CO₂ IMPACT ON FECO₃ CORROSION PRODUCT

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Abstract

Reduction of the emissions of CO_2 and other greenhouse gases is a global challenge. Carbon capture and storage (CCS) is one of the most ready to use technologies applicable for industries such as biogas upgrading, cement, and in general, gas cleaning. Even though the technology is mature, optimization is still needed to reduce costly production losses and shutdowns. CO_2 corrosion is a significant problem in the industry, and therefore, fundamental information regarding the corrosion product, $FeCO_3$, is needed. $FeCO_3$ creates a protective barrier on the steel surface under the right conditions, and therefore information on the solubility is important. In this study, the solubility of $FeCO_3$ in water and under the influence of CO_2 is investigated. Results revealed that the $FeCO_3$ solubility in water (with and without the presence of CO_2) is constant with temperature. A global maximum in the $FeCO_3$ solubility was seen when increasing CO_2 pressure. This phenomenon is not seen in the typical carbonate systems.

Keywords: CO₂, FeCO₃, Corrosion, Solubility

1. Introduction

To combat greenhouse gas emissions and significantly reduce the CO_2 content in the atmosphere, carbon capture and storage (CCS) technology is one of the most viable options.

The CCS technology is easily retrofitted to existing plants, however, optimization is still important to minimize costs and shutdowns.

CO_2 corrosion is a huge problem as it can lead to expensive production losses and shutdowns due to maintenance. In the process of capturing CO_2 from a process stream, the CO_2 is absorbed using a chemical solvent at approximately 40 °C. The CO_2 rich solvent can be regenerated heating the solvent to 120 °C and to a pressure of approximately 1.8 bar. Corrosion in the CCS technology would be seen when the solvent is loaded with CO_2 and also near the reboiler due to the heating. Transporting CO_2 after the capture process would also lead to the risk of corrosion if water is not removed from the gas stream.

As gaseous CO_2 dissolves in aqueous solutions, carbonic acid is formed. As it diffuses to the steel surface, it reacts electrochemically, and Fe^{2+} is released [1], [2]. Released Fe^{2+} reacts with carbonates in the aqueous solutions and leads to the formation of a solid corrosion product, $FeCO_3$. Under the right conditions (pH, temperature, particle size), precipitation of $FeCO_3$ creates a protective layer on the steel surface, which will create a barrier for further corrosion [3]–[10].

Detailed knowledge about the solubility of $FeCO_3$ is needed to understand and predict CO_2 corrosion. The literature is sparse about experimental $FeCO_3$ solubility data. In the review by Fosbøl et al. [11], he summarizes available literature data on solubility. A conclusion is that the lack of anoxic conditions biases the experimental data. Another conclusion was that the purity of the synthesized $FeCO_3$ was questionable.

In this study, the solubility of $FeCO_3$ in water is measured experimentally as a function of:

- Temperature
- CO_2 pressure
- Equilibrium time

The aim is to understand the impact of CO_2 on the $FeCO_3$ solubility to predict when the protective layer is formed. The data would help further optimization processes related to preventing CO_2 corrosion in pipelines.

2. Methods

2.1 Materials

For the synthesis of $FeCO_3$, the chemicals: $FeCl_2·4H_2O$, $NaHCO_3$, and Na_2HCO_3 were purchased from Sigma-Aldrich. All chemicals had a purity of ≥99.0 %.

Solutions of $FeCl_2·4H_2O$, and $NaHCO_3/Na_2HCO_3$ were prepared with degassed with N_2 ultra-pure Milli-Q water.

2.2 FeCO₃ synthesis

The synthesis of $FeCO_3$ was prepared in a glovebox (MBRaun) with an anoxic environment of less than 0.1 ppm.

Solutions of $FeCl_2·4H_2O$ and $NaHCO_3/Na_2CO_3$ were mixed. The prepared solutions were added to a titanium piston-cylinder. The piston cylinder was removed from the glovebox and pressurized to 10 bar. The cylinder was placed in an oven at 130 °C for 24 h.

After 24 h the cylinder was cooled to room temperature and transferred to the glovebox. Here solution was filtered and the solid $FeCO_3$ product was washed several times and let to dry. The product was confirmed by x-ray powder diffraction (XRPD) to be $FeCO_3$, see Figure 1.
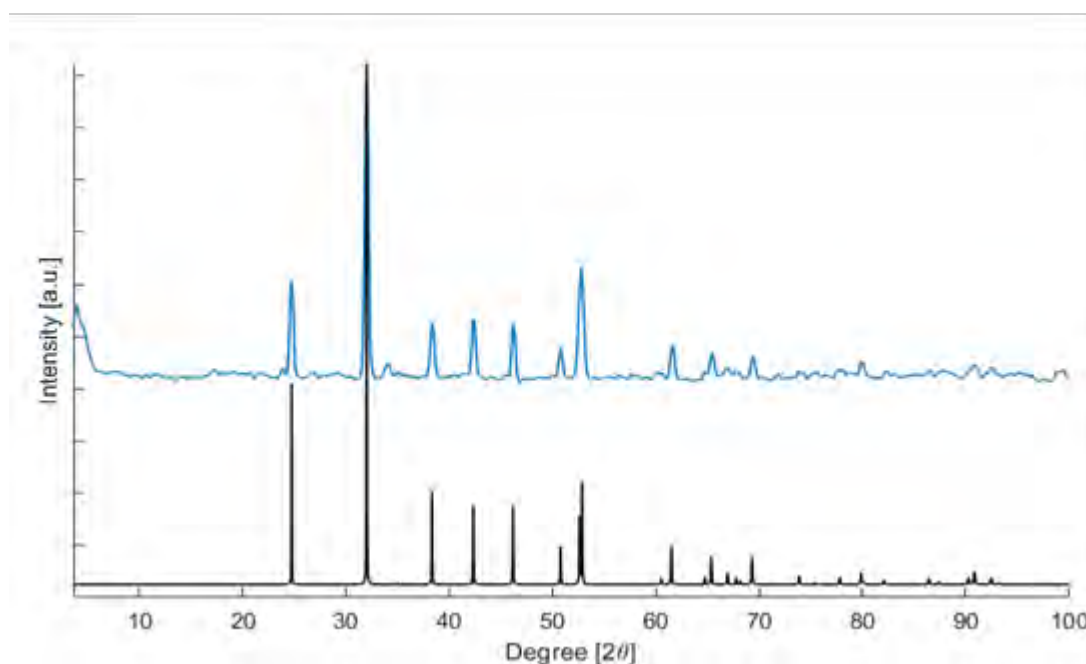

Figure 1. XRPD of $FeCO_3$

2.3 FeCO₃ solubility

All samples were prepared in the glovebox.

The solubility of $FeCO_3$ in water was conducted at ambient pressure in the temperature range 25 to 80 °C. The experiments were performed on the setup equivalent to the setup previously described by Fosbøl et al. [17]. The setup consists of an equilibrium unit with up to 5 cells connected parallel to a heating/cooling circulation bath (Julabo).

15 mg of $FeCO_3$ and 22 g of degassed Milli-Q water were added to a 25 mL blue-cap bottle. Silicon oil was transferred to the blue-cap bottle to prevent oxygen contamination and evaporation of the sample. Each sample solution was submerged in the cell and set to equilibrate for up to 35 days.

To determine the impact of CO_2 on the $FeCO_3$ solubility, pressure reaction vessels (Andrews Glass) were used. Approximately 15 g of $FeCO_3$ and 22 g degassed water were added to the glass reaction vessel together with a magnet. The vessel was closed and removed from the glovebox. All vessels were pressurized with CO_2 and left to equilibrate for 14 days.

All samples were filtrated using 0.22 μm PVDF membrane (Merck Millipore Ltd.).

Iron content was determined spectrophotometrically (Hach Lange, DR 3900) using iron test kits from Hach Lange (LCK321, LCK320).

3. Results and Discussion

3.1 FeCO₃-H₂O

The solubility of $FeCO_3$ in water as a function of equilibrium time is presented in Figure 2 at temperatures 25, 40, 60, and 80 °C. Equilibrium was reached when the Fe concentration did not significantly change over time.

Equilibrium was obtained between 3 to 5 days, as shown in Figure 2b, Figure 2c, and Figure 2d. The kinetics of reaching equilibrium was affected by temperature. This

is seen as the sample held at 25 °C reached an almost constant Fe concentration after more than ten days.

Comparing the equilibrium Fe concentrations at 25-80 °C reveal that the $FeCO_3$ solubility is constant with

temperature. This phenomenon is also seen in the $CaCO_3$ system when no CO_2 is present [12].

The results give an initial impact of the influence of temperature on the $FeCO_3$ solubility.
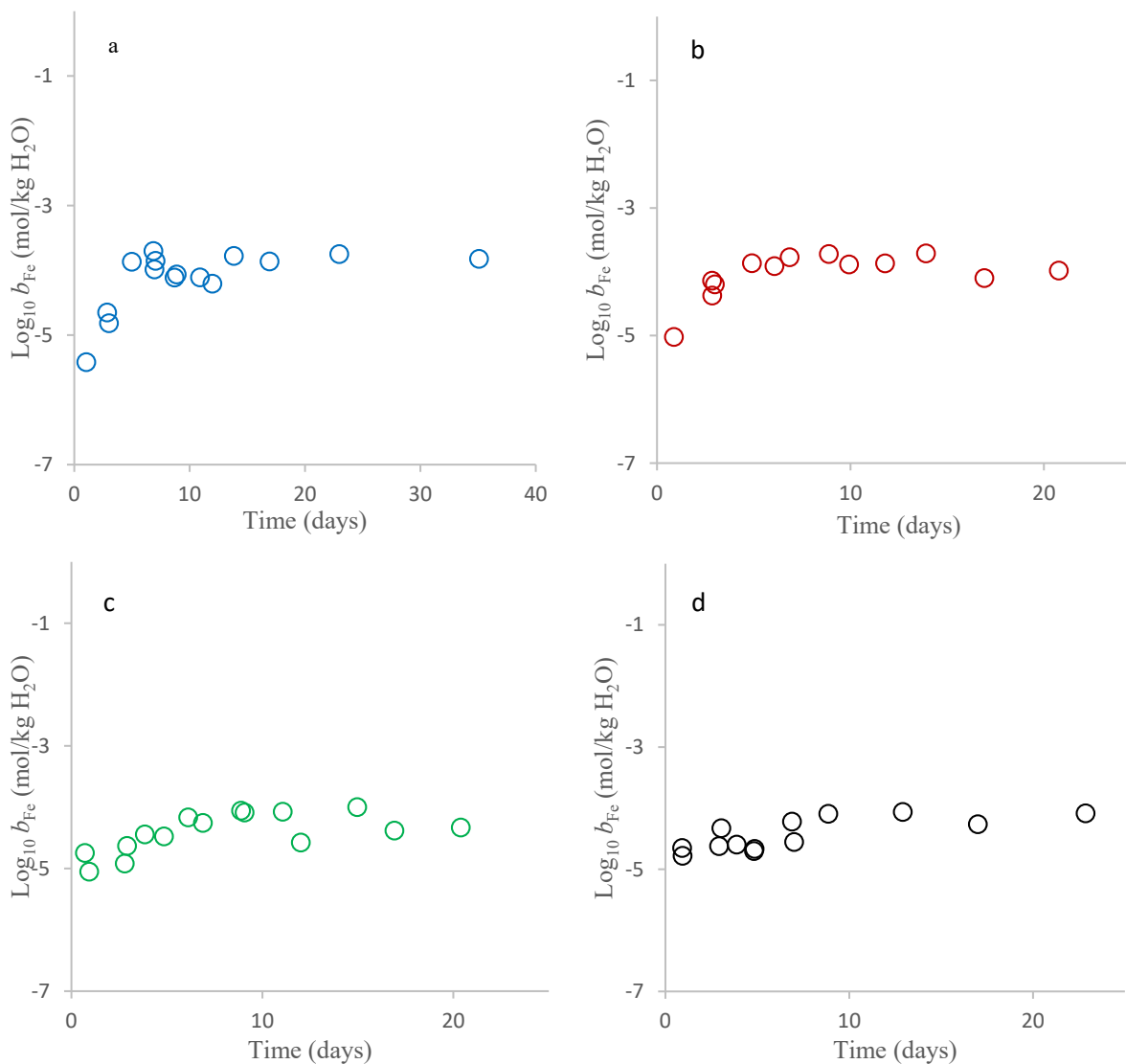

Figure 2. $FeCO_3$ solubility in water as a function of equilibrium time. (a) 5 °C, (b) 25 °C, (c) 40 °C, (d) 60 °C, and (d) 80 °C.

3.2 FeCO₃-CO₂-H₂O

The impact of CO_2 on the $FeCO_3$ solubility at 25 and 40 °C is shown in Figure 3. The full circles are the Fe^{2+} concentration, and the circles without is the Fe^{3+} concentration.

The temperature ranging from 25 to 40 °C has little impact on the solubility. However, the partial pressure of CO_2 affects solubility. A global maximum of the solubility of $FeCO_3$ was measured at 1.5 bar of CO_2. Hereafter the solubility curves are decreasing, increasing the pressure. There was not found a global minimum in the conditions investigated in this study.

The initial results of the impact of CO_2 on the $FeCO_3$ solubility gives some initial knowledge on how the CO_2 affects the solubility. The results at 40 °C mimic at rich loaded solvent after leaving the absorption column. This is a stage where corrosion would be expected as the CO_2 content is high in the liquid solvent.

The impact of CO_2 on the $FeCO_3$ solubility is not comparable to the trends in other carbonate systems [13], [14], and therefore the $FeCO_3$-CO_2-H_2O system needs to be studied further.

The oxidation of $FeCO_3$ is, with minor outliers, relatively stable around -4.5 mol/kg.
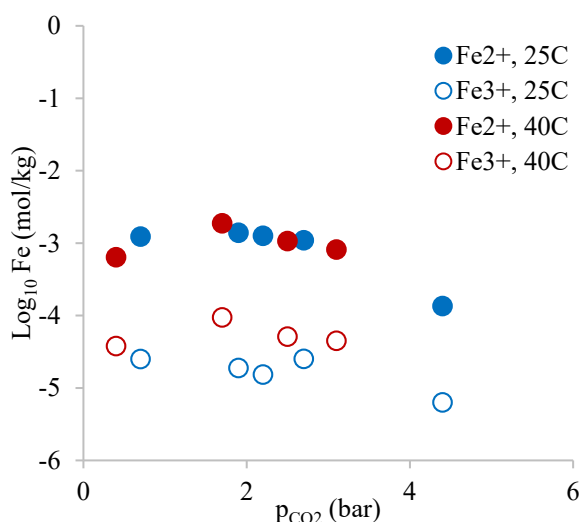
Figure 3. CO₂ impact on FeCO₃ solubility.

4. Conclusion

The solubility of FeCO₃ in water with and without the impact of CO₂ was measured in this study.

The results show that the FeCO₃ solubility is constant with temperature, which is also seen CaCO₃ system whit no air present.

The impact of CO₂ was also studied. The preliminary results showed that the CO₂ pressure influences solubility. The solubility increases up to a CO₂ pressure of 1.5 bar, and increasing the pressure above 1.5 bar, the solubility decreases. This is contrary to typical carbonate solubility phenomena.

There is a need for more experiments investigating the mechanism and the impact of CO₂ on solubility.

Acknowledgements

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