

Influence of Impurity Adsorption and Condensation on the Initial Corrosion Mechanism of CO₂ Transport Pipeline Steel

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ABSTRACT

The present study was designed to study the role of impurity adsorption and condensation behaviors in the corrosion mechanism of CO₂ transport pipeline steel, based on the hypothesis that the impurity adsorption and condensation play a critical role in inducing the formation of aqueous electrolyte in the initial stage of the corrosion processes. The impurity adsorption and condensation behaviors including water adsorption, adsorption of sulfurous species (SO₂/H₂SO₃), and H₂SO₃ condensation onto the Fe-coated quartz crystals were measured by the Quartz Crystal Microbalance (QCM) technique in water-unsaturated CO₂/H₂O flow and CO₂/H₂O/H₂SO₃/SO₂ flow at 45°C and 1 bar. The connections between the water adsorption and acid condensation behavior onto Fe-coated quartz crystals with Fe corrosion were also studied by utilizing SEM and EDS techniques. The results showed that Fe suffered no corrosion in the water-unsaturated CO₂/H₂O gas flow but suffered localized corrosion in the water-unsaturated CO₂/H₂O/H₂SO₃/SO₂ gas flow. It was suggested that the acid condensation initiated the Fe corrosion at water-unsaturated conditions with impurities instead of the pure water adsorption behavior.

Key words: Carbon Capture and Storage, CO₂ corrosion, carbon steel, SO₂, acid condensation

INTRODUCTION

CO₂ captured from different sources for carbon capture and storage (CCS) will contain impurities. Although it is technologically possible to treat CO₂ to near 100% purity in the gas conditioning process, it is preferable to have fewer rigid specifications to reduce both operational and capital costs. From a corrosion point of view, SO_x, NO_x, H₂S, and O₂ are considered to be the most aggressive impurities. There are no field cases that analyzed the effect of impurities on corrosion,

however, laboratory experiments have shown that noticeable, and potentially severe, corrosion occurs at water-unsaturated conditions in dense phase CO₂ with the presence of those impurities due to synergistic interactions between chemical species.¹⁻¹¹

Although many experimental works have been conducted to investigate the effects of water and various impurities on the corrosion behavior of pipeline steels in dense phase CO₂, there is little study on the evaluation of corrosion mechanisms for the corrosion behavior of pipeline steels in dense phase CO₂, especially for the corrosion mechanism in the water-unsaturated conditions.

The corrosion process for carbon steel exposed to wet CO₂ mainly consist of three stages: the initial stage for the electrolyte formation, the intermediate stage for the chemical and electrochemical reactions that occur both on the steel-electrolyte interface and in the bulk phase, and the final stage for the nucleation and growth of the corrosion products. For the corrosion mechanism at the water-unsaturated conditions with dense phase CO₂, the initial corrosion mechanisms play the most important role in initiating the corrosion process and determining the extent of general corrosion and localized corrosion. However, it remained unknown that how the electrolyte formed and how corrosion was initiated at water-unsaturated conditions in dense phase CO₂ with impurities, in which case the free water phase was not supposed to exist.

There are four possible explanations for the initial corrosion mechanism from the literature.¹²⁻¹⁷ The first explanation argued that the impurities (SO₂, O₂, NO₂, etc.) could decrease the water solubility in the dense phase CO₂,¹² thus inducing the water condensation onto the steel surface. However, the existing studies showed that small amounts of impurities could not significantly decrease the water solubility. Take O₂ as an example,¹³ it was reported that the presence of 2.5 mol.% O₂ in CO₂ lowered the actual water solubility limit by approximately 100 ppm_v at 38°C, 12 MPa, comparing with the theoretical water solubility in pure CO₂. The decreased water solubility is not large enough to induce the water condensation when the water amount is far below the theoretical water solubility. The second explanation argued that because the temperature and pressure might vary during the operation processes, especially in the field,¹⁴ the water solubility in the CO₂ phase would change with the temperature and pressure, thus the water condensation would occur. Dugstad et. al.,¹⁵ also pointed out in some applications, when the liquid or supercritical CO₂ leaked out, the pressure would drop and induce the water condensation. The above two explanations focused on how water condensation could occur when the water contents are below the theoretical water solubility in the CO₂ phase at the theoretical conditions, and the motivation for water condensation is the change of actual water solubility, which either derived from the impact of impurities or the change of environments. However, these two explanations could be used as the possible reasons, but not the general reasons for the electrolyte formation at the water-unsaturated conditions. The third explanation argued that it was the water adsorption and accumulation at the pipeline steel-CO₂ interface that induced the electrolyte formation due to the hydrophilic nature of the steel surface.¹⁶ But it remains doubt as to whether the amount of adsorbed and accumulated water is sufficient to initiate corrosion. The fourth explanation is proposed herein that the electrolyte formation at the water-unsaturated conditions in the CO₂ with acid gas impurities is derived from the acid condensation,¹⁷ and the evaluation of this hypothesis is the focus of the present work.

In order to investigate the initial corrosion mechanism, this work was designed to study the role of impurity adsorption and condensation behavior in CO₂ corrosion mechanism, based on the hypothesis that the impurity adsorption and condensation play a critical role in inducing the formation of aqueous electrolyte in the initial corrosion stage for the CO₂ corrosion processes at water-unsaturated conditions. Before stepping into the high pressure CO₂ conditions, this work mainly addressed with the corrosion at the low pressure in 1 bar CO₂ gas flow. It was suggested

that there are some similarities for the corrosion mechanisms between the low pressure CO₂ conditions and high pressure CO₂ conditions including characteristics of CO₂ corrosion product scale and the variation rule of corrosion rate with temperature.¹⁸

EXPERIMENTAL PROCEDURE

Quartz Crystal Microbalance

In the present work, Fe-coated quartz crystal of 5 MHz resonant frequency with 1.37 cm² of effective area was used (Figure 1 (a)). The Fe-coated quartz crystal was selected to investigate the connections between the water and impurity adsorption with corrosion initiation.

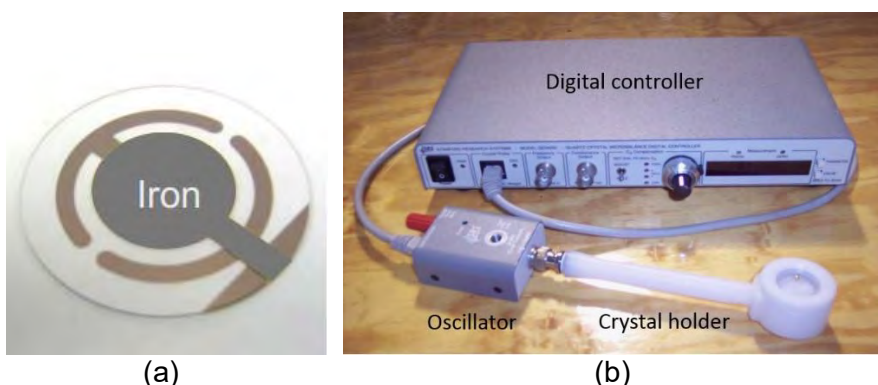


Figure 1: Images of quartz crystals and Quartz Crystal Microbalance (QCM) system: (a) Fe-coated quartz crystal, (b) Quartz Crystal Microbalance (QCM)

A sensitive QCM technique, which can yield a mass sensitivity of 10⁻⁹ g/cm² and detect a mass change in nano gram scale, has been widely used to study adsorption, condensation, and deposition processes, because of its economical, usable and reliable characteristics.^{19,20} QCM is an acoustic-wave sensor in which the acoustic wave propagates in the direction perpendicular to the quartz crystal surfaces. The basic principle behind all acoustic-wave sensors is that adding mass on the quartz crystal surface of the sensor causes the resonant frequency to decrease.²¹ Thus, QCM technique is utilized to measure the mass change per unit area by measuring the change in frequency of a quartz crystal. The mass change on the Fe-coated surfaces of the resonator due to the resonant frequency change in the gas phase is given by the Sauerbrey equation:²²

$$\Delta f = -C_f \cdot \Delta m \quad (1)$$

where Δf is the frequency change (Hz), C_f is the sensitivity factor for the quartz crystal (56.6 Hz $\mu\text{g}^{-1}\text{cm}^2$ for a 5 MHz AT-cut quartz crystal), and Δm is the change in mass per unit area (g·cm⁻²).

Experimental Set-up for Water Adsorption Tests

A 2 L glass cell containing deionized water was used as a water bath to control the temperature of the QCM chamber at 45.0 ± 0.1°C. The QCM chamber with 200 ml volume acted as a confined space, where water and impurity could adsorb onto the quartz crystal surface. Figure 2 shows a schematic diagram of the experimental set-up for the water adsorption tests using QCM. It mainly consisted of a CO₂ gas cylinder and gas lines, a saturator, QCM chamber, and humidity

measurement device. After the dry CO₂ gas left the cylinder, the gas flow rate was kept constant at around 40 mL/min for each test.

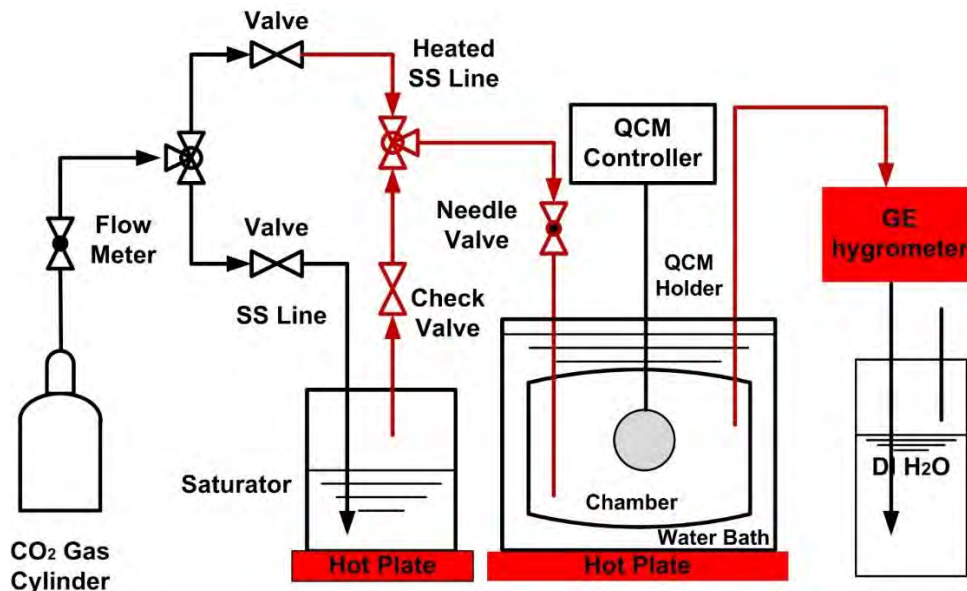


Figure 2: The Experimental Set-up for Water Adsorption Tests with the Fe-coated quartz crystals.

Once the gas source was opened, the dry CO₂ gas either passed through the dry gas line into the QCM chamber or passed through the saturator to be saturated with water vapor. The dry and wet gas paths were controlled by a three-way valve. The dry CO₂ gas was used to remove the moisture inside the QCM chamber before conducting the test, while the wet CO₂ gas was used to conduct the water adsorption tests. After the wet gas mixture left the saturator, it passed through the heated stainless steel gas lines and entered the QCM chamber. The stainless steel gas lines were heated to above 50°C to minimize the moisture loss along the gas paths due to the potential water condensation, which might derive from the temperature differences between the gas mixture and gas lines.

The water-unsaturated CO₂ gas flow with various relative humidities was generated by utilizing the two-temperature difference method. By bubbling CO₂ in the saturator, which contained deionized water at the temperature of T_s , the water vapor with saturated vapor pressure at T_s was added into the CO₂ gas flow. Afterwards, the wet CO₂ gas flowed from the saturator into the QCM chamber at higher temperature (T_b) of 45°C, thus the CO₂ gas flow became water-unsaturated ($T_s < T_b$). The relative humidity (RH) of the CO₂ gas flow was calculated by the division of the saturated water vapor pressure at T_s to the saturated water vapor pressure at T_b (Equation 2). T_s ranged from 9°C to 40°C, while T_b was kept constant at 45°C, thus the relative humidity in CO₂/H₂O gas flow ranged from 10% to 75%.

$$RH (\%) = \frac{p_{sat}(T_s)}{p_{sat}(T_b)} \times 100 \quad (2)$$

where $p_{sat}(T)$ represents the saturated vapor pressure of water at temperature of T (°C) and can be calculated by Equation 3:

$$p_{sat}(T) = 10^{A-B/(C+T)} \quad (3)$$

where A, B, C represent Antoine Constants for Water. When water temperature is in the range of 1 to 100°C, A = 8.07131, B = 1730.63, C = 233.426.²³

The relative humidity was also measured by using a humidity measurement device in the gas downstream. The device was a microprocessor-based, single-channel hygrometer that measured moisture content in gases, and it was suitable for a wide range of process conditions requiring real-time moisture measurement. The measured relative humidity was usually $\pm 5\%$ difference from the calculated relative humidity, which implied that the measured relative humidity showed a good match with the calculated relative humidity.

Experimental Set-up for the Adsorption and Condensation of Sulfurous Species Tests

The experimental set-up for the sulfurous species ($\text{H}_2\text{SO}_3/\text{SO}_2$) tests was basically identical to that for the water adsorption tests, except that 6% w/v H_2SO_3 solution was added into the saturator instead of the deionized water. In this way, the 1 bar CO_2 flow would be contaminated by the impurities of $\text{H}_2\text{O}(\text{g})$, $\text{SO}_2(\text{g})$ and $\text{H}_2\text{SO}_3(\text{g})$ when it passed through the saturator to turn into $\text{CO}_2/\text{H}_2\text{O}/\text{SO}_2/\text{H}_2\text{SO}_3$ gas flow. Since H_2SO_3 solution was volatile acid, $\text{SO}_2(\text{g})$ would be generated by the decomposition of H_2SO_3 , according to the Equation 4:



It is worthy to mention that $\text{H}_2\text{SO}_3(\text{g})$ probably existed in the CO_2 gas mixture because stable $\text{H}_2\text{SO}_3(\text{g})$ in the gas phase was once detected by Sulzle et al.²³

Since the relative humidity sensor in the humidity measurement device was easily corroded by the sulfurous species, the hygrometer was removed from the set-up. Thus, T_s was respectively set as 32°C and 38°C, while T_b was kept constant at 45°C, thus the relative humidity of 45% and 70% in $\text{CO}_2/\text{H}_2\text{O}/\text{SO}_2/\text{H}_2\text{SO}_3$ gas flow was respectively achieved in the QCM chamber. As a H_2SO_3 solution rather than pure water is used, the actual values of humidity may differ from the calculated results. Therefore, experiments were conducted on 45% and 70%, which can show a sufficient difference. For the tail gas treatment, NaHCO_3 aqueous solution was used to absorb the gas mixture to prevent the SO_2 pollution.

Surface analysis

Apart from the QCM technique, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were employed to investigate the corrosion initiation on the Fe-coated quartz crystals. Before and after the Fe-coated quartz crystals were exposed to the $\text{CO}_2/\text{H}_2\text{O}$ and $\text{CO}_2/\text{H}_2\text{O}/\text{SO}_2/\text{H}_2\text{SO}_3$ gas flow, the SEM technique was used to observe the crystal surface morphology to examine whether corrosion was initiated and furthermore to study the corrosion products morphology once corrosion did occur. EDS technique was also used to detect the elemental composition of the crystal surfaces before and after the QCM tests.

RESULTS

Test Results for Fe-coated Quartz Crystal Exposed to $\text{CO}_2/\text{H}_2\text{O}$ gas flow

The water adsorption behavior onto the Fe-coated quartz crystals was measured upon exposure to the water-unsaturated $\text{CO}_2/\text{H}_2\text{O}$ gas flow with various humidities. The series of water adsorption