Effect of Oxygen on CO₂ Corrosion of Mild Steel

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ABSTRACT

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In oil and gas production, O_2 contamination can occur in pipeline systems. Trace amounts of aqueous O_2 can cause a significant increase in corrosion rates normally due to dissolved CO_2 . To understand this effect, measurements were conducted under aqueous CO_2 saturated conditions with contaminant being O_2 , with concentrations ranging from 10 ppb to 3 ppm. The role of oxygen (O_2) in CO_2 corrosion was investigated using linear polarization resistance (LPR), potentiodynamic sweeps, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and infinite focus microscopy (IFM) techniques. It has been shown that galvanic corrosion will occur between mild steel exposed to pure CO_2 and mild steel exposed to a mixture of CO_2 and O_2 . It was also found that this galvanic corrosion which is initially very high slowly decreased over time.

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CHAPTER 1: INTRODUCTION

In the oil and gas industry, carbon dioxide corrosion is a major problem associated with mild steel pipelines and associated equipment. Although many corrosion-resistant materials have been developed, mild steel is still the most extensively used construction material for pipelines due to its economical advantages. The cost of stainless steel is usually 5 to 7 times more than traditional mild steel, since the nickel used in stainless steel is of limited availability. These factors restrict the wide use of stainless steel to combat CO_2 corrosion.

Oil and gas do not come out of the ground pure; there are always various byproducts. Typically they are: water, carbon dioxide (CO₂), various salts (Na⁺ K⁺ Ca²⁺ SO₄⁻ Cl⁻, etc), organic acid and in some cases hydrogen sulfide (H₂S). Oxygen (O₂) is not present in produced fluids, but it can be introduced into the oil and gas flow in various ways: during processing operations, with fluids that are added (inhibitors, biocides, etc.), during temporary shutdowns of the system for maintenance, etc. The service life of the mild steel structures is greatly reduced if the CO₂ corrosion process is ignored. Every year, the premature failure of equipment causes billions of dollars of direct losses in the oil and gas industry, not to mention the indirect cost such as lost production, possible human injury, and environmental impact. It is estimated that 4% of the total GDP is lost due to the corrosion each year.

As oxygen is a very strong oxidizer, it will aggravate the usual CO₂ corrosion process. Table 1.1 shows the relevant physical and chemical properties of oxygen.

Chemical Formula	O_2
Molecular Weight	31.9988
CAS (chemical abstract number)	7782-44-7
Melting Point (1 atm.)	-182.97°C
Boiling Point	-218.4°C
Critical Temperature	-118.6°C
Critical Pressure	49.77 atm.
Density (gas) @ 0°C	1.429 g/L
Density (liquid) @ -183°C	1.14 g/L
Viscosity of Liquid @ -183°C	0.1958 cp
Solubility in 100 parts (Cold water)	$2.35^{0^{o}C}cc$
Solubility in 100 parts (Hot water)	$1.55^{20^{o}C}cc$

Table 1.1. Oxygen Physical and Chemical Properties ++

⁺⁺ Perry's Handbook¹

As it is normally assumed that oxygen is not present in oil and gas production pipelines, studies of simultaneous effect of oxygen and CO_2 on mild steel corrosion are very limited, especially compared with the extensive research done in pure aqueous CO_2 systems. Preliminary laboratory research conducted by John² has shown that under high flow conditions, a low concentration of O_2 (<20 ppb), in a CO_2 saturated water solution, can cause a significant corrosion rate increase when compared with the corrosion rate in a pure CO_2 environments without O_2 .

Galvanic corrosion is an electrochemical process in which one metal with a low potential (less noble) corrodes preferentially when in electrical contact with another metal with a higher potential (more noble). The less noble metal will corrode much faster and is called an anode, while the more noble metal that corrodes less is called a cathode. The driving force is the potential difference between the two metals. The galvanic attack will be intensified if the surface ratio between the cathode and anode is large. With regard to pipeline systems, some parts of the inner pipe surface areas may be covered by surface deposit, while the rest of the bare surface is in more or less direct contact with the fluid. It can be speculated that small amounts of oxygen are quickly depleted in these isolated environment beneath the surface deposit which in the absence of CO₂ would cause the occluded environment to become very acidic. This is a typical oxidation cell. With CO_2 present in the fluid being a very strong buffer, it will virtually prevent the acidification process. However, the corrosion potential of the metal in contact with O₂ is higher than that in the occluded area under the deposit. Thus, it is hypothesized that a potential difference is created and galvanic corrosion ensues. The severity of the galvanic corrosion is determined amongst other things by the magnitude of this potential difference. However, while this hypothesis is clearly possible, it is not clear how severe the galvanic corrosion could be in a pipeline systems under given conditions. This makes it an interesting topic to investigate. Before describing the experimental program devised to investigate this phenomenon, a brief literature review covering the past few decades will help explain CO₂ corrosion and possible effects of oxygen.

CHAPTER 2: LITERATURE REVIEW

2.1 CO₂ Corrosion Mechanism

CO₂ corrosion, which is also called "sweet corrosion" in the industry, is by far the most common scenario associated with the internal pipeline corrosion in the oil and gas industry. The mechanism of CO₂ corrosion has been intensively studied over the past few decades, especially with reference to pipeline failures in oil and gas industry. The researchers have already identified the key influencing factors like CO₂ partial pressure, pH, flow, inhibitors, and surface deposits/films.

The most significant advances in research of CO_2 corrosion of mild steel have been made by de Waard et al³⁻⁶ in the 70's and 80's, by Dugstad et al⁷⁻⁸ and Grey et al¹² in the 90's, and Nesic's group over the past 10-15 years⁹⁻¹¹. Based on their collective arguments, CO_2 corrosion of mild steel is an electrochemical process which involves the anodic dissolution of iron and cathodic evolution of hydrogen.

The overall reaction is an electrochemical reaction and it can be described as follows:

$$\operatorname{Fe}(s) + \operatorname{CO}_{2}(g) + \operatorname{H}_{2}O(l) \to \operatorname{FeCO}_{3}(s) + \operatorname{H}_{2}(g)$$
(1)

The overall reaction can be separated into anodic and cathodic half reactions, with both reactions happening simultaneously at the metal surface. Anodic reaction, iron dissolution being:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-1}$$
⁽²⁾

The cathodic reduction involves two reactions depending on the pH. At a pH lower than 4, the proton reduction is the dominant cathodic reaction, while at a pH higher than 4, the dominant reaction is the reduction of carbonic acid.

Proton reduction:

$$2\mathrm{H}^{+}(\mathrm{aq}) + 2\mathrm{e}^{-} \to \mathrm{H}_{2}(\mathrm{g}) \tag{3}$$

Carbonic acid reduction:

$$2H_2CO_3(aq) + 2e^- \rightarrow H_2(g) + 2HCO_3^-(aq)$$
⁽⁴⁾

In the CO₂ saturated system, six homogenous chemical equilibria are possible. Gaseous carbon dioxide dissolves in water:

$$\operatorname{CO}_2(\mathbf{g}) \longleftrightarrow \operatorname{CO}_2(\mathbf{aq})$$
 (5)

Dissolved carbon dioxide CO_{2 (aq)} will hydrate to form carbonic acid:

$$\operatorname{CO}_{2}(\operatorname{aq}) + \operatorname{H}_{2}\operatorname{O}(l) \xleftarrow{\operatorname{Khyd}} \operatorname{H}_{2}\operatorname{CO}_{3}(\operatorname{aq})$$
 (6)

The carbonic acid H_2CO_3 (aq) will dissociate and give off a proton and a bicarbonate ion:

$$H_{2}CO_{3}(aq) \xleftarrow{kca} H^{+}(aq) + HCO_{3}^{-}(aq)$$
(7)

The bicarbonate ion will also dissociate to release another proton and a carbonate ion:

$$HCO_{3}^{-}(aq) \xleftarrow{Kbi} H^{+}(aq) + CO_{3}^{2-}(aq)$$
(8)

The water also dissociates to give off a proton and a hydroxide ion:

$$H_2O(l) \longleftrightarrow^{K_W} H^+(aq) + OH^-(aq)$$
(9)

Based on the reactions and equilibrium equations provided above, water chemistry can be calculated as a function of temperature, the partial pressure of CO_2 and pH.

2.2 Some CO₂ Corrosion Factors

2.2.1 Temperature Effect

Temperature has two conflicting effects in the corrosion of steel. On one hand, an increasing temperature will accelerate the kinetics of CO_2 corrosion as well as speeding up the mass transfer process. On the other hand, increased temperature facilitates the FeCO₃ film forming process under film forming conditions as the solubility (K_{sp}) of FeCO₃ decreases with an increased temperature¹³.

$$\log[K_{sp}] = -59.3498 - 0.041377 \times T - \frac{2.1963}{T} + 24.5724 \times \log(T) + 2.518 \times I^{0.5} - 0.657 \times I$$

The new effect can result in the formation of a protective iron carbonate scale that reduces the rate of CO₂ corrosion. Under the film forming conditions, between 30°C and 70°C, corrosion increases with the temperature as there is little FeCO₃ filmed formed. There is a critical point between 70°C and 80°C at which the corrosion rate reaches a maximum. The corrosion rate decreases between the temperature 80°C and 90°C. This is commonly cited as a critical temperature range by previous researchers. This FeCO₃ film could be affected by flow rate, bulk solution chemistry and temperature^{7, 10}.

2.2.2 pH Effect

The pH represents the hydrogen ion concentration in a given solution. Changing pH has a very strong effect both on the localized corrosion and general corrosion. As mentioned above, at a pH lower than 4, the hydrogen ion reduction is the dominant

cathodic reaction, while at a pH higher than 4, the dominant reaction is the reduction of carbonic acid. Generally speaking, an increase in pH will decrease the corrosion rate under non-film-forming conditions¹². At film forming conditions, decreasing the pH would cause the dissolution of the FeCO₃ film formation¹⁰. It is considered to be non-film-forming conditions below the pH value of 5. Above the pH of 6, it is relatively easy for FeCO₃ film to grow on the metal surface after reaching FeCO₃ supersaturation. The high pH level may also facilitate the passivation process, causing a sharp decline in corrosion rate.

2.2.3 Flow Effect

Under surface film forming conditions, there are two direct flow effects on the corrosion process. First, high flow rates may prevent the FeCO₃ film from growing on the metal surface. It can also damage or remove the existing film at some extremely high velocities¹⁰. High flow is also associated with high mass transfer rate which can help to accelerate the CO₂ corrosion process due to increased mass transfer. On the other hand, if the transport of the corrosive species is not fast enough to support the electrochemical reactions at the steel surface, then the corrosion rate is under mass transfer control.

2.2.4 Oxygen Effect

There is little published research regarding effects of O_2 in CO_2 corrosion; some typical papers looking at O_2 effect are listed below¹⁶⁻²⁹. The first oxygen reduction model, which was derived from a study of the kinetics of oxygen reduction on a rotating disk,

was introduced by Zecevic et al¹⁶⁻¹⁷. The O_2 reduction on iron in a borate and bicarbonate buffered solution at pH 9.8 occurs on the oxidized as well as on the oxide-free surface, which would depend on the corrosion potential. On the oxidized surface, O_2 reduction proceeds via a series of complicated mechanisms. The processes are much faster at less oxidized surfaces than at more oxidized surfaces. This suggests that oxidation film provides some protection against corrosion.

The presence of natural gas and CO_2 was combined with oxygen in a corrosion study by Durr¹⁸. It was found that with the presence of oxygen in natural gas, the highest corrosion rate was measured at the vapor/liquid interface, followed by the liquid- and then the gas phase. This suggests that a high corrosion rate would need a sufficient supply of O_2 and the electrolyte to be sustained. The corrosion rate stabilized after the first week of tests. This is due to the corrosion product formation process within the first week. The corrosion rates reached a maximum when the O_2 concentration was at 100 ppm in gas phase.

Rogne¹⁹ concluded that oxygen would increase the bare metal potential by 150-175 mV vs. the SCE when there was only a 50 ppb O_2 in the liquid phase. This corrosion potential increase with the O_2 addition formed a foundation for the research on galvanic corrosion between the CO₂ saturated and O_2/CO_2 saturated systems presented in this thesis.

There are other studies investigating the oxygen contamination on the inhibition of CO_2 corrosion²² as well as on the corrosion consequences of oxygen entry into oilfield

brines²³. These investigations do not relate directly to the present research, but indicated the importance of O_2 contamination from a practical point of view.

As O_2 is a very strong oxidizer; when present in a CO_2 system, the following reactions will happen in addition to CO_2 related reactions listed above.

The key cathodic reaction is the reduction of oxygen:

$$O_2 + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$$
⁽⁹⁾

The electrons needed for the above reaction are provided by the oxidation of iron:

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-1}$$
(10)

The following reactions also occur in the presence of oxygen and are crucial to the formation of rust:

$$4Fe^{2+} + 4H^{+} + O_{2} \rightarrow 4Fe^{3+} + 2H_{2}O$$
 (11)

$$Fe^{2+} + 2H_2O \rightarrow Fe(OH)_2 + 2H^+$$
(12)

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$$
(13)

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$$2Fe(OH)_2 \Leftrightarrow 2FeO + 2H_2O$$
 (14)

$$Fe(OH)_3 \Leftrightarrow FeO(OH) + H_2O$$
 (15)

$$2\text{FeO(OH)} \Leftrightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O}$$
(16)

Besides the few parameters mentioned above which are essential for this work, there are many other parameters associated with mild steel. The following graph is a general summary of all the key parameters in CO_2 corrosion; however their detailed analysis exceeds the scope of this thesis.



Figure 2.1 Important parameters in CO₂ Corrosion³¹

CHAPTER 3: RESEARCH OBJECTIVES AND TEST MATRIX

3.1 Research Objectives

This work is targeted at understanding the effect of oxygen on CO₂ corrosion of mild steel under various test conditions. Two specific goals were targeted:

1. The general effect of oxygen contamination on CO₂ dominated corrosion of mild steel.

2. Galvanic effects between a CO₂ saturated system and a mixed O₂/CO₂ saturated system.

3.2 Test Matrix

To determine the general effects of O_2 on mild steel corrosion in a CO_2 saturated environment and the galvanic effect between the CO_2 purged O_2/CO_2 purged systems, the following series of tests were planned and conducted under non-FeCO₃-film-forming conditions at pH 5.0. The test matrices were designed to address the research objectives listed above. It is necessary to point out that not all the combinations of the parameters were tested, only what were considered the essential experiments were conducted in a way that a reference (baseline) test was conducted first and then one parameter at a time was varied.

Parameter	Condition
Temperature	25°C
Electrolyte	1 wt% NaCl
рН	5.0 adjusted by NaHCO ₃ and HCl
Steel Coupon Surface Area	5.4 cm^2
Coupon Specification	X-65 Mild steel
Test Time	5 hours, 1 day, 3 days, 5 days
Rotation Speed	100 rpm, 1000 rpm, 6000 rpm
Purging Gas	CO ₂ , N ₂ , or O ₂
Oxygen Concentration	10 ppb, 40 ppb, 100 ppb, 1 ppm, 2 ppm, 3 ppm

 Table 3.1
 Single Cell Test Matrix

Table 3.2 Galvanic Corrosion Test Matrix

Parameter	Condition
Temperature	25°C
Electrolyte	1 wt% NaCl
pH	5.0 adjusted by NaHCO ₃ and HCl
Steel Coupon Surface Area	0.016 cm^2 for anode 16 cm^2 for cathode
Coupon Specification	1008 Mild steel
Test Time	6 days
Purging Gas	$CO_{2,} N_{2,}$ or O_{2}
Oxygen Concentration	3 ppm

Al	As	В	С	Ca	Со	Cr	Cu	Mn	Мо	Nb
0.0032	0.005	0.0003	0.05	0.004	0.006	0.042	0.019	1.32	0.031	0.046
Ni	Р	Pb	S	Sb	Si	Sn	Та	Ti	V	Zr
0.039	0.013	0.02	0.002	0.011	0.31	0.001	0.007	0.002	0.055	0.003

 Table 3.3 Chemical Composition of X-65 Mild Steel (wt%, balance being Fe)

CHAPTER 4: EXPERIMENTAL SETUP AND PROCEDURE

All the experiments were carried out in the glass cell system³². A schematic representation of a typical glass cell is shown in Figure 4.1. A saturated Ag/AgCl reference electrode was connected with the glass cell via a Luggin capillary. A platinum ring was used as a counter electrode. The glass cell was filled with two liters of 1 wt% NaCl in de-ionized water. The salt solution was purged with CO₂ (in some cases premixed with O₂ and N₂). The total pressure of the system was 1 bar. The N₂ was added to adjust the partial pressure of CO₂ to 0.5 bar. After the system had been purged with the mixed gas and reached equilibrium, the pH of the solution was adjusted to 5.0 by using deoxygenated sodium bicarbonate solution. Before the mild steel specimen was immersed into the test solution, it was polished with 240, 400, and 600 grit silicon carbide sand paper, rinsed with isopropyl alcohol, and ultrasonically cleaned in isopropyl alcohol.

As the aqueous oxygen concentration increased from ppb level to ppm level in various experiments, and the total pressure was maintained at 1 bar, the partial pressure of CO_2 would have to be reduced. In order to make the results easier to compare, the partial pressure of CO_2 was fixed at 0.5 bar. This was achieved by using a mixing gas rotameter and by adding N₂. The CO_2 partial pressure was checked by using a colorometric sampling kit from CHEMetrics. The O₂ concentration was read directly from the O₂ meter.

To study the general O_2 effect in CO_2 system, an X-65 mild steel cylindrical coupon was used as shown Figure 4.3. The glass cell setup is shown in Figure 4.1 and Figure 4.2. Linear polarization measurements were performed using a scan rate of 0.125mV/s from -5 mV to +5 mV with respect to the corrosion potential. Potentiodynamic scans were performed at a scan rate of 0.125 mV/s, from -0.7 V to +0.2 V with respect to the measured corrosion potential. The oxygen concentration was measured directly with a high accuracy oxygen meter. The model was Orbisphere 410 with a sensor range from 0.5 ppb to 20 ppm. The measurements were occasionally checked by using the CHEMetrics kit.

To study the galvanic corrosion in an O_2/CO_2 system, a modified artificial pit³² was used as shown in Figure 4.4. Figure 4.5 and Figure 4.6 are the cross-section and bottom view of the artificial pit. The test solution within the artificial pit was purged with CO_2 only while the test solution outside the artificial pit was purged with O_2/CO_2 . The small working electrode was immersed in the CO_2 purged environment which made it to be an anode while the large working electrode in contact with O_2/CO_2 purged solution became a cathode. The two environments were separated by a porous glass plug to prevent O_2 leakage. This setup is shown in Figure 4.7. The anode and cathode were externally connected via a zero resistance ammeter (ZRA) to measure the galvanic current. Occasionally, the ZRA was temporally disconnected to make LPR and EIS measurements.



 Ag/AgCl reference electrode; 2- gas rotameter; 3- platinum counter electrode;
 4- luggin capillary; 5- X-65 carbon steel working electrode; 6-shaft; 7- pH probe; 8- bubbler; 9- hot plate.

Figure 4.1. Schematic of the glass cell setup (Design one)

(courtesy of Daniel Mosser)



Figure 4.2. Schematic of the glass cell setup (With rotameter,

oxygen meter and gear pump)



Figure 4.3. X-65 carbon steel coupon configuration



Figure 4.4. Artificial pit

(courtesy of Jiabin Han)





Figure 4.6. Artificial pit bottom view (courtesy of Jiabin Han)



1- Ag/AgCl reference electrode; 2- thermo couple; 3- artificial pit; 4- luggin capillary; 5- C-1008 carbon steel working electrode (anode); 6- pH probe; 7- bubbler; 8- hot plate.

Figure 4.7. Schematic of the glass cell setup (Design two, with artificial pit)

(courtesy of Jiabin Han)

CHAPTER 5: RESULTS AND DISCUSSION

Experiments were carried out at a constant pH of 5.0 in the presence of CO_2 and O_2 . The value of pH was selected at 5.0 to distinguish the effect of the O_2 reduction from the effect of H⁺ reduction on the cathodic reaction as well as to maintain a non- FeCO₃-film-forming environment. The oxygen concentrations were increased gradually up to 3 ppm to allow observation of the oxygen effect. The rotation speed varied from 100 to 1000 and 6000 rpm in order to observe the interfering flow effect.

5.1 Baseline Test Results

Baseline tests were conducted in the absence of oxygen at pH 5.0 to determine the corrosion mechanism. These sets of tests would serve as a means of comparison for tests with O₂ presented subsequently.

Linear polarization resistance and potentiodynamic sweeps measurements at electrode rotation speeds of 100 and 1000 rpm (pH 5.0, 0.5 bar CO_2 , 25°C) were performed. The LPR was monitored every 20 minutes for 5 hours and potentiodynamic sweeps were performed at the end of the experiment.

The corrosion potential and corrosion rate vs. time measurement are shown in Figure 5.1 and 5.2 respectively. Under non scaling conditions, the corrosion potential and corrosion rate were relatively stable and consistent. There was no significant change with rotation speed between 100 and 1000 rpm; the average potential change was only about 5 mV. As seen in Figure 5.2, by increasing the rotation speed from 100 rpm to 1000 rpm, there was no significant increase in the corrosion rate. This suggested that the corrosion



was not under mass transfer control when there was no O2 in the aqueous environment.

Figure 5.1. Average corrosion potential variation with time in tests without adding O_{2.} (pH 5.0, 25 °C, 100 rpm, 1000 rpm and non FeCO₃ film forming conditions)



Figure 5.2. Average corrosion rate variation with time in tests without adding O_{2.} (pH 5.0, 25 °C, 100 rpm, 1000 rpm and non FeCO₃ film forming conditions)

5.2 Flow Results

The potentiodynamic sweeps were performed in 1 wt% sodium chloride electrode at pH 5.0 purged with CO_2 and "contaminated" by O_2 . The rotation speed varied from 100 rpm to 6000 rpm. A more detailed test matrix pertaining to these experiments is shown in Table 5.1.

Parameter	Condition
Temperature	25°C
Electrolyte	1 wt% NaCl
рН	5.0 adjusted by NaHCO ₃ and HCl
Steel Coupon Surface Area	5.4 cm^2
Coupon Specification	X-65 Mild steel
Test Time	1 hour for cathodic sweep, 20 minutes for anodic sweep
Rotation Speed	100 rpm, 1000 rpm, 6000 rpm
Purging Gas	CO_2 , N_2 and O_2
Oxygen Concentration	0-3 ppm

 Table 5.1 Test Matrix for Potentiodynamic Sweeps

The results are shown in Figure 5.3 to Figure 5.5. There is a clear acceleration of the cathodic limiting current density with increased concentration of O_2 . The anodic reaction was inhibited with an increase in O_2 concentration. At 40 ppb of O_2 concentration seen in Figure 5.3, increasing the flow rate from 100 rpm to 6000 rpm caused the limiting current density increase "only" by a factor of 2. The dots in Figure 5.6 to Figure 5.8 represent the average LPR results measured. The three lines are relative

close with each other and the difference is small in Figure 5.3. This suggests that 40 ppb O_2 concentration would not significantly affect the CO_2 dominated corrosion process. However at 3 ppm of O_2 seen in Figure 5.5, an order of magnitude increase in the limiting current is seen upon increasing the flow rate from 100 rpm to 6000 rpm, suggesting that this level of O_2 has significantly affected the CO_2 corrosion process.

It is known that the corrosion potential should not change with flow rate under pure charge transfer control. Under mass transfer control, the limiting current density obtained from potentiodynamic measurement should increase with flow and equal the corrosion current from LPR measurement. The corrosion current density measured by LPR in Figure 5.6 to Figure 5.8 does not match and is much less than the limiting current density showing in the potentiodynamic sweeps. This indicates the corrosion mechanism at high O_2 concentration is under mixed charge and mass transfer current control.

As it is seen from the potentiodynamic sweeps that the limiting current density is very sensitive to the flow rate with high O_2 concentration. In order to verify if the corrosion process is under pure mass transfer control, a calculation is used to verify the corrosion mechanism. For a rotating cylinder flow system, the following relationship can be used as a means to calculate the mass transfer coefficient:

$$Sh_r = 0.079 \times \mathrm{Re}^{0.7} \times Sc^{0.356}$$

Where the Sherwood number (Sh_r) is defined as:

$$Sh_r = k_m d_n / D$$

Reynolds number (Re) is defined as:

$$\operatorname{Re} = v \rho_{H_{2}O} d / \mu_{H_{2}O}$$

Schmidt number (Sc) of a given species is defined as:

$$Sc = \mu_{H_{2}O} / (\rho_{H_{2}O}D)$$

Finally the limiting current (i_{lim}) can be calculated as:

$$i_{\lim} = nFk_mC_b$$

There is a general increase in the cathodic current indicating the reaction is partially mass transfer controlled. However, the reaction is not fully under mass transfer controlled because the increase in the cathodic limiting current is not in proportional to the $v^{0.7}$ as theory would have it (seen from Figure 5.3 to Figure 5.5).



Figure 5.3. Potentiodynamic sweeps in bubbling CO₂ solutions with 40 ppb contaminant O_{2.} (pH 5.0, 25 °C, 1 wt% NaCl, 100 rpm 1000 rpm 6000 rpm, non FeCO₃ film forming conditions)


Figure 5.4. Potentiodynamic sweeps in bubbling CO₂ solutions with 1 ppm contaminant O_{2.} (pH 5.0, 25 °C, 1 wt% NaCl, 100 rpm 1000 rpm 6000 rpm, non FeCO₃ film forming conditions)



Figure 5.5. Potentiodynamic sweeps in bubbling CO₂ solutions with 3 ppm contaminant O_{2.} (pH 5.0, 25 °C, 1 wt% NaCl, 100 rpm 1000 rpm 6000 rpm, non FeCO₃ film forming conditions)



Figure 5.6. Current density comparison in bubbling CO₂ solutions with 40 ppb contaminant O₂ using LPR measurement (pH 5.0, 25 °C, 1 wt% NaCl, 100 rpm 1000 rpm 6000 rpm, non FeCO₃ film forming conditions)



Figure 5.7. Current density comparison in bubbling CO₂ solutions with 1 ppm contaminant O₂ using LPR measurement (pH 5.0, 25 °C, 1 wt% NaCl, 100 rpm 1000 rpm 6000 rpm, non FeCO₃ film forming conditions)



Figure 5.8. Current density comparison in bubbling CO₂ solutions with 3 ppm contaminant O₂ using LPR measurement (pH 5.0, 25 °C, 1 wt% NaCl, 100 rpm 1000 rpm 6000 rpm, non-FeCO₃ film forming conditions)

Figure 5.9 shows the corrosion potential response at increased flow rates at elevated O_2 concentrations. At low oxygen concentrations (<5 ppb and 100 ppb), the flow does not seem to have a strong influence on the corrosion potential, while at relatively high oxygen concentrations (1 ppm and 3 ppm), the increase of flow significantly increases the corrosion potential. At 3 ppm of O_2 , the corrosion potential jumps approximately by 200 mV with increased rotation speed from 100 rpm to 6000 rpm.



Figure 5.9. Corrosion potential comparision by changing flow rate and O₂ concentrations. (pH 5.0, 25 °C, 1 wt% NaCl, pCO₂ =0.5 bar, non FeCO₃ film forming conditions)

5.3 Oxygen Concentration Results

This series of tests was performed in 1 wt% sodium chloride solutions at pH 5.0 purged with CO₂ and contaminated by O₂ in an aqueous concentration range from 0 to 3 ppm. Figure 5.10 to Figure 5.12 show the potentiodynamic sweeps performed at 100 rpm, 1000 rpm and 6000 rpm respectively. The figures clearly indicate that the dissolved oxygen strongly affects the limiting current. By increasing the oxygen concentration, the corrosion mechanism switches from pure charge transfer control to mixed control as both the corrosion potential and limiting current density increased. At 100 rpm rotation speed, the corrosion potential increases only by 20 mV when increasing the O₂ from 40 ppb to 3 ppm as seen in Figure 5.10. At 6000 rpm rotation speed, the corrosion potential increased more than 200 mV (Figure 5.12). At 100 rpm rotation speed, increasing the O₂ concentration from 40 ppb to 3 ppm did not cause a change in the limiting current. At 6000 rpm rotation speed, the limiting current jumped almost 6 times when increasing the O₂ concentration from 40 ppb to 3 ppm. This suggests the flow strongly affects the corrosion rate when sufficient O₂ is introduced.



Figure 5.10. Potentiodynamic sweeps in bubbling CO₂ solutions with 100 rpm rotation speed (pH 5.0, 25 °C, 1 wt% NaCl, 40 ppb, 1 ppm, 3 ppm O₂ contaminant, non FeCO₃ film forming conditions)



Figure 5.11. Potentiodynamic sweeps in bubbling CO₂ solutions with 1000 rpm rotation speed (pH 5.0, 25 °C, 1 wt% NaCl, 40 ppb, 1 ppm, 3 ppm O₂ contaminant, non FeCO₃ film forming conditions)



Figure 5.12. Potentiodynamic sweeps in bubbling CO₂ solutions with 6000 rpm rotation speed (pH 5.0, 25 °C, 1 wt% NaCl, 40 ppb, 1 ppm, 3 ppm O₂ contaminant, non FeCO₃ film forming conditions)

5.4 High Oxygen Concentration Test Results

5.4.1. 3 ppm Oxygen Concentration Effect

It can be seen in the above results that at high O_2 concentration and high flow rates, the limiting current would increase by a factor of 6-7. In the following tests, the experimental duration was extended from a few hours to at least 24 hours to monitor the corrosion potential and corrosion rate development and identify the corrosion products.

The first set of experiments was performed at 3 ppm of O_2 and 6000 rpm, in a 1day test. In the rotating cylinder electrode (RCE) assembly, the rotation speed of 6000 rpm equals 3.79 m/s and a shear stress (τ) of 32 Pa.

The corrosion potential and corrosion rate measured by LPR are shown in Figure 5.13 and Figure 5.14. The initial corrosion potential is -450 mV when the coupon was newly polished and immersed into the solution. This is around 220 mV higher compared with results under the same conditions without O₂ present. The corrosion potential slowly dropped from -450 mV to -620 mV with the formation of a red oxide layer, which was later identified as Fe₂O₃. By the end of the test period, a visible oxide layer had been well formed, covering the whole coupon surface. The corrosion potential stabilized after about 12 hours, according to Figure 5.14. The corrosion rate increased during the first few hours and then declined and reached equilibrium at around 12 hours according to Figure 5.13. This could be explained due to the formation of surface oxide film, which acts as a diffusion barrier, and the oxygen had limited access to the coupon, thus leading to the corrosion rate and the corrosion potential decreasing correspondingly. SEM photograph of the film are shown in Figure 5.15.



Figure 5.13. General corrosion rate measurement by LPR on X-65 carbon steel coupon in bubbling CO₂ solutions with 3ppm O₂, 6000 rpm rotation speed (pH 5.0, 25 °C, 1 wt% NaCl, non FeCO₃ film forming conditions)



Figure 5.14. Corrosion potential measurement on X-65 carbon steel coupon in bubbling CO₂ solutions with 3ppm O₂, 6000 rpm rotation speed (pH 5.0, 25 °C, 1 wt% NaCl, non FeCO₃ film forming conditions)

Figure 5.15 shows the morphology of the surface film after a 1 day test period with 3 ppm of O_2 . There are many features on the surface. The SEM picture reveals the oxide film loose structure and also its approximate thickness. The loose and porous oxide layer explains why the general corrosion rate still persisted at 1 mm/year even though the film has been developed over the first 12 hours the coupon surface remained unprotected.



(a)



(b)

Figure 5.15. Oxidation film on X65 carbon steel coupon. 3ppm O₂, 6000 rpm rotation speed after 24 hours (pH 5.0, 25 °C, 1 wt% NaCl, non FeCO₃ film forming conditions)

EDS analysis confirmed that the film was composed mainly of iron (Fe) and oxygen (O); there was barely any carbon (C) in Figure 5.16, which suggests that very little iron carbonate (FeCO₃) film was formed. This can be explained by the fact that the formation of iron carbonate film requires supersaturation with respect to FeCO₃ formation. As O_2 is a very strong oxidizer and continues to be purged into the solution with CO_2 , any amount of Fe²⁺ is rapidly oxidized to Fe³⁺ and forms iron oxide (Fe₂O₃). As there was always a sufficient supply of O_2 , the Fe²⁺ was not able to reach saturation values for FeCO₃ precipitation.



(b)

Figure 5.16. Analysis of surface film using EDS (CO₂ solutions with 3ppm O₂, 6000 rpm rotation speed, 1 day test, pH 5.0, 25 °C, 1 wt% NaCl, non FeCO₃ film forming conditions)

After SEM investigation and the film composition EDS analysis, the film was removed using the Clark (inhibited acid) solution to obtain a clear view of the steel surface. (See Appendix B for typical coupon cleaning procedure). SEM micrograph reveals pits present in large numbers which were also visible by naked eye. Figure 5.17 shows two well formed pits at 200 and 1000 magnification respectively. The average pit diameter was around 45 μ m with one day exposure to 3 ppm of O₂. Besides the two large pits, there are many other smaller pits scattered over the 550 μ m × 550 μ m areas.



(a)



(b)

Figure 5.17. Two pits on X65 carbon steel coupon in bubbling CO₂ solutions with 3 ppm O₂, after 1 day test. Magnification at 200 and 1000 (6000 rpm, pH 5.0, 25 °C, 1 wt% NaCl, non FeCO₃ film forming conditions)

The infinite focus microscopy (IFM) provides an efficient way of measuring the pit depth without cutting the coupon using conventional methods. The average pit depth measured following a one-day exposure in the solution under test conditions is around 50 μ m; the maximum pit depth measured was 70 μ m, which corresponds to 18.2 mm/year and 25.5 mm/year, respectively. Examples of pits depth determination are shown in Figure 5.18.



(b)

Figure 5.18. Pit depth analysis using IFM. (X-65 carbon steel, CO₂ solution with 3 ppm O₂, 6000 rpm, 1 day test period. Magnification X1000 pH 5.0, 25 °C, 1 wt% NaCl, non FeCO₃ film forming conditions)

The comparison between LPR, and average pit depth analysis is shown in Figure 5.19. The pitting corrosion is significantly larger than the general corrosion rate, resulting in a pitting factor of 18.



Figure 5.19. Comparison between the general corrosion and localized corrosion

5.4.2. 1 ppm Oxygen Concentration Effect

Figure 5.20 and Figure 5.21 depicts a comparison in the change in corrosion rate and corrosion potential respectively for 1 ppm and 3 ppm O_2 in the CO_2 saturated brine solution. At 3 ppm O_2 , the general corrosion rate increased at the first 2 hours and then declined to 1 mm/year. At 1 ppm O_2 , the general corrosion rate is much more stable and maintained at 1 mm/year. The plausible explanation is that with less O_2 , it took a much longer time for an oxide film to form on the coupon surface. The 3 ppm of O_2 addition caused a very high corrosion potential initially which then declined, while the corrosion potential with 1 ppm of O_2 was much more stable at around -620 mV. Within a 24-hour test period, the variation was only about 10 to 15 mV. This is much less than the 200 mV increases obtained with the 3 ppm O_2 addition.



Figure 5.20. Corrosion rate comparison on X-65 carbon steel coupon in bubbling CO₂ solutions with 1 ppm O₂ and 3 ppm O₂, respectively (6000 rpm rotation speed, pH 5. 0, 25 °C, 1 wt% NaCl, non FeCO₃ film forming conditions)



Figure 5.21. Corrosion Potential on X-65 carbon steel coupon in bubbling CO₂ solutions with 1 ppm O₂ and 3 ppm O₂, 6000 rpm rotation speed comparison (pH 5.0, 25 °C, 1 wt% NaCl, non FeCO₃ film forming conditions)

Figure 5.22 shows the morphology of the surface film after 24-hour test period with 1 ppm of O_2 in CO_2 saturated brine. The film formed at 1 ppm of O_2 is considerably thinner than the film formed in the presence of 3 ppm of O_2 in the flow. The steel surface was not fully covered with film and some areas of bare metal were still visible. Although there was less film present, the structure of the film did not change. It still exhibited a porous and loose morphology. After removing the specimen from the test solution, the oxide film spalled off readily during drying.



Figure 5.22. Oxidation film on X-65 carbon steel coupon in bubbling CO₂ solutions with 1 ppm O₂, 6000 rpm rotation speed (pH 5.0, 25 °C, 1 wt% NaCl, non FeCO₃ film forming conditions)

SEM pictures shown in Figure 5.23 reveal that pitting corrosion was still widespread even though the oxygen concentration had decreased from 3 ppm to 1 ppm. In the small surface area (700 μ m ×700 μ m) shown in Figure 5.23 (a), there are approximately 20 pits present. Decreasing the O₂ concentration from 3 ppm to 1 ppm does not prevent initiation of pitting corrosion. The diameter of the pits was about 8 μ m compared with the average pit diameter of 45 μ m obtained with 3 ppm of O₂.



(a)



(b)

Figure 5.23. Three pits on X65 carbon steel coupon in bubbling CO₂ solutions with 1 ppm O₂, 6000 rpm rotation speed X200 (pH 5.0, 25 °C, 1 wt% NaCl, non-FeCO₃ film forming conditions)

The general corrosion and localized corrosion rates for 1 ppm and 3 ppm O_2 tests are shown in Figure 5.24. The average pit depth measured using IFM for 1 ppm of O_2 addition is 20 µm after the one-day test period, which equates to 7.3 mm/year. The pitting factor is approximately 7, i.e. the pitting corrosion rate is still 7 times larger than the general corrosion rate. The general corrosion rate for 1 ppm and 3 ppm of O_2 addition are relatively close.



Figure 5.24. Comparison between the general corrosion and localized corrosion at 1 ppm and 3 ppm of O₂ contaminant in CO₂ flow

In summary, after 24 hours of exposure in a system with either 1 ppm or 3 ppm of O_2 in the aqueous phase, pitting corrosion was identified. The oxide films formed were loose, porous and unprotective. After the film had been removed, the SEM tests revealed that pitting was developed and evenly distributed across the metal surface. The IFM show the average pit depth for 1 ppm and 3 ppm of O_2 addition was about 20 µm and 50 µm respectively, which corresponds 7mm/year and 18 mm/year. A protective iron carbonate

film (FeCO₃) could not form under these test conditions. The presence of oxygen and formation of the very insoluble Fe_2O_3 prevented the formation of a protective iron carbonate film.

5.5 Test Time Results

As described above, at 1 ppm or 3 ppm of O_2 in the aqueous phase, pitting corrosion/initiation could be identified within 24 hours. As pitting initiation does not necessarily lead to pitting propagation, a longer test period was necessary. Therefore 3-day and 5-day test periods were introduced and results are shown in Figure 5.25.

Figure 5.25 shows a comparison of the general corrosion rate obtained at 1 ppm and 3 ppm O_2 tests for 1-day, 3-day and 5-day exposures. The tests at 3 ppm O_2 showed that the general corrosion rates in all cases reached a steady state after about 20 hours. Before reaching the steady state, it increased for the first few hours and then declined. The steady state general corrosion rates at 1 ppm of O_2 and 3 ppm of O_2 are not significantly different despite the O_2 concentration being 3 times larger. In all cases, a red oxide film formed, and the general corrosion rate dropped from the maximum of 3 mm/year to 1 mm/year.



Figure 5.25. Corrosion rate variation with time and O₂ concentration (6000 rpm pH 5.0, 25 °C, 1 wt% NaCl, non FeCO₃ film forming conditions)



Figure 5.26. Average corrosion potential variation with time and O₂ concentration (6000 rpm pH 5.0, 25 °C, 1 wt% NaCl, and non FeCO₃ film forming conditions)

A red oxidation layer formed on the steel surface, shown in Figure 5.27, was not dense and provided little corrosion protection.



Figure 5.27. Stress Cracking on X-65 carbon steel coupon in bubbling CO₂ solutions with 3 ppm O₂, 3 days, 6000 rpm rotation speed X200 (pH 5.0, 25 °C, 1 wt% NaCl, non FeCO₃ film forming conditions)

According to the EDS analysis, most of the film was composed of Fe and O, and there was a trace amount of C and Cl. The C is most likely introduced from the parent mild steel. The Cl is from NaCl, which was remained on the surface after drying. The area between the crack lines seen in Figure 5.27 is the bare metal.



(b)

Figure 5.28. Composition analysis on X-65 carbon steel coupon in bubbling CO₂ solutions with 3 ppm O₂, 3 days 6000 rpm rotation speed X200 (pH 5.0, 25 °C, 1 wt% NaCl, non FeCO₃ film forming conditions)

Figure 5.29 shows the SEM results from the 3 day test at 3 ppm O_2 . According to this picture, the whole surface area is indicating a general corrosion scenario, although some pitting is still visible. The pitting corrosion does not seem to propagate after the initial 24 hours.



Figure 5.29. X-65 mild steel coupon surface exposed in saturated CO₂ solutions with 3 ppm O₂, 3 days 6000 rpm rotation speed X100 (pH 5.0, 25 °C, 1 wt% NaCl, non FeCO₃ film forming conditions)

Figure 5.30 shows the SEM image following film removal in the 5 day test at 3 ppm of O_2 . The same conclusion can be drawn as before: the corrosion mechanism has switched from pitting corrosion to general corrosion after the initial 24 hours of heavy pitting corrosion.



Figure 5.30. Stress Cracking on X-65 carbon steel coupon in bubbling CO₂ solutions with 3 ppm O₂, 5 days 6000 rpm rotation speed X100 (pH 5.0, 25 °C, 1 wt% NaCl, non FeCO₃ film forming conditions)

The IFM surface analysis of the specimen from the 5 day test at 3 ppm O_2 shows the roughness of the bare metal surface in Figure 5.31. There are no pits visible. Depth analysis shown in Figure 5.32 indicates there has been no sharp decline in depth, which also suggests that initial pitting corrosion has been replaced by general corrosion.



(a)



(b)

Figure 5.31. The IFM surface sweep analysis at 3 ppm O₂, 5 days (pH 5.0, 25 °C, 1 wt% NaCl, non FeCO₃ film forming conditions)



Figure 5.32. Depth analysis by IFM at 3 ppm O₂, 5 days (pH 5.0, 25 °C, 1 wt% NaCl, non FeCO₃ film forming conditions)

In summary, even if in short periods of time (24h) the presence of oxygen caused severe localized corrosion (pitting) initiation, this did not continue, i.e. no pitting propagation was detected and only general corrosion could be seen.

5.6 Galvanic Corrosion Results

Galvanic corrosion is an electrochemical process in which two metal surfaces are immersed in an electrolyte. One metal surface (called an "anode") corrodes faster when in electrical contact with another metal surface (called a "cathode"). The two metal surfaces can be but do not necessarily need to be two different kinds of metals. If the surrounding environment is different, this can also cause galvanic corrosion even if the same metal is exposed. The driving force which causes this type of corrosion is the different corrosion potentials between the two metal surfaces. Appendix A describes a typical galvanic corrosion scenario caused by a differential oxidation cell. In the tests presented here, adding O_2 into a CO_2 saturated solution caused the increase in potential and established a galvanic cell.

In the oil and gas pipelines, some surface deposits/films would cause O_2 to be quickly depleted beneath them potentially creating a galvanic cell. In order to mimic the real-life situation, an artificial pit was designed to accommodate the aerobic and anaerobic conditions seen underneath a deposit/film, as described above. The artificial pit was placed inside a glass cell. Within the artificial pit the solution was purged only with CO_2 , simulating the environment underneath a deposit, while the brine solution in the glass cell was purged with a mixture of CO_2 and O_2 simulating a bare steel surface around the deposit. The two systems in the experiments were separated by a porous glass plug simulating the porous deposit. As the addition of O_2 into the CO_2 -purged system would cause the increase of the potential (described above), the potential difference between the aerobic and anaerobic systems would cause electrical current flow from the anode to the cathode. The electron flow would cause the anode to corrode preferably, while the cathode would be protected. In the experiments the anode and cathode were externally connected using the ZRA to measure the galvanic current.

In order to expedite the galvanic effect, the O_2 concentration in the mixture was maintained at 3 ppm level. The surface area ratio between the anode and cathode was 1:1000 to mimic the real large cathode and small anode scenario that can be expected in a real life situation. The galvanic current was monitored continuously for 6 days. The uncoupled corrosion potential and corrosion rate for both the anode and the cathode were measured by temporarily disconnecting the ZRA. EIS was measured to compensate for the solution resistance effect. The galvanic current was later converted to corrosion rate to better identify the corrosion implications.

As can be seen from Figure 5.33, the uncoupled corrosion potential for the cathode decreased from initially -607 mV to -660 mV within the first day and then stabilized for the rest of the testing period. The corrosion potential for the anode was more stable than the cathode, and the total increase of the potential was 30 mV after the end of the 6-day test. The anode potential increase could be explained due to the formation of an oxide layer on the coupon surface. The initial potential difference between the cathode and anode was almost 90 mV after the first day of exposure due to the ferric oxide film which was formed within the first day of exposure. Due to the initially high potential difference, the peak galvanic corrosion rate was around 45 mm/year shown in Figure 5.34. As the driving force is the potential difference, the decrease in potential difference caused the average galvanic corrosion rate to decrease to

about 4-5 mm/year after reaching a steady state. This was still significant as this rate was still 3-4 times higher than the uncoupled cathode or anode corrosion rate. From Figure 5.33 and Figure 5.34, it is estimated that 20 mV of potential difference would cause 4-5 mm/year galvanic corrosion under test conditions. Had there been a flow effect for the cathode part, the galvanic current would be expected to be even higher than the current measured in the present experiment because of the mass transfer effect.



Figure 5.33. Uncoupled cathode and anode corrosion potential comparison. (Measured respectively by temporarily disconnecting the anode and cathode)



Figure 5.34. Galvanic corrosion rate and galvanic corrosion potential variation with time. (O₂ 3 ppm for cathode, pH 5.0, 25 °C, 1 wt% NaCl)

Since only a fraction of the galvanic current contributes to the increase in the corrosion rate of the anode, the coupled corrosion rate for both anode and cathode were calculated as following:

Anode:

Coupled CR= Uncoupled CR + 3/4 Galvanic CR

Cathode:

Coupled CR= Uncoupled CR - 1/4 Galvanic CR

In Figure 5.35, the total coupled corrosion rates are significantly higher than the uncoupled corrosion rates for anode. For cathode, they are not distinguishable in Figure

5.36. This could be explained that due to the large cathode and small anode scenario (1000:1), where the galvanic effect for cathode is minimized.



Figure 5.35. Uncoupled and coupled corrosion rate comparison for anode (O₂ 3 ppm for cathode, pH 5.0, 25 °C, 1 wt% NaCl)



Figure 5.36. Uncoupled and coupled corrosion rate comparison for cathode (O₂ 3 ppm for cathode, pH 5.0, 25 °C, 1 wt% NaCl)

As observed in Figure 5.33, the uncoupled anode corrosion potential increased by 30 mV within 6 days test period. This could be explained by the surface deposit which formed on the anode as shown in Figure 5.37 and Figure 5.38. For cathode, the composition of the deposit is shown in Figure 5.41, being primarily Fe and O. During the film forming process, the potential for the cathode increased due to limited O_2 access. For anode, an oxide was formed on the surface. The decrease of the potential difference between anode and cathode caused the decrease of the total corrosion rate.


Figure 5.37. Anode surface film morphology (pH 5.0, 25 °C, 1 wt% NaCl)



Figure 5.38. Anode surface film composition (pH 5.0, 25 °C, 1 wt% NaCl)



Figure 5.39. Cathode surface film morphology (3 ppm O₂, pH 5.0, 25 °C, 1 wt% NaCl)



Figure 5.40. Cathode surface film composition (3 ppm O₂, pH 5.0, 25 °C, 1 wt% NaCl)

Figure 5.41 and Figure 5.42 correspond to the steel surface morphology of the anode and cathode after film removal. There are some shallow pits formed. However, the pitting corrosion rates were significantly smaller than the coupled corrosion rate and the calculated pitting factor for the anode and cathode were 0.4 and 0.6 respectively. Therefore, no pitting corrosion was found on anode or cathode. Based on the surface roughness, the steel surfaces of both anode and cathode were heavily corroded due to the O_2 attack and the galvanic effect.



Figure 5.41. Bare metal surface morphology for anode (O₂ 3 ppm for cathode, pH 5.0, 25 °C, 1 wt% NaCl)



Figure 5.42. Bare metal surface morphology for cathode (O₂ 3 ppm for cathode, pH 5.0, 25 °C, 1 wt% NaCl)

CHAPTER 6: CONCLUSIONS

The oxygen effect on CO_2 corrosion of mild steel has been studied in a glass cell system by using a rotating cylinder and an artificial pit test setup. The oxygen concentration varied from 0 ppb to 3 ppm. Based on the results, the following conclusions can be made:

- 1. At 1 bar CO₂ and low oxygen concentrations (below 100 ppb), the dominant corrosion mechanism is still CO₂ corrosion which is under charge transfer. At high oxygen concentrations (higher than 1 ppm), the corrosion mechanism is affected by the presence of oxygen and is under mixed charge and mass transfer control.
- With 3 ppm of O₂ in the CO₂ saturated aqueous system, pitting initiation was seen within a 24-hour test period. However pitting did not propagate and the dominant corrosion scenario was general corrosion.
- 3. The film formed on the steel surface in the presence of oxygen was mainly a ferric oxide. Its thickness depended on the dissolved O₂ concentration. Due to its porous nature, it provides very little corrosion protection. In the experiments conducted in this work, there was no iron carbonate film that formed as the pH was maintained at pH 5.0 which is below the supersaturation level for iron carbonate.
- 4. When a differential oxidation cell was established, galvanic corrosion was detected, and the coupled corrosion rate for the anode was severe.

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APPENDIX A: GALVANIC CORROSION SCENARIO

The galvanic corrosion happened at the inner pipeline surface could cause severe corrosion if not take well care of. There are a few steps associated with galvanic corrosion in pipelines. They are introduced as follows:

At time zero, there is no oxygen concentration gradient in the bulk solution.



Stage one: the oxygen content in the flow is the same everywhere.

As time goes by, the impurities in the flow could deposit at the surface of the pipeline, resulting in the iron carbonate film. Sometimes it will create a bulk at the bare metal surface.



Stage two: impurities or iron carbonate deposit on the bare pipeline surface creating a bunker.

The oxygen diffusion into the bunker is now restricted due to the separation from the bulk solution, and a differential aeration cell tends to be created between the microenvironment and the external surface. The stagnant condition will initiate the change of solution chemistry in the microenvironments. The change of chemistry could be caused not only by depletion of oxygen, but also by depletion of inhibitor, a shift to acid conditions, and a build-up of aggressive ion species (e.g. chloride).



Stage three: Due to the separation from the bulk solution, a differential aeration cell tends to be created between the crevice (microenvironment) and the external surface (bulk environment).

Because of the geometry of the microenvironment, oxygen consumed by normal uniform corrosion is quickly depleted.

Anode $\operatorname{Fe}(s) \to \operatorname{Fe}^{2+}(aq) + 2e^{-}$

Cathode $O_2 + 2H_2O(aq) + 4e \leftrightarrow 4OH^-(aq)$

Thus the cathodic oxygen reduction reaction cannot be sustained due to the limited amount of oxygen inside the microenvironment, causing it becoming an anodic in the concentration cell. Besides that, the large surface ratio between the cathodic surface (Sc) and anodic surface (Sa) (Sc/Sa) will further increase the servility of the corrosion. The metal ions produced by the anodic corrosion reaction readily hydrolyze, giving off protons (acid) and forming corrosion products (Fe(OH)₃). The corrosion product will block any small openings on the film, and the proton concentration will build up. The acidification will further intensify the corrosion.

APPENDIX B: METHODS OF SAMPLE CLEANING

B.1 Ultrasonic Cleaning

It is possible the coupon will contact with dirt in the air, and the isopropyl alcohol used to polish the coupon will not remove all the dirt still attached to the coupon surface. The method to get rid of any impurities attached to the coupon before testing is by using the ultrasonic cleaner.

After the coupon has been polished using sandpaper and rinsed with isopropyl alcohol, the coupon is placed into a beaker, and the beaker is filled up with isopropyl alcohol, in which the coupon is completely immersed. The beaker is placed into an ultrasonic cleaner and will be ultrasonically cleaned for 2 minutes.

B.2 Clark Solution Cleaning

It is crucial to do bare surface analysis when there is oxidation film present. In this case, removing this oxidation film without damaging the bare surface is important. Clarke solution is prepared and used to remove the oxidation film.

Table A-1 shows the chemical composition and amount of Clarke solution.

Chemical Component	Amount
Antimony Trioxide (Sb ₂ O ₃)	20 g
Tin(II) Chloride (SnCl ₂)	50 g
Hydrochloride Acid (HCl)	1 Liter

Table B-1 Chemical composition and amount of Clarke solution

Steps for coupon cleaning:

- 1. After the Clarke solution is prepared, the coupon should be immersed into the solution for no more than 10 seconds.
- 2. The coupon is taken out of the solution and rinsed with water and isopropyl alcohol, then rubbed with a rubber eraser to remove any visual surface deposit.
- 3. The coupon is weighed, and the mass weight is recorded.
- 4. Repeat step one to step three for up to three times until the weight does not change.
- 5. The wasted Clarke solution should be recycled for environmental purposes.

APPENDIX C: TAFEL SLOPE

It was described by Stern and Geary³⁰ that β_a and β_c are the slopes of logarithmic local anodic and cathodic polarization curves individually. β_a and β_c are expressed as the following two equations:

$$\beta_{\rm a} = \frac{2.303 \rm RT}{\alpha_a F}$$
C-1

$$\beta_{\rm c} = \frac{2.303 \rm RT}{\alpha_c F}$$
C-2

Where,

R is the universal gas constant (8.314 J/mol K),

T is the absolute temperature in K,

 α_a and α_c are the symmetry factors for anodic and cathodic reactions, the typical value of α_a and α_c are 1.5 and 0.5,

F is Faraday's constant (96485 coulombs/equivalent)

Based on the above two equations, the B value can be calculated as follows:

$$B = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)}$$
C-3

From the above equations (B-1, B-2, B-3), the average value of B in the temperature range of 20 $^{\circ}$ C to 100 $^{\circ}$ C could be calculated as 14.3 mV/dec.

APPENDIX D: CORROSION RATE MEASUREMENT

Weight Loss (WL) and Linear Polarization Resistance (LPR) are the two most commonly used corrosion-monitoring techniques used in the lab. In the following the two methods are introduced.

D.1 Weight loss (WL)

Corrosion rate calculated based on weight loss is determined by measuring the coupon's total mass loss over the test period of time, then it is converted to the thickness lost per year, usually in millimeters per year. By using the density of the mild steel and the total coupon surface area, the conversion equation can be shown as follows:

$$\frac{\text{Total mass loss (g)}}{\text{Total test period (hr)}} \times \frac{8760 \text{ (hr)}}{\text{year}} \times \frac{\text{cm}^3}{7.86g} \times \frac{1}{5.4\text{cm}^2} \times \frac{10\text{mm}}{1\text{cm}} = \frac{\text{mm}}{\text{year}}$$

D.2 Linear Polarization Resistance

The linear polarization measurement is made by using a potentiostat, a piece of electrochemical equipment. The polarization resistance is defined as the slope of the potential-current density curve at the free corrosion potential, yielding the polarization resistance Rp, which can be related to the corrosion current. Measurements are taken at intervals of at least 20 minutes to prevent any potential instability. Generally, 30 minutes is preferred. The current density can be calculated as follows:

$$R_{p} = \frac{B}{I_{corr}} = \frac{(\Delta E)}{(\Delta i)}_{\Delta E \to 0}$$
D-2

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Or

$$i_{corr} = B \times \frac{1}{R_p} \times \frac{1}{A}$$
 D-3

Where:

Rp is the polarization resistance

 I_{corr} the corrosion current

 i_{corr} the corrosion current density

A is the surface area of the coupon.

The proportionality constant B is introduced in Appendix B

The corrosion rate can be calculated via the following equation listed below:

$$CR = \frac{m}{AT\rho} = \frac{i_{corr}M_{w}}{\rho nF} = 1.16 \times i_{corr}$$
D-4

Where,

m is the mass loss in gram,

A is the surface area in m^2 ,

T is the test time,

M_w is the molecular weight,

F is the Faraday constant.