Corrosion Science 134 (2018) 149–161

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Flow dependence of steel corrosion in supercritical CO_2 environments with different water concentrations

An Qing Liu[a,b], Chen Bian[a,b], Zi Ming Wang[a,*], Xia Han[a], Jian Zhang[a]

[a] Sinopec Energy and Environmental Engineering Co., Ltd., No. 49 Jinan Road, Dongying 257026, PR China
[b] College of Science, China University of Petroleum (Beijing), No. 18 Fuxue Road, Beijing 102249, PR China

ARTICLE INFO

Keywords:
A. Mild steel
B. SEM
B. Weight loss
C. CO_2 corrosion
C. Interfaces

ABSTRACT

The corrosion behavior of mild steel in water contaminated supercritical CO_2 fluids was investigated by weight-loss measurements and surface morphology observations. It is found that a higher flow rate induces a higher corrosion rate in various water containing conditions, which becomes much obvious with increasing the water concentration. By a detailed comparison of the surface corrosion morphologies formed in different supercritical CO_2 fluids, the flow dependence is attributed to a mechanism of water droplet entrainment and its impact on steel surfaces. This observation is helpful for the understanding and the control of steel corrosion in CO_2 transportation and injection conditions.

1. Introduction

Carbon capture, utilization and sequestration (CCUS) is currently a feasible and economic method for reducing the greenhouse gas emissions. In recent years, a huge amount of CO_2 was captured from the industrial plants and injected into deep reservoirs for enhancing oil recovery or for the permanent carbon storage [1,2]. Pipeline was generally suggested to be the best choice for large-quantity, high-pressure CO_2 transportation [3]. Corrosion would happen when CO_2 meets water at steel surfaces, especially for the conditions of CO_2 transportation at a supercritical state where carbonate acid may form with very low pH values [4,5]. This may lead to a high risk of pipeline leakage [6]. Clearly, it is essential to evaluate the corrosion risk of CO_2 transportation and injection pipelines.

Absolutely dry CO_2 would not chemically or electrochemically corrode carbon steel at relatively low temperatures of CO_2 transportation and injection conditions. However, for long-term operation the occasional ingress of a limited amount of water in CO_2 transportation and injection pipelines is possible [6,7]. For the CO_2-enhanced oil recovery (EOR) production, CO_2 and water may be alternatively flooded into the injection wells. Residual water will be dissolved in the supercritical (SC) CO_2 phase gradually and the well tube would be periodically immersed in corrosive CO_2 fluids with different degrees of water saturation. Plenty of works have reported on the critical water concentration that may trigger corrosion in SC CO_2 conditions [4,8,9]. Generally speaking, corrosion would be very weak and practically acceptable if water concentration is well below the saturation limit in CO_2. It seems that both of the general corrosion and the localized attacks are highly dependent on the water concentrations. A higher water concentration induces a higher corrosion rate. Although it was found that molecular water solvated in SC CO_2 is very reactive to steel surfaces [7], these measured corrosion rates of mild steel samples in water bearing SC CO_2 are relatively small compared to the cases in high-pressure CO_2 saturated aqueous phase [6,10]. They are generally in a range from 0.01 mm/y to 1.0 mm/y depending on the experimental conditions [11].

Besides the degree of water ingress, many factors may affect the corrosion behavior of mild steel in SC CO_2 conditions. SO_x and NO_x were identified as the primary impurities that would greatly increase corrosion, because water may be easier to be precipitated on steel surfaces in the presence of these impurities [12–14]. Other impurities, such as H_2S and O_2, may also significantly affect the corrosion behavior of steels in SC CO_2 conditions [15]. A higher temperature and a higher pressure may result in more aggressive corrosion damages of steel surfaces in water saturated SC CO_2 phase [10,16]. However, it has pointed out that temperature drop [11] and pressure drop [4] in the pipeline system would increase the corrosion risk. In high-pressure CO_2-saturated aqueous fluids or SC CO_2–water mixed conditions, the measured corrosion rate was found to be very sensitive to flow rates, especially when the flow rate was higher than 1.0 m/s [4]. It presents an enhancement of corrosion with increasing flow rates, similar to that has observed in other aqueous fluids, which can be explained by a mechanism of the flow accelerated corrosion attack. However, there are very limited data on the corrosion behavior of steels in flowing SC CO_2

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[*] Corresponding author. Present address: College of Materials, Xiamen University, 422 South Siming Road, Xiamen 361005, PR China.
E-mail address: zmwang@xmu.edu.cn (Z.M. Wang).

https://doi.org/10.1016/j.corsci.2018.02.027
Received 10 October 2016; Received in revised form 10 February 2018; Accepted 16 February 2018

conditions. According to the production data in Shengli oilfield, the flow rates of CO_2 fluids can be varied from 0.05 m/s to 1.0 m/s as a function of the injection depth, owing to the changes of pressure and temperature along the depth from wellhead. For the CO_2 transportation pipelines, a higher flow rate was generally used to improve the operation efficiency [4]. Obviously, flow rate is an important factor in corrosion evaluation and pipeline design for the transportation and injection of CO_2.

Regarding the corrosion mechanism of pipeline steel in water-bearing SC CO_2 conditions, water condensation or precipitation on steel surface was generally viewed as the control process [5]. Water film or droplets may be formed on steel surfaces in a manner like the mechanism of water condensation during atmosphere corrosion [17]. It was believed that the variation of temperature and pressure near to the steel surface was essential for the condensation of water [5]. However, it should be noticed that pipeline corrosion in SC CO_2 fluids is quite different from that in a high-pressure natural gas phase, since the density of CO_2 phase is relatively high. In view of the mixing state, the water-containing SC CO_2 fluids might be similar to the crude oil-water mixtures, *i.e.*, water might be preferentially settled on the pipeline bottom from the mixtures other than condensed as water droplets on the top of pipelines. This assumption is consistent with the field observation of corrosion damages of CO_2 transportation pipelines, where internal corrosion always happens at the bottom of pipelines. It is noticed that the formation of a water-in-SC CO_2 emulsion is possible without the addition of surfactants [18]. One may be noticed from previous researches that the corrosion rates of mild steel in water saturated SC CO_2 conditions were closely relied on the degree of water super-saturation or the quantity of water entrainment [19,20]. It seems hard to explain these corrosion phenomena based on the water condensation mechanism in SC CO_2 conditions. It is still demanded to thoroughly understand the corrosion phenomena in water bearing SC CO_2 conditions.

The industrial background of our research is the CCUS project in Sinopec Shengli oilfield. A pilot scale CO_2-EOR project was started since 2007. Some corrosion problems have been observed in the whole oil production system, owing to the presence of high pressure CO_2 gas. Our purpose is to identify the corrosion risk and to mitigate the potential corrosion damages. Previously, most of the works were related to the corrosion control in oil production and oil transportation systems [21–23]. Corrosion risk analysis of the CO_2 transportation and injection systems is also highly demanded for ensuring the whole chain security of CO_2 EOR process. In this paper, the influence of water concentration and flow rate on steel corrosion in SC CO_2 fluids was systematically investigated, attempting to make an insight into the corrosion mechanisms in CO_2 transportation and injection conditions. According to the corrosion rate measurements and surface morphology observations, a flow dependence of steel corrosion was clearly presented and a corrosion mechanism in water bearing SC CO_2 fluids was proposed. Correlating the flow rate of SC CO_2 with corrosion phenomena is helpful for the corrosion control in CO_2 transportation and injection systems.

2. Experimental details

2.1. Materials and testing solution

The steel samples used in corrosion experiments were N80 steel with a composition of C: 0.36%; Si: 0.23%; Mn: 1.61%; P: 0.01%; S: 0.004%; Cr: 0.05%; Mo: 0.18%; Ni: 0.05; V: 0.002%; Cu: 0.11% and Fe balanced (in weight percentage). The steel surface was ground with 800-grit silicon carbide paper, rinsed with distilled water and acetone, and then dried gently with compressed air. Samples were weighted by an electronic balance with an accuracy of 0.1 mg and then stored in a desiccator before using for corrosion tests.

The composition of the aqueous solution was (0.1 mol NaCl + 0.01 mol $NaHCO_3$ + 0.01 mol $CaCl_2$)/L to mimic the produced water in the CO_2-EOR field condition. In Shengli oilfield, this brine solution may be directly used for periodic reinjection into the CO_2 wells.

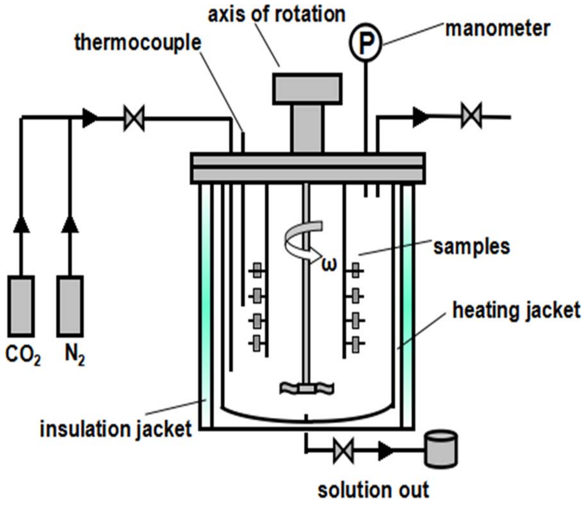

Fig. 1. Schematic illustration of the autoclave setup.

2.2. Weight-loss measurement

Weight-loss experiments were conducted in an autoclave with a maximum temperature of 150 °C and a highest pressure of 60 MPa. The autoclave was made up of C276 Nickel Alloy. Fig. 1 provides a schematic illustration of the experimental system. The entire system consists of an autoclave with 5.2 L in volume, a thermocouple, a CO_2 pump and a series of valves for CO_2 flow and liquid control. The inner diameter and the height of the autoclave are 15 cm and 29 cm, respectively. The length of stir shaft is 27 cm and the shape of autoclave bottom is an arc. Test specimens were prepared in a size of 50 mm (length) × 13 mm (width) × 1.5 mm (thickness) for each weight-loss experiment. The specimens were fixed on a non-conductive holder to avoid the galvanic coupling effect. Generally, six parallel specimens were tested in one experiment, where three were used for weight-loss measurements and the other three were used for surface morphology analysis. The autoclave was firstly cleaned with alcohol and finally wiped with acetone to remove the possible water adsorbed on autoclave wall. The brine solution was deaerated by CO_2 bubbling for 2 h and then introduced into the bottom of autoclave by a precise syringe at ambient pressure and temperature. At this stage, the autoclave was kept open and protected by flowing CO_2 gas. To generate different degrees of water saturation in SC CO_2 phase for different test conditions, the amount of the brine solution added to the autoclave was 2.4 mL, 4.8 mL, 9.6 mL and 24 mL, respectively. As can be seen from Table 1, these addition volumes can produce a series of water-saturated states. According to a previous literature [5], at the 10 MPa and 50 °C condition, the water saturation limit is about 4.3×10^{-3} in mole fraction. Therefore, the degree of water saturation can be estimated as listed in Table 1.

All lines connected to the autoclave were purged with CO_2 gas and

Table 1
The amount of aqueous solution added in autoclave in different test conditions.

Amount of water	Case 1	Case 2	Case 3	Case 4
Solution volume mL	2.4	4.8	9.6	24
Mole fraction	2.97×10^{-3}	5.95×10^{-3}	1.19×10^{-2}	2.97×10^{-2}
Degree of saturation	0.69	1.38	2.77	6.9

Notes: Autoclave volume 5.2 L; density of CO_2: 0.379 g/mL; water solubility in CO_2: 4.3×10^{-3} mol fraction (4300 ppm); The degree of saturation is relative to the solubility limit of water in CO_2.