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Synergistic effect of O_2, H_2S and SO_2 impurities on the corrosion behavior of X65 steel in water-saturated supercritical CO_2 system

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ABSTRACT

The synergistic effect of O_2, H_2S and SO_2 impurities on the corrosion behavior of X65 steel corrosion was evaluated in the water-saturated supercritical CO_2 system. Weight loss measurements showed that the synergistic effect of multiple impurities significantly increased the corrosion rate of steel. Surface characterization of corrosion scales using SEM, EDS and XRD showed that low concentrations of impurities notably changed the characteristics of corrosion scales. The interactions among O_2, H_2S and SO_2 resulted in additional formation reactions of elemental sulfur, sulfuric acid and water and consequently accelerated the corrosion of steel consistent with the high synergistic interaction impact factors.

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1. Introduction

Global climate change caused by CO_2 emission has become increasingly prominent with the growing demand for fossil energy. Emissions from fossil fuel-fired power plants and other industrial processes constitute a great source of the greenhouse gas CO_2. Carbon capture and storage (CCS) is considered to be an important technique to alleviate global warming [1,2]. The CCS process includes: Capturing CO_2 from industrial and energy-related sources (e.g., coal-fired power plants, cement production, refineries), transporting CO_2 (e.g., pipeline, shipping) to storage locations (such as oil and gas fields, coal seams, deep saline formations and deep ocean), where CO_2 is stored for long-term isolation from air [3]. Transmission of CO_2 is a vital part of CCS process [4]. It was estimated that, by 2050, about 10 Gt/year of CO_2 needs to be transported for geological storage to alleviate global climate change [5]. Carbon steel pipelines are considered to be the most cost-efficient solution for transmitting large quantities of CO_2 over moderate or long distances [6,7]. In this case, CO_2 is typically compressed into supercritical state (The pressure and temperature are respectively over 7.38 MPa and 31.1 °C) or liquid state [8,9].

It is well known that dry CO_2 does not corrode carbon steel. However, a range of impurities such as H_2O, O_2, H_2S and SO_2 may exist in supercritical CO_2 depending on the gas source, capture process and budget constraint [10,11], which poses great risk to security and stability of pipelines. In recent years, the corrosion problem of supercritical CO_2 transport pipeline is attracting the attention from researchers. Previous research considering the effect of O_2, SO_2 and H_2S impurities is summarized in Table 1. At present, in-depth studies on the corrosion of CO_2 transport pipeline mainly focus on several impurities such as O_2 and SO_2, suggesting that the presence of O_2 or SO_2 can increase the corrosion rate of carbon steel [7,12–18]. Choi and Nesic [7] investigated the effect of adding O_2 at partial pressures of 0.16, 0.33 and 0.51 MPa in water-saturated CO_2 at 8 MPa and 50 °C and obtained a maximum corrosion rate of 1 mm/y at the partial pressure of 0.33 MPa. The investigation revealed that O_2 provides an additional cathodic reaction pathway and inhibits the formation of a protective iron-carbonate layer. SO_2, which has a high solubility in H_2O, results in the formation of H_2SO_3 and consequently lowers the pH ($\sim$2) of the aqueous phase [21]. When O_2 and SO_2 appear simultaneously in CO_2 fluid, SO_2 can be oxidized into SO_3, and then H_2SO_4 can form to further lower the pH of the aqueous phase and notably increase the corrosion rate of the pipelines [7,12–14].

H_2S, which can form a weak acid when dissolved in water, is also a source of corrosion. Under certain conditions, the mixture of CO_2 and H_2S is more corrosive than H_2S alone [22–27]. In view of the high toxicity of H_2S, DYNAMIS CO_2 quality specification on the limitation of H_2S concentration (less than 200 ppm) in CO_2 is mainly based on health and safety concerns [11]. Weyburn pipeline

Table 1
Summary of corrosion research of CO_2 transport pipeline considering O_2, SO_2 and H_2S impurities in recent years.

Steel	Temperature (°C)	Pressure (MPa)	Time (h)	H_2O (ppm)	O_2	SO_2	H_2S (ppm)	Corrosion rate (mm/y)	Reference
X65	50	8	24	Sat.	0.16–0.51 MPa		–	0.6–1	[7]
X65	50	8	24	Sat.	–	0.08 MPa	–	5.6	[7]
X65	50	8	24	Sat.	0.33 MPa	0.08 MPa	–	>7	[7]
X70	50	10	120	Sat.	0.01 MPa	0.02–0.2 MPa	–	0.2–0.9	[12]
X70	25–75	10	120	Sat.	0.01 MPa	0.2 MPa	–	1.1–3.1	[13]
X65	35	8	48	Sat.	20 ppm	0–100 ppm	–	0.1–0.72	[14]
X65	35	8	48	300–1170	0–20 ppm	0–100 ppm	–	0.003–0.07	[14]
X65	50	8	24	650	–	0.008–0.08 MPa	–	0.03–3.48	[15]
X65	25	10	240	1220	–	500 ppm	–	0.02	[16]
X65	25	10	336	488–1220	–	100–344 ppm	–	0.005–0.02	[17]
1010	45	7.58	–	2440	100 ppm	–	–	2.3	[18]
1010	45	7.58	–	2440	–	100 ppm	–	4.6	[18]
X65	80	10	240	Sat.	–	–	50	0.24	[19]
UNS K03014	80	12	48	Sat.	–	–	200	0.41	[20]
UNS K03014	80	12	24	100	–	–	200	0.01	[20]

operated by Dakota Gasification Company transports CO_2 with up to 9000 ppm H_2S, but no significant corrosion occurred due to the strict limitation of H_2O (less than 20 ppm) [28]. However, Choi et al. [20] investigated the presence of 200 ppm H_2S in water-saturated supercritical CO_2 at 12 MPa and 80 °C and obtained that the corrosion rate was 0.41 mm/y. Dugstad et al. [29] pointed out that elemental sulfur could form in the simultaneous presence of O_2 and H_2S, which can further complicate the corrosion process of carbon steel. However, the corrosion of CO_2 transport pipeline in the simultaneous presence of O_2 and H_2S has rarely been reported, especially that of O_2, H_2S and SO_2, which may be a common phenomenon encountered in the future transmission operation.

The aim of this work is to understand the synergistic effect of multiple impurities such as O_2, SO_2 and H_2S on the corrosion behavior of X65 pipeline steel in water-saturated supercritical CO_2 system. To achieve this objective, the corrosion rate was determined by weight loss tests. The morphology and composition of corrosion scales were characterized by scanning electron microscope (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). Accordingly, the synergistic interaction impact factors of multiple impurities concerning the corrosion of X65 steel were proposed.

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 × 15 mm × 3 mm. Prior to the tests, the working surface of each specimen was abraded with silicon carbide paper of decreasing roughness (up to 1000 grit) until the surface roughness reached about 10 μm. After that, the specimen were firstly washed with deionized water and then with acetone, placed in a vacuum desiccator for 24 h to remove water, and weighed using an electronic balance with a precision of 0.1 mg.

2.2. Weight loss test

Weight loss tests were carried out in a 3 L autoclave to investigate the corrosion rate of X65 steel in water-saturated supercritical CO_2 containing impurities. A schematic diagram of the apparatus for the corrosion test is shown in Fig. 1, which mainly consisted of a gas source supply device, a booster pump, a 3 L autoclave, a controller and a waste gas treatment device. As listed in Table 2, two tests were designed:

Test 1 (conditions 1–4) was employed to determine the effect of single impurities on the corrosion of X65 steel for comparison with the Test 2.

Test 2 (conditions 5–8) was employed to investigate the synergistic effect of multiple impurities on the corrosion of X65 steel.

According to the related literature [30,31], it was calculated that about 0.74 g (4333 ppmv) water could be 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 in the tests. In each test, four parallel specimens were hung on the polytetrafluoroethylene holder (To ensure that the specimens were insulated from the autoclaves) in the autoclave. When the autoclave was sealed, purging CO_2 was adopted to remove the air for 2 h. After the autoclave was heated to 50 °C, the mixed gases of impurity/CO_2 (O_2/CO_2, H_2S/CO_2 and SO_2/CO_2, with a proportion of 1/4) were respectively injected into the autoclaves to the desired concentrations through dedicated pipelines, as shown in Fig. 1. The pressure of mixed gases injected into autoclaves was respectively 0.05 MPa corresponding to 1000 ppmv (0.01 MPa) impurity. Then the booster pump was used to inject CO_2 gas into the autoclave via another pipeline to a pressure of 10 MPa. The pressure indicator with a precision of 0.001 MPa on the controller in Fig. 1 was used to control the injected pressure. According to the compiled data of CO_2 transport pipelines [28] and published reference data [13] as well as the actual operating condition, the test parameters were chosen to be 10 MPa and 50 °C. All the tests were carried out under static condition.

After the heated autoclave naturally cooled down to room temperature, the specimens were taken out, rinsed in deionized water, dehydrated in alcohol and dried in air respectively. One of the four specimens was retained for surface characterization of corrosion scales. The rest three specimens were 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 [32], and then processed as above. After that, the specimens were weighed again to determine the weight loss. The corrosion rate was calculated through the following equation [33]:

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

where V_{CR} is the corrosion rate, mm/y; ΔW 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 average corrosion rate with error bars was calculated from the three parallel specimens for each test.