

Corrosion Resistance of Super Duplex Stainless Steel for CCS Usage under Supercritical CO₂ Conditions with Impurity Gas

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ABSTRACT

In carbon capture and storage (CCS), the CO₂ emitted from various industries containing impurities is captured and injected to underground in dense or supercritical phase through a tubing. In order to evaluate corrosion resistance of the tubing materials in supercritical CO₂ environment with impurity, corrosion tests were performed in the conditions of CO₂, containing 5 wt% NaCl with O₂ or SO₂ at total pressure of 130 bar and temperature of 100 °C. The corrosion rates of UNS S41426 (13Cr super martensitic stainless steel) were higher than 1 mm/y in the solution saturated CO₂ with 2% O₂, as well as with 0.02% SO₂. On the other hand, UNS82551 (25Cr duplex stainless steel) and UNS S39274 (25Cr super duplex stainless steel) showed the corrosion rates of 0.1 mm/year or less and no pitting corrosion when the impurity gas concentration was 0.02% SO₂. UNS S39274 showed the same results even in the condition with 4% O₂ or 0.50% SO₂. The authors conducted the analysis by X-ray photoelectron spectroscopy and confirmed that Cr concentrated in the passivation film of S39274 after the corrosion test. Therefore, it is considered that UNS S39274 would be a suitable material even in the supercritical CO₂ environment contaminated with impurities (O₂ or SO₂).

Key words: CCUS; CCS; Supercritical CO₂; Corrosion; Pitting; Stainless steel;

INTRODUCTION

Carbon capture, utilization and storage (CCUS) is one of the key technologies to achieve the net-zero emission. One of the CCUS method is CO₂ injection to depleted oil and gas wells or aquifers and storage (CCS). The CO₂ emitted from fossil fuel-based powers and industrial plants are captured and transported to the injection point by ships or pipe line. Following that, the dense phase or supercritical phase CO₂ will be injected to depleted oil and gas wells or aquifers through oil country tubular goods, for examples, seamless pipe.

Since the transported CO₂ is dehydrated, there are little risk of corrosion to pipe line materials. On the other hand, it is necessary to consider the risk of corrosion when it comes to injection pipes, because formation water is present in depleted oil and gas wells or aquifers and there is a possibility of flow back. In addition that the captured CO₂ from various industries includes impurities, for instance O₂, SO_x, and NO_x, which are reported that they accelerate general corrosion of steels^{1,2,3}.

Therefore 25Cr duplex stainless steel (DSS) with high corrosion resistance has been applied to CCS project for instance Sleipner CO₂ Storage Project⁴. However, there are few reports describing the corrosion resistance of 25Cr DSS in supercritical CO₂ with impurities.

In order to evaluate the corrosion resistance of 25Cr DSS and various stainless steel tubing materials, corrosion tests were performed in the conditions of CO₂ with impurity gas of O₂ or SO₂ and 5 wt% NaCl (31,200 mg/L Cl⁻) at total pressure of 130 bar and temperature of 100 °C.

EXPERIMENTAL PROCEDURE

Materials

UNS S41426 (13Cr super martensitic stainless steel), UNS S82551 (25Cr duplex stainless steel) and UNS S39274 (25Cr super duplex stainless steel) were used for the investigation into the effect of contaminations in supercritical CO₂ on resistance to general corrosion and pitting at 100 °C.

The materials were seamless pipes that were melt and hot rolled in a mill. After hot rolling, UNS S41426 was quenched and tempered to control the yield strength of 110 ksi grade, UNS S82551 was solution heat treated to control the yield strength of 80 ksi grade, and UNS S39274 was solution heat treated and cold worked to control the yield strength of 125 ksi grade.

Experimental methods

Immersion test

Coupon specimens with dimensions of 30 mm long, 20 mm width, and 2 mm thickness with a 5 mm hole were used. The specimens were machined parallel with the rolling direction of the materials and were polished with silicon carbide No.600 paper.

The specimens were immersed in 5 wt% NaCl aqueous solution saturated with supercritical CO₂ with or without O₂ or SO₂. Details of the immersion test conditions are shown in Table 1. Total pressure and temperature were 130 bar and 100 °C, respectively. The contamination ratio of O₂ ranged from 1 to 4% and the contamination ratio of SO₂ ranged from 0.02 to 0.5%.

The specimens were hooked on an UNS N10276 plate with hook parts wrapped by Teflon tape and placed in the autoclave. The 5 wt% NaCl aqueous solution were transferred in the autoclave, after that the solution were bubbled with CO₂ with purity of 99.999% to be deaerated.

The condition without impurity was prepared by heating to 100 °C and pressurized by CO₂ to the total pressure of 130 bar. As to the test conditions with impurity of O₂, O₂ gas was filled to a pressure that produces the specified mole fraction under the test environment. Then the test vessel was heated to 100 °C and pressurized by CO₂ to the total pressure of 130 bar. As to the test condition with SO₂, SO₂ and CO₂ mixed gas was filled to a pressure that produces the specified mole fraction under the test environment. Then the test vessel was heated to 100 °C and pressured by CO₂ to the total pressure of 130 bar. The pH value calculated by OLI software ranged from 3.1 to 1.9 in these conditions. The immersion duration was 96 hours. All test conditions are show in Table 1.

Table 1
Test conditions

#	Temperature (°C)	Total Pressure (bar)	Mole fraction of CO ₂ (%)	Mole fraction of O ₂ (%)	Mole fraction of SO ₂ (%)	Test solution	pH	Duration (hours)
1	100	130	100	N/A	N/A	5 wt% NaCl	3.1	96
2	100	130	99	1	N/A	5 wt% NaCl	3.1	96
3	100	130	98	2	N/A	5 wt% NaCl	3.1	96
4	100	130	96	4	N/A	5 wt% NaCl	3.1	96
5	100	130	99.98	N/A	0.02	5 wt% NaCl	2.6	96
6	100	130	99.85	N/A	0.14	5 wt% NaCl	2.2	96
7	100	130	99.50	N/A	0.50	5 wt% NaCl	1.9	96

After the testing, the specimens were removed from the autoclave and the general corrosion rate was calculated by using the weight loss method. In addition that the specimens were visually or microscopically examined for any sign of pitting. One of the immersed test specimens of S39274 was used to confirm the passivation film structure by X-ray photoelectron spectroscopy.

RESULTS

Effect of O₂ contamination

The test results are summarized in Table 2. The appearances of tested specimens and the corrosion rate of them are shown in Figures 1 and 2, respectively. As to S41426, any pit were not observed on the specimens after the testing in the condition without O₂, however, pits were observed after the testing including more than and equal to 1% O₂ as shown in Figure 1.a). In addition that the general corrosion rate was drastically increased to 0.98 mm/year in the condition with 2% O₂ as shown in Figure 2.

On the other hand, any pit were not observed on S39274 even in the condition with 4% O₂ as shown in figure 1.b) and the corrosion rate was less than 0.1 mm/year as shown in Figure 2.

Effect of SO₂ contamination

The appearances of tested specimens and the corrosion rate of the materials are shown in Figures 3 and 4, respectively. Even in the condition with 0.02% SO₂, the corrosion rate of S41426 was significantly high, more than 1 mm/year. In contrast the corrosion rate of S82551 and S39274 were 0.01 mm /year or less and any pitting were not observed on the specimens. As to S39274, the corrosion rate were 0.03 mm/year in the conditions with 0.14% and 0.50% SO₂ and any pitting were not observed.

The corrosion rate of S82551 tested in the condition with 0.02% SO₂ was less than 0.01 mm/year and any pit were not observed on the tested specimens as shown in Figure 3.