

Experimental Evaluation of Corrosion Modeling on Carbon Steel in Sub-critical and Supercritical CO₂ Environments

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Abstract

This study is aimed to compare the corrosion rate predictions obtained from CO₂ corrosion models with experimental results on mild carbon steel (C1018) exposed in brine solutions in both sub-critical CO₂ and supercritical CO₂ (SC-CO₂) environments. Corrosion behavior of mild carbon steel is investigated by immersing in a still 1 wt.% NaCl solution at temperatures from 60 – 120°C in both 400 psi (Sub-critical CO₂) and in 1600 psi (Supercritical CO₂), respectively. The experimental results are evaluated by comparing with the CO₂ corrosion calculation algorithms developed by Anderko et al. The corrosion mechanism kinetics are studied by Linear Polarization Resistance (LPR) and Electrochemical Impedance Spectrum (EIS). Surface morphology, element distributions on the surface, and crystal structures of the mild carbon steel are evaluated. The results indicate that the corrosion rate of C1018 in the sub-critical environment at steady state in the LPR measurement showed higher corrosion rate than its theoretical value at high temperature, whereas the corrosion rate of C1018 in supercritical environment at steady state was found to decrease with the temperature and was found consistently lower than the predicted value.

Keywords: Supercritical CO₂, mild carbon steel, CO₂ corrosion, ferrous carbonate (FeCO₃)

INTRODUCTION

CO₂ corrosion is one of the main corrosion mechanisms paid with great concern in the Oil and Gas industry ¹. This type of corrosion is commonly found in fields related to carbon capture and storage (CCS), enhanced-oil recovery (EOR), deep water oil and gas applications, and refineries as a high amount of CO₂ gas is frequently injected to reservoirs to increase the longevity of oil fields. In these fields, the environment is usually maintained dry to prevent corrosion attack from water as the existence of water would rise high risk of corrosion damage. Hence, the effect of water plays an important role in the severity of corrosion in the co-existence of CO₂ gas, especially in supercritical CO₂ (SC-CO₂) condition.

It is well-known that CO₂ gas itself is not corrosive unless a relative humidity of water is involved with the existence of CO₂ gas ². Hence, sufficient water removal is required to fulfill

before the pipelines are used for CCS, EOR, and so on as a small amount of water is tricky enough to cause serious corrosion damage on the pipelines and shorten their longevity. When water is present in a system, CO₂ gas dissolves into water and combined with water molecule, leading to the formation of carbonic acid (H₂CO₃), which lowers the pH of a solution and makes the material of interest susceptible to corrosion attack.

In the past decade, more research interest is enabled to focus on studying corrosion behavior on pipeline materials in liquid or supercritical CO₂ phase with the availability of novel technologies and facilities than before. Carbon steel, undoubtedly, is one of the most popular materials used for multiple purposes due to its availability, great balance of ductility and strength, and cost-efficiency. Among all the carbon steel materials, API 5L X65 carbon steel³⁻⁶, a high strength low carbon material, was studied for its corrosion behavior with great interest in supercritical CO₂ environment as it has been broadly used in CCS because of its excellent corrosion-resistive ability from being corroded in harsh environment, or API 5CT L80 carbon steel was studied in water-saturated supercritical CO₂ phase regarding the effect of temperature and pressure⁷, and the effect of different water cuts in a flowing condition⁸.

Modeling used to accurately predict CO₂ corrosion in dense liquid phase of CO₂ gas or supercritical CO₂ state has developed since 1990s^{9,10}. Starting with the “worst case” corrosion rate prediction - the deWaard-Milliams equation, it was widely accepted to predict the corrosion rate of carbon steel in environment full of CO₂. Waard⁹ introduced several correction factors that could quantitatively verify effects caused by corrosion product scale and environmental factors including temperature, pressure, condense water phase, and more. Among all the factors, temperature is profound in high temperature environment as it has the direct impact on surface morphology of protective corrosion product film like FeCO₃ or Fe₃O₄ at 60°C and up, further decreasing the corrosion rate in the system.

In 2000, Anderko^{11,12} developed a comprehensive model that was used to simulate the effect of FeCO₃ on general corrosion of iron and carbon steel by combining thermodynamic prediction and electrochemical simulation found on the mixed-potential theory. The effect of the protective corrosion film scale shouldn't merely be explained based on the surface reactions between the carbon steel and the active bulk solution as it contains the formation scale of FeCO₃ corrosion product on the surface, and the dissolution of iron ion and the iron precipitate in the solution. Both the experimental and simulated results show consistent that the effect of temperature tremendously influenced the solubility of FeCO₃ in water, which decreased with increasing temperature, and the enlarged protectiveness of FeCO₃ scale with increase in temperature. Nonetheless, it is important to clarify that the precipitation of solid iron in solution is not necessarily equivalent to the formation of FeCO₃ corrosion product adhered on the steel surface, but the ratio of the FeCO₃ formation to the iron precipitate could decide the protective scale of FeCO₃ corrosion product, which leads to the FeCO₃ coverage fraction on the steel surface. By far, this comprehensive model is the only one available to simulate CO₂ corrosion of supercritical CO₂ condition, covering the effect of temperature, pressure, flow rate, thermodynamic prediction and electrochemical kinetics of each possible chemical reaction.

The objective of this study focused on comparing corrosion rate predictions of CO₂ corrosion, which was simulated by the state-of-the-art CO₂ corrosion model developed by Anderko, with experimental results on mild carbon steel in brine solution for both sub-critical and SC-CO₂ environments. The experimental conditions were set up at 60°C, 80°C, 100°C, and 120°C, and in 400 psi for sub-critical CO₂ condition and in 1600 psi for SC-CO₂ condition, respectively, to monitor in-situ corrosion behavior of mild carbon steel using LPR and EIS. Surface morphology

and element distribution of the formed layer on the steel was examined via SEM and EDS, and crystal structure of it was analyzed by XRD and XPS.

EXPERIMENTAL APPROACH

Experimental Preparation, Equipment, and Operation of Mild Carbon Steel

Experimental design

Overall, this study targeted on measuring the real corrosion rate on mild carbon steel in brine solution for sub-critical and water-saturated supercritical CO₂ conditions, and compare with theoretical values at 60°C, 80°C, 100°C, and 120°C. To do that, the sub-critical and supercritical CO₂ environments were created using an autoclave system where 2.8 liters of 1 wt.% NaCl solution was pulled in before sealing with a lid attached with a three-electrode pole. After sealing and purging with N₂ gas, the real-time corrosion behavior of the mild carbon steel was monitored by LPR and EIS. Microstructure, element distribution, chemical composition, and electronic structure of the mild carbon steel were analyzed by SEM, EDS, XRD, and XPS, respectively, after the specimens were taken out from the autoclave system. More details about experimental information are elaborated below.

Materials Sources

Due to economic efficiency and widespread acceptability in the Oil & Gas industry, mild-low carbon steel (C1018) was selected to study the corrosion behavior in both the sub-critical CO₂ and supercritical CO₂ environments in this study. C1018 is a commercial material and well-known that it represents a good balance of toughness, strength, and ductility. In addition, it has excellent weldability and can produce a solid and uniform product easily. The chemical composition of mild-low carbon steel consists C (0.14 – 0.2% in weight), Fe (98.81 – 99.26%), Mn (0.6 – 0.9%), P ($\leq$ 0.04%), and S ($\leq$ 0.05%). The C1018 was a cylindrical coupon dimensioned using 43.688 mm x 6.35 mm (1.72 inch x 0.25 inch) and finished with a centerless ground.

Testing Equipment

In order to process the study in the supercritical condition successfully, an autoclave system was employed for all tests. The autoclave system was composed of a 4-liter autoclave, a three-electrode system for conducting electrochemical testing, A booster pump was used to bring the pressure to supercritical level. A heating pad was wrapped around the autoclave body to increase the temperature to 60°C, 80°C, 100°C, and 120°C. A thermometer, pressure monitor, and draining outlet were installed at the bottom side of the autoclave.

Experimental Procedure

Each test included two carbon steel specimens; one was examined with Linear Polarization Resistance (LPR) to calculate the corrosion rate in both sub-critical and supercritical CO₂ environments, and the other specimen was performed with Electrochemical Impedance Spectroscopy (EIS) on it to study the kinetics of corrosion behavior. Prior to the test, all specimens were polished mechanically with 400, 600, and 800 grit silicon carbide (SiC) sandpapers respectively, and then were degreased and cleaned with acetone, ethanol and deionized water (DI water) step by step.

A probe of the three-electrode system was used for the electrochemical testing in the autoclave with the carbon steel sample as working electrode (WE). Hastelloy C-2000 alloy (UNS N06200), was used as the counter electrode (CE) and a tungsten/tungsten oxide was employed as the reference electrode (RE). The autoclave was filled up to 2.8 L of fluid, with a solution containing sodium chloride (NaCl) was 1% (%w/w) for conducting the electrochemical testing.

To remove air bubbles from the solution, a research grade nitrogen (N₂) cylinder with 99.9999% purity was used to de-aerate the autoclave for 1 hour in the process of increasing the temperature to 60°C. A research grade of carbon dioxide (CO₂) cylinder with 99.9995% purity was followed to clear the nitrogen out for 10 minutes before the pressurizing process started.

After the temperature was increased to the value of interest, which was set to 60, 80, 100, and 120°C respectively, the high-purity CO₂ gas was injected to increase the pressure in the autoclave vessel. The pressure was targeted at 2.75 MPa (400 psi) for the sub-critical environment and 11.03 MPa (1600 psi) for the supercritical environment.

All the specimens were processed for 72 hours, and the specimens were taken out one day later after the autoclave vessel was cooled down for analyses of X-ray Diffraction (XRD), Scanning Electron Spectroscopy & Energy Dispersive Spectroscopy (SEM & EDS), and X-ray photoelectron Spectroscopy (XPS).

Electrochemical measurements

Electrochemical Impedance Spectroscopy (EIS) and Linear Polarization Resistance (LPR) were employed as electrochemical measurements to study corrosion behavior. Open Circuit Potential (OCP) testing was grouped in the series of testing to monitor the steady state of the potential for 30 minutes first before the EIS measurement started. It was applied for both the EIS and LPR testing. The EIS measurement was set up with 10 mV AC perturbations vs. the open circuit potential and in the frequency from 100k Hz to 0.01 Hz. The Linear Polarization Resistance (LPR) was scanned from -0.005 V to 0.005 V vs. the OCP at a scanning rate of 0.1 mV/s.

All specimens, prior to any further material analysis, were cleaned with anhydrous ethanol and de-ionized water after the autoclave test was finished. The final step to store them was to dehydrate them with high purity nitrogen gas.

RESULTS and DISCUSSION

Morphology and Microstructure Characterization

Characterization of Formed Layers in Sub-critical CO₂ condition

Iron-oxidized corrosion products were generated on the surface of the cylindrical carbon steel specimen after the specimen was sealed and processed in both sub-critical and supercritical CO₂ environments for 72 hours. In macro level, the corrosion products were loose and could be easily removed from the surface of the carbon steel specimen at 60 and 80°C. The structure of the corrosion products became more condensed after the temperature was increased beyond 95°C at which temperature a phase transition of iron-oxidized product was expected in low acidic environment with brine solution.

Figure 1 showed surface morphology of the cylindrical carbon steel specimen after it was processed in the sub-critical CO₂ condition at (a)60°C, (b)80°C, (c)100°C, and (d)120°C. The SEM images showed that at all temperatures solid squarish corrosion products were produced on the surface of the specimen in the sub-critical CO₂ environment. At 60°C, the corrosion products were generated but not sound. As the temperature was increased to 80°C, the corrosion products became more integrated with clear edges and boundaries. When the temperature was increased to 100°C, the grain size of the corrosion products was certainly enlarged to over 8 μm , but the size of each grain was not consistent.

Figure 2 shows chemical composition of the corrosion products on the surface of the cylindrical carbon steel specimen at 60, 80, 100, 120°C, respectively, in correlation of the SEM images above. The types of elements in every corrosion product at all temperatures is mainly

composed of carbon, iron, and oxygen, whereas a fair amount of molybdenum was also shown at 100 and 120°C. The plausible reason that could explain this unexpected phenomenon was contamination from the autoclave vessel body, which in this case was composed of Hastelloy C-2000 alloy (UNS N06200). The net amount of each element of the corrosion products were found to be where C 23.65%, Fe 55.95%, and O 20.39% were contained at 60°C. At all temperatures, the amount of carbon element in the corrosion products was remained consistent with less than one order of fluctuation. In addition, oxygen seemed to decrease from 55.95% to 45.35% as the temperature increased. On the other hand, iron increased to 31.34% from 20.39% when the temperature rose.

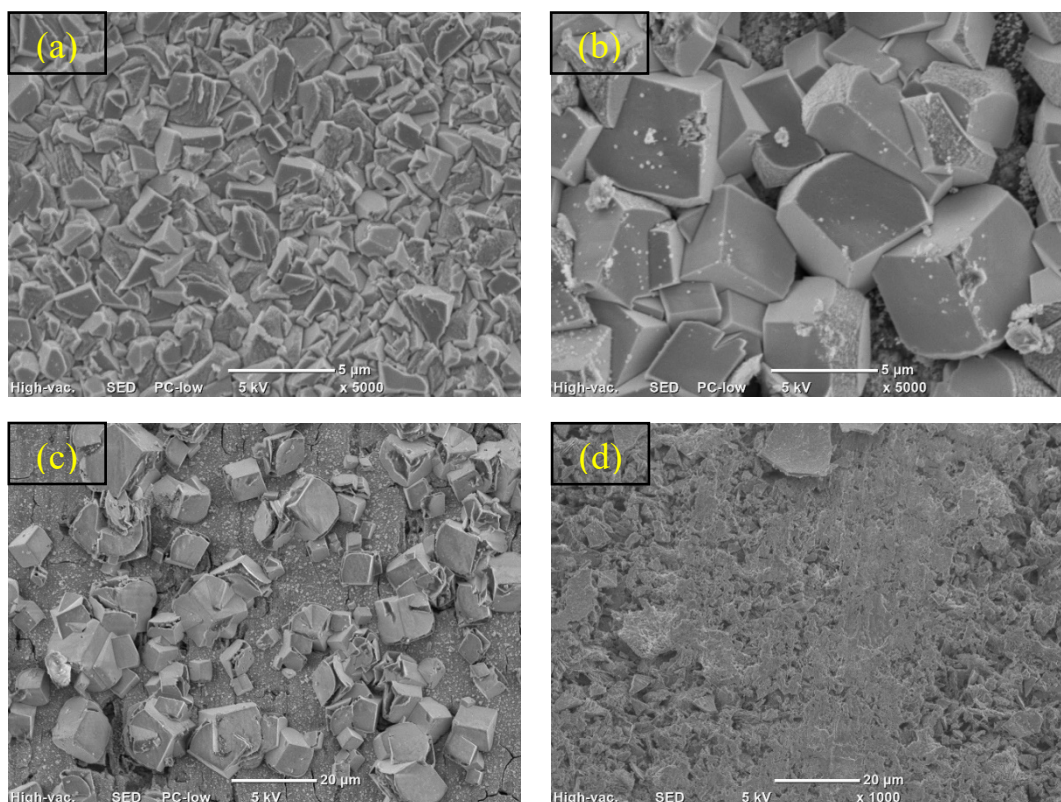


Figure 1: Surface morphology of SEM images of iron oxide corrosion product processed in a sub-critical CO₂ gas environment at 60°C, 80°C, 100°C, and 120°C, respectively.

Energy-Dispersive Spectroscopy of the Corroded Products in Sub-critical CO₂ condition

