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The effect of dissolved sulphate on calcite precipitation kinetics and consequences for subsurface CO₂ storage

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Abstract

Steady state calcite precipitation rates were measured in mixed-flow reactors at 25 °C and pH ~9 in the presence and absence of aqueous sulphate. Two aqueous inlet solutions were used to provoke precipitation 1) containing NaHCO₃ and Na₂CO₃ and 2) a second containing CaCl₂. 0-20 mM of Na₂SO₄ was added to this second solution to assess the effects of the presence of aqueous sulphate on rates. The presence of aqueous sulphur is found to decrease calcite precipitation rates; the presence of 20 mM lowers calcite dissolution rates by a factor of 2 at a constant Ω of 2.6. The slowing of calcite precipitation may aid subsurface carbon storage efforts as it will slow pore clogging of injected rock formation. In addition as the rate limiting step of mineral carbonation is the dissolution of divalent-metal bearing silicate solids such as basaltic glass or olivine, it seems likely that a decrease of carbonate precipitation rates of a factor of 2 will negligibly effect mineral carbonation efforts.

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Keyword: Calcite, precipitation, mineral carbonation, aqueous sulphate.

1. Introduction

Calcite precipitation rates are a prerequisite for the understanding of the global carbon cycle, and to optimising the conditions for carbon sequestration through carbonate mineralization (e.g. [1] [2]). It is known that the presence of some trace species in solution can have dramatic effects on calcite precipitation rates which could strongly influence the success of carbon mineralization efforts [3][4][5][6].

A major challenge to sequestering carbon in subsurface geologic formations is that numerous other gases are commonly produced during hydrocarbon combustion (c.f.[7]). Sulphuric gases are one of these common by-product gases of hydrocarbon combustion. The high reactivity and oxidation capacity of sulphuric species make them difficult to store on land. By their co-injection with CO₂ it may be possible to store the sulphate safely underground. One of the potential consequences of the co-injection of sulphuric gases with CO₂ during carbon storage efforts is that the presence of this gas might alter the reactivity of the minerals present in the subsurface. The presence of

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aqueous sulphate has been shown to accelerate the dissolution of basaltic glass [8]. This acceleration favours the mineral carbonation of CO₂ by making available divalent cations to aqueous solution more rapidly where they can form stable carbonates. The effect of the presence of sulphate in calcite precipitation, however, has yet to be measured. This study is aimed at determining the effect of dissolved sulphate on calcite precipitation rates at conditions present at subsurface carbon sequestration sites. As calcite precipitation is the goal of mineralogical storage efforts, any inhibition of rates could have detrimental effects on such storage efforts.

2. Theoretical background

Calcite dissolution and precipitation kinetics have traditionally been described as a function of the degree of disequilibrium of the aqueous solution by using a mechanistic model [9], which describes the elementary reactions controlling dissolution in different pH regions. This approach generally employs the following empirical equation for precipitation reactions:

$$r = k(\Omega - 1)^n \quad (1)$$

where r represents the specific precipitation rate, k stands for an apparent rate constant, $(\Omega - 1)$ represents the degree of supersaturation of the reactive fluid and n designates an empirical reaction order, which is indicative of the growth mechanism of mineral surfaces. Ω defines the saturation state of solution, equal to the ratio of the ion activity product of dissolved mineral components (Q) to the thermodynamic solubility product (K_{sp}). For calcite, the saturation state is defined as:

$$\Omega = \frac{Q}{K_{sp}} = \frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{K_{sp}} \quad (2)$$

where a_i refers to the activity of the subscripted aqueous species.

3. Methods

Large transparent Iceland spar calcite crystals, collected from hydrothermal veins in basaltic traps in Central Siberia as described by Pokrovsky et al. [10], were used in these experiments. Electron microprobe and total chemical analysis showed that the samples contained less than 0.5% impurities and no other phases were detected using X Ray Diffraction. These samples were ground and then sieved to obtain the 100 to 200 μm size fraction. The calcite powder was then reacted for several seconds in a 1% aqueous HCl solution, ultrasonically cleaned in alcohol to remove adhering fine particles, rinsed repeatedly with distilled water, then dried overnight at 60 °C. The specific surface area of the resulting calcite powder was 370 cm²/g as determined by multi-point krypton absorption using the B.E.T. method on a Quantachrome Autosorb-1. Images of the calcite powder taken before the precipitation experiments using a JEOL JSM 6460LV Scanning Electron Microscope (SEM) are shown in Figure 1.

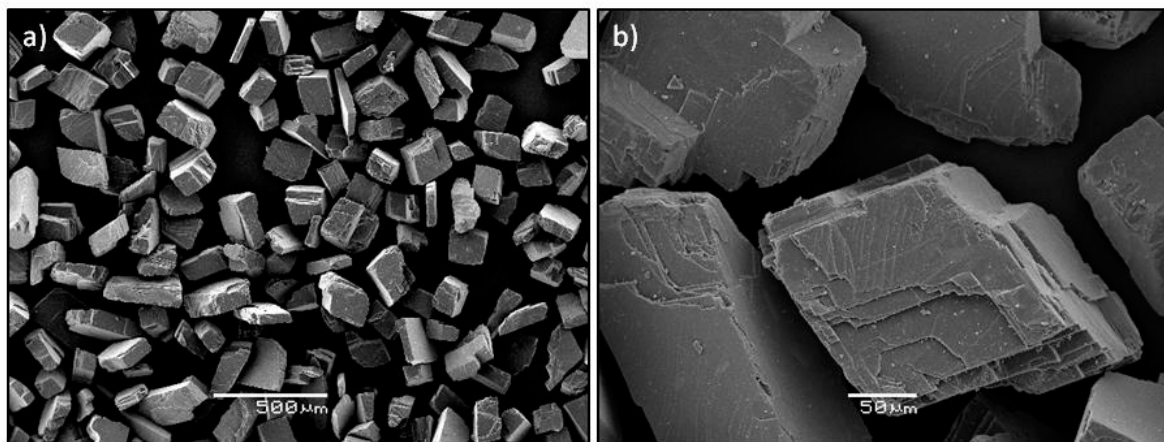


Figure 1 Scanning electron microscope images of the calcite seeds used in the present study. Image b) is an enlargement of a) showing fine scale surface roughness.

Calcite precipitation experiments were performed on the calcite seeds described above in 30 mL mixed flow polypropylene reactor systems at pH \sim 9.0. The experiments were all performed at 25 ± 2 °C. The reactors were continuously stirred with floating Teflon stirring bars. The solution left the reactor through a $2.5 \mu\text{m}$ polypropylene filter. No additional filtering was performed on outlet fluid samples obtained from either reactor before chemical analysis.

Calcite precipitation was induced by mixing together two distinct solutions 1) an aqueous Na-carbonate solution and 2) an aqueous CaCl_2 solution. This first solution was comprised of demineralised H_2O , NaHCO_3 (99.5%) and Na_2CO_3 (> 99%) from Sigma-Aldrich. The concentration of NaHCO_3 and Na_2CO_3 in the carbonate solution was 0.0169 and 0.00129 mol/kg, respectively. The second solution was comprised of CaCl_2 (1000 ppm standard) and Na_2SO_4 (99%) from Merck. The acidic CaCl_2 stock solution was neutralized using 1 M NaOH from Merck. In the CaCl_2 solution, the amount of Ca was 0.277 mmol/kg and the concentration of Na_2SO_4 varied between 0 and 40 mmol/kg.

The two inlet solutions were injected simultaneously into the reactors using Gilson peristaltic pumps to inject simultaneously two distinct solutions at identical flow rates. These pumps allow fluid flow rates from 0.01-10 g/min [11]. The injection of two separate solutions was essential to avoid calcite precipitation prior to solution entry into the reactor. At the onset of each experiment, the reactor was filled with 0.25 g of calcite seed crystals and a 1:1 mixture of the two inlet solutions. The flow rate was held constant until the outlet solution contained a steady state Ca concentration. Steady-state dissolution rates were obtained after 1-4 days. The sulphate was added to some of the CaCl_2 solution.

The Ca content of the inlet and outlet solutions was determined using a Varian SpectrAA 300 atomic absorption spectrometer. The reproducibility of chemical analyses was $\pm 2\%$. The outlet solution pH was measured at 23°C immediately after sampling. Solution alkalinity was fixed by the large concentration of bicarbonate in the reactive solution and the solution pH.

4. Results

Steady state calcite precipitation rates (r) were computed from the measured steady-state Ca concentration using

$$r = \frac{\Delta[\text{Ca}]F}{s_{\text{BET}}M} \quad (4)$$

where $\Delta[\text{Ca}]$ stands for the concentration difference between the inlet and outlet of Ca in solution (mol/kg), F represents the fluid mass flow rate, s_{BET} denotes the BET specific surface area of the initial glass, and M signifies the initial mass of glass in the reactor. An example of the approach of an experiment to steady state is illustrated in Figure 2. This figure shows the temporal evolution of the Ca concentration inside the reactor during an experiment with a total fluid flow rate of 0.1 g/min. The residence time of this experiment, defined as the volume of the reactor divided by the fluid flow rate, is 5 h; steady state Ca concentration is apparent after 4 days.

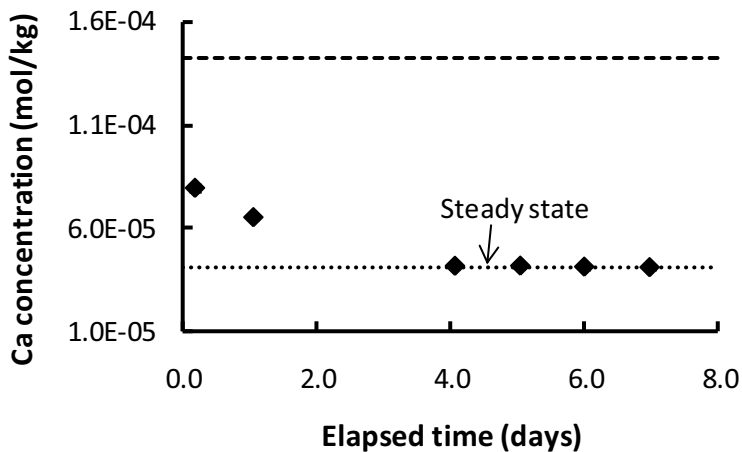


Figure 2 Temporal evolution of the Ca concentration inside the reactor during an experiment. The thick dashed line shows the inlet concentration of Ca while the diamonds show the outlet concentration of Ca from the reactor.

The concentration of Ca in the output fluid versus the reactive fluid flow rate for all experiments performed are shown in Figure 3. The estimated uncertainty of these experiments is ± 0.2 log units. As the Figure shows, the concentration of Ca in the output fluids are all less than that of the inlet fluids consistent with calcite precipitation. Moreover the outlet fluid Ca concentrations increase with increasing aqueous sulphate concentration, indicating that calcite precipitation rates decrease as sulphate concentration increases.

The saturation state of calcite inside the reactor changes with reactive fluid flow rate and dissolved sulphate concentration. The logarithm of measured calcite precipitation rates are plotted as a function of $\log(\Omega-1)$ in Figure 4. The saturation states were calculated using the PHREEQC computer code [12] together with its `l1n1.dat` database. Calcite precipitation rates decrease rapidly with decreasing saturation state at relatively high supersaturation ($\log(\Omega-1) = 0-0.3$, depending on the amount of sulphate present), while the precipitation rate tend to be independent of saturation state closer to equilibrium. The presence of aqueous sulphur decreases constant saturation state calcite precipitation rates; the presence of 20 mM lowers calcite dissolution rates by a factor of 2 at a constant Ω of 2.6.

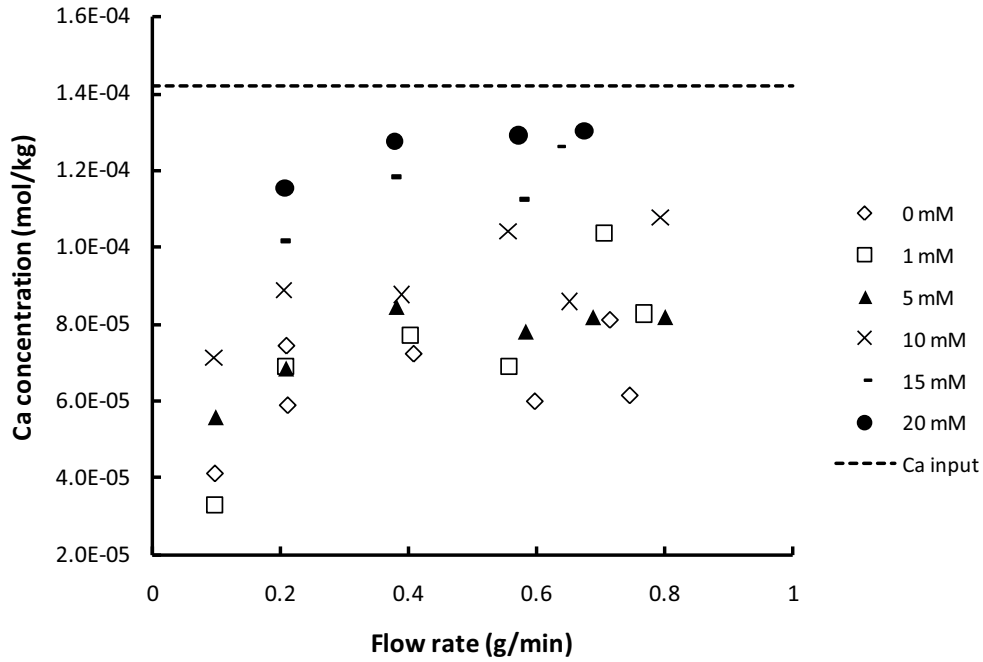


Figure 3 The concentration of Ca in the output versus flow rate for all experiments performed in this study. Aqueous sulphate concentrations of the outlet solution ranged from 0 to 20 mM. The estimated uncertainty of the measured concentrations are approximated by the symbol size.

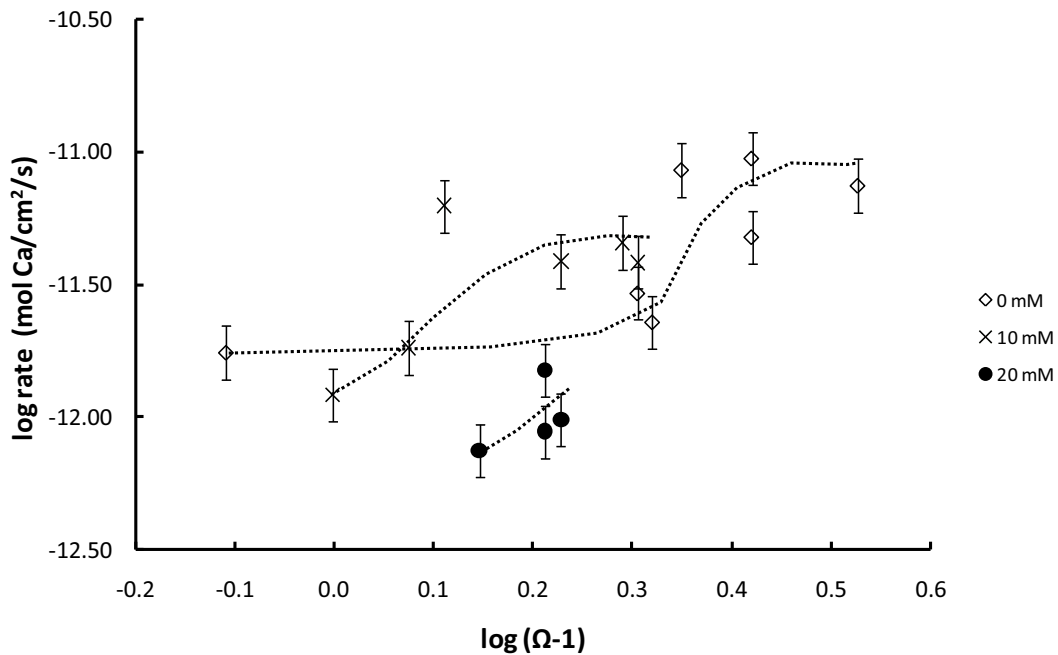


Figure 4 The logarithm of the measured steady state calcite precipitation rates versus $\log(\Omega-1)$ and the indicated concentrations of sulphate. The dashed curves are for the aid of the reader.

5 Discussion and conclusions

The observation that sulphate slows somewhat calcite precipitation has both positive and negative consequences for CO₂ storage. A positive consequence is that if the presence of sulphate slows calcite precipitation this might prevent pore clogging and decreasing permeability in the target reservoir. On the other side, a negative consequence is that less CO₂ might be mineralized as calcite.

A number of recent studies have suggested that basalts and ultramafic rocks might be excellent CO₂ injection hosts for a number of reasons. These rocks are rich in divalent cations and have high dissolution rates which would promote mineral carbonation [13][14][15][16]. It has been shown that the rate limiting step in the carbonization process in these types of rock is the dissolution of the primary minerals and the following release of divalent cations. A recent study [8] has shown that the dissolution rate of basaltic glass can be enhanced by the addition of sulphate. As calcite precipitation rates are still far faster than the dissolution rates of the divalent metal bearing minerals present in basalts and ultra mafic rocks [17][18][19][20], the observation that the presence of sulphate might decrease calcite precipitation rates by a factor of two has likely negligible effects on mineral carbonation rates in these systems.

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