

Corrosion of Carbon Steel in High CO₂ Environment: Flow Effect

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Abstract

At first glance, the need to explore and develop hydrocarbon gas fields which contain high CO₂ contents (up to 80 mole %) would call for the use of expensive corrosion resistant alloys. This would have the potential to render project development costs untenable. An alternative approach would be to evaluate the technical feasibility of using carbon steels. Unlike transportation and sequestration of supercritical CO₂, where the amount of water is normally negligible or comes from condensation, field development has to consider the presence of formation water. This water has the potential to contain multiple corrosive species. In addition to the action of such species during carbon steel corrosion, evaluations that involve the effect of flow on corrosion rates are required as flow has the possible effects of challenging the protectiveness of the corrosion product films and increasing the mass transfer rates close to the pipe wall.

In the present study, flow-sensitive CO₂ corrosion has been investigated using a high-pressure high-temperature rotating cylinder electrode (RCE) autoclave and a pipe flow loop system. Corrosion rates are measured via weight loss and by electrochemical methods at various pH's (3 to 5), temperatures (25 to 50°C), near critical and supercritical CO₂ partial pressures and at equivalent fluid velocities from 0 to 1.5 m/s.

Keywords: Supercritical CO₂, rotating cylinder electrode, flow-sensitive corrosion

Introduction

South East Asia has about 182 Tcfg undeveloped hydrocarbon gas reserves. One of the reasons that these reserves have not been fully harnessed is that they reside in high CO₂ fields; for example, Natuna D-Alpha field in Indonesia contains about 70 mole percent of CO₂ [1]. At the outset, the development of these fields would call for the use of expensive corrosion resistant alloys due to the possibility of high CO₂ corrosion. This would potentially render the project development costs untenable. An alternative approach would be to evaluate the technical feasibility of using carbon steels. Unlike transportation and sequestration of supercritical CO₂, where the amount of water is normally negligible or comes from condensation [2], field development has to consider the presence of formation water which has the potential of containing multiple corrosive species. For offshore installation, it would be costly to dry the gas stream or to remove the CO₂ gas prior to transportation of hydrocarbon gas via pipelines. It is even impractical to remove water and CO₂ from the full stream coming from the wells. While the presence of dissolved CO₂ and other corrosive species itself renders the environment corrosive to carbon steel, the flowing of the corrosive liquid over the metal surface could possibly enhance the corrosion rate. This is because flow has the possible effects of increasing the corrosion rate by increasing the mass transfer rates of the corrosive species to the pipe wall and challenging the protectiveness of the corrosion product films [3][4].

There have been a lot of studies on the effects of flow on CO₂ corrosion of carbon steel [5-8]. However, only few studies have attempted to address the flow effect in high partial pressure CO₂, *i.e.*, 10 bar and above. This is especially true for flow effects in supercritical CO₂; despite the wide interest in CO₂ transport in carbon capture and storage (CCS) and enhanced oil recovery (EOR), almost all studies in CO₂ corrosion at supercritical CO₂ were carried out in stagnant conditions [9-15]. Although one study [16] simulated the effects of velocity on supercritical CO₂ corrosion, the focus of the study was more on the effects of crude oils/water mixture on super-critical CO₂ corrosion at one particular velocity: 1 m/s. The authors did not study the hydrodynamic and mass transfer effects on corrosion. Some of the studies that have attempted to address effect of flow in high partial pressure CO₂ environment are given below.

Denpo and Ogawa [17] studied the effect of flow on corrosion of N80 carbon steel and stainless steel at various CO₂ partial pressures (1, 10, and 40bar), dissolved oxygen concentrations (10 to 5000 ppb) and velocities using a flow loop (2m/s to 17m/s) and a rotating cylinder electrode (0.1m/s to 1m/s); the test temperature was set at 80°C. The test pH was not stated, but was most probably at autogenous pH: 4.24 at 1 bar, 3.62 at 10 bar and to 3.32 at 40 bars as calculated using an in-house thermodynamic model [18]. The work employed weight loss specimens for the corrosion rate measurement in the flow loop and electrochemical tests for the measurements of the corrosion rate and determination of the corrosion mechanism under the influence of flow. They found no formation of protective films on all carbon steel specimens for the pipe flow at the velocity ranges studied. They also observed that the corrosion rate of carbon steel increased with the increase of velocity with the power law of 0.6; the corrosion rate also increased with the increase in dissolved oxygen concentration. By setting the mass transfer rates of pipe and RCE equal, they were able to relate the RCE linear velocity to pipe linear velocity which would yield a similar corrosion rate. It is interesting that the work indicates the flow sensitivity of CO₂ corrosion even at high CO₂ partial pressure. However, this sensitivity was observed probably because the natural autogenous pH studied corresponded to the relatively high proton concentration which would lead to a dominant mass transport controlled corrosion process [19]. The work did not address the effect of flow as a function of pH. Nor did the work study the effect of flow as a function of temperature. More importantly, the presence of dissolved oxygen might have increased the effect of mass transport, thus possibly contributing to the flow sensitivity observed.

Dugstad and co-workers [3] studied the corrosion of carbon steel at various CO₂ partial pressures (0.5 bar to 21 bar), temperatures (20 to 90°C), pH values (4-6), and flow velocities (0.1m/s to 13m/s). They observed that the corrosion rate increased with the increase in flow at low pH, but the corrosion rate became less sensitive to flow as the pH increased; this was due to a lower proton concentration and the dominance of carbonic acid reduction at a high pH. They also found that the effect of flow on corrosion rate was more observable at higher temperature. Nevertheless, all the flow-related data presented in this work corresponded to low CO₂ partial pressure (less than 3 bar); no effect of flow at 21 bar was mentioned. Furthermore, the given mechanism by which flow affects corrosion rate was not clear; while they attributed the removal of iron carbide by flow at 20 to 40°C as the cause of *decrease* in corrosion rate as a result of less galvanic effects, they also attributed the flow-induced removal of iron carbide which served as the mass transfer resistance as the reason for the *increase* in corrosion rate at higher temperature. They also ruled out the possibility of interrelating hydrodynamics to mass transport from the data obtained in evaluating the effects of flow [3].

Hara and co-workers [20] studied the effect of flow on carbon steel (N80), low alloy steel and stainless steels in a flow loop tester: an autoclave equipped with solution circulation and an external test section; static experiments were run in the autoclave while flow experiments were run in the external test section. The experiments were carried out in non-film forming conditions at various CO₂ partial pressures (4 to 40 bar), temperatures (45 to 180°C), and velocities (2 m/s to 17 m/s). Corrosion rate was determined from weight loss. Their results suggested that the corrosion rate of carbon steel and low alloy carbon steel was under mass transfer control and was proportional to $Re^{0.83}$. They also found that the corrosion rate increased with the increase in temperature. This work is useful as the analysis relates the corrosion rate and the hydrodynamic parameters. The analysis, however, only considered the reduction of proton and neglected the contribution of carbonic acid reduction to the total cathodic current density, yet the Sh number calculated from weight loss must have incorporated the direct reduction of carbonic acid. Without electrochemical measurements, particularly from potentiodynamic sweeps, it is hard to deduce that the corrosion rate came mainly from proton reduction; the order of magnitude of the change in corrosion rate due to the change in proton concentration alone is much larger when carbonic acid reduction is also considered. At 40 bar, the effect of flow was observed most probably because the test pH was at the autogenous pH value of 3.47 [18]. At this pH, the proton concentration was relatively high. Moreover, the effect of flow at 40 bar was restricted to 120° C where diffusion coefficient is relatively high. It may be worthwhile to see whether the flow effect could be similarly observed at a lower temperature corresponding to the field temperature. The work also did not address the flow effect as a function of pH as it was most probably carried out at fixed pH [20].

Wang and co-workers [21] studied the effects of velocity (0.2m/s, 1 m/s, and 2 m/s) and CO₂ partial pressure (3, 10 and 20 bar) at pH 5 and 60°C on corrosion rate of X-65 carbon steel in a single-phase flow using a 0.16m I.D inclinable stainless steel high pressure flow loop. They found that flow did not affect the anodic reaction at these three CO₂ partial pressures as it was under charge transfer control. They also observed that the cathodic limiting current density became less flow-sensitive with the increase in CO₂ partial pressure although its value increased with the increase in CO₂ partial pressure; this was probably because at such high CO₂ partial pressures, the cathodic limiting current density came largely from the slow chemical reaction of the hydration of dissolved CO₂ into carbonic acid. It must be noted that the study focused only on a single pH value of 5 where the effects of flow even in low CO₂ partial pressure are less dominant [19]. It would be interesting to know if the same observation is applicable at a lower pH, particularly at pH less than 4 in which the proton concentration is relatively higher. Likewise, the scope of the study could be expanded to see the effect of flow at various temperatures and at much higher CO₂ partial pressure [21].

The present work attempts to contribute to the study on the effect of flow at high partial pressure CO₂. As such, the aim of the study is to evaluate the effects of flow in high partial pressure CO₂ environment at various pCO₂, pH values and temperatures. However, the focus is only on a single-phase turbulent flow, and the current paper will limit its findings to 10 bar data. To accomplish the above objective, the hydrodynamic effects on CO₂ corrosion of carbon steel were evaluated using a high pressure and high temperature (HPHT) rotating cylinder electrode (RCE) shown in Figure 1. Corrosion rates are measured via weight loss and electrochemical methods at various pH values (3 to 5), temperatures (25 to 50°C), 10 bar CO₂ partial pressures, and at liquid velocities of 0, 0.1, 0.5 and 1.0 m/s.

Methodology and Experimental Setup

Test Specimen

The cylindrical test specimen, shown **Figure 1**, had an outside diameter of 2 cm and a length of 2 cm.



Figure 1: Specimen for HPHT rotating cylinder electrode

It was made of API X65 carbon steel machined from a retrieved line pipe. Its chemical composition is given in **Table 1**. Its total exposed surface area was 15.96 cm². Prior to exposure to test solution, the specimen was polished first with 400 grit and then with 600 silicon carbide papers. It was then rinsed with de-ionized water, washed with iso-propanol and finally dried using a heat gun.

Table 1: Chemical composition (in %) of X65 carbon steels (balance Fe)

C	Mn	Si	P	Cr	Cu	Ni	Mo	Al
0.065	1.54	0.25	0.013	0.001	0.05	0.04	0.007	0.041

Test Solution

The test solution used in the experiment was 1 wt.% NaCl so as to factor out the effects of electromigration on transport processes. Prior to transferring the test solution into the autoclave, it was fully de-aerated using CO₂ for at least four hours. The pH of the test solution was subsequently adjusted to the desired value using de-aerated NaOH or HCl solution after the test solution had been fully saturated with carbon dioxide at the desired temperature and CO₂ partial pressure; a pH adjustment assembly mounted on the RCE lid, as shown in **Figure 2**, was used to adjust the pH.

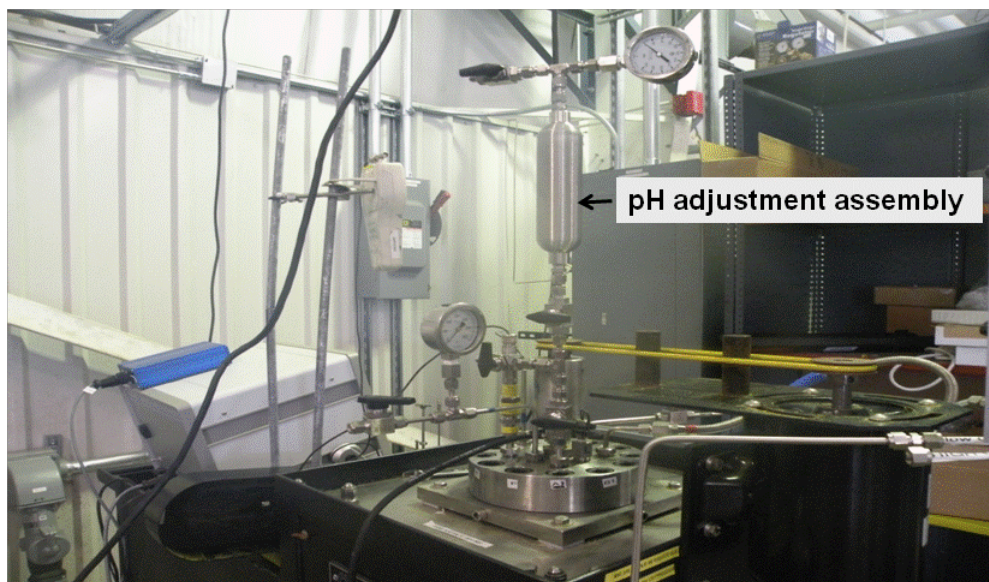


Figure 2: The experimental set up showing the pH adjustment assembly

Equipment

The experiments made use of a 7.5-L high pressure and high temperature (HPHT) autoclave equipped with a RCE assembly. For pH and electrochemical measurements, high pressure and high temperature (HPHT) glass pH probe and Ag/AgCl reference electrode probe were used; a platinumized niobium electrode served as the counter electrode in a three-electrode electrochemical set up. The working electrode was mounted on a rotating shaft in which its speed could be controlled to be between 0 to 1750 rpm. A potentiostat/galvanostat was employed for electrochemical measurement and data acquisition.

For weight loss tests, a spectrophotometer was used to determine the concentration of ferrous ions in ppm. The value was then converted to corrosion rate.

Test Procedure

After the lid was mounted on the vessel and the probes were installed, the vessel was purged with CO₂ gas for 15 minutes. Then, five liters of de-aerated test solution was transferred to the autoclave vessel. Once the temperature of the test solution reached the desired temperature, the vessel was pressurized to the required CO₂ partial pressure. Since the vapor pressure at the highest test temperature of 50°C is small, the total pressure was assumed to correspond to the CO₂ partial pressure. Once the pH reading indicated that the test solution had reached the autogenous pH, this was adjusted to the desired value using either NaOH or HCl solution.

For electrochemical tests, the open-circuit potential of the specimen was first measured until it became stable. Polarization resistance (R_p) and corrosion potentials were then measured over a period until they showed rather stable values. Once stable, linear polarization resistance (LPR) tests were carried out first at ascending velocities and then at descending velocities; in LPR tests, the specimen was polarized within ± 5 mV from the open-circuit potential with a scan rate of 0.125 mV/s. It was followed by EIS tests at a test frequency of 100 kHz to 1 MHz and an applied potential of 5 mV; the velocity was set at 0 rpm. The specimen was then cathodically swept at a scan rate of 0.2 mV/s from the open circuit potential to a potential which was 700 mV more negative for each velocity. Finally, the specimen was anodically swept from the open-circuit potential to a potential 300 mV more positive at 0 rpm.

Weight loss test was also carried out, but only at a rotation rate of 500 rpm with an exposure period of 24 hours. The purpose was to cross validate the results from the electrochemical experiments. At the end of the experiment, test solution was collected and analyzed for iron ion count; the value was then converted to corrosion rate.

Results and Discussion

Figure 3, Figure 4, and Figure 5 show the comparison of the LPR data between 25°C and 50°C (pH4; $pCO_2=10$ bar), pH 3 and 4 ($pCO_2=10$ bar; 25°C), and pCO_2 of 10 bar and 70 bar (25°C; pH 3), respectively; the R_p values from LPR were first corrected for solution resistance (R_s) from EIS results before being converted to corrosion rates.

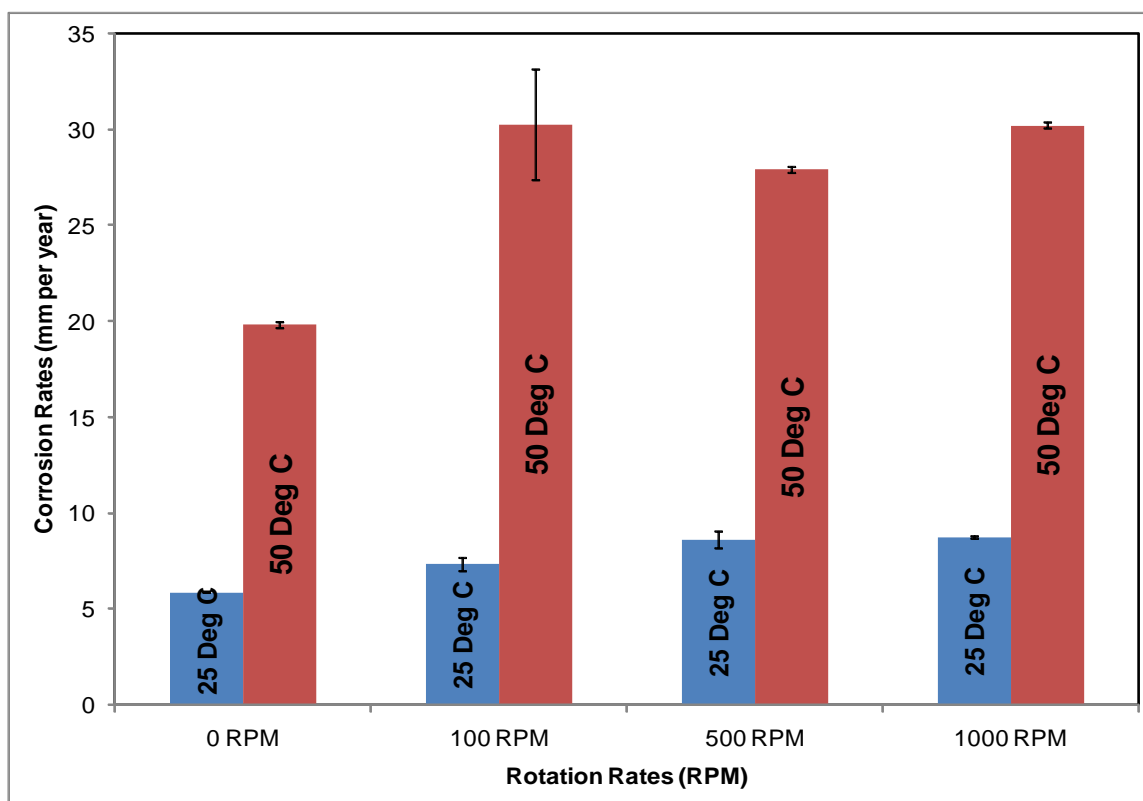


Figure 3: Comparison of corrosion rate from LPR tests between 25°C and 50°C at $pCO_2=10$ bar and pH 4.

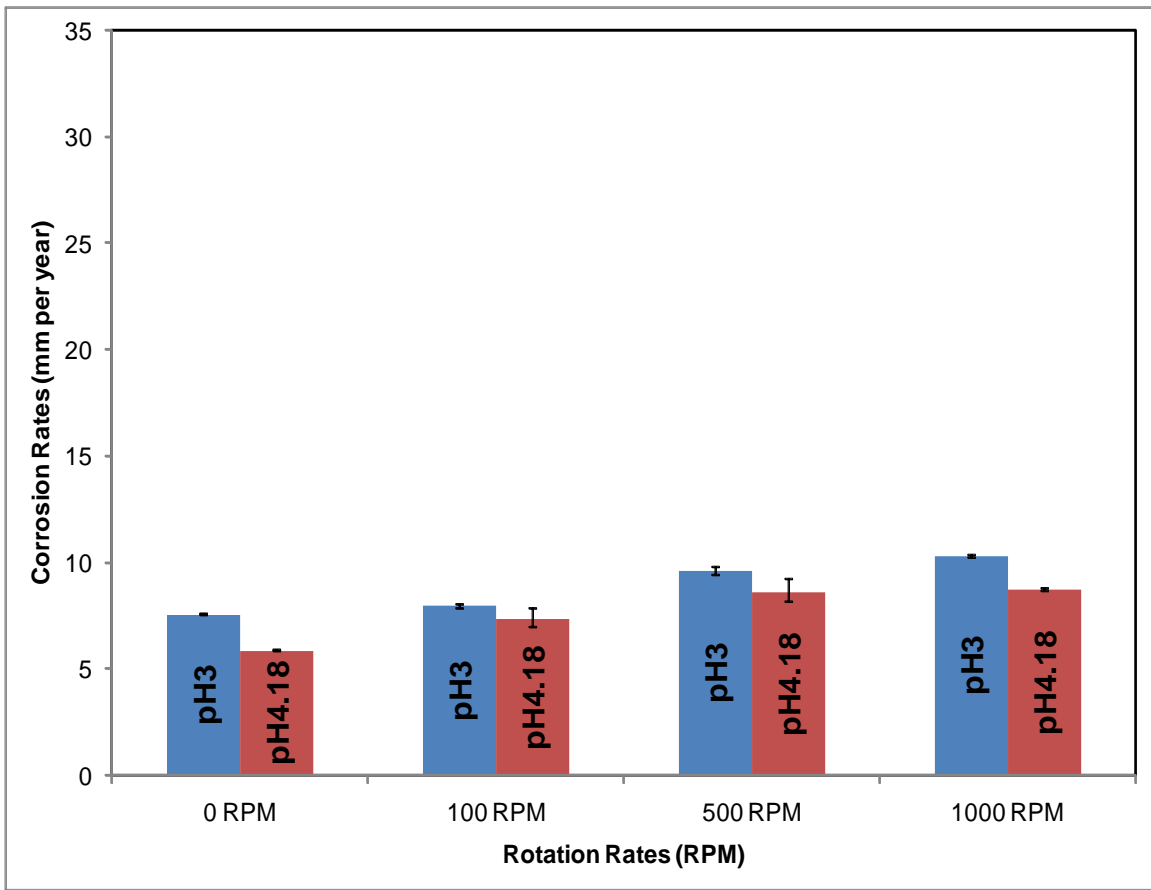


Figure 4: Comparison of corrosion rate from LPR tests between pH 3 and pH 4 at $p\text{CO}_2=10$ bar and 25°C .

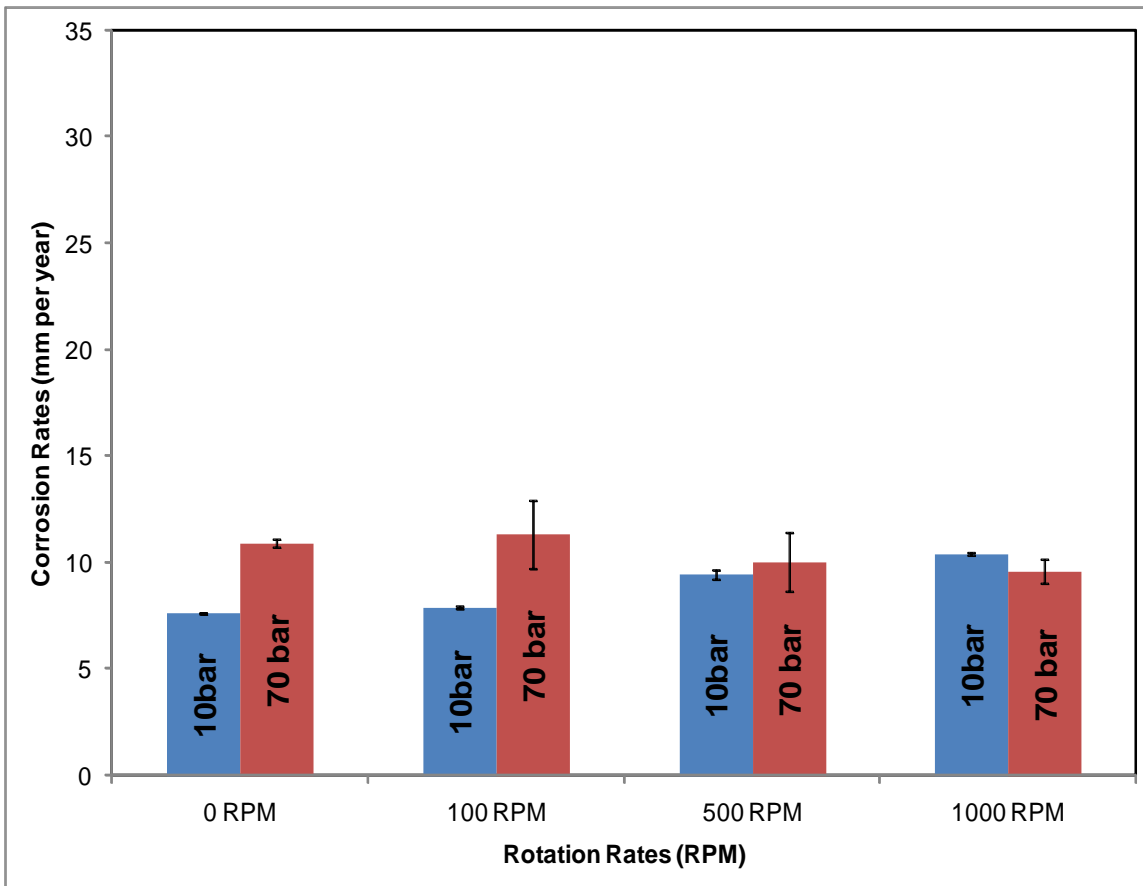


Figure 5: Comparison of corrosion rate from LPR tests between $p\text{CO}_2=10$ bar and 70 bar at 25°C and pH 3.

The results indicate slight sensitivity of the corrosion rate to the change in velocity at each test condition. This could also be observed from potentiodynamic results shown in Figure 6, Figure 7, and Figure 8.

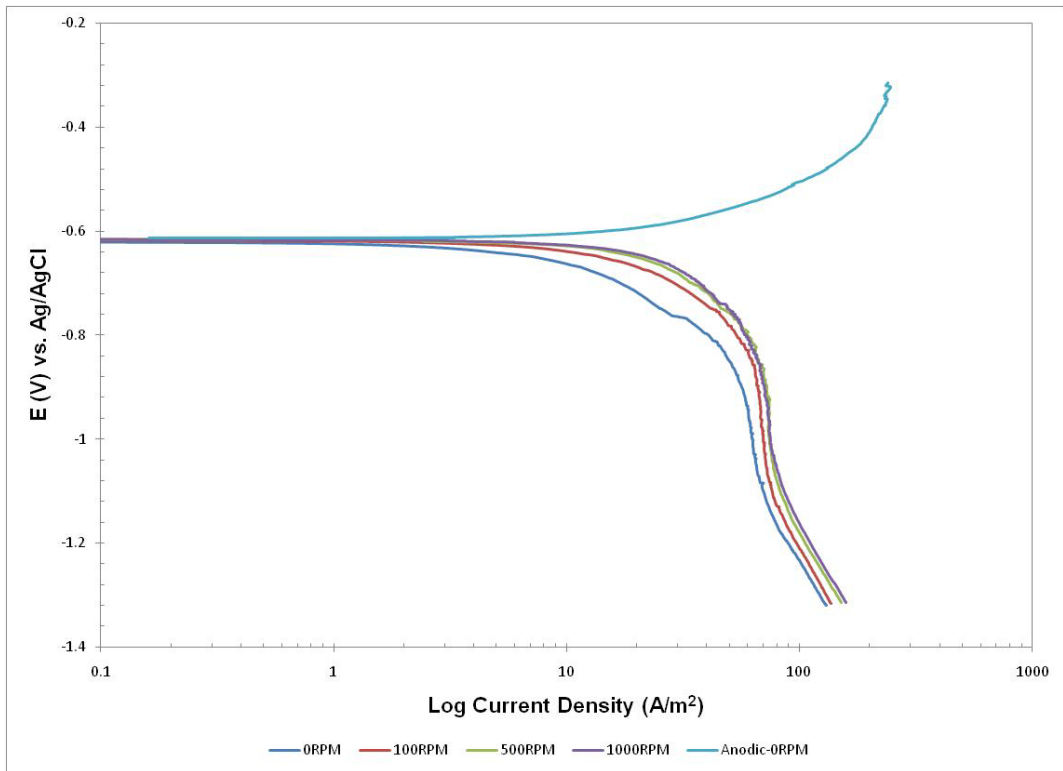


Figure 6: Cathodic polarization curves at various velocities; $p\text{CO}_2=10\text{bar}$, $\text{pH } 3$ and 25°C .

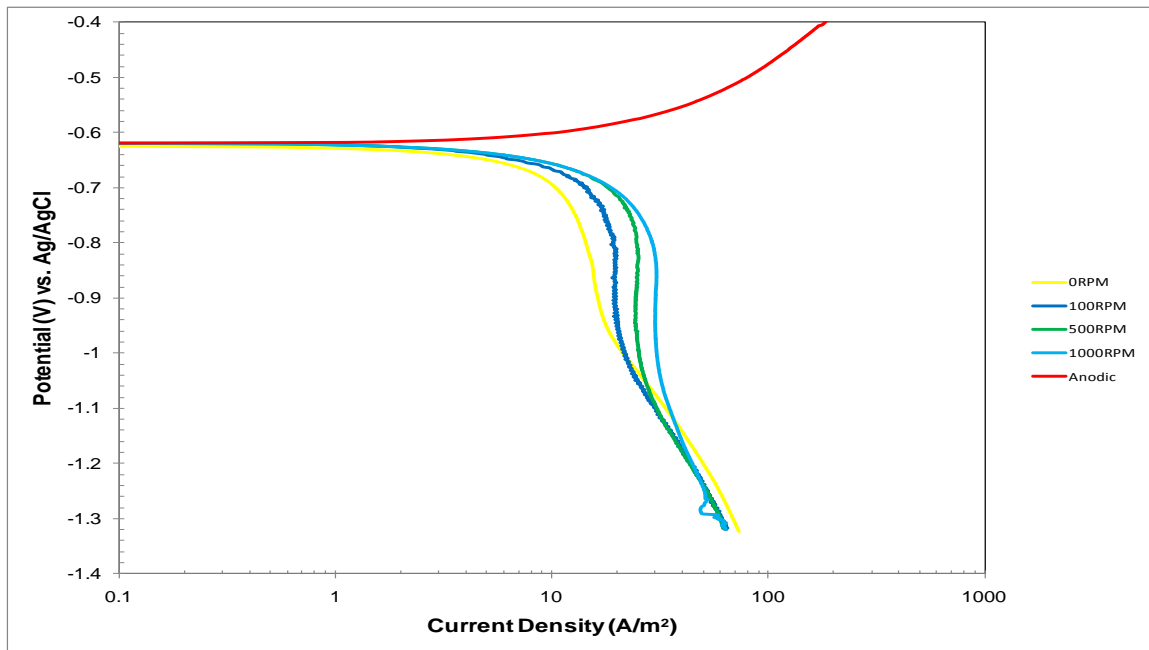


Figure 7: Cathodic polarization curves at various velocities; $p\text{CO}_2=10\text{ bar}$, $\text{pH } 4$ and 25°C .

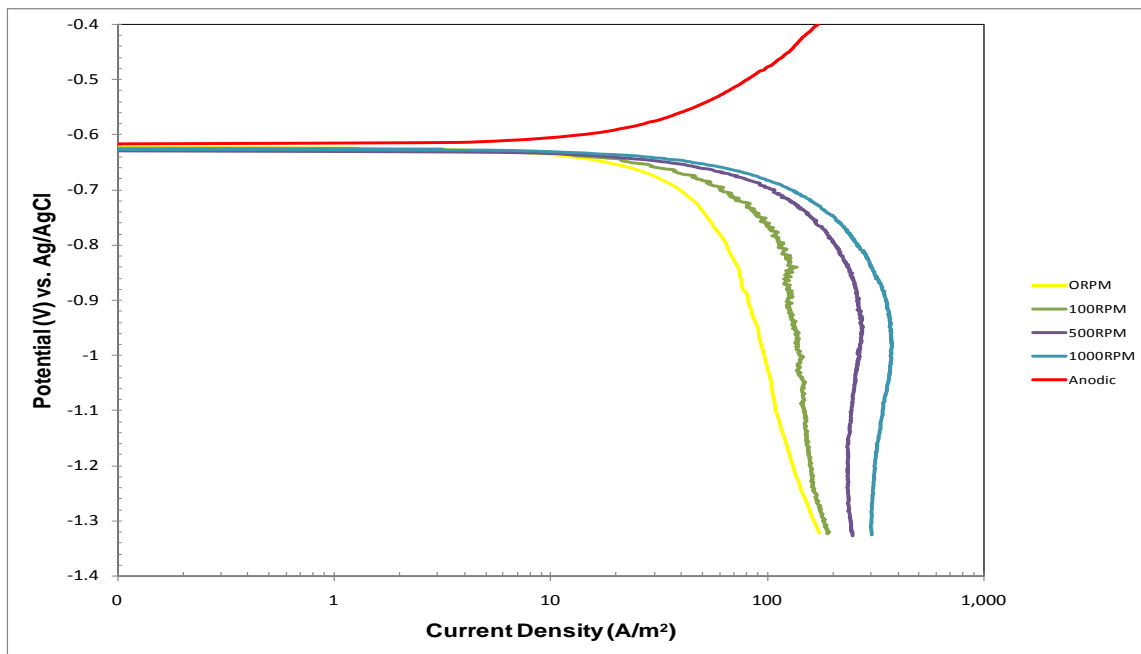


Figure 8: Cathodic polarization curves at various velocities; $p\text{CO}_2=10$ bar, pH 4 and 50°C .

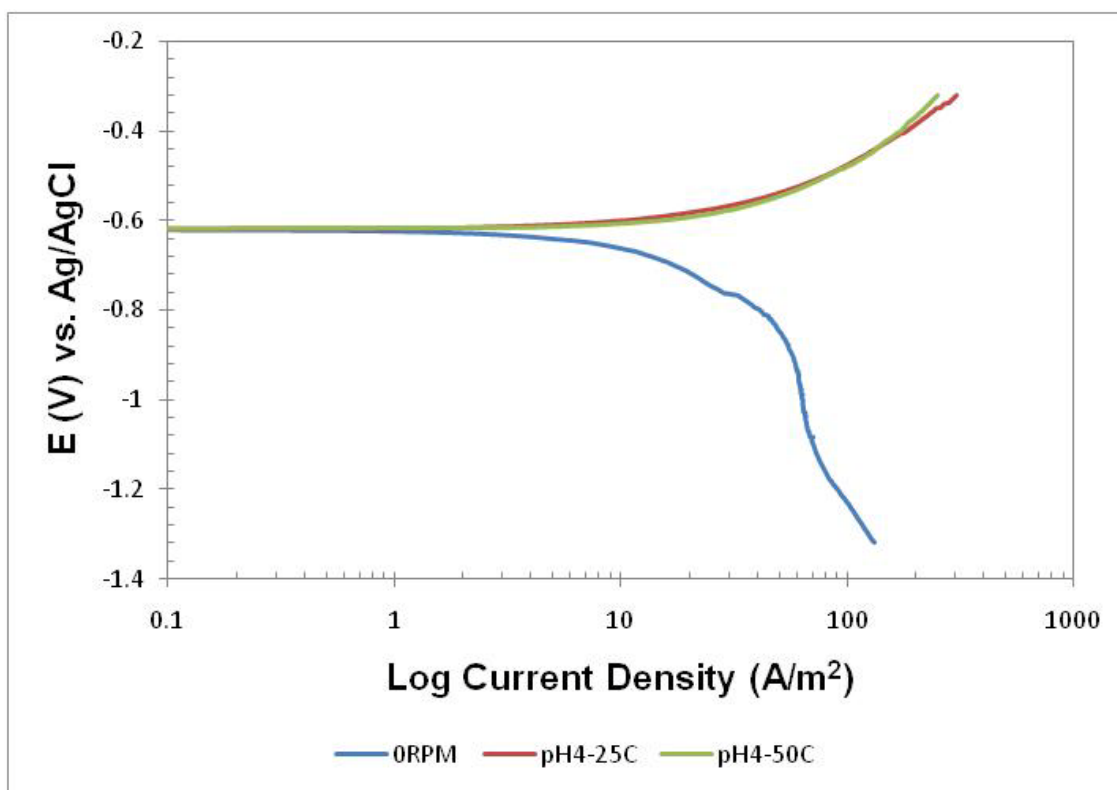


Figure 9: Comparison of anodic curves between 25°C and 50°C ; $p\text{CO}_2=10$ bar and pH 4

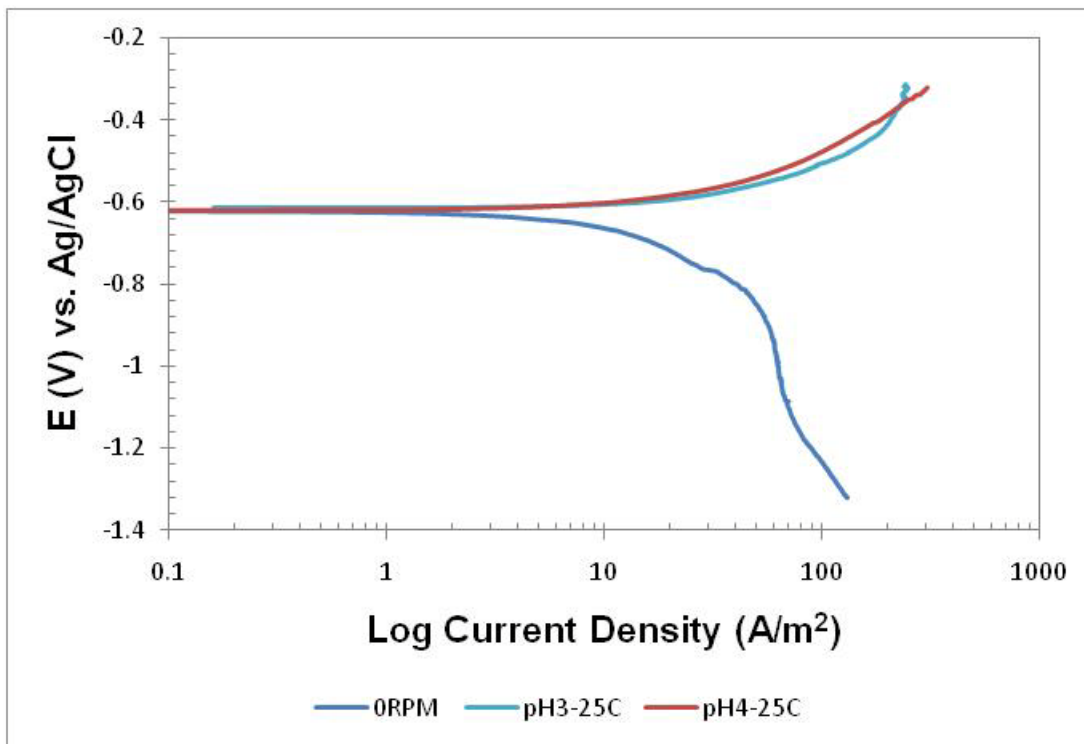


Figure 10: Comparison of anodic curves between pH 3 and pH 4; $p\text{CO}_2=10$ bar and 25°C

All potentiodynamic sweep results were corrected for IR-drop errors. Figure 9 and Figure 10 show the superimposition of anodic curves at various tests conditions; the two figures suggest that anodic reaction was not much affected by the change in pH and temperature.

Figure 3, Figure 4 and Figure 5 also suggest that temperature has more pronounced effects on corrosion rate than pH and $p\text{CO}_2$. The LPR data at each test condition were cross-validated with weight loss and iron count results at 500 rpm as well as with results from previous in-house work (where available). Figure 11, Figure 12 and Figure 13 show, respectively, the cross-validation data for the following test conditions:

- 10bar, 25°C , pH3.19
- 10bar, 25°C , pH4.08
- 10bar, 50°C , pH4.05

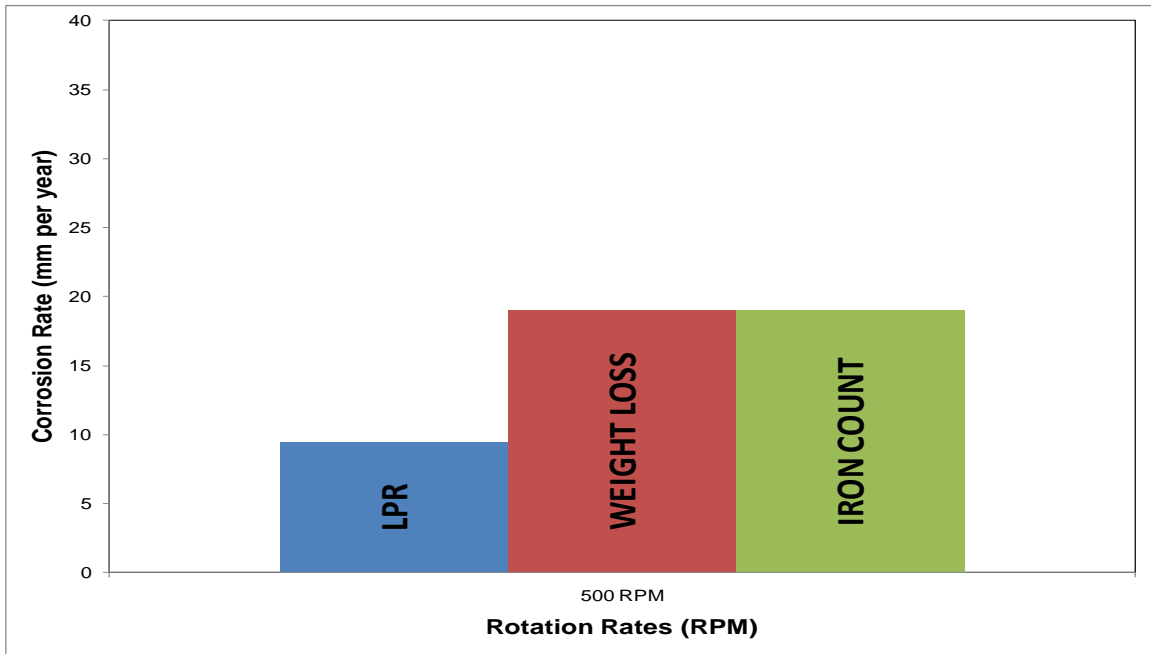


Figure 11: Data cross validation for $p\text{CO}_2=10$ bar, $T=25^\circ\text{C}$, and $\text{pH}=3.19$ at 500 rpm

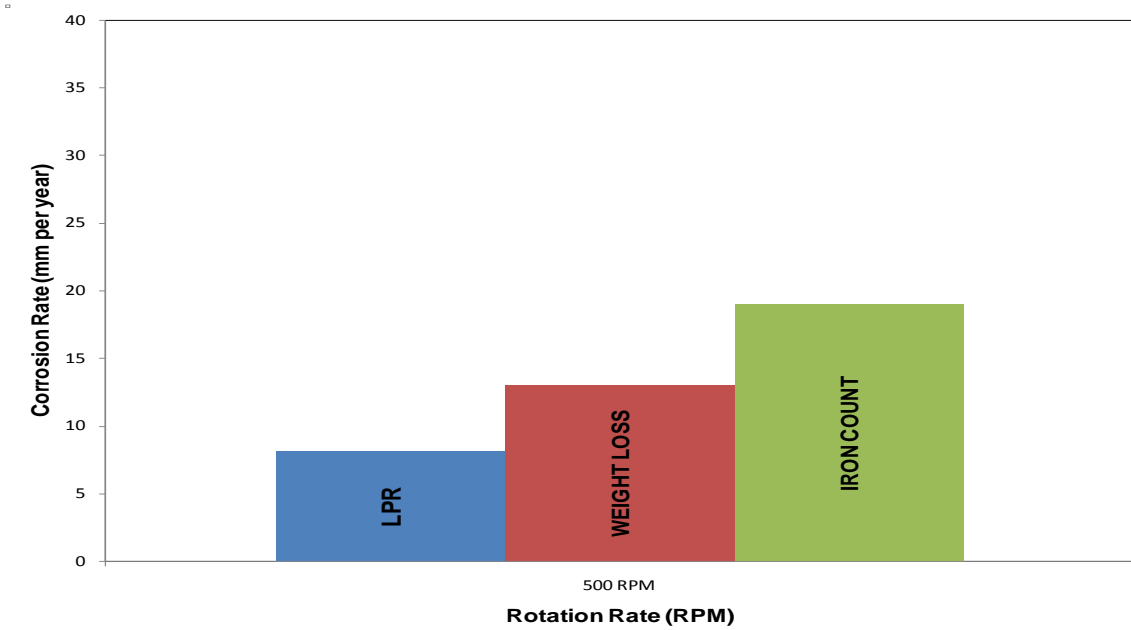


Figure 12: Data cross validation for $p\text{CO}_2=10$ bar, $T=25^\circ\text{C}$ and $\text{pH}=4.08$ at 500 rpm

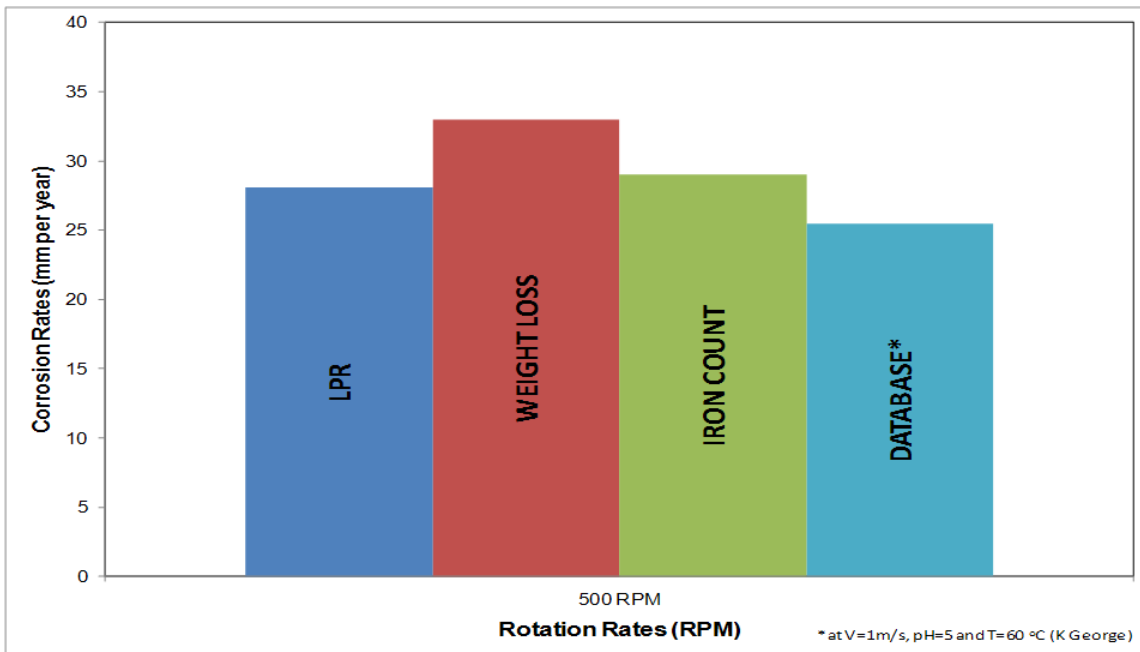


Figure 13: Data cross validation for $p\text{CO}_2=10$ bar; $T=50^\circ\text{C}$; $\text{pH}=4.05$ at 500 rpm

The data suggest that the LPR corrosion rate was generally lower than those of weight loss and iron count. It is not clear why this was so. Wang and co-workers also observed a similar trend in their data, albeit with acetic acid [21]. It must be noted that the calculation of corrosion rate made use of 26 mV as the Stern-Geary coefficient (B value) which is the same value proposed in another work [22]. Figure 13 suggests that the value yields corrosion rate that correlates well with corrosion rate from weight loss and iron count. The SEM/EDAX results for all the test conditions indicate that the films formed were mainly iron carbide (Fe_3C), which was porous and non-protective. Figure 14 shows an example of surface film analysis which was at 10 bar, 25°C and pH 3 test conditions.

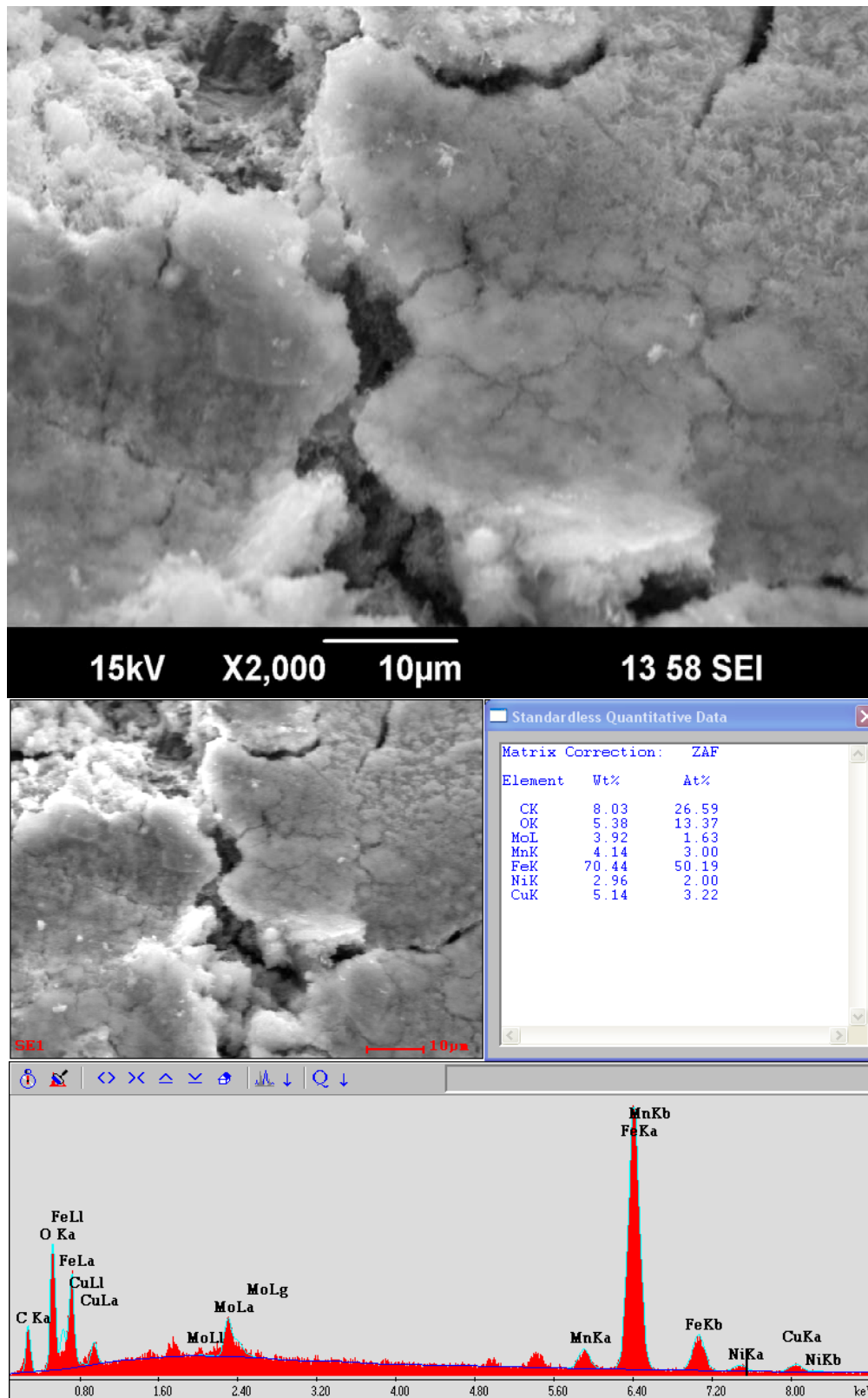


Figure 14: Surface analysis at $p\text{CO}_2=10$ bars, $\text{pH}=3$ and $T=25^\circ\text{C}$ indicating iron carbide films covering the substrate.

Furthermore, when the cementite films were removed, the substrate seems to have experienced general corrosion as shown by Figure 15 below:

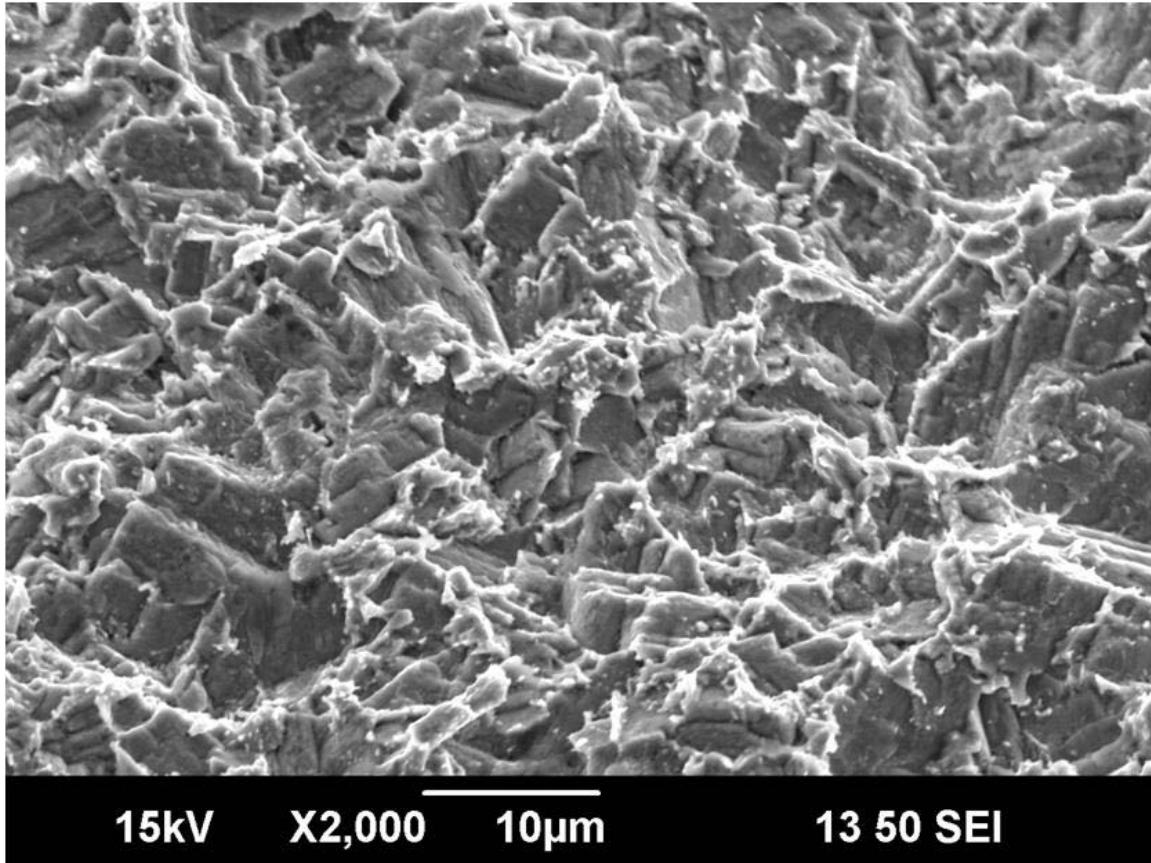


Figure 15: Surface analysis at $p\text{CO}_2=10$ bars, $\text{pH}=3$ and $T=25^\circ\text{C}$ after removal of iron carbide films indicating general corrosion.

The slight sensitivity of corrosion rate to flow at all the test conditions could be due to the fact that at higher CO_2 partial pressure, the slow chemical reaction of aqueous CO_2 hydration was more dominant than that of mass transport process of proton and carbonic acid. The flow sensitivity could be expected to become less with the increase in pH as the proton concentration was reduced further [3]. The observation agreed with that of Wang [3] and Dugstad [3, 21]. Similarly, although temperature seemed to have a more pronounced effect on corrosion rate than did pH , it does not seem to have increased flow-sensitivity of the corrosion rate. This is similar to what has been observed at low CO_2 partial pressure [6]. As for anodic reaction, it was not flow sensitive because its reaction rate was under charge transfer control. It did not show much pH dependence probably because the surface was already saturated with hydroxyl ions [23]. However, it remains unclear why the anodic reaction was not temperature dependent [19].

Conclusions

Thus, the above results suggest the following:

1. The increase in CO_2 partial pressure reduced the flow-sensitivity of CO_2 corrosion rate most probably due to the increase in carbonic acid concentration whose reduction is limited by hydration of dissolved CO_2 .

2. Under the test conditions, only iron carbide seems to have formed, and it did not provide sufficient corrosion protection.
3. The flow-sensitivity of CO₂ corrosion was not clearly observed even at a low pH (pH 3). This is opposite to what has normally been observed at a low CO₂ partial pressure.
4. Even at a relatively high CO₂ partial pressure, anodic reaction seems not to have been flow-sensitive probably because it was under charge-transfer control.

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