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Effect of O_2 and H_2S impurities on the corrosion behavior of X65 steel in water-saturated supercritical CO_2 system

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ABSTRACT

The corrosion behavior of X65 steel in water-saturated supercritical CO_2 containing O_2 and/or H_2S impurities was investigated by means of weight loss measurements and surface characterization. The results showed that the addition of O_2 or H_2S impurities increased the corrosion rate of X65 steel in water-saturated supercritical CO_2 system. The effect of H_2S on the corrosion of X65 steel was greater than that of O_2. The corrosion was more severe with the coexistence of O_2 and H_2S. The change in corrosion behavior was attributed to the fact that low concentrations of O_2 and/or H_2S can notably change the corrosion mechanism.

1. Introduction

Global climate change caused by CO_2 emission has become increasingly prominent with the growing demand for fossil energy. Carbon capture and storage (CCS) is considered to be one of the important techniques to reduce CO_2 emission [1].

During the CCS process, the captured CO_2 is usually transported from the CO_2 source to the storage location via a safe, reliable and cost-effective method. In order to avoid two-phase flow regime and increase the density of CO_2, the captured CO_2 is typically compressed into a supercritical state or liquid state before being transported by pipelines [2,3]. However, due to the constraints of gas source, capture process and economic cost [4–7], it is inevitable that some impurities such as H_2O, O_2, SO_x, NO_x and H_2S will be found in the captured CO_2. Free water, once existing in the pipeline, will be saturated and acidified by CO_2 and cause the corrosion of pipeline steel. Relevant researches on the corrosion of CO_2 transmission pipelines in recent years are summarized in Table 1. As indicated in the table, no corrosion attack is detected in CO_2–H_2O system where the water content is low enough [8,9]. However, corrosion still occurs when impurities exist in the system. The presence of impurities such as O_2, SO_2 or NO_2, may increase the corrosion rate of carbon steel [6,8,11–17], and pose great risk to the security and stability of pipeline. Therefore, enough attention shall be paid to the internal corrosion of pipeline in the supercritical CO_2 system containing impurities, which probably constrains the development and application of CCS.

The present studies on the corrosion of supercritical CO_2 transmission pipeline mainly focus on several impurities such as O_2, SO_2 and NO_2, but the effect of H_2S on the corrosion behavior of pipeline steel has rarely been reported. Some CO_2 quality specifications on the limit of H_2S concentration in CO_2 are mainly made in the respect of health and safety concerns because of the high toxicity of H_2S [4]. It is well known that H_2S is an important factor that affects the corrosion of carbon steel in oil and gas fields [18,19]. Therefore, it is necessary to have a good study of the corrosion effect of H_2S, especially the coexistence of H_2S and other impurities, on supercritical CO_2 transmission pipeline.

The aim of this work is to understand the impact of O_2 and H_2S impurities on the corrosion behavior of X65 pipeline steel in water-saturated supercritical CO_2 system. To achieve this objective, the corrosion rate was determined through weight loss tests. The morphology and composition of corrosion scales were characterized by scanning electron microscope (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Accordingly, the corrosion mechanism of

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Table 1
Summary of corrosion research of CO_2 transmission pipeline in recent years.

Steel	Temperature (°C)	Pressure (MPa)	H_2O (ppm)	O_2 (ppm)	SO_2 (ppm)	NO_2 (ppm)	Corrosion rate (mm/y)	Reference
X65	25	10	500	0	0	0	No	[8]
X70	22	6.3	610	0	0	0	No	[9]
X70	22	6.3	998	0	0	0	Slight	[9]
X65	20	10	500	0	0	0	No	[10]
X65	50	4 – 8	Saturability	0	0	0	~0.2	[1]
X65	50	8	Saturability	0	0	0	0.38	[11]
X65	50	8	Saturability	0.33 MPa	0.08 MPa	0	>7	[11]
X65	25	10	500	0	500	1	0.02	[8]
X65	25	10	500	0	0	500	1.6	[8]
1010	45	7.58	1000	100	0	0	2.3	[12]
1010	45	7.58	1000	0	100	0	4.6	[12]
1010	45	7.58	1000	0	0	100	11.6	[12]
X65	50	8	650	0.33 MPa	0.08 MPa	0	3.7	[13]
X70	50	10	Saturability	1000	0.02 –0.2 MPa	0	0.2 – 0.9	[6]
X65	25	10	488	0	100–344	96 – 478	0.005 – 1.6	[14]
X70	50	10	RH:50 – 60%	1000	0.2 MPa	0	~0.1	[15]
X70	25 – 75	10	Saturability	1000	0.2 MPa	0	1.1 – 3.1	[16]
X52	60	10	500 – 1000	8100	70	100	0.004 – 0.0013	[17]

X65 steel in water-saturated supercritical CO_2 system containing O_2 and/or H_2S impurities was illustrated.

2. Experimental

2.1. Material and pretreatment

X65 pipeline steel, with a composition (mass fraction) of 0.06% C, 0.288% Si, 1.52% Mn, 0.012% P, 0.003% S, 0.048% Cr, 0.008% Ni, 0.178% Mo, 0.007% Cu, 0.057% Al, 0.031% V and Fe balance, was used in this test. The specimens were machined into a size of 40 mm × 20 mm × 3 mm. Before the tests, the working surface of each specimen was abraded with silicon carbide papers of decreasing roughness (up to 1000 grit), rinsed with deionized water, and degreased with acetone. After that, the specimen was weighed using an electronic balance to a precision of 0.1 mg, and then stored in a desiccator.

2.2. Weight loss test

Weight loss tests were carried out in a 3 L autoclave to investigate the corrosion rate and corrosion morphology of X65 steel in supercritical CO_2 system containing impurities. The test conditions are listed in Table 2. According to the literature [20], the solubility of H_2O in supercritical CO_2 is about 4600 mol ppm under the present experimental conditions, and the density of supercritical CO_2 is about 394 kg/m^3, as calculated through the equation of state for CO_2 formulated by Span and Wagner [21]. The results show that about 0.74 g water was dissolved in 1 L supercritical CO_2 under the test conditions. Thus, 10 g deaerated deionized water was added into the autoclave to ensure full moisture saturation of supercritical CO_2 during the tests. Four specimens were installed on the specimen holder (made of polytetrafluoroethylene (PTFE)) in the autoclave. After the autoclave was sealed, purging CO_2 was adopted to remove the oxygen for 2 h. After the autoclave was heated to 50 °C, the gas impurities were injected into the autoclave to a desired concentration. Then a booster pump was used to add CO_2 gas into the autoclave to reach a pressure of 10 MPa. All the tests were carried out under static conditions.

After each corrosion test, the specimens were respectively taken out of the autoclave, rinsed with deionized water, dehydrated with alcohol, and dried in the air. Three specimens were respectively descaled in the solution consisting of hydrochloric acid (100 mL, density is 1.19 g/mL), hexamethylene tetramine (5 g) and deionized water (900 mL) at room temperature, and then rinsed with deionized water, dehydrated with alcohol and dried in the air. After that, the specimens were weighed again to determine the weight loss. The corrosion rate was calculated through the following equation:

$$V_{CR} = \frac{8.76 \times 10^4 \Delta W}{S\rho t} \tag{1}$$

where V_{CR} is the corrosion rate, mm/y; $\triangle W$ is the weight loss, g; S is the exposed surface area of specimen, cm^2; ρ is the density of specimen, g/cm^3; t is the corrosion time, h; 8.76×10^4 is the unit conversion constant. The corrosion rate with error bars was averaged from the corrosion rates of the three parallel specimens.

2.3. Characterization of corrosion scales

The surface morphology and elemental compositions of the corrosion scales on specimen surface were analyzed using SEM and EDS with a scanning voltage of 15 kV. The phase compositions of the corrosion scale were identified by using XRD with a Cu Kα X-ray source operated at 40 kV and 150 mA, and the surface chemistry of the corrosion scales were also measured by using XPS with an Al Kα (hv = 1486.6 eV) X-ray source.

3. Results

3.1. Corrosion rate and corrosion morphology

Fig. 1 shows the effect of O_2 and H_2S on the average corrosion rate of X65 steel in the water-saturated supercritical CO_2 environment. It can be seen that the corrosion rate was only 0.0037 mm/y in the water-saturated supercritical CO_2 system. The corrosion rate increased from 0.0037 mm/y to 0.0066 mm/y with the addition of 2000 ppmv O_2, and increased by about 15 times (0.0551 mm/y) with the addition of 2000 ppmv H_2S. However, the corrosion rate increased dramatically to 0.3396 mm/y (by about 92 times) with the addition of the mixture of 2000 ppmv O_2 and 2000 ppmv H_2S. This indicated that a low concentration of O_2 or H_2S impurities had a great impact on the corrosion of X65 steel in water-saturated supercritical CO_2 system.

See Fig. 2 for the macroscopic morphology of X65 steel after being corroded for 240 h in water-saturated supercritical CO_2 system containing different impurities. It can be seen that the corrosion characteristic of X65 steel is closely related to impurity types. X65 steel was locally covered with a small amount of black corrosion products in supercritical CO_2–H_2O system (Fig. 2a), while a very thin layer of rust was formed on the steel surface when O_2 was added into the system (Fig. 2b). In contrast, the steel surface was completely covered with grey corrosion scales (Fig. 2c) when