

How to Maintain a Stable Solution Chemistry when Simulating CO₂ Corrosion in a Small Volume Laboratory System

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ABSTRACT

In laboratory experiments, corrosion of mild steel specimen in glass cells or autoclaves with a relatively small internal volume (of the order of 1 liter or less), will usually lead to a change in solution chemistry, (i.e., increase in ferrous ion concentration and solution pH) which will affect the corrosion product formation and ultimately the corrosion rate. However, in much larger field systems that are being simulated in the laboratory, such as for example oil and gas mild steel pipelines, the solution chemistry at any specific location does not change significantly over the same time period, since it is governed by the flow coming from further upstream. Therefore, it is very important to be able to maintain a stable solution chemistry in small scale laboratory experiments, in order to get a better simulation of corrosion seen in the field. In this work, a stable solution chemistry system was developed using ion exchange resins. H-form and K-form exchange resins were successfully tested in long term experiments aiming to keep pH and ferrous ion concentration reasonably stable. The results show that pH can be controlled within ± 0.02 pH units and ferrous ion concentration within ± 3 ppm. The results of electrochemical measurements and surface analysis show that there is a significant difference in both corrosion rate and corrosion product layer formation when a stable solution chemistry system is used.

INTRODUCTION

In small scale constant inventory laboratory experiments, CO₂ corrosion of mild steel will often lead to a change in aqueous solution chemistry (i.e. increase in ferrous ion concentration and solution pH). As an example, Figure 1 shows the changes in ferrous ion concentration and solution pH during a small scale lab experiment with an API 5L X65 specimen with surface area of 5.4 cm² in 2 liters of CO₂ purged, 1 wt.% NaCl solution at 40 °C and initial pH 4.0. It was found that ferrous ion concentration increased from 0 to 54 ppm during 72 hours. At the same time, the solution pH increased more than 1 pH unit, from pH 4.0 up to pH 5.1.

However, for a field system,¹ such as an oil or gas pipeline, the solution chemistry at a any given location inside the line does not change significantly over time, as there is always fluid flow coming from upstream. It is well known that the increase in pH and ferrous ion concentration will affect the CO₂ corrosion rate and the precipitation rate of corrosion products such as iron carbonate.²⁻⁴ Therefore, it is not trivial to conduct and interpret corrosion results from small scale lab experiments that are meant to simulate field corrosion data.

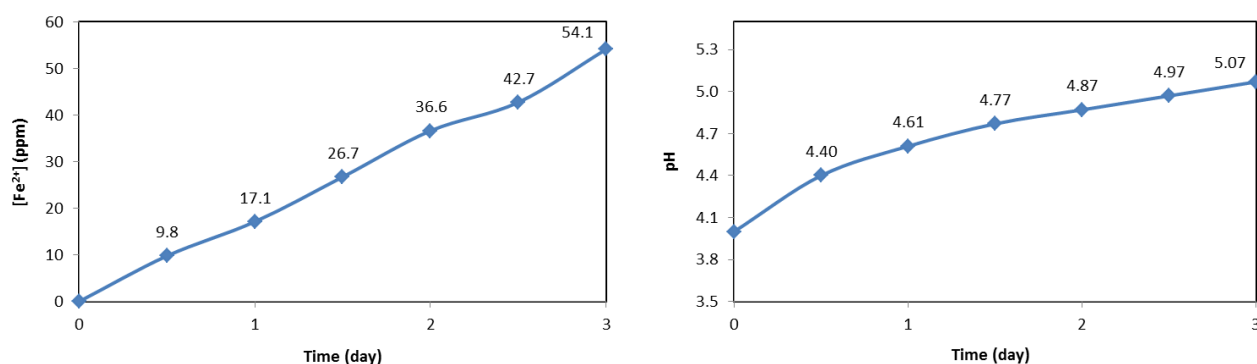


Figure 1: Changes of ferrous ion concentration and solution pH during the corrosion of X65 in CO₂ purged 1 wt.% NaCl solution at 40 °C and initial pH 4.0.

In order to get a better simulation of corrosion in small scale constant inventory laboratory systems, the effect of solution chemistry changes needs to be minimized. Since small scale apparatus are typically used due to their cost effectiveness, and long term studies (> 1 week) are often required, an implementation of a system that can maintain stable solution chemistry by controlling the ferrous ion concentration and pH is desirable.

There are multiple methods used to control the solution chemistry in corrosion experiments. One way would be to use a large ratio of solution volume to specimen surface area, so that the solution chemistry is maintained.⁵ In large scale systems⁶ this is straightforward to achieve, as this ratio is often larger than 100 L/cm². However, most laboratory corrosion tests are conducted in vessels less than 2 liters in volume with corroding specimen ranging from 1 to 10 cm² in surface area and require constant attention during experimentation. Another method is based on deployment of a high temperature precipitator to control the ferrous ion concentration during the corrosion of mild steel.^{7,8} For this method, complicated equipment is required and solution pH needs to be separately maintained by using a pH controller connected to a chemical injection pump. The third method used in small scale experiments is a flow-through system where purged, pH adjusted solution at the desired temperature is constantly added to the test cell which uses an overflow or solenoid controlled valve to maintain a continuous volume in the test cell.⁹ Finally one can use an ion exchange resin – as probably the simplest solution. Although this method has been deployed in some previous studies,¹⁰ details related to the use of resins have not been reported, and this is the topic of the present paper.

Some basic questions related to the use of ion exchange resins in typical small scale CO₂ corrosion laboratory experiments need to be answered:

- What kind of ion exchange resin can be used to control the ferrous ion concentration?
- Can the same ion exchange resin be used to control the solution pH?
- Can an automatic system be deployed?
- Is there truly a large effect on the corrosion of mild steel when pH and ferrous ion concentration are controlled?

Ion exchange resins are typically cross-linked porous polymer substances containing functional groups with mobile ions which may be replaced with ions of the same charge dissolved in the surrounding liquid media. For example, if the Na-form resin is added into Ca²⁺ containing aqueous solution, Na⁺ (the mobile ion in the resin) will be replaced by Ca²⁺. In this case, Ca²⁺ will be removed from the solution and Na⁺ will be given back to the solution, as schematically illustrated in Figure 2.

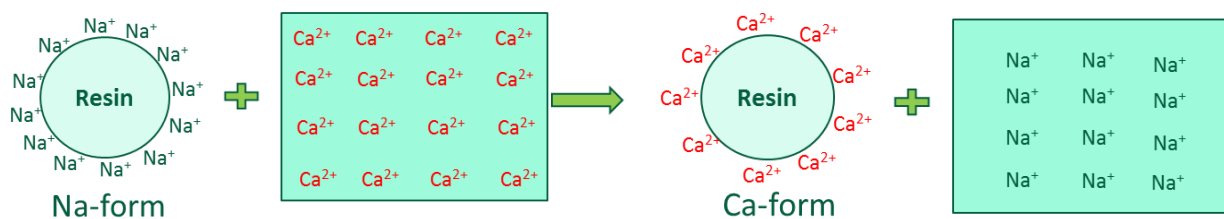


Figure 2: Schematic diagram of exchanging process between Na-form resin and Ca²⁺.

The exchange capability of resin depends on the properties of the functional group and the affinity of the mobile ions to exchange with the resin. For the resins with the same functional group, the affinity of the mobile ions varies with the ionic size and charge of the ion. Generally the affinity is greatest for large ions with high valence. For example, the affinity of H⁺, Na⁺ or K⁺ is lower than Fe²⁺ or Fe³⁺. The ion with a lower affinity can generally be replaced by an ion with a higher affinity. This characteristic of ion exchange resins is very important for selecting of suitable resins to control the ferrous ion concentration and solution pH.

In the present work, the primary aim was to build and test a system for maintaining stable solution chemistry in a small scale CO₂ corrosion experiment by using ion exchange resins. The following issues are addressed in the text below: (i) selection of ion exchange resins for solution pH control and ferrous ion concentration control, (ii) automatic control for the stable solution chemistry system, and (iii) effect on corrosion behavior of mild steel when using the new system.

EXPERIMENTAL

A 2 liter glass cell was used for the experiments. Cylindrical mild steel specimen (API[†] 5L X65 with an outer diameter 12.0 mm and length of 14.4 mm) were used for each corrosion test. Before the test, the specimens were evenly polished by sand paper with 400 and 600 grit sequentially, and then cleaned in an ultrasonic bath with isopropanol. Specimens were then taken out and dried by nitrogen gas and immediately used in the experiments. The test matrix is shown in Table 1:. Before each test, a 1 wt.% NaCl solution was prepared in the glass cell, deaerated with a continuous CO₂ gas flow purge and heated to the required temperature by a hot plate. After the designated temperature was achieved, the bulk pH was adjusted by addition of NaOH (0.1 M).

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Ferrous ion concentration in the glass cell was measured ex-situ by a UV/Vis spectrophotometer. A three-electrode system was employed for electrochemical measurements using an Ag/AgCl electrode and platinum wire as the reference electrode and counter electrode, respectively. Open circuit potential (OCP) and linear polarization resistance (LPR) were conducted using a potentiostat (Gamry[‡] Reference 600). For the LPR measurement, the scan rate was 0.125 mV/s and the polarization range was from -5 mV to 5 mV (vs. OCP). The corrosion rate was calculated from the LPR data using a B value of 26 mV. The morphology and composition of the specimen surface and the cross section of the corrosion product layer were examined using scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS). In this work, two types of ion exchange resins were used, including the so called “H-form” and “K-form”. The resins were first rinsed with deionized water before use.

Table 1: Test matrix for a stable solution chemistry system

Initial pH	4.0, 5.8
Initial ferrous ion concentration	0, 20 ppm
Temperature	25, 50, 80 °C
Supporting electrolyte	1 wt.% NaCl solution
CO ₂ partial pressure	0.97, 0.88, 0.53 bar
Testing material	API X65

RESULTS AND DISCUSSION

The Use of Resin for Solution pH Control

In laboratory experiments using small volume glass cells or autoclaves, corrosion of mild steel specimen will lead to a change in solution pH. i.e., the H⁺ ions will be depleted and the solution pH will increase compared to the initial pH. The H⁺ ions can be replenished in the solution through ion exchange with the resin, and the pH returned close to the original value. It should be noted that usually NaCl is used as supporting electrolyte, so there is a large amount of Na⁺ in the test solution. For the resins with the same functional group, the affinity of the mobile ions varies with the ionic size and charge of the ion; generally the affinity is greatest for large ions with high valence. Therefore, the affinity of Na⁺ is higher than H⁺. If the H-form resin is used to exchange with Na⁺, the following reaction will occur:



where R represents the functional group of the H-form resin. This way H⁺ will be regenerated, but the problem of increasing amounts of ferrous ions due to corrosion remains, and will be discussed further below.

The H-form resin was placed into a column where solution from the glass cell was pumped through and then returned back to the glass cell. The pump could be manually controlled based the measured solution pH as indicated by the pH meter. This labor intensive exercise was deployed first to test the whole concept. Figure 3 shows the solution pH evolution during the corrosion of X65 in CO₂ purged, 1 wt.% NaCl solution, with and without the use of H-form resin at 25 °C. It was found that the pH increased gradually with time in the absence of pH control. During the 9 hours experiment, the solution pH increased from pH 4.0 to more than pH 4.2. However, in the presence of H-form resin, the solution pH was controlled very close to the initial value pH 4.0. The deviation was only ±0.03 pH units when the pump was manually controlled. This result undoubtedly indicated that the H-form resin can be used to

[‡] Trade name.

control the solution pH in a small scale glass cell experiment. Compared with the standard practice of adjusting solution pH by addition of an acid, no new ions or contaminants are brought into the original corrosion system by using H-form ion exchange resin.

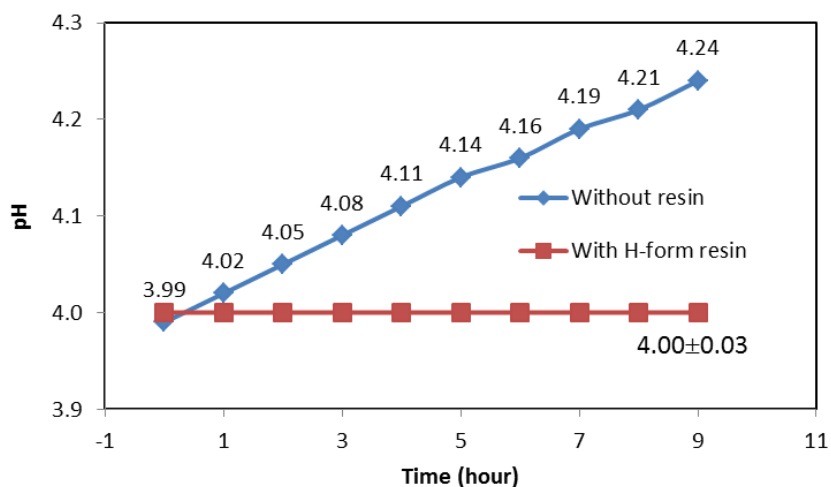


Figure 3: The solution pH as a function of time during the corrosion of mild steel. (API 5L X65, 1 wt.% NaCl solution, 25 °C, initial pH 4.0, pCO₂ = 0.97 bar, 20 g H-form resin was used in the control of control of solution pH.)

The Use of Resin for Control of Ferrous Ion Concentration

Just like the pH of the solution, the ferrous ion concentration also increases with time in a small scale experimental vessel such as a glass cell or an autoclave. In order to maintain the ferrous ion concentration at a desired value, some ferrous ions have to be removed from the solution. The affinity of K⁺ is lower than Fe²⁺, so a K-form resin is expected to exchange with Fe²⁺ in a NaCl solution. In this case, the following reaction would occur:



where R is the functional group of K-form resin, and K⁺ will be given back to the solution. Therefore, the K-form resin was prepared and then placed into the column. The ferrous ion concentration was measured by taking a 10 mL sample of solution and testing in a UV/Vis spectrophotometer after reacting with phenanthroline.

Figure 4 shows the ferrous ion concentration as a function of time during corrosion of an X65 specimen with surface area of 5.4 cm² in 2 liters of CO₂ purged, 1 wt.% NaCl solution with and without K-form resin at 50 °C and initial pH 4.0. In the absence of K-form resin, the ferrous ion concentration increased with time. When the K-form resin was used, the increase in the ferrous ion concentration was not as pronounced. This result indicated that the K-form resin can be used to remove ferrous ion from NaCl solution, but that a larger amount needed to be deployed for a better result.

In summary, it was found that both H-form and K-form ion exchange resins could be used to successfully control the solution pH and ferrous ion concentration, respectively.

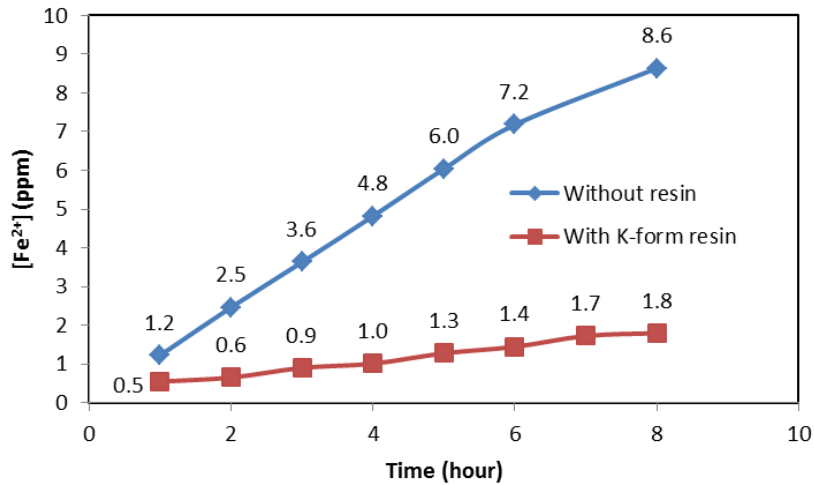


Figure 4: Ferrous ion concentration as a function of time during the corrosion of mild steel with and without K-form resin. (API 5L X65, 1wt.% NaCl solution, 50 °C, initial pH 4.0, pCO₂ = 0.88 bar, 30 g K-form resin was used in the control of ferrous ion concentration.)

The Use of Resins for Simultaneous Control of pH and Ferrous Ion Concentration

In order to control the solution pH and simultaneously control the ferrous ion concentration during corrosion, two external flow loops needed to be added to the standard glass cell setup. Since there is no known method available to measure the in situ concentration of ferrous ions in solution, an Omega[§] timer-controller was used to turn the pump on and off at a preset rate determined empirically and linked to the measured corrosion rate. The ratio between on time and off time can also be adjusted based on the measured ferrous ion concentration measurements done by a UV/Vis spectrophotometer.

For the pH control, a controller was used to automatically control the pump. During a corrosion experiment, the controller was set to turn the pump on automatically when the pH exceeded the desired value by 0.01 pH units. When the pH returns to the original value, the pump will automatically be turned off.

Corrosion Behavior of X65 with and without the Stable Solution Chemistry System

A series of long term glass cell experiments were carried out to verify the difference in corrosion behavior with and without the stable solution chemistry system in place. The target values was 0 ppm dissolved ferrous ion concentration and pH5.8. All of the experiments were conducted for 220 hours (~9 days) in a CO₂ purged, 1 wt.% NaCl solution at 80 °C. The solution pH, ferrous ion concentration, corrosion potential, and corrosion rate were measured during the experiment. After the experiment, the morphology and composition of the specimen surface and cross section of corrosion product layer were also examined.

Figure 5 shows the ferrous ion concentration vs. time during the corrosion of X65 in CO₂ purged 1 wt.% NaCl solution with and without the stable solution chemistry system, respectively. Without the use of resins, the ferrous ion concentration first increased and then decreased over time. The anodic dissolution of iron increases the ferrous ion concentration at the beginning, while at the later stage, the formation and precipitation of solid iron carbonate will consume large amount of Fe²⁺, resulting in a

[§] Trade name.

decrease in ferrous ion concentration. With the use of resins, the ferrous ion concentration was maintained. It can be seen that ferrous ion concentration was always < 2 ppm over the course of the experiment. At 80 °C and pH 5.8, at saturation for iron carbonate the ferrous ion concentration should be about 6 ppm.¹¹ Therefore, with the stable solution chemistry system in place, the solution remained undersaturated and no formation of iron carbonate was expected.

Figure 6 shows the solution pH vs. time during the corrosion of X65 in CO₂ purged 1 wt.% NaCl solution with and without the stable solution chemistry system. It was found that without the use of resins, the solution pH first increased and then decreased, closely following the change of ferrous ion concentration. With the use of resins, the solution pH during the whole test period was maintained around the pH 5.8± 0.02 as shown in Figure .

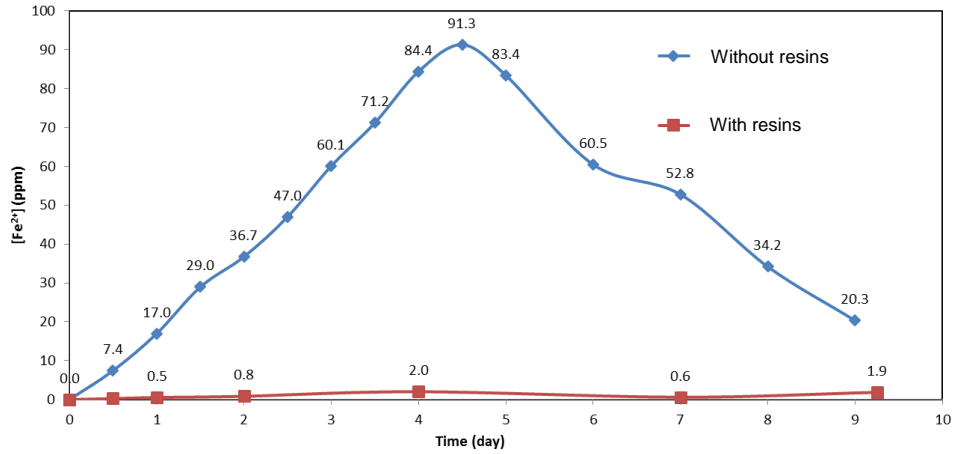


Figure 5: The ferrous ion concentration as a function of time during the corrosion of mild steel. (API 5L X65, 1 wt.% NaCl solution, 80 °C, initial pH 5.8, pCO₂ = 0.53 bar, 400 g K-form resin was used in the control of ferrous ion concentration.)

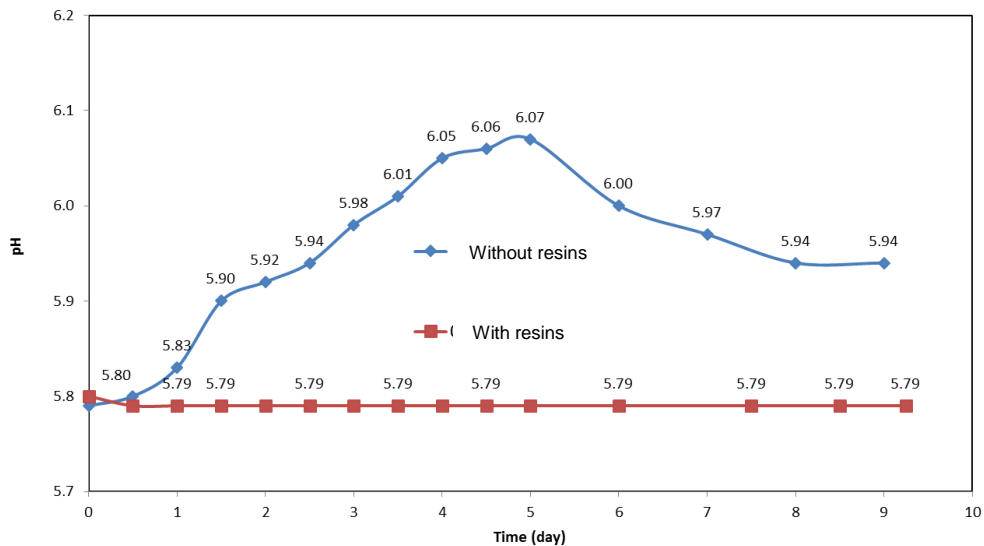


Figure 6: The solution pH as a function of time during the corrosion of mild steel. (API 5L X65, 1wt.% NaCl solution, 80 °C, initial pH 5.8, pCO₂ = 0.53 bar, 60 g H-form resin was used in the control of ferrous ion concentration.)

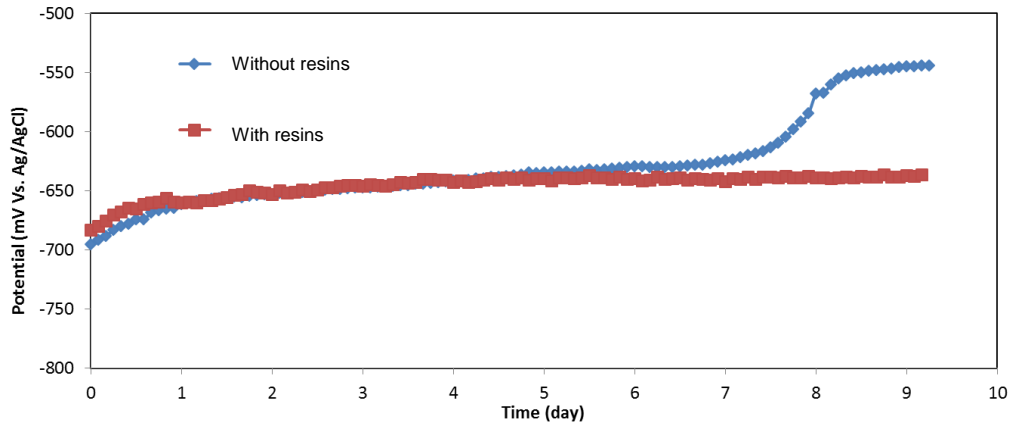


Figure 7: The corrosion potential (vs. Ag/AgCl) as a function of time during the corrosion of mild steel. (API 5L X65, 1 wt.% NaCl solution, 80 °C, initial pH 5.8, $p\text{CO}_2 = 0.53$ bar. With the stable solution chemistry system, 400 g K-form resin and 60 g H-form resin were used.)

Figure 7 shows the corrosion potential change during the corrosion of X65 in CO_2 purged 1 wt.% NaCl solution with and without the use of resins. The corrosion potential increased over the course of the first week. In the absence of water chemistry control by the resins, after about a week the corrosion potential suddenly increased from about -620 mV (vs. Ag/AgCl) to more than -550 mV (vs. Ag/AgCl) in about 24 hours due to the formation of a protective iron carbonate layer on the surface of specimen. With the stable solution chemistry system in place (use of resins), corrosion potential did not change much during this time.

Figure 8 shows the corrosion rate vs. time of X65 in CO_2 purged 1 wt.% NaCl solution at 80 °C and initial pH 5.8. Without the use of resins, the corrosion rate first increased and then decreased sharply after about a week, with the final corrosion rate < 0.4 mm/y. This sharp decrease in corrosion rate is attributed to the formation of a protective iron carbonate layer on the specimen surface, hindering corrosion. When ferrous ion concentration was maintained close the 0 ppm by the resins, the corrosion rate also increased initially and then was rather stable with an average value of 8-9 mm/y. This clearly indicates that no protective layer was formed on the specimen surface.

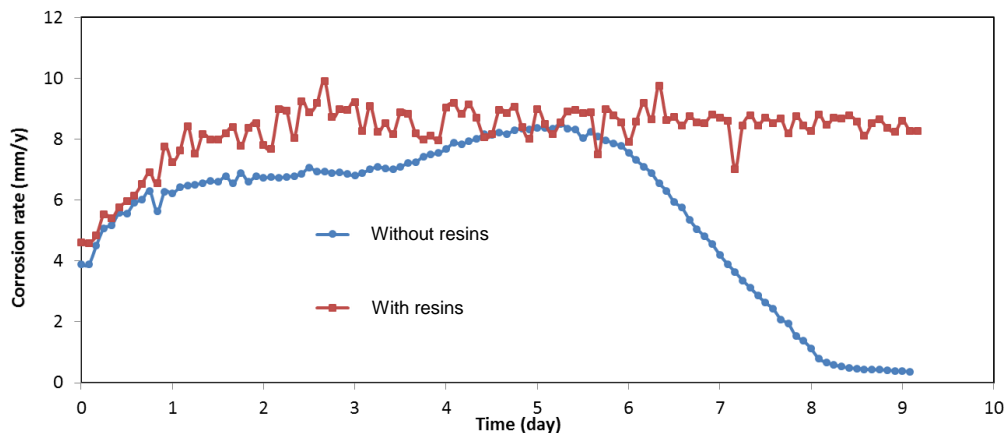


Figure 8: The corrosion rate as a function of time during the corrosion of mild steel. (API 5L X65, 1 wt.% NaCl solution, 80 oC, initial pH 5.8, $p\text{CO}_2 = 0.53$ bar. With the stable solution chemistry system, 400 g K-form resin and 60 g H-form resin were used.)

After 220 hours of testing, the specimen surface and the cross section were examined by using SEM. It is seen that a dense prism-shaped iron carbonate crystals formed on the surface of the steel specimen in the solution without the use of resins (Figure 9a and Figure 9b). According to the cross section, this formed layer was compact and totally covering the substrate surface, indicating a very good protectiveness (Figure 9c). This is consistent with the electrochemical results, which show a very low corrosion rate in the later stages of the test.

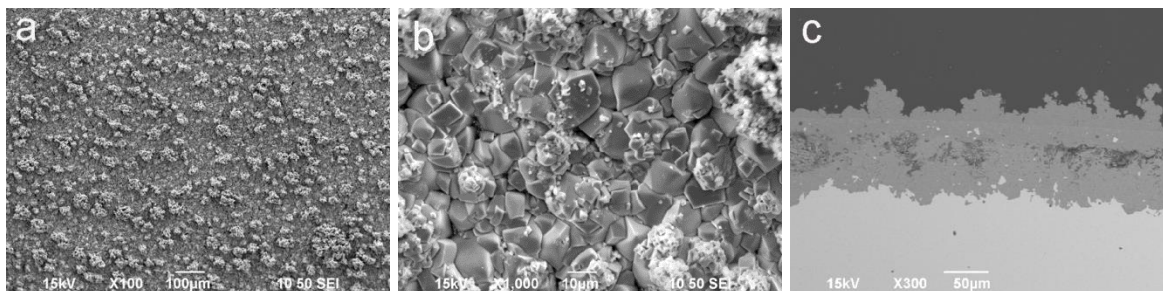


Figure 9: SEM images of (a) and (b) surface and (c) cross section taken at the end of the test, 0 ppm Fe^{2+} , without the stable solution system. (API 5L X65, 1 wt.% NaCl solution, 80 °C, initial pH 5.8, $\text{pCO}_2 = 0.53$ bar.)

In the experiment where a very low ferrous ion concentration was maintained by the use of resins, the SEM images of corroded surface and cross section are quite different. No iron carbonate crystals can be seen on the surface (Figure 10a and Figure 10b) as the solution was undersaturated. The observed layer is most likely iron carbide – which is the uncorroded portion of the mild steel. It also appears that the adhesion between the steel substrate and this corrosion product layer is not good, and an obvious gap can be observed in the cross section image (Figure 10c). The images of the steel specimen surface and cross section confirm that when the ferrous ion concentration is maintained very close to zero, the formed corrosion product layer does not lead to effective protection.

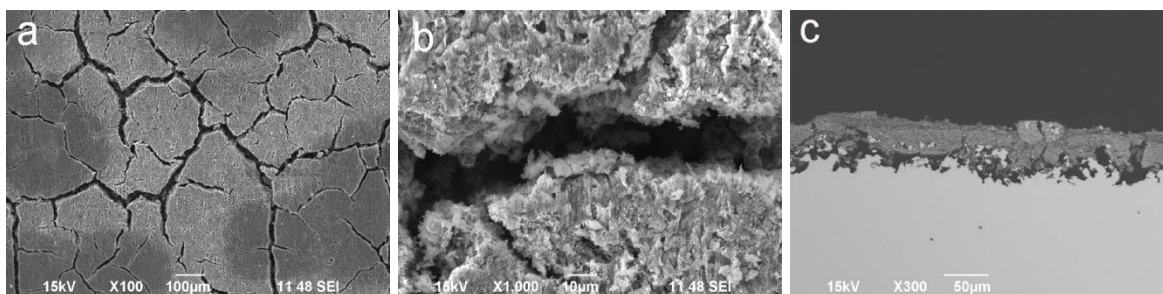


Figure 10: SEM images of (a) and (b) surface and (c) cross section taken at the end of the test, 0 ppm Fe^{2+} , with the stable solution system. (API 5L X65, 1 wt.% NaCl solution, 80 °C, initial pH 5.8, $\text{pCO}_2 = 0.53$ bar.)

CONCLUSIONS

A stable solution chemistry system for small scale corrosion experiments has been developed in this work. The selection of suitable resins, construction of control loops and study the corrosion behavior of mild steel with and without this stable solution chemistry system have been conducted. The following conclusions have been drawn:

- 1) This stable solution chemistry system can be successfully used to control the solution pH and ferrous ion concentration during the corrosion in the small scale lab experiments.
- 2) H-form resin can be employed to control the solution pH during the corrosion of mild steel. The change in solution pH can be automatically controlled within ± 0.02 pH units.
- 3) K-form resin can be used to control the ferrous ion concentration during the corrosion of mild steel in CO₂ purged 1 wt.% NaCl solution. The change in ferrous ion concentration can be controlled within ± 3 ppm.
- 4) A large difference in corrosion behavior is seen in two nominally identical tests, one with and the other without the stable solution chemistry system in place. Without the stable solution chemistry system, the corrosion rate first increased and then decreased to very low values (<0.2 mm/y) what can be attributed to the formation of a compact iron carbonate layer on the specimen surface. The measured pH, ferrous ion concentration, potential and SEM images all corroborate these findings. Without the stable solution chemistry system in place, the corrosion rate first increased slightly and then remained stable at an average value over 9 mm/y. After the experiment, no iron carbonate was observed as the formed corrosion product layer did not provide adequate protection for the steel substrate.

ACKNOWLEDGEMENTS

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