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GHGT-12

## Study of mineral trapping of CO<sub>2</sub> and seal leakage mitigation

Qi Liu<sup>a,\*</sup> and M. Mercedes Maroto-Valer<sup>a,b</sup>

<sup>a</sup> Centre for Innovation in Carbon Capture and Storage (CICCS), School of Engineering and Physical Sciences, Heriot-Watt University, UK.

<sup>b</sup> Institute of Petroleum Engineering, Heriot-Watt University, UK.

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### Abstract

Mineral trapping of carbon dioxide is the safest and the most permanent sequestration mechanism. Brine composition, brine pH, system temperature and pressure have been reported to have significant effects on mineral trapping of CO<sub>2</sub> in brines. It has also been reported that iron cation in brine could cause pH instability that may lead to lower carbonation conversion rate. This study aims to investigate whether ferric or ferrous iron caused this pH instability. pH stability studies and high temperature/high pressure carbonation experiments (150°C, 100bar) with the addition of 1.0M KOH were conducted using different synthetic brines with Fe<sup>3+</sup>, Fe<sup>2+</sup>, and without Fe. It can be concluded from this study that ferrous iron causes pH instability. However, ferrous iron might promote carbonate precipitation in non-pure CO<sub>2</sub> streams in iron oxyhydroxide-containing saline aquifers as seal leakage mitigation.

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*Keywords:* CO<sub>2</sub> storage; mineral trapping; pH instability; leakage mitigation

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### 1. Introduction

CO<sub>2</sub> geological storage is a promising mitigation technology essential in tackling global climate change, and ensuring secure energy supply [1]. In order to accelerate its deployment, trapping mechanisms of underground CO<sub>2</sub>

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\* Corresponding author. Tel.: +44 131 4513299  
E-mail address: [q.liu@hw.ac.uk](mailto:q.liu@hw.ac.uk)

storage need to be fully understood. CO<sub>2</sub> can be stored permanently by mineral trapping via the formation of carbonate, and this would require a massive supply of easily obtained, appropriate calcium and/or magnesium sources in close proximity to the CO<sub>2</sub> emission source. However, it should be noted that brines normally have high concentrations of Ca, Mg and Fe, in addition to the dominant Na and Cl ions [2]. The permanent storage (mineral trapping) of CO<sub>2</sub> in brines takes significantly long periods of time, as the formation and precipitation of carbonates is very slow, and therefore, the main parameters affecting mineral trapping kinetics need to be further understood and when possible optimised. It has been suggested that the precipitation of mineral carbonates is mostly dependent on brine pH [3-4].

Previous studies by the authors concluded that iron in natural brines causes pH instability, but it was not ascertained whether ferric or ferrous iron caused pH instability [5]. Accordingly, the aim of this work is to study synthetic brines mimicking the major ions found in natural brines and including different concentrations of ferric and ferrous iron. Three brines prepared were as follows: Brine 1 containing ferric iron, Brine 2 with ferrous Fe<sup>2+</sup> iron and Brine 3 prepared with no iron. A series of pH stability studies and high pressure high temperature carbonation reactions were conducted using the above three brines.

## 2. Methodology

Three synthetic brines were prepared in this study (see Table 1). The target concentrations of the major ions were chosen from the authors' previous work [5].

- B 1 –containing the first five cations and Fe<sup>3+</sup>.
- B 2 - containing the first five cations and Fe<sup>2+</sup>.
- B 3 – containing the first five cations only.

Table 1. The target concentrations of the major ions in synthetic brine

Target Ion	Ca <sup>2+</sup>	K <sup>+</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	Sr <sup>2+</sup>	Fe <sup>3+</sup> /Fe <sup>2+</sup>
Conc. (ppm)	19350	1180	48500	2055	1800	476

In order to investigate the effect of iron concentration on carbon sequestration, pH stability studies and carbonation experiments were conducted using B1, B2 and B3 with 1.0M KOH. pH stability studies were run at ambient temperature and pressure in open atmosphere. Brine pH was adjusted to an initial pH of 6.3 or 9.0 by adding KOH solution. pH 6.3 was chosen as anything higher than pH 6.8 cause iron hydroxide precipitate while pH 9.0 is favourable for mineral trapping [6]. A 600 ml Parr reactor (model series 4544, Hastelloy C-276) was used to conduct the hydrothermal CO<sub>2</sub>-brine experiments under high temperature/high pressure (150°C,100bar), which

were the same conditions selected in Druckenmiller and Maroto-Valer's previous work (2005). The operational procedure of the high pressure reactor followed the authors' previous study [6]. Liquid samples were analysed by ICP-MS, and solid samples were analysed by XRD.

### 3. Results and discussion

pH stability studies were conducted using the synthetic brines B1, B2 and B3 with KOH until brine pH was stabilised. Figure 1 shows the results of pH stability studies of brines B1 and B2 in over 192 hours. The pairs B1A and B1B, B2A and B2B represent duplicates of brines B1 and B2, respectively.

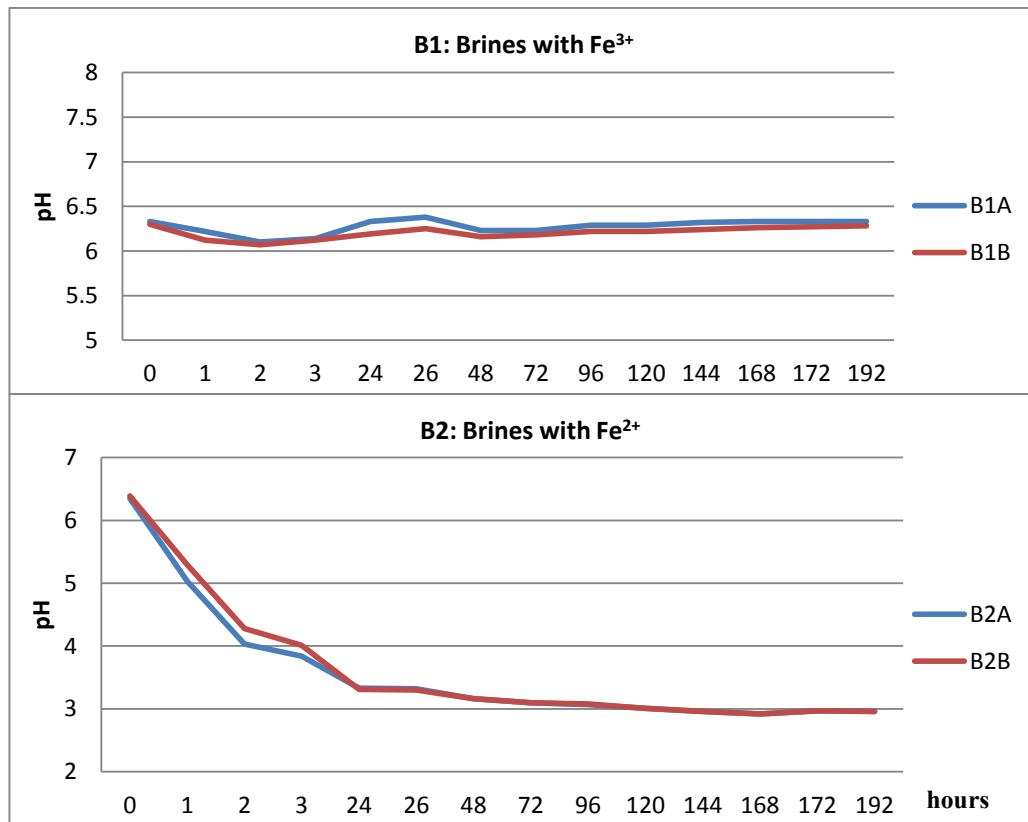


Fig. 1. pH stability studies of B1 and B2 with 1.0M KOH

From Figure 1, it can be observed that the pH of brines B1 (with  $\text{Fe}^{3+}$ ) fluctuated around the initial pH value of 6.3 in the first 48 hours, but they were then stable afterwards. However, the pH of brines B2 (with  $\text{Fe}^{2+}$ ) fell off quickly from 6.3 to around 3.3 in the first day. Then pH for B2 decreased gradually and was stable at around 3.0. The trends of brine pH variation were similar in all duplicate experiments. Therefore, the results obtained in this study proved that ferric iron does not contribute to any pH instability, and this is in contrast with the role of ferrous

iron in brine pH.

Six hydrothermal CO<sub>2</sub>-brine experiments were conducted using B1, B2 and B3 with 1.0M KOH at 150°C and 100bar. The precipitate obtained when using B2 was analysed by XRD with the major peaks identified, as halite (NaCl) and hematite (Fe<sub>2</sub>O<sub>3</sub>), which is consistent with the large drop of Fe<sup>2+</sup> concentration in the ICP-MS results. It could be further concluded that the oxidative precipitation of iron oxide (hematite), which is the transition of the soluble divalent ferric ion Fe<sup>2+</sup> to the oxidized insoluble trivalent form Fe<sup>3+</sup> oxide may be responsible for the pH instability [5]. There was also small amounts of dolomite ferroan (Ca(MgFe)(CO<sub>3</sub>)<sub>2</sub>), which explained the small drop in cation concentration of Mg<sup>2+</sup> and Ca<sup>2+</sup>.

The authors have also investigated sequestration of non-pure CO<sub>2</sub> streams in iron oxyhydroxide-containing saline aquifers and showed that the mineral trapping process is faster when iron is present in the water-rock interactions and carbonate precipitation (siderite) would occur with increasing distance from the well, within the higher pH regions [7-8]. The understanding gained on the effect of brine composition on mineral trapping of CO<sub>2</sub> is now utilised to develop a novel self-sealing process.

#### 4. Conclusion

In summary, this study aimed to investigate whether ferric or ferrous iron caused brine pH instability. It is concluded from this study that the ferrous iron is the reason to cause the instability of brine pH, while ferric iron might promote carbonate precipitation in non-pure CO<sub>2</sub> streams. A further understanding of the effect of employed brines on mineral trapping will result from this work.

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