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Investigation of pipeline corrosion in pressurized CO₂ containing impurities

Aki S. Ruhl^{a,b,*}, Axel Kranzmann^aBAM Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin, Germany^bBerlin Institute of Technology, Water Quality Control, Straße des 17. Juni 135, 10623 Berlin, Germany

Abstract

Transmission of captured CO₂ in pipelines is an essential part of the carbon capture and sequestration process chain. Dependent of the fuel, the combustion process and the capture technology the resulting gas contains impurities that might cause corrosion effects in pipelines constructed of low alloyed steels. Corrosion testing under simulated conditions therefore is a prerequisite for the installation of reliable and safe CCS systems. Sulfur and nitrogen oxides together with water vapor form corrosive acids. Their behaviours and corrosive effects in static pressurized experiments were critically investigated in the present study. The results indicate that experimental limitations might influence the predictive capability of corrosion tests with sulfur dioxide. The limited supply of corrosive constituents in static test might lead to an underestimation of the corrosion risk.

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1. Introduction

Economic transmission of captured carbon dioxide (CO₂) to the receiving geological formation requires a pressurized dense fluid, either in a liquid or supercritical state. Constituents in the fluid can cause corrosion and pressure inside the pipe causes additional mechanical stress in the pipeline walls that are typically constructed of low alloyed carbon steels with ferritic-pearlitic micro-structure. Safe operation of CO₂ transmission pipelines requires long-term resistance towards any type of corrosion and rupture.

Resulting concentrations of impurities in captured CO₂ are dependent on many influencing factors such as fuel type, combustion regime, gas cleaning, capturing technologies and others. The impurity

* Corresponding author. Tel.: +49-30-314-25493; fax: +49-30-314-23313.
E-mail address: aki.s.ruhl@tu-berlin.de.

levels are not fully clarified yet but residual impurities can be expected [1]. Sulfur di- or trioxide (SO_2 or SO_3) or nitrogen dioxide (NO_2) can react with water vapor (H_2O) to corrosive acids. The dew points of the resulting acids can be much lower than that of water. Therefore it is necessary to consider potential reaction products and their phase behavior. Corrosive effects of SO_2 and NO_2 with regard to atmospheric corrosion are well known [2,3].

In the present investigations pipeline steels were exposed in autoclaves of different volumes to pressurized CO_2 at 100 bar and 60°C. Varying gas compositions were mixed using CO_2 , SO_2 , NO_2 and oxygen (O_2). Defined volume flows of the gaseous compounds were adjusted with mass flow controllers. The real-time gas mixture was pressurized with two subsequent compressors. The humidity was simulated by injecting a defined volume of deionized water into the autoclave prior to pressurization.

The results indicate that the continuous supply of impurities could cause severe corrosion, dependent on their concentrations and the humidity level. However, the molar amount of corrosive constituents in static experiments is limited since the fluid can not be refreshed without changing the boundary conditions such as temperature or pressure.

Gravimetric analyzes were employed to quantify the corrosive material loss. However, weight losses cannot be extrapolated to achieve long-term corrosion rates due to the decrease and depletion of corrosive constituents in the static experiments.

2. Materials and Methods

A number of corrosion tests were conducted in two types of autoclaves with inner volumes of 1.0 and 1.9 litres, respectively. The experimental setup has been previously described, both in words and schematically [4]. Roughly, specimens were positioned on a glassware level to avoid direct contact with the autoclave material. Humidity was added as droplets of water supported on another glassware level prior to insertion and pressurization with a pre-mixed gas composition. Gas constituents were mixed with mass flow controllers as previously described [5,6]. The necessary molar amount of water was calculated according to the molar density of CO_2 at 60°C and 100 bar. The pre-heated autoclaves were not flushed with CO_2 before pressurization to avoid a loss of water. Since the initial gas in the autoclave consisted of ambient air, small amounts of nitrogen and oxygen were included in all experiments. Reported autoclave volumes used for corrosion testing in pressurized CO_2 range from 140-200 mL [7, 8], over 1.0 L [9,10], 1.8 L [11], 2.2 L [12, 13], 4 L [14], 8.9 L [15,16] to 9 L [17], thus the autoclave used here are comparable to other studies.

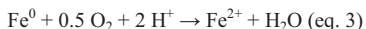
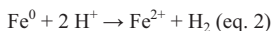
3. Results and Discussion

3.1 Theoretical considerations

Possible corrosion reactions can be balanced on the basis of molar amounts of precursor substances such as SO_2 or SO_3 and H_2O . Equation 1 describes the formation of sulfurous ($x=2$) or sulfuric acid ($x=3$) and indicates that two moles protons (H^+) are formed per mole SO_x .



Protons are reduced during corrosion according to net equations 2 (anaerobic) or 3 (aerobic). Two moles of protons are required per mole of corroded iron (Fe^0 or Fe^{2+}). In the presence of O_2 ferrous iron (Fe^{2+}) can be further oxidized to ferric iron (Fe^{3+})



Combining equation 1 with equation 2 or 3, corrosive dissolution of iron requires an equivalent molar amount of SO_x . Hence it can be assumed that the concentration of SO_x is the limiting factor in pressurized experiment when concentrations of O_2 and H_2O are comparably higher. The maximum corrosive material loss can be estimated from the initial molar amount of SO_x that can be derived from its concentration or partial pressure and the applied pressure P and temperature T or the according fluid density ρ , respectively.

3.2 Experimental complexity of SO_2

Preliminary test were conducted to investigate the reliability of corrosion testing with low concentrations of impurities such as SO_2 . We have previously reported [4] that no corrosion occurred with addition of sulfuric acid or mixtures of sulfuric acid and H_2O (omitting direct contact with the steel specimen) in supercritical CO_2 . This observation indicated that no significant diffusion of sulfuric acid (towards the steel specimen) occurs in supercritical CO_2 , most likely due to low solubility of H_2SO_4 in supercritical CO_2 .

In autoclave experiments humidity is typically adjusted by adding a calculated amount of H_2O into the autoclave expecting that H_2O completely dissolves in the subsequently added CO_2 with SO_2 . However, during gas addition and pressurization with CO_2 containing SO_2 and O_2 , all gas constituents readily partition into the H_2O that is initially present in the autoclave. The dissolution of SO_2 in the H_2O leads to the formation and dissociation of sulfurous acid according to equation 1. In the presence of oxygen, sulfurous acid might be further oxidized to sulfuric acid. Subsequently, dissolution of the resulting liquid phase containing sulfurous or sulfuric acid is inhibited. A residual liquid phase was observed after 120 hours exposure in several corrosion tests conducted with CO_2 containing SO_2 . In order to clarify the origin of the liquid phase, the total amount of 225 μL H_2O (corresponding to a target humidity of approximately 1000 ppm) was added as 9 symmetrically positioned droplets of 25 μL H_2O each. All 9 drops were still found after the experiment as shown in Fig. 1. The vaporization and dissolution in the CO_2 therefore was not complete. Hence the target concentration in the supercritical fluid was not achieved but significant molar amounts of both corrosive SO_2 and H_2O were immobilized in the residual acidic droplets. A low pH value in the droplets was confirmed with a pH indicator. This effect is relevant for static and circulated corrosion tests with humidification by addition of liquid H_2O . Alternatively, humidity can be adjusted by vaporization of H_2O into CO_2 (compare [5,6]) prior to pressurization. However, solubility of H_2O decreases with increasing pressure (up to the critical point) and condensation with the above discussed dissolution of SO_2 can not be excluded either.

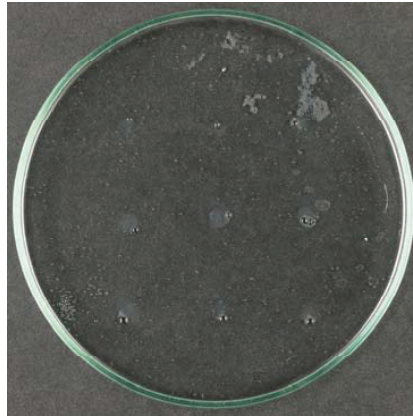


Fig. 1: Photograph of the glassware (diameter ca. 100 mm) after 120 hours exposure in supercritical carbon dioxide containing 200 ppm SO₂, 200 ppm NO₂ and 1000 ppm O₂. Water was placed before the experiment in a specific pattern with 9 spots with 25 µL H₂O corresponding with a target humidity of 1000 ppm.

According to the previous discussion no corrosive effect was observed in static corrosion tests with H₂O addition followed by pressurization with 100 ppm SO₂ and 100 ppm O₂ in CO₂. Corrosion effects were neither visually nor gravimetrically observed. Both the limited molar amount of corrosive species and its immobilization might have inhibited corrosive effects.

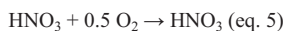


Fig. 2: Photographs of specimens after 120 hours exposure 200 ppm H₂O, 100 ppm SO₂, 100 ppm O₂ (left) and after 240 hours exposure to 400 ppm H₂O, 100 ppm SO₂ and 100 ppm O₂ (right).

The results obtained here indicate that continuous corrosion tests under ambient pressure but with constant supply of corrosive constituents as previously conducted [5,6] are an valuable complement to pressurized but static corrosion tests with inherent experimental difficulties.

3.3 Corrosion tests with nitrogen oxides

Nitrogen dioxide also forms corrosive acids. According to equations 4 and 5 nitrogen dioxide might completely react to nitric acid with an equivalent molar amount.



According to previous findings nitric acid completely diffuses into supercritical CO_2 and reacts with steel specimens [4]. A molar amount of CO_2 of 6.59 mol in the autoclave volume (1000 mL) at 100 bar and 60°C was assumed according to thermodynamic data [18]. Thus a molar amount of 329 μmol is equivalent to 50 ppm mole fraction. The constituents of nitric acid as purchased (65 wt%) were 14.5 mol/L HNO_3 and 27 mol/L H_2O . A dosage of 22.7 μL nitric acid therefore yields concentrations of 50 ppm HNO_3 and 94 ppm H_2O in the pressurized CO_2 . In order to investigate the reaction kinetic in static autoclave experiments, a series of tests with differing exposure durations were conducted.

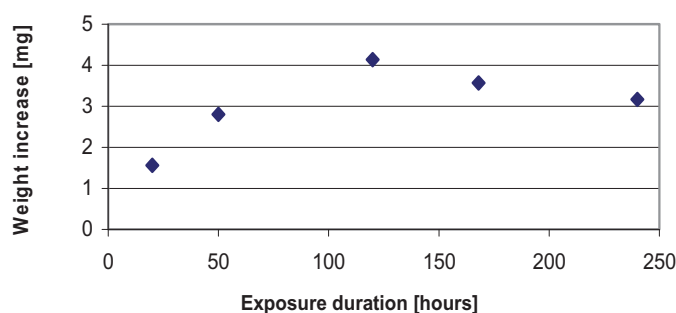


Fig. 3: Weight increase of specimens after corrosion in supercritical CO_2 and 22.7 μL nitric acid corresponding with 50 ppm NO_2 and 94 ppm H_2O .

The results shown in Fig. 3 indicate that corrosion was caused by the addition of nitric acid. The maximum weight increase was observed after 120 hours. The variation was probably caused by variations of the volumetric addition of nitric acid and thus varying molar amounts of corrosive constituents. However, according to the results the corrosive effects of the impurities in the supercritical CO_2 are depleted after a few days. Exposure durations of 5 days therefore appear to be sufficient and no further corrosion can be expected in long-term static exposure tests.

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