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Interaction between CO_2-rich sulfate solutions and carbonate reservoir rocks from atmospheric to supercritical CO_2 conditions: Experiments and modeling

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ABSTRACT

A test site for CO_2 geological storage is situated in Hontomín (Burgos, northern Spain) with a reservoir rock that is mainly composed of limestone. During and after CO_2 injection, the resulting CO_2-rich acid brine gives rise to the dissolution of carbonate minerals (calcite and dolomite) and gypsum (or anhydrite at depth) may precipitate since the reservoir brine contains sulfate. Experiments using columns filled with crushed limestone or dolostone were conducted under different P–pCO_2 conditions (atmospheric: 1–$10^{-3.5}$ bar; subcritical: 10–10 bar; and supercritical: 150–34 bar), T (25, 40 and 60 °C) and input solution compositions (gypsum-undersaturated and gypsum-equilibrated solutions). We evaluated the effect of these parameters on the coupled reactions of calcite/dolomite dissolution and gypsum/anhydrite precipitation. The CrunchFlow and PhreeqC (v.3) numerical codes were used to perform reactive transport simulations of the experiments.

Within the range of P–pCO_2 and T of this study only gypsum precipitation took place (no anhydrite was detected) and this only occurred when the injected solution was equilibrated with gypsum. Under the P–pCO_2–T conditions, the volume of precipitated gypsum was smaller than the volume of dissolved carbonate minerals, yielding an increase in porosity ($\Delta\phi$ up to $\approx$4%).

A decrease in T favored limestone dissolution regardless of pCO_2 owing to increasing undersaturation with decreasing temperature. However, gypsum precipitation was favored at high T and under atmospheric pCO_2 conditions but not at high T and under 10 bar of pCO_2 conditions. The increase in limestone dissolution with pCO_2 was directly attributed to pH, which was more acidic at higher pCO_2.

Limestone dissolution induced late gypsum precipitation (long induction time) in contrast to dolostone dissolution, which promoted rapid gypsum precipitation. Moreover, owing to the slow kinetics of dolomite dissolution with respect to that of calcite, both the volume of dissolved mineral and the increase in porosity were larger in the limestone experiments than in the dolostone ones under all pCO_2 conditions ($10^{-3.5}$ and 10 bar).

By increasing pCO_2, carbonate dissolution occurred along the column whereas it was localized in the very inlet under atmospheric conditions. This was due to the buffer capacity of the carbonic acid, which maintains pH at around 5 and keeps the solution undersaturated with respect to calcite and dolomite along the column.

1D reactive transport simulations reproduced the experimental data (carbonate dissolution and gypsum precipitation for different P–pCO_2–T conditions). Drawing on reaction rate laws in the literature, we used the reactive surface area to fit the models to the experimental data. The values of the reactive surface area were much smaller than those calculated from the geometric areas.

1. Introduction

CO_2 injection into deep saline aquifers is one of the three main options of geological storage of CO_2. Several studies in the past have shown that deep saline aquifers provide the largest storage capacity because of their size and distribution with respect to the two other major options (depleted hydrocarbon reservoirs and deep un-mineable coal seams; Bachu, 2003; Bradshaw et al., 2007; Michael et al., 2010).

CIUDEN (CIUDad de la ENergía Foundation) currently runs a technology development plant for CO_2 geological storage in a deep saline aquifer located in Hontomín (Burgos, northern Spain). CO_2 will be injected in a reservoir rock which is mainly composed of limestone. The native saline solution is sulfate-rich, equilibrated with calcite, dolomite and gypsum and with an ionic strength of 0.6 M. CO_2 injection at depth, where CO_2 will be in a supercritical state (total pressure $P > 74$ bar and temperature $T > 31$ °C), will lead to the formation of a CO_2-rich acid solution which will promote the dissolution of carbonate minerals (calcite and dolomite). Secondary mineral precipitation (gypsum or anhydrite) may occur since the solution contains sulfate.

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These reactions imply changes in the porosity and pore structure of the repository rocks.

Hydrodynamic and geochemical processes responsible for trapping CO_2 in geological formations over long time frames have been extensively studied (e.g., Bachu et al., 1994; Gunter et al., 1997; Johnson et al, 2001; Bachu and Adams, 2003; Gunter et al., 2004; Kaszuba et al., 2005; Knauss et al., 2005; Xu et al., 2005; Gaus, 2010; Espinoza et al., 2011). In deep saline aquifers, the interaction between dissolved CO_2 in groundwater and carbonate and siliciclastic minerals controls the aqueous inorganic system (Bachu and Adams, 2003). Uncertainties in the mineral reaction rates may generate unreliable estimations of the CO_2-sequestration capacity. It is essential, therefore, to understand the dissolution and precipitation kinetics of the carbonate minerals (calcite, dolomite, magnesite or siderite).

Several studies have focused on the dependence of dissolution rates of pure carbonate minerals on pH, temperature, CO_2 partial pressure, presence of inhibitor ions and ionic strength (Plummer et al., 1978; Sjöberg and Rickard, 1984; De Giudici, 2002; Morse and Arvidson, 2002; Pokrovsky et al., 2005, 2009; Gledhill and Morse, 2006; Xu and Higgins, 2011). Earlier works have shown that calcite dissolution kinetics is strongly pH dependent at high undersaturations and pH $\leq$ 4, and Pokrovsky et al. (2005, 2009) demonstrated that the effect of CO_2 partial pressure is not significant compared with that of pH. Research on the influence of reactor inhibitors on calcite dissolution kinetics has shown that calcite dissolution is retarded in the presence of aqueous divalent cations at neutral to basic pH (Morse and Arvidson, 2002; Martin-Garin et al., 2003; Arvidson et al., 2006), but it does not seem to be affected under acidic conditions (Alkattan et al., 2002).

In the framework of CO_2 geological storage, CO_2–water–rock interaction at elevated temperature and pressure has been studied in detail in closed reactors (Kaszuba et al., 2003, 2005; Palandri and Kharaka, 2005; Rosenbauer et al., 2005; Rimmelé et al., 2010; Chopping and Kaszuba, 2012; Lu et al., 2012). However, the transport processes that are able to control or at least affect the reaction paths during CO_2 injection have not been taken into account. This transport effect has been studied in reactive flow-through experiments (e.g., Noiriel et al., 2004, 2005, 2009; Luquot et al., 2013; Nogues et al., 2013). Luquot and Gouze (2009) performed percolation experiments under different P–T–pCO_2 conditions that are found in deep saline aquifers. This enabled them to describe mass transfer processes at different distances from the injection well. Smith et al. (2013) conducted core-flood experiments at 30 bar of pCO_2 and 60 °C with dolostone and limestone cores to gain insight into the effect of physical and chemical heterogeneities on the development of distinct reaction fronts. Elkhoury et al. (2013) performed experiments and numerical simulations to shed light on the influence of coupled geochemical alteration and mechanical deformation on calcium carbonate fracture geometry. However, in none of these studies was the importance of the coupled reactions of carbonate dissolution and gypsum precipitation assessed since the injected solutions consisted of sulfate-free brines. Singurindy and Berkowitz (2003) studied the effect of simultaneous calcium carbonate dissolution and gypsum precipitation on the evolution of hydraulic conductivity and flow patterns using column experiments. Atanassova et al. (2013) evaluated the inhibitory effect of gypsum precipitation on calcite dissolution in acid, sulfate-rich solutions in flow-through experiments. However, these two studies were limited to atmospheric pCO_2 conditions.

There is very little experimental knowledge about the overall process of gypsum precipitation at the expense of carbonate mineral dissolution in CO_2-rich solutions and its implication for porosity and permeability changes in limestone and dolostone reservoir rocks. The present study seeks to better understand these coupled reactions by assessing the effect that P, pCO_2, T, mineralogy, acidity and solution saturation state exert on the reactions. Thus, experiments using columns filled with limestone or dolostone were conducted under different P–pCO_2 (atmospheric: 1–$10^{-3.5}$ bar; subcritical: 10–10 bar; and supercritical: 150–34 bar) and T (25, 40 and 60 °C) conditions. Input solutions were injected varying the sulfate content (gypsum-undersaturated and gypsum-equilibrated solutions) and the acidity source (strong HCl and weak H_2CO_3 acids).

In addition, the experimental data were reproduced by means of 1D reactive transport calculations to evaluate mineral reaction rates in the system (fitted in the model through the reactive surface area term) and to quantify the porosity variation. The CrunchFlow (Steefel, 2009) and PhreeqC (v.3, Parkhurst and Appelo, 2013) numerical codes were used to conduct the simulations.

2. Materials and methods

2.1. Experimental methodology

2.1.1. Sample characterization

Two samples were used in this study: limestone and dolostone. The limestone was provided by CIUDEN and belongs to the Bercedo series (Puerto de la Palombera Formation; Pujalte et al., 1998) where CO_2 injection will take place. The dolostone was provided by the Department of Mineralogy (Faculty of Geology, Barcelona University) and comes from Peñarroya, Teruel (Spain).

According to X-ray diffraction (XRD), which was performed using a Bruker diffractometer model D-5005 with Cu K-α1 radiation, and to the Rietveld analysis (Young, 1995), the mineralogical composition of the limestone was 90.7 wt.% calcite and 9.3 wt.% dolomite and that of the dolostone was 100% dolomite. X-ray fluorescence analysis of the limestone and dolostone samples was carried out using a Bruker spectrometer model AXS-S2 Ranger to identify minor-element composition. In the limestone sample, Ca and Mg were the major elements. Si (0.37 wt.%) and Fe (0.20 wt.%) appeared as minor components and S and Sr as trace elements (<0.1 wt.%). In the dolostone sample, Al, Si, S, Mn and Cl appeared as minor components (from 0.1 wt.% to 1 wt.%) and Cu, Pb and K as trace elements. Fe (1.48 wt.%) was the only element, besides Ca and Mg, with a concentration higher than 1 wt.%.

Flow-through experiments with the dolomite sample were conducted to obtain dolomite dissolution rates at different pH values from 1.5 to 3.5. Assuming stoichiometric dolomite dissolution, the Ca/Mg ratio measured from the steady-state output Ca and Mg concentrations was used to obtain the structural formula of dolomite ($Ca_{1.048}\,Mg_{0.952}(CO_3)_2$).

The two rock samples were crushed to grain sizes between 1 and 2 mm for the atmospheric and 10 bar pCO_2 experiments. For the 34 bar pCO_2 experiment, the limestone was ground to grain sizes between 250 and 500 μm owing to the smaller diameter of the column. Thereafter, in order to remove microparticles due to grinding, the crushed and ground samples were washed three times with pH 1 solution (HCl) and three times with deionized water. Finally, the washed samples were dried in the oven at 40 °C. Scanning electron microscopy (SEM) was performed on C-coated samples before and after the experiment using a Hitachi H-4100 instrument under a 15–20 kV potential. The surface of the unreacted limestone grains was rough, whereas the surface of the unreacted dolostone grains was flat and terraced (Fig. 1a and b). Microparticles attached onto the surfaces were not observed.

2.1.2. Injected solutions

Two types of solution were prepared. The first type was a synthetic version of the Hontomín groundwater, which is nearly in equilibrium with calcite, dolomite and gypsum/anhydrite, with a 0.6 M ionic strength and neutral pH. Four modifications of this solution were performed varying gypsum saturation state and acidity (Table 1), yielding one solution undersaturated with respect to gypsum (not equilibrated brine, *nEb*) and three gypsum-equilibrated solutions (brine, *b*; pH 2.1 acid brine, *ab2.1*; pH 3.5 acid brine, *ab3.5*). TDS of these solutions was around 30 g/L. Synthetic brines were prepared by adding appropriate amounts of reagents $CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, NaCl, KCl, Na_2SO_4 and NaBr to Millipore MQ water (18 MΩ·cm). The amounts of reagents