

Electrochemical and Morphological Investigation of Corrosion Behavior of C1018 in a Subcritical and Supercritical CO₂ Environment with Presence of H₂S

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ABSTRACT

The corrosion behavior of a C1018 carbon steel in supercritical CO₂ environment with different amount of H₂S (5 ppm-200 ppm) was investigated in both *ex-situ* morphological analysis and *in-situ* electrochemical methods. The corrosion rates were measured using both linear polarization resistance (LPR), weight loss method and electrochemical impedance spectroscopy (EIS), at temperatures from 60°C up to 120°C with an interval of 20°C, the experiments were performed at 400 psi (sub-critical) and 1600 psi (supercritical) of CO₂ partial pressure. The corroded surfaces and the corrosion products were analyzed using various techniques, including scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS), and X-ray Diffraction (XRD). The results show that the slight presence of H₂S in a supercritical CO₂ environment plays an insignificant role in terms of the observed corrosion rates. The types and the thickness of corrosion products changed as temperature increased. Under the effect of time, the corrosion rates decreased with exposure time gradually due to the formation of corrosion products.

Key words: Supercritical CO₂ corrosion, Subcritical CO₂ corrosion, H₂S, Iron sulfides.

INTRODUCTION

Supercritical CO₂ storage has been gaining more attention due to its wider application. It is one of the desirable solutions for reducing CO₂ emission, which is an important contributor to the global climate crisis. In other cases, some of the early applications were focused on the oil and gas industry, by using supercritical CO₂ to sequence the mature wells for better production [1],[2]. In those environments, C1018 carbon steel was extensively used, due to its good balance of toughness, strength, and ductility as well as its excellent weldability. However, C1018 is not known to be rather corrosion resistant. Moreover, corrosion can be severe in a supercritical CO₂ system, which can reach high temperature (up to 150°C) and high pressure (1000MPa) range and sometimes contain H₂S. Therefore, the corrosion behavior can be the biggest challenge to the fitness of C1018 steel in the oil and gas supercritical CO₂ environment.

Due to the significant existence of CO₂/H₂S in the production of oil and gas and its notorious role in the corrosion of carbon steels, many researchers had investigated corrosion behavior, kinetics, and materials microstructure of carbon steels in a CO₂/H₂S environment by various techniques. As a result, many models have been established to simulate corrosion behavior under different environments[3],[4]. However, most of the effort is made for sub-critical environment, instead of supercritical environment. Additionally, many factors limited the understanding of supercritical CO₂ corrosion in with the presence of H₂S. The environment is more complex, with multiple chemical/electrochemical reactions occur at the same time and different corrosion products formed at the surfaces [5]. In addition, because the complicated phases and extra harsh testing environment, traditional in-situ electrochemical testing may not work properly. Therefore, most of the research on super-critical CO₂ corrosion was ex-situ weight loss method. As a result, the information obtained in such test is rather limited.

In the author's earlier effort [6], a tungsten/tungsten oxides electrode was developed as a stable reference electrode to perform electrochemical test at a harsh environment. Therefore, it is expected to obtain more insight to the corrosion behavior of carbon steel in a supercritical CO₂ with presence of H₂S. In the current research, the corrosion behavior of a C1018 carbon steel is investigated using both in-situ electrochemical test (LPR and EIS) and ex-situ weight loss method. The effect of temperature and amount of H₂S was studied in water-saturated sub-critical and super-critical CO₂ systems. The surfaces of steel coupons were examined and analyzed by various techniques, including SEM/EDS, XRD.

EXPERIMENTAL

Materials and its preparation

In the current research, the tested material is an AISI C1018 carbon steel. Its chemical composition can be found in Table 1.

Table 1. Chemical composition of C1018

Element	C	Mn	P	S	Fe
Concentration/%	0.14-0.2	0.6-0.9	≤0.04	≤0.05	Balance

The steel was machined into cylindrical shape with a height of 1.72" (4.37cm) and a diameter of 0.25" (0.635cm). The samples were polished with 200, 400, 600, 1000 grit sand paper, progressively. After that, the samples were immersed and ultra-sounding in acetone. Later, the samples were rinsed with alcohol and water consequently so that the surfaces are uniform and

oxides-free. Finally, the samples were dried with N₂ and kept in a vacuum container before experiment.

Experimental procedures and matrix

The autoclave body was rinsed with testing solution (1 wt.% NaCl) prior to test. Then the desired amount of solution was poured into the autoclave and purged with N₂ to remove oxygen dissolved in the solution. After two hours of purging, the freshly polished C1018 samples were mounted to the lid through threads and worked as working electrode. Hastelloy C-2000 alloy (UNS N06200), was used as counter electrode (CE) and a tungsten/tungsten oxide was employed as the reference electrode (RE). After that, the lid was installed properly and the system was purging with CO₂ to further remove N₂. The different amounts of acids were added after this step. Here, notice that the H₂S was generated through in-situ chemical reaction between Na₂S and acids. The required amount of Na₂S and acids (HCl and HAc) were calculated through OLI software according to different testing environment (desired temperature and H₂S content).

After the temperature was increased to the desired temperatures, which were 60, 80, 100, and 120°C respectively, the high-purity CO₂ gas was injected to increase the pressure in the autoclave vessel through a booster pump. 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. Once the desired condition was achieved, electrochemical tests were started, including OCP and EIS. 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 XRD, SEM and EDS. All specimens, prior to any further 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.

The purpose of current research is to understand the effect of H₂S concentration and temperature on the corrosion behavior of C1018 at subcritical and supercritical conditions. Therefore, the test matrix is summarized as in Table 2.

Table 2. Testing matrix

Parameters	Description			
Temperatures/°C	60	80	100	120
H ₂ S concentration/ppm	5	50	100	200
CO ₂ pressure/psi	400 (Water-saturated sub-critical CO ₂ condition)		1600(Water-saturated supercritical CO ₂ condition)	
Electrolyte	1 wt.% NaCl			
Testing methods	Weight loss, OCP, EIS.			

RESULTS AND DISCUSSION

Effect of temperature and CO₂ pressure

Figure 1 shows the corrosion rates of carbon steel measured by the weight loss method after exposure in a subcritical/supercritical CO₂ environment at (a) 60°C, (b) 80°C, (c) 100°C, and (d) 120°C for 2 days. With all H₂S concentrations (5 ppm, 50 ppm, 100 ppm, and 200 ppm), the

trend of the corrosion rates on carbon steel were similar for all tested temperatures; the corrosion rates reached their maximum at 100°C and then decreased at 120°C with 5 ppm, 50 ppm, and 200 ppm of H₂S gas, except for the corrosion rate with 100 ppm of H₂S which still increased as the temperature rose to 120°C.

Additionally, the corrosion rates were compared in subcritical and supercritical conditions. With 5 ppm of H₂S, the corrosion rates on C1018 in the sub-critical CO₂ environment were higher than the ones in the supercritical CO₂ environment at low temperatures (60°C and 80°C) where the corrosion rates are reversed at higher temperatures (100°C and 120°C), as shown in Figure 1(a). It was suggested that the addition of 5 ppm H₂S helped lower down the corrosion rate in the supercritical CO₂ environment at low temperatures but at higher temperatures the effect of temperature still outweighed the low H₂S concentration as a more dense form of iron carbonate occurred at 95°C [6]. The corrosion rates of C1018 in the supercritical CO₂ environment were all lower than the ones in the sub-critical CO₂ environment at all temperatures, indicating that the H₂S concentration increasing to 50 ppm could be beneficial to the corrosion rate even at higher temperatures. However, with the presence of 100 ppm and 200 ppm of H₂S concentrations, the corrosion rates in the supercritical CO₂ environment were higher than the ones in the sub-critical CO₂ environment at all temperatures.

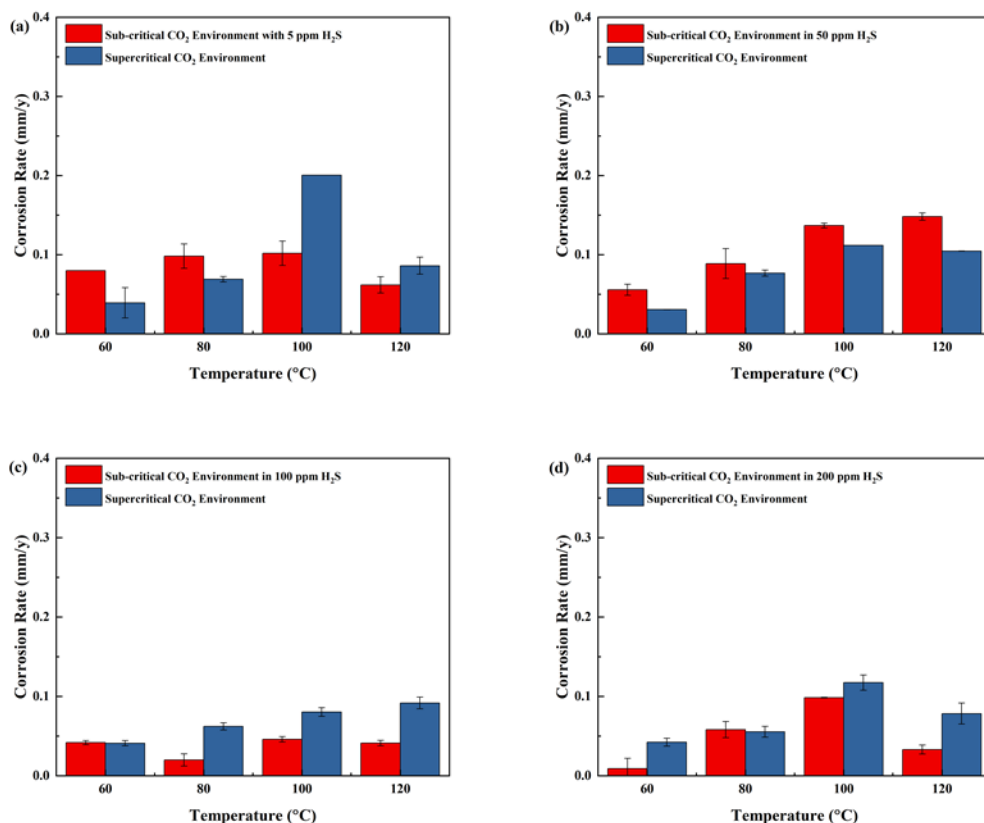


Figure 1. Corrosion rates of C1018 from Weight Loss method after exposed in the subcritical/supercritical CO₂ condition at 60°C, 80°C, 100°C, and 120°C with H₂S gas of (a)5 ppm, (b)50 ppm, (c)100 ppm, and (d)200 ppm for 2 days.

Figure 2 shows the XRD spectrums of C1018 after 2 days experiments in the supercritical CO₂ environment with the presence of 5ppm H₂S. It clearly shows that as the temperature increases, a series of phase transformations occurred from 80°C to 120°C. At 60°C and 80°C, the major