

## Effect of Cr on Corrosion Performance of Steels in Supercritical CO<sub>2</sub> Environments

Kaiyang Li, Xue Han, Yimin Zeng  
CanmetMATERIALS  
183 Longwood Rd South  
Hamilton, ON L8P 0A5 Canada

### ABSTRACT

As a promising technology, carbon capture and storage (CCS) can significantly reduce CO<sub>2</sub> emissions while retaining the core value of fossil fuel power plants. CO<sub>2</sub> transportation is a crucial step to ensure the successful deployment of CCS, which is achieved by pipeline network. However, the impurities in the captured supercritical CO<sub>2</sub> (s-CO<sub>2</sub>) may cause severe corrosion damages to pipeline steels. As a control strategy, Cr-bearing steels are proposed as potential candidate materials to mitigate corrosion, especially at the crucial parts of the transportation system. In this paper, corrosion behaviors of steels with different Cr contents were studied in s-CO<sub>2</sub> streams with impurities (H<sub>2</sub>O, SO<sub>2</sub>, O<sub>2</sub>, etc.) at 10 MPa and 45 °C. The corrosion rates were measured by mass loss method and the corrosion products were characterized. The effect of Cr on corrosion behavior of steels was also discussed.

**Key words:** supercritical carbon dioxide, corrosion, Cr-bearing steels

### INTRODUCTION

In recent years, several novel technologies have been proposed and developed to produce energy in a clean and sustainable way. However, in the foreseen future, fossil fuel will still be the major source to meet our needs on energy.<sup>1</sup> The combustion of fossil fuel for power and heat is always accompanied by CO<sub>2</sub> emission, which is believed to be in large correlation to global warming.<sup>2</sup> To control the CO<sub>2</sub> emission and reduce the negative effects, carbon capture and storage (CCS) has been rapidly developed in fossil fuel combustion power plants.<sup>3, 4</sup> One of the crucial parts of CCS is the long-distance transportation of CO<sub>2</sub>, during which a large amount of captured CO<sub>2</sub> is transported to storage sites. Pipeline network is chosen as transportation system due to its high efficiency and moderate cost.<sup>5</sup> And the transported CO<sub>2</sub> streams are usually compressed into supercritical CO<sub>2</sub> (s-CO<sub>2</sub>).<sup>6</sup>

Due to the wide accessibility and relatively low price, some high-strength carbon steels from API<sup>(1)</sup> Grade 5 were selected as the construction materials for the pipeline network.<sup>7</sup> However, the integrity of pipeline steels is threatened by impurity-induced corrosion issues. These impurities, including H<sub>2</sub>O, H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>S, SO<sub>x</sub>, NO<sub>x</sub>, CO, and acids, originate from the combustion or capture processes and often cause great corrosion damage to pipeline steels.<sup>8</sup> Among them, SO<sub>2</sub> seems to be one of the most notorious impurities. It is generated when sulfur-containing fossil fuels are combusted. It arouses severe degradation of pipeline steels even at ppm level and the corrosive effect is proportional to its concentration.<sup>9</sup> Some researchers attributed the high corrosive effect of SO<sub>2</sub> to its conversion to sulfuric acid and the dissociated H<sup>+</sup> in the presence of H<sub>2</sub>O.<sup>10</sup> Other researchers found that corrosion damage is further enhanced by the synergistic effect of SO<sub>2</sub> with other impurities.<sup>11</sup> Up to now, a lot of researchers have been made and several review articles have been tried to summarize the corrosive effects of SO<sub>2</sub>.<sup>1, 12</sup> More efforts should be made to ensure the safe operation of s-CO<sub>2</sub> transportation system.

One possible mitigation strategy to prevent SO<sub>2</sub>-induced severe corrosion in s-CO<sub>2</sub> is exploring the possibility of using Cr-bearing steels in the pipeline systems. Cr-bearing steels are known for the good mechanical behavior and improved corrosion resistance due to the addition of Cr. Related studies showed that when adding Cr into steels, the corrosion resistance to CO<sub>2</sub> environment increased up to 40 times while the cost only increased 1.5 times.<sup>13</sup> So far, a lot of efforts have been made to study the corrosion performance of Cr-bearing steels in oil and gas fields.<sup>14, 15</sup> Generally, Cr-bearing steels improve the corrosion resistance by developing a protective scale containing Cr and its compounds.<sup>16</sup> All those features make Cr-bearing steels suitable candidates as transport materials in s-CO<sub>2</sub> environments, and several researchers have been studying the corrosion behavior of Cr-bearing steels in s-CO<sub>2</sub> environments with different types of impurities. However, the results are not enough to form a clear image and sometimes the results are contradictory. For instance, one study showed that 5 Cr steel had lower corrosion rates than X65 steel in s-CO<sub>2</sub> + O<sub>2</sub> + H<sub>2</sub>O environments since the former developed a Cr-rich surface layer (Cr<sub>2</sub>O<sub>3</sub> and Cr(OH)<sub>3</sub>).<sup>17</sup> Another study, on the contrary, revealed that the addition of Cr may not be effective to improve the corrosion resistance in H<sub>2</sub>O saturated s-CO<sub>2</sub> + SO<sub>2</sub> + O<sub>2</sub> since the corrosion rates of 13Cr steel and X65 carbon steel exhibited no obvious difference.<sup>10</sup> Therefore, it comes to a question whether the addition of Cr helps to improve the corrosion resistance of steels and a systematic study on the effect of Cr on corrosion of steels are highly desired.

This study investigates the effect of Cr contents on the corrosion performance of steels in H<sub>2</sub>O-saturated saturated s-CO<sub>2</sub> with SO<sub>2</sub> and O<sub>2</sub> impurities, which is relevant to oxy-fuel combustion in CCS. To fulfill this goal, three steels with different types (carbon steel, ferritic steel, and stainless steel) were chosen due to their different Cr contents. The corrosion rates were measured through both weight gain and weight loss methods and the morphology of corrosion scales was characterized to identify the corrosion model.

## EXPERIMENTAL PROCEDURE

### Sample Preparation

Three steel plates (K03104, S50200, and S31600) were purchased from commercial manufacturers and machined into plates with a size of 32 mm long × 6 mm wide × 2 mm thick or metal coupons with a size of 20 mm long × 10 mm wide × 2 mm thick. The chemical compositions of the steels are shown

<sup>(1)</sup> American Petroleum Institute (API) 1220 L Street, NW, Washington, DC 20005-4070

in Table 1. The Cr content in these steels follows an increasing trend from ~0 to ~16 wt.%. Therefore, these steels are named as 0 Cr, 4.5 Cr, and 16.6 Cr for short in the following. Prior to corrosion tests, all the samples were polished with SiC papers of #120, #240, #360, #480 and #600 grits. Then, all the samples were ultrasonically cleaned with distilled water and ethanol, and dried with compressed air. Then, the samples were weighted by a microbalance with a precision of 0.001 mg and dimensioned by a caliper with a precision of 10  $\mu\text{m}$ . After weight and size measurements, the pristine samples were stored in a vacuum container to prevent oxidation by air.

**Table 1**  
**Chemical composition of tested alloys (wt.%).**

| Steel  | Short as | Cr     | Ni     | Mo     | Fe   | C     | Si    | Mn   | S       |
|--------|----------|--------|--------|--------|------|-------|-------|------|---------|
| K03104 | 0 Cr     | 0.023  | 0.012  | 0.0026 | Bal. | 0.075 | 0.210 | 1.36 | <0.0010 |
| S50200 | 4.5 Cr   | 4.550  | 0.142  | 0.4570 | Bal. | 0.093 | 0.327 | 0.29 | 0.0004  |
| S31600 | 16.6 Cr  | 16.600 | 10.000 | 2.000  | Bal. | 0.022 | 0.320 | 1.20 | 0.0010  |

### Experimental Setup and Procedures

The flue gas analysis results from the pilot-scale oxy-fuel combustion system show that the concentrations of  $\text{O}_2$  and  $\text{SO}_2$  are 1-6% and <800 ppm, respectively, and the content of  $\text{H}_2\text{O}$  could be up to the saturated point.<sup>18</sup> Thus, water-saturated s- $\text{CO}_2$  with 100 ppm  $\text{SO}_2$  + 3%  $\text{O}_2$  was used to simulate the typical oxy-fuel combustion environment. The total pressure is 10 MPa while the testing temperature is 45 °C. Given the high solubility of  $\text{SO}_2$  in water and its possible conversion into  $\text{H}_2\text{SO}_4$  in the presence of  $\text{O}_2$ , the amount of added  $\text{H}_2\text{O}$  should be carefully controlled so tests are conducted under the designed conditions. To ensure the accuracy in gas/water charging, commercial software and experimental data published in other references were combined to decide the  $\text{H}_2\text{O}$ -saturation point in 10 MPa s- $\text{CO}_2$  at 45 °C.<sup>2, 19</sup> Besides, calculations were performed to determine the amount of charged  $\text{O}_2$  and  $\text{SO}_2$ .<sup>20</sup>

**Figure 1** shows the experimental setup for corrosion tests, which is mainly composed of three parts, namely gas supply, autoclave and heating system. Different gases ( $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{O}_2$ , and so on) were charged into the autoclave and the pressure inside the autoclave was monitored by a digital pressure gauge. Note that a s- $\text{CO}_2$  pump was used to assist the charging of  $\text{CO}_2$ . A heating jacket connected to a controller was used to control the temperature during the corrosion tests.

Prepared sample steels were accommodated on a self-made sample holder, which was placed in the autoclave. After sealing, the autoclave was purged with  $\text{CO}_2$  gas for several times. Then, 5.3 g  $\text{CO}_2$ -saturated water was injected into the autoclave by a self-made apparatus driven by  $\text{CO}_2$  gas. The temperature inside the autoclave was maintained at 25 °C, when  $\text{O}_2$  was added to 0.179 MPa. The autoclave was then heated to 45 °C, and a mixture of  $\text{SO}_2$  and  $\text{CO}_2$  (774 ppm  $\text{SO}_2$  + bal.%  $\text{CO}_2$ ) was charged to make the total pressure of 3.25 MPa. Afterward,  $\text{CO}_2$  was pumped in until the total pressure reached 10 MPa. This remarks the beginning of the corrosion test. After 120 h, the heater was turned off and the autoclave was cooled down to room temperature. Degassing was performed by letting the emitted gas pass through a homemade rig for toxic gas capture before venting. All the samples were taken out for weight measurement. Three samples of each steel were kept while the remaining ones were sent back to the autoclave for another cycle of test. There are four cycles in total and the total exposure time was 120 h/cycle  $\times$  4 cycles = 480 h. The samples after 120 and 480 h were selected as typical examples for corrosion rate assessment and corrosion products characterization.

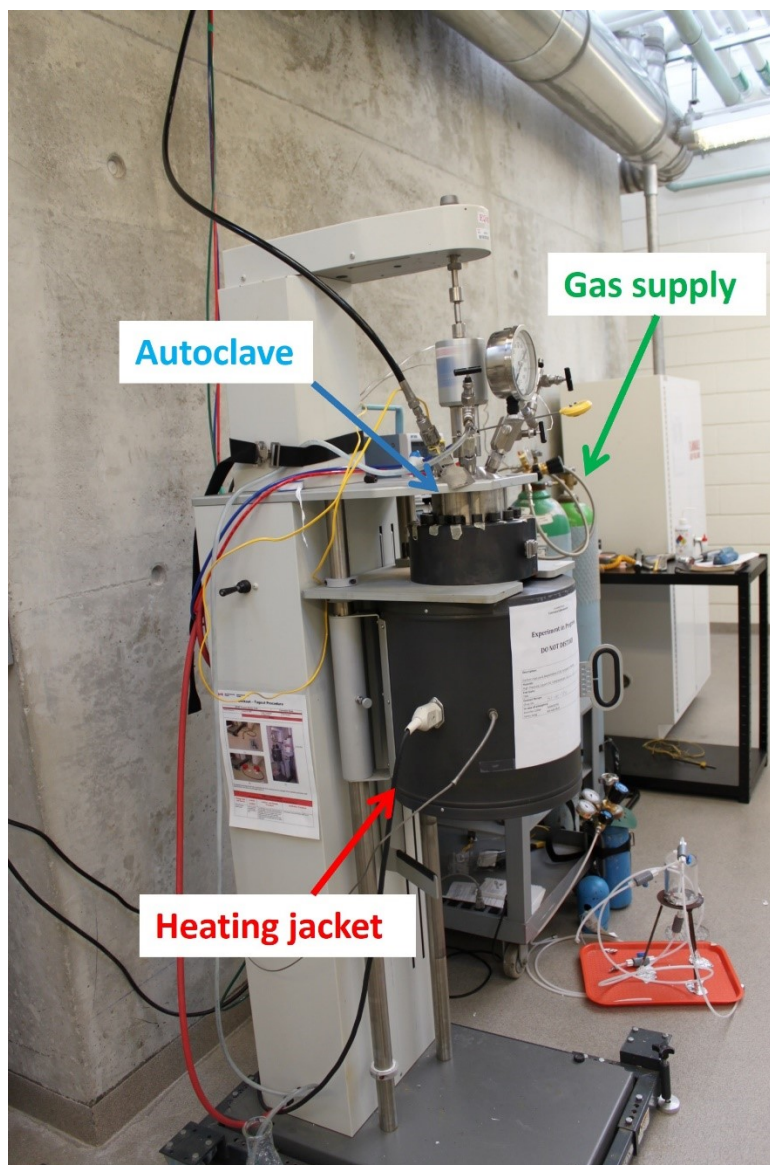


**Figure 1: Photographic images of testing facilities for corrosion.**

### **Corrosion Products Characterizations and Corrosion Rate Measurements**

After each cycle, photographic images of samples were taken to observe the microscopic changes on sample surfaces. The cross-sectional observation was also made by mounting corroded and grinding. Both mass change and mass loss methods were used to evaluate the degree of corrosion. The mass change method measures the mass difference per surface area of each sample before exposure and after a certain time period of corrosion. Mass loss measurements were performed by chemically removing the formed corrosion products and calculating the amount of consumed metals during corrosion. Based on ASTM G1,<sup>21</sup> the corrosion products were completely removed by a pickling solution of 500 ml hydrochloric acid + 3.5 g hexamethylene tetramine + 500 ml deionized water. Corrosion rate in mm per year (mm/y) of each steel sample was then calculated by:

$$\text{Corrosion rate} = \frac{8.74 \times 10^4 \Delta m}{A d t} \quad (1)$$

where  $\Delta m$  is the mass loss of the sample after a corrosion test, g; A is the exposed surface area, cm<sup>2</sup>; d is the density in g/cm<sup>3</sup> (K03104: 7.86 g/cm<sup>3</sup>, S50200: 7.80 g/cm<sup>3</sup>, S31600: 7.87 g/cm<sup>3</sup>); t is the exposure time, h.