edge of each specimen to facilitate the suspension inside of the autoclave of capacity 2.2 liter. The faces of the samples were initially coarse grounded on a SiC belt grinder machine then consequently machine polished in the successive grade of emery papers (220, 400, 600 800 and 1000). The initial weight and area of each sample was measured using digital weighing machine upto an accuracy of four digits. Four different experiments were carried out at different temperature (30 °C, 60 °C, 90 °C and 120 °C) for each measured sample at a constant partial pressure of 50 psi. The velocity of fluid was maintained at a constant speed of 1.5 m/s for 96 hours. The oxygen solubility of the system was maintained below 40 ppb using the Ar gas purging in the system. In the beginning of the test, the actual temperature of the machine was set as 30°C, 60°C, 90°C and 120°C separately and respectively and then created the actual partial pressure of carbon dioxide by releasing the carbon dioxide gas inside the autoclave. The exposed samples were taken out from the system washed in distilled water, rinsed in acetone and then dried in air. After cleaning, the coupon weighed again and finally the corrosion rates of the samples were measured in mills per year using the formula;

Corrosion rate (mpy) = Weight loss (g) X Constant (K)/Metal density (gm/cm^3) X Metal Area (A) X Exposure time (hrs.)

Where K is 5.34 x 10^5. Also, the exposed samples were characterized by using different techniques such as environmental scanning electron microscope (ESEM) and X-ray diffraction (XRD)

Table 1: Chemical composition of the as received materials (in wt %)

Elements	Sample 1 (L-80) (Wt %)	Sample 2 (API X-52) (Wt %)	Sample 3 (API X-56) (Wt %)	Sample 4 (API X-60) (Wt %)
C	0.19	0.17	0.14	0.12
Mn	1.22	1.23	1.27	1.25
Si	0.36	0.37	0.035	0.037
S	0.003	0.003	0.0031	0.003
P	0.004	0.004	0.0039	0.0038
Cr	0.07	0.080	0.010	0.015
Mo	-	0.0001	0.00025	0.00034
Cu	0.16	0.09	0.22	0.23

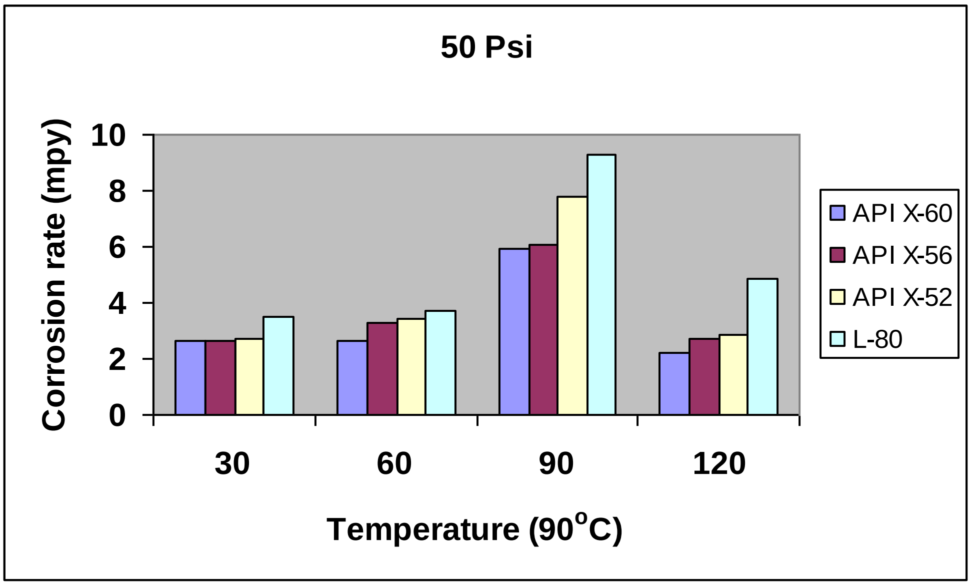

Fig. 1: Corrosion rate patterns of exposed samples in CO_2 environment

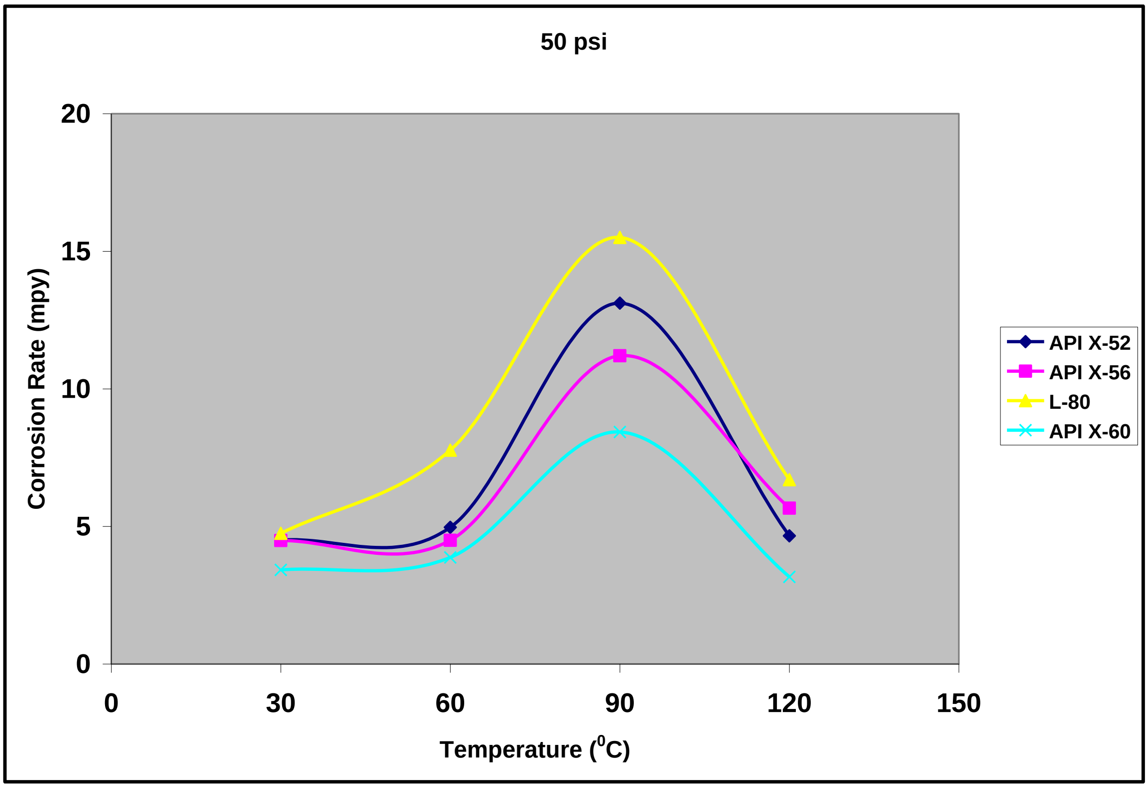

Fig. 2: Weight loss graph patterns of exposed samples in CO_2 environment

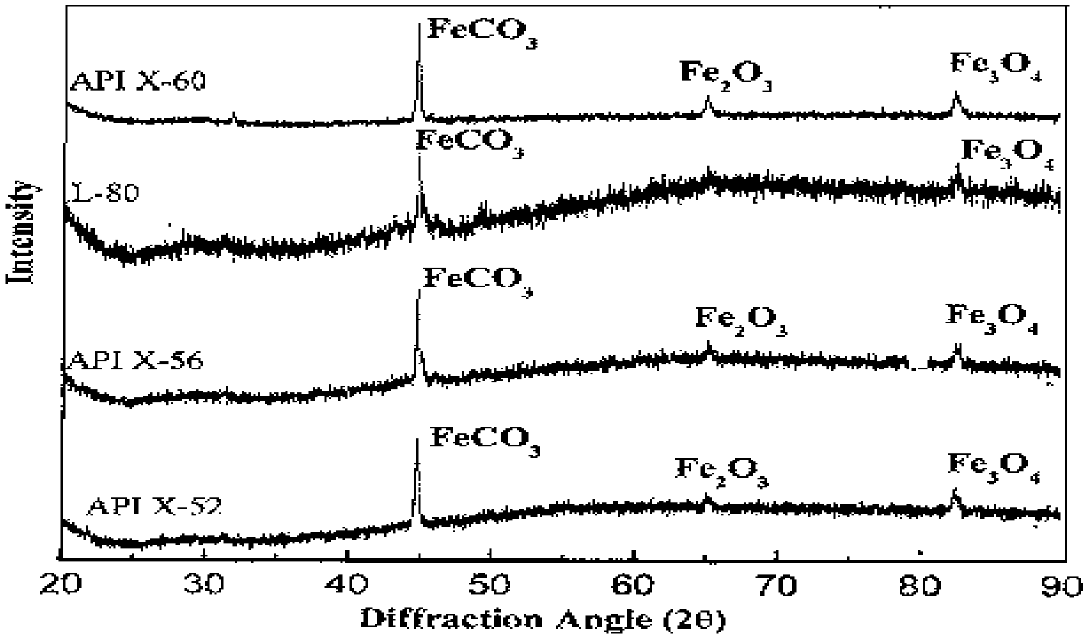

Fig. 3: XRD Patterns of all the four exposed samples exposed at 90ºC and in CO_2 environment

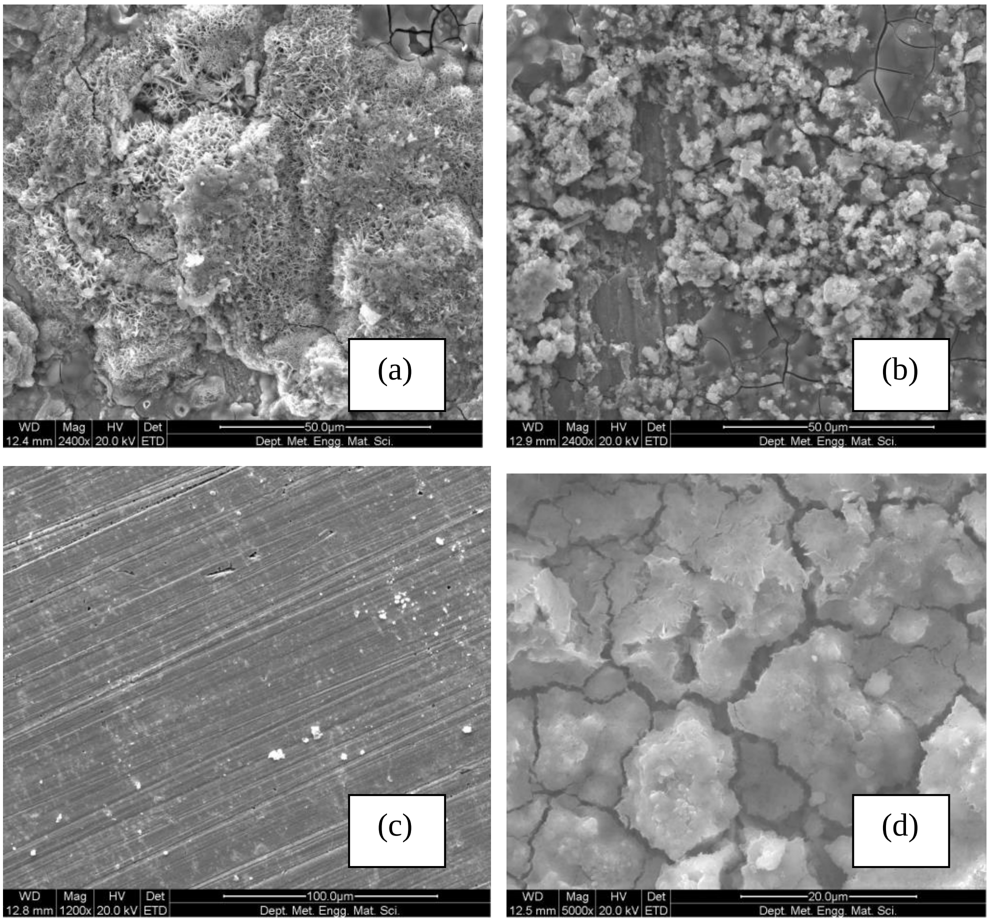

Fig. 4: ESEM micrographs of exposed samples (a) API X-52 (b) API X-56 (c) API X-60 and (d) L-80 at 90ºC and in 50 psi CO_2

IV. RESULTS AND DISCUSSION

The corrosion rate patterns of exposed samples in CO_2 environment are shown in Fig. 1. The results indicated that all the steel exhibit corrosion in mildly acidic condition, however, the severity of corrosion is different in different compositional steel. All exposed samples shown higher corrosion rate at the 90^{o}C due to formation of porous layer of siderite and their spallation from the metal surface. Also, the results indicated that the corrosion rate decreases at higher temperature near about 100-120^{o}C due to formation of adherent and dense layer of protective iron carbonate films that protect the metal from further reaction of corrosion. The formations of iron carbonate scales on the metal surface were confirmed by using X-ray diffraction analysis and are shown in Fig.3. The other phases observed are Fe_3O_4, Fe_2O_3 and Fe_3C respectively are also indicated in Fig. 3. The micrographs of corroded samples were captured in environmental scanning electron microscope and presented in Fig.4.

V. CONCLUSIONS

The corrosion rate patterns of all the steels increases with increasing temperature upto 90^{o}C due to formation of porous layer on the surface of the metal. The weight loss data as a function of temperature at a constant partial pressure of carbon dioxide are shown in Fig. 2. Beyond this temperature the corrosion rate again fall down due to formation of dense and adhered layer of siderite with magnetite films on the metal surface which acts as protective in nature. At aggressive temperature the layer formed on the surface dissolving continuously and the reaction rate becomes faster and shown higher corrosion rate while at higher temperature the iron carbonate films formed are very dense in nature and compact on the surface results in slower corrosion rate.

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