



## Experimental investigation of CO<sub>2</sub>-brine-calcite interactions under reservoir conditions



Luc Steel, Eric Mackay, M. Mercedes Maroto-Valer\*

Research Centre for Carbon Solutions (RCCS), Heriot-Watt University, UK

### ARTICLE INFO

#### Keywords:

CO<sub>2</sub> geological storage  
Fluid-rock interactions  
Mineral carbonation  
Geochemical modelling

### ABSTRACT

Deep geological formations such as saline aquifers and depleted oil and gas fields are potential sites for CO<sub>2</sub> geological storage. The local host rock in these formations can have significant quantities of calcite present, such as in limestone or where carbonate formations have overlying chalk intervals. Therefore, the objective of this work is to understand how CO<sub>2</sub>-saturated brine interacts with calcite under reservoir conditions. Hydrothermal experiments were carried out over a 6 month period to assess the potential for calcite to buffer brine and promote mineral carbonation over time. In addition, as the system had yet to reach equilibrium at 6 months, geochemical modelling using PHREEQC was performed to calculate the equilibrium state. The dissolution and precipitation of minerals were investigated to determine the effect that these processes have on the properties of the rock, such as porosity. The addition of calcite to the brine resulted in a significant increase in brine pH from 2.03 to 5.72. However, once CO<sub>2</sub> had been injected there was only a slight initial increase in pH, and therefore, the buffering effect of calcite is not sufficient to promote mineral carbonation. The formation of anhydrite, celestite and hematite was observed after 3 months, although dissolution and precipitation were still taking place after 6 months. The PHREEQC modelling conducted estimated an overall decrease in mineral volume of 2.3%, leading to an increase in porosity that is dependent on the SO<sub>4</sub><sup>2-</sup> concentration in the original brine. Therefore, brine composition needs to be considered when injecting CO<sub>2</sub> into reservoirs containing calcite bearing rock.

### 1. Introduction

When injecting CO<sub>2</sub> into deep geological formations, such as saline aquifers and depleted oil and gas fields, it is important to understand how the CO<sub>2</sub> will be stored *via* trapping mechanisms. Moreover, the local host rock in these geological formations may present significant quantities of calcite present, *e.g.* as limestone or where carbonate formations have overlying chalk intervals. However, there is a lack of experimental work that focuses on the interactions between CO<sub>2</sub>-saturated brine and calcite bearing host rock over extended periods of time.

There are two different mechanisms by which CO<sub>2</sub> can be trapped following storage: physical trapping and geochemical trapping [1]. The former is split into three separate mechanisms; static (structural and stratigraphic), hydrodynamic and residual gas trapping, whereas the latter consists of mineral and solubility trapping. Upon injection, CO<sub>2</sub> is generally trapped first by physical trapping mechanisms, as geochemical trapping occurs over a longer time period [2]. Geochemical trapping is preferred as it does not depend on the integrity of the cap rock, unlike physical trapping, and so is a more secure method of storage.

Due to the formation of solid immobile carbonates, mineral trapping is the safest and most permanent means of CO<sub>2</sub> geological storage, and follows on from solubility trapping since it depends on CO<sub>2</sub> dissolution in brine. Mineral trapping in these deep formations usually takes place at temperatures between ~40–200 °C and pressures ranging from 70 to 280 bars [3]. Previous studies have shown that higher pressure and temperature conditions result in an increase in the formation of mineral carbonates, with temperature having a greater effect than pressure [4]. The contribution of pressure and temperature are, however, minor in comparison with the effect that brine pH has on mineral trapping.

The optimal pH level for the formation of mineral carbonates is over 9.0 due to the high concentration of carbonate (CO<sub>3</sub><sup>2-</sup>) ions present [5]. Brine pH in deep formations usually ranges from 2 to 7 and at pH < 7, formation of mineral carbonates is unlikely due to too few or no carbonate ions being present [6]. The brine pH, however, after initially reducing on the injection of CO<sub>2</sub>, does subsequently increase due to geochemical reactions between the host rock and the injected CO<sub>2</sub> [7]. When CO<sub>2</sub> dissolves in brine, it forms a weak acid. This acid will then react with calcite from the host rock, resulting in an overall loss of

\* Corresponding author.

E-mail address: [m.maroto-valer@hw.ac.uk](mailto:m.maroto-valer@hw.ac.uk) (M.M. Maroto-Valer).

calcite and the formation of bicarbonate ( $\text{HCO}_3^-$ ), which is alkaline [7]. This will then cause the pH of the brine to increase. Therefore, as more  $\text{CO}_2$  is injected and dissolved in the brine, the brine pH will further increase due to the increased concentration of  $\text{HCO}_3^-$  ions. Consequently, calcite should act as a buffer and may promote mineral carbonation [8]. Buffering of acid brine in chalk formations due to calcite dissolution and any resulting changes in porosity will be of interest in carbonate formations where there are chalk intervals overlying many of the potential aquifer stores.

In addition, the dissolution and precipitation of minerals may affect the properties of the rock, such as the porosity. Changes in porosity will have a direct effect on  $\text{CO}_2$  storage security. For example, if the porosity decreases then this will result in increased  $\text{CO}_2$  storage security as the extent of the  $\text{CO}_2$  migration will be reduced by the reduced flow capacity [9]. In contrast, a reduction in porosity will require greater injection pressure to displace  $\text{CO}_2$  into the formation.

Therefore, the aim of this study is to understand how  $\text{CO}_2$ -saturated brine interacts with calcite under reservoir conditions. Hydrothermal experiments were conducted over a 6 month period to assess the potential for calcite to buffer  $\text{CO}_2$ -saturated brine and promote mineral carbonation. In addition, as the system had yet to reach equilibrium at 6 months, geochemical modelling using PHREEQC was performed to calculate the equilibrium state. The effect of dissolution of calcite and precipitation of other minerals on the porosity of the host rock is also investigated.

## 2. Materials and methods

### 2.1. Brine preparation

The brine composition used for these experiments was that obtained from a North Sea oil field where seawater injection had taken place and information on the brine composition had been recorded over a 12 year period. The objective was not to consider  $\text{CO}_2$  Enhanced Oil Recovery, but injection of  $\text{CO}_2$  into an aquifer which may have been swept (or partially swept) by seawater during oilfield operations, and for which the brine composition was well characterised. It is assumed that oilfield operations would have ceased, that the system would thus be closed, and that enough time had elapsed for it to be fully equilibrated before  $\text{CO}_2$  injection commenced. The ion concentrations of the brine were achieved by dissolving the following seven salts, namely NaCl, KCl,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NaHSO}_4$  in Milipore water. The salts were weighed and dissolved in a 2 l beaker using Milipore water to make a 1 l solution. The sequence in which the salts are added is an important part of the brine preparation. Adding the salts in the wrong order can lead to the formation of precipitates, and can make the desired brine composition impossible to achieve. Each salt was added and dissolved before the addition of the next salt. A clear, colourless solution was obtained, with no precipitates forming, by adding the salts in the following order;  $\text{NaHSO}_4$ , NaCl, KCl,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 6\text{H}_2\text{O}$  and finally  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ . The  $\text{NaHSO}_4$  was added and dissolved in the distilled water first, since in previous attempts the  $\text{SO}_4^{2-}$  ions reacted with the metal cations already dissolved in the water. Once the  $\text{SO}_4^{2-}$  ions were dissolved, the monovalent salts were added in order of quantity, followed by the divalent salts.  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$  was added last, as it was calculated that the saturation ratio (SR) was 15.79 for  $\text{SrSO}_4$ , meaning that the formation of  $\text{SrSO}_4$  was thermodynamically favourable, although no precipitate formed [10].

### 2.2. Characterisation of brine

Once a clear solution was obtained the pH of the brine was measured using a Thermo Scientific Orion 3-star benchtop pH meter, with an analytical error of  $\pm 0.02$ . Two samples of the brine were then taken for Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES) analysis to measure the major ion concentrations. Each sample

was diluted with Milipore water by a factor of 10 and 2% nitric acid was added so as to prevent any reactions between the ions. ICP-OES is a very effective analytical tool for determining trace metal elements at concentrations of 0.0002–1000 ppm [11]. It can also be used to detect several non-metallic elements such as sulphur and phosphorus.

The ICP-OES used is a Perkin Elmer Optima 5300 DV ICP-OES and was selected as it can detect and measure the concentrations of  $\text{SO}_4^{2-}$  and has a relatively high total dissolved solids tolerance of 5–10% [12]. The concentration range for this particular instrument is 0.01–1000 ppm and that is why the brine samples had to be diluted by a factor of 10.

### 2.3. Calcite preparation

For these experiments, 1 kg of 100% calcite chips were purchased from the Geological Superstore. These chips were then ground up using a pestle and mortar so that a powder was obtained. Particle size has a direct and significant effect on reaction rates [13]. Reducing particle size results in increased surface area and hence quicker reaction rates. For example, when Rahmani et al. (2014) prepared calcite from red gypsum for mineral carbonation they noted that decreasing the particle size from  $> 200 \mu\text{m}$  to  $< 75 \mu\text{m}$ , increased the amount of Ca converted to calcite from 37.0% to 98.8% [14]. Consequently, if the intention is to maximise reaction rates then the particle size should be as small as possible. However, it is also important that the prepared particles are within a specific size range to enable a direct comparison between different experiments. This is where the importance of defining and analysing particle size distribution is evident.

The desired particle size for these experiments was chosen to be in the range 45–75  $\mu\text{m}$ . The 45  $\mu\text{m}$  and 75  $\mu\text{m}$  sieves were the smallest available in the laboratory, and since previous work has shown that reaction rates can be maximised at particle sizes  $< 75 \mu\text{m}$ , it was considered an appropriate choice [14].

### 2.4. Characterisation of calcite

Once the 45–75  $\mu\text{m}$  calcite had been prepared, 1 g of sample was taken for particle size distribution analysis. For the particle size distribution analysis, a laser diffraction particle size analyzer (Mastersizer 3000) was used. The laser diffraction technique can be used to measure both dry and wet samples, ranging from 10 nm up to 5 mm [15]. Along with particle size distribution, another extremely important factor that affects reaction rates is the powder's specific surface area [16]. Specific surface area can be calculated using the Brunauer, Emmett and Teller (BET) method. The equipment used to perform the BET analysis was a Micromeritics' Gemini VII 2390 Series Surface Area Analyzer. Before sampling can take place the sample must undergo degassing so as to remove any vapours or gases that may have been adsorbed onto the surface. Approximately 0.4 g of powder is added to a sampling tube and the overall weight is measured. The sample is placed in a heater at a temperature of 200 °C and nitrogen gas is pumped through it for a period of 24 h. After this point the sample is weighed again (noting any weight loss) and can now be used for analysis.

X-ray Diffraction (XRD) was used to identify the mineral phases present in the sample and to confirm that the calcite chips were 100% pure, as stated upon purchase. The analysis was performed over a  $2\theta$  range of 5° to 85° and the equipment used was a Bruker Nonius X8-Apex2 CCD. The data obtained was then compared with that from the International Centre of Diffraction Data (ICDD) so as to identify what crystalline mineral phases were present. For the XRD analysis, 1 g of sample was provided and the particle size was already within the required size of  $< 75 \mu\text{m}$ .

Scanning Electron Microscopy/Energy Dispersive X-ray Spectroscopy (SEM/EDS) was performed to construct an image of the sample surface as well as for chemical characterisation and elemental analysis. The equipment used was a Quanta FEG 650 Suite which is

Download English Version:

<https://daneshyari.com/en/article/4914324>

Download Persian Version:

<https://daneshyari.com/article/4914324>

[Daneshyari.com](https://daneshyari.com)