Reactions During CO₂ Geological Sequestration: Dissolution of Calcite and Dolomite Coupled to Gypsum Precipitation

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INTRODUCTION.

CO_2 geological sequestration consists in injecting supercritical CO_2 into a deep saline aquifer (CO_2 should be in supercritical state to ensure a high density, around 800 kg/m³, and an efficient use of pore space). This requires pressures nearing 100 bar, which explains why injection needs to be deep.

Supercritical CO_2 is less dense and much less viscous than resident saline water. Therefore, it will tend to float until it reaches a low permeability, high entry pressure, mechanically stable caprock that traps it. As a result, a CO_2 phase bubble will tend to form at the aquifer top. At the injection pressure, CO_2 is quite soluble (around 3% in mass; Garcia, 2003). Therefore, it will dissolve. At first, dissolution is limited by diffusion and dispersion away from the CO_2 bubble. However, as time passes, unstable gravity fingers develop below the CO_2 bubble because CO_2-saturated brines are denser than resident brines. The onset of convection as a transport mechanism increases mineral dissolution rates significantly (Riaz et al, 2006). The coupling of flow and chemical reaction can significantly modify the original porosity, permeability and degree of heterogeneity of the rock (e.g. formation of wormholes). Therefore, there is a need to quantify the mineral reaction rates in the rock, the nature of the secondary minerals precipitating, the volumes of reaction and the consequent changes in porosity. With this aim, we have initiated an experimental study of calcite and dolomite dissolution and gypsum precipitation, which are likely reactions to occur in the reservoir rock.

The repository rocks for CO_2 injection at the Hontomín (Burgos) test site are predominantly limestones and dolostones, with clays containing evaporites at the bottom (Keuper). The seal on top of the reservoir is composed mainly of shales and marls, with chlorite and illite as the dominant clay minerals. With this lithology, groundwater (brine) is nearly equilibrated with respect to calcite, dolomite and gypsum/anhydrite.

EXPERIMENTAL METHODOLOGY.

Two types of experiments were carried out at room T and atmospheric P_{CO2}: (1) flow-through experiments with calcite and dolomite grains (1 – 2 mm) at pH between 1.5 and 3 and (2) in-situ AFM experiments with Iceland spar (calcite) at pH 2.5. Flow rates ranged from 0.030 to 0.035 mL min⁻¹. In the flow-through experiments HCl and H_2SO_4 solutions were continually injected into the cells containing a known mass of calcite or dolomite. In the AFM experiment, a H_2SO_4 solution was reacting with calcite. All the HCl and H_2SO_4 solutions were equilibrated with respect to gypsum.

RESULTS AND DISCUSSION.

Experimental.

Experimental work started with the study of the kinetics of the dissolution of calcite and dolomite coupled to the precipitation of gypsum. The injection of CO_2 will cause the formation of CO_2-rich acid brines, which will induce the dissolution of the carbonate minerals. Since the brine contains sulfate (from the dissolution of evaporites), gypsum (or anhydrite at depth) will precipitate, which may cover the surface of the dissolving carbonate causing its passivation:
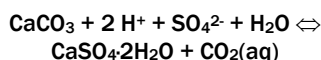
$$CaCO_3 + 2\,H^+ + SO_4^{2-} + H_2O \Leftrightarrow CaSO_4 \cdot 2H_2O + CO_2(aq)$$

Fig. 1 shows the variation of output pH and Ca and S concentrations in an experiment of calcite dissolution at pH 1.6.
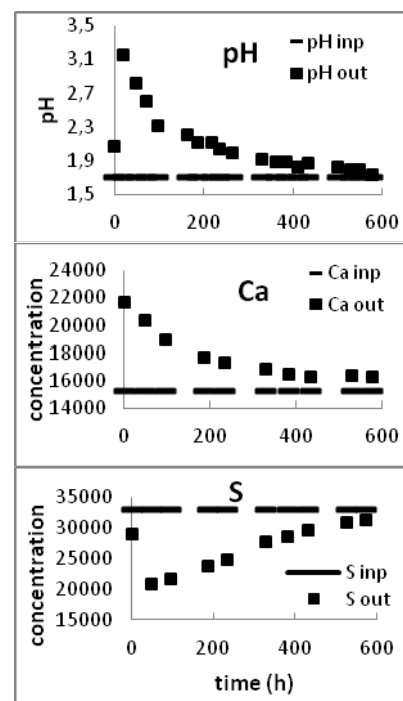

fig 1. Variation of input and output pH, calcium and sulfur concentrations (microM) with time in an experiment at pH 1.6.

The increase (output > input) in calcium concentration indicates that calcite dissolves, whereas sulfur concentration shows gypsum precipitation (output < input). After approximately 600 h, output and input pH and Ca and S concentrations are the same, indicating that the calcite surface is passivated (Fig. 2). Likewise, dolomite grains reacted with a H_2SO_4 solution equilibrated with respect to gypsum and pH 1.5. The system behavior was similar to that of calcite dissolution. However, after approximately 600 h, the dolomite surface was not passivated yet (Fig. 2c, 2d).

In the in-situ AFM experiments,

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formation of etch pits was observed when the cleaved surface of Iceland spar reacted with dionized water (Fig. 3a), whereas when reacted with the sulfate solution equilibrated with respect to gypsum at pH 2.5, gypsum started to precipitate on the calcite surface (Fig. 3b).

Modeling.

In the flow-through experiments, knowing the dissolution rate law for calcite (e.g. Palandri and Kharaka, 2004), its surface area (0.5 m²/g, measured by BET), the volume of solution in the cell (40 mL) and the flow rate (0.035 mL/min), it is possible to calculate the expected evolution of the solution composition at the outlet of the reaction cell. The calculated evolution of solution composition overestimated the dissolution rate of calcite (large increase in pH and Ca concentration; Fig 4). Moreover, a rapid decrease in sulfate concentration was caused by the precipitation of gypsum. The model predicted the complete dissolution of calcite at ≈ 750 h (fast dissolution).
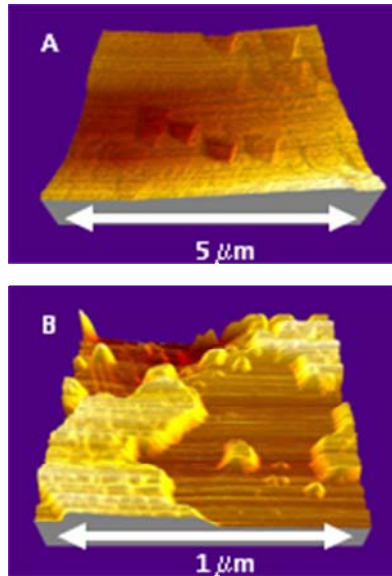
fig 3. AFM images that show (a) dissolution of calcite after 20 min in deionized water, and (b) precipitation of gypsum after 40 min in a gypsum-equilibrated H_2SO_4 solution. Calcite dissolution was characterized by etch pit formation. Gypsum precipitation took place at preferred sites over the reacted surface before calcite surface became fully passivated.

The refinement of the model required the reactive surface area of calcite to be decreased (several orders of magnitude) until a match between model and experimental results was achieved (Fig. 4). The reason for this apparently small reactive surface area probably resides in the effect caused by gypsum precipitating directly on the surfaces of the calcite grains, causing a passivation of the reacting calcite. The evolution of solution composition indicated that the ratio between the volumes of gypsum precipitated and calcite dissolved equaled 1.4 (V_{gyp}/V_{cc-dis} = 1.4), which would translate into a decrease in porosity of the rock matrix.

These results clearly show that even for such a simple system, reaction rates (including the important passivation effects) have to be studied first in the laboratory. Otherwise, model predictions may be significantly off.

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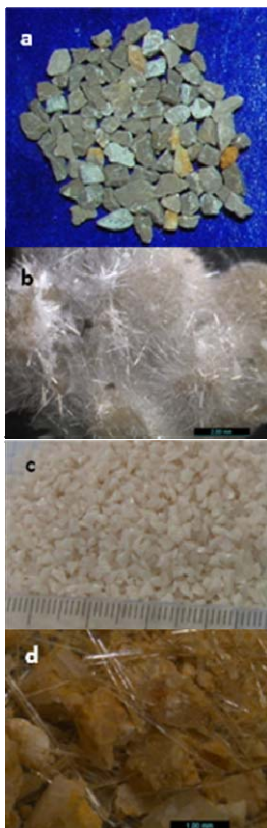
fig 2. Calcite grains before (a) and after reaction (b). Calcite surface was passivated by precipitation of needle-shaped gypsum crystals. Dolomite grains before (c) and after reaction (d). Dolomite surface was not fully passivated after 600 h of reaction.
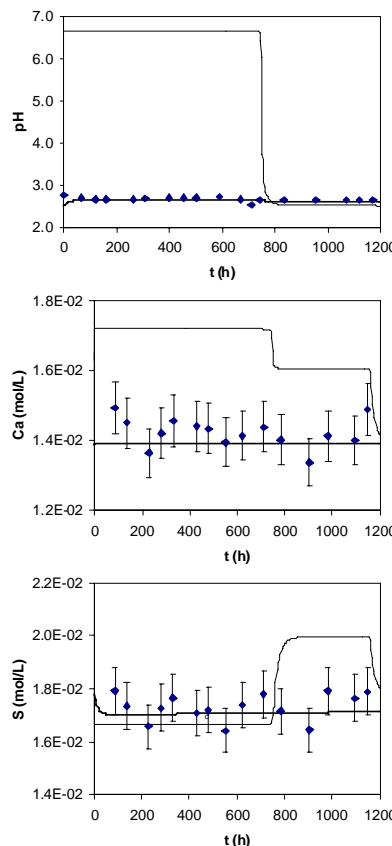
fig 4. Experimental (initial pH 2.7) and model results (output pH, Ca, S). Symbols: Experimental data. Thin lines: First model results. Thick lines: Refined model.