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Experimental studies of CO_2-water-rock interaction under hydrothermal conditions appropriate for CO_2 sequestration into geothermal fields

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Abstract. Experiments on CO_2-water-rock interaction at hydrothermal temperatures have been performed to investigate dissolution and precipitation phenomena, including Ca extraction from rocks, that might occur during CO_2 sequestration into geothermal fields. The rock samples, granodiorites from the Ogachi hot/dry rock field, were reacted in distilled water with and without CO_2 being present. The results indicate that Ca concentration in the solutions quickly increase within 2 days and become constant for 30 days. The concentration of Ca in the solutions reacted with CO_2 is 50 mg/L higher than those without CO_2 (with N_2 gas). These results indicate that Ca can be released from rocks (silicates) easily and might be removed as $CaCO_3$ and/or $CaSO_4$ during CO_2 sequestration into geothermal fields.

1 Introduction

In most Japanese geothermal fields, carbonate-rich formations are observed. In the Sumikawa field, Akita, Japan, for example, CO_2-rich groundwaters are thought to have reacted with reservoir rocks to form a carbonate and kaolinite alteration assemblage by the reaction (Ueda et al., 2001):

$$CaAl_2Si_2O_8(\text{plagioclase}) + H^+ + HCO_3^- + H_2O = CaCO_3(\text{calcite}) + Al_2Si_2O_5(OH)_4(\text{kaolinite}) \quad (1)$$

An isotopic investigation of calcites at Sumikawa, indicated that the above reaction (1) occurred at 100 to 250°C by interaction of reservoir rocks with meteoric waters (Ueda et al., 2001).

The reaction (1) moves towards the right side at higher temperature, while at the same time calcite can be deposited more easily because the solubility of calcite decreases with increasing temperature. The calcite and kaolinite (smectite)-rich formation that is produced acts as a caprock to the geothermal reservoir. These considerations, together with the increasing reaction rates as temperatures are elevated and CO_2 fixation in solid carbonate minerals, suggests that CO_2 sequestration by injection into geothermal fields could be practicable (Fig. 1).

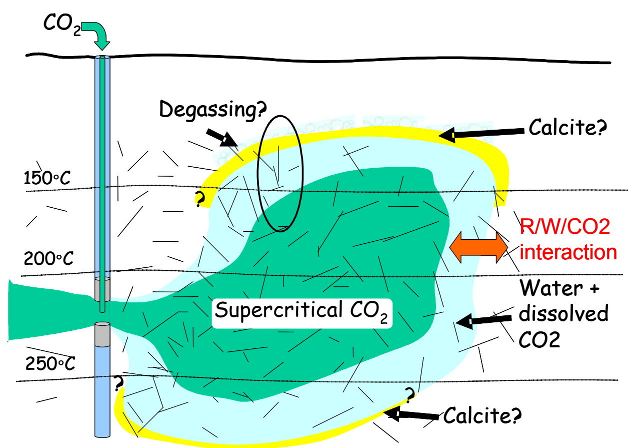

Fig. 1. General scheme of CO_2 sequestration into geothermal fields.

This study has evaluated the capacity of geothermal fields in Japan to sequester CO_2 by storage of a free CO_2 phase and by fixation in carbonate minerals. The characteristics of Ca extraction from rocks during reactions with CO_2-charged water has been evaluated experimentally and theoretically.

2 Experimental procedure

A drill core (OGC-2) from the Ogachi hot/dry rock field, Akita, Japan was sampled at a depth of 1061 m. The samples were fine grained graniodiorites, composed of quartz, plagioclase, K-feldspar, mica, epidote, chlorite, anhydrite, pyrite and calcite. These were sealed with distilled water and CO_2 gas at 7 MPa in a teflon beaker covered by a SUS reaction vessel (Fig. 2). The reaction vessel was then heated and kept at 150°C for between one and 30 days while rotating (1 rpm). After reaction, the solution was collected directly

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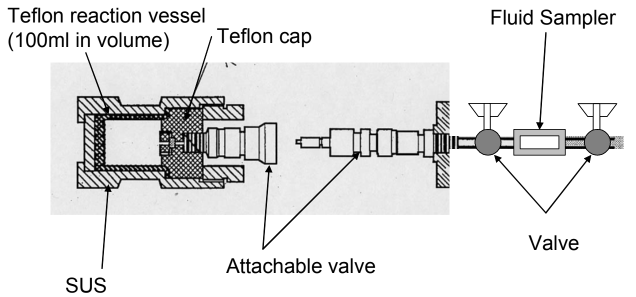

Fig. 2. Reaction vessel for CO_2/rock/water interaction.

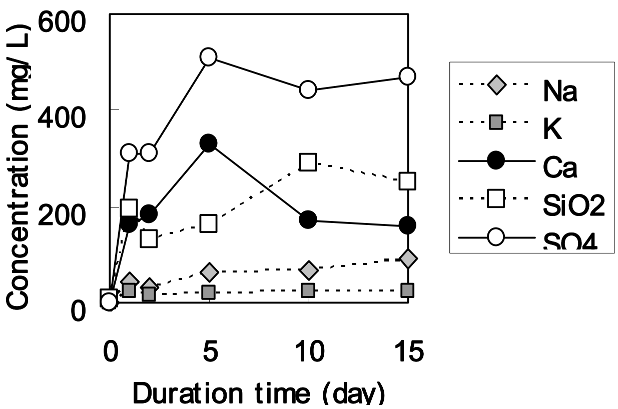

Fig. 3. Chemical concentrations in solutions after CO_2/rock/water interaction.

into a sample collctor (SUS) through a valve and analyzed for its chemical composition.

3 Results and discussion

3.1 Capacity of CO_2 storage

The capacity for CO_2 storage in 15 geothermal areas in Japan is estimated to be 19.7 billion tons CO_2 (17 times the total annual CO_2 emission in Japan) on the basis of estimated rock porosities (average 4%) and the density of supercritical CO_2 (100 kg/m^3). During CO_2/rock/water interaction, carbonate can be deposited as shown in reaction (1). The (Ca + Mg)/CO_2 mole ratios of andesitic and granitic rocks in Japan exceed 45.6 and 15.3, respectively. These results strongly support the view that CO_2 sequestration into geothermal fields is technically feasible.

3.2 Experimental results

Initially, concentrations of chemical constituents in the solutions that reacted with the Ogachi rocks and CO_2 (7 MPa) at 150°C increased with increasing reaction time. However, after 5 days Ca and SO_4 concentrations decreased (Fig. 3). In this experiment, Ca can be released from both anhydrite ($CaSO_4$) and silicates such as plagioclase. To calculate the

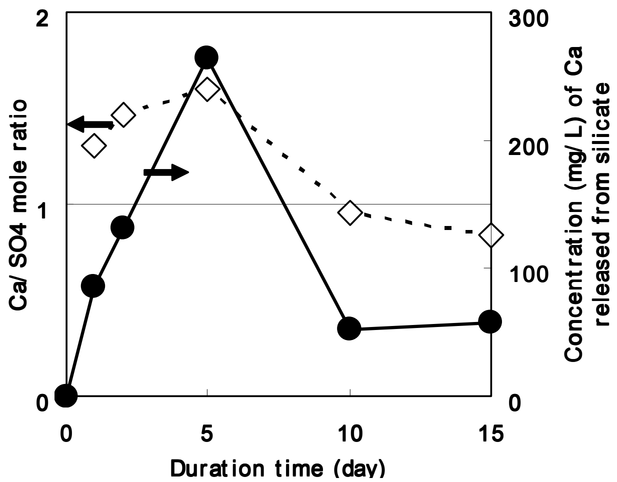

Fig. 4. Aqueous Ca/SO_4 mole ratios and concentrations of Ca released from silicates after CO_2/rock/water interaction.

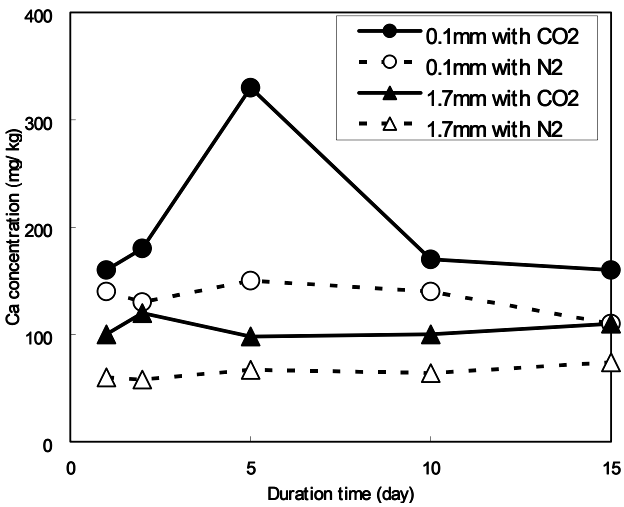

Fig. 5. Ca concentrations in solutions after reaction with and without CO_2 – water/rock interaction.

concentrations of Ca released from silicates, the observed Ca concentrations are adjusted on the basis of the Ca/SO_4 mole ratios in the solutions (Fig. 4). These results indicate that Ca can be released easily from rocks (silicates) and might be removed as $CaSO_4$ and/or carbonate during CO_2 sequestration into geothermal fields.

Figure 5 shows the experimental results when the Ogachi granodiorite was reacted with distilled water at 150°C, with and without CO_2. The concentration of Ca in the solutions reacted with CO_2 is 50 mg/L higher than those without CO_2 (purged with N_2 gas). These observations indicate that Ca can be released readily from rocks by the action of CO_2-charged water.

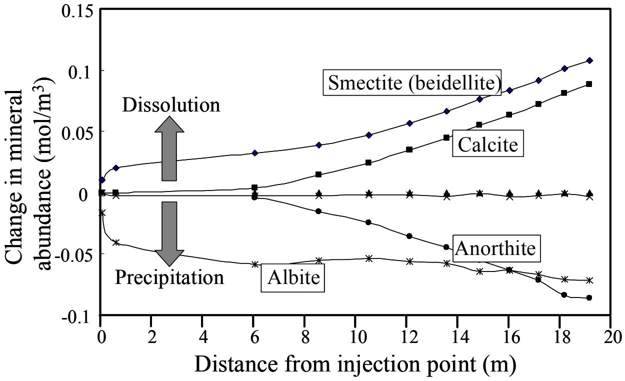

Fig. 6. Illustrative theoretical results for CO_2/rock/water interaction.

3.3 Theoretical consideration

The feasibility of high-temperature sequestration was evaluated by theoretical modeling using a purpose-designed, fully-coupled, flow-reaction code incorporating reaction kinetics. Coupled "moving window" simulations evaluated diffusion, dispersion and water-rock interactions as CO_2 is injected into a granodiorite at 225°C and 10 MPa. There remain uncertainties, notably concerning high-temperature CO_2 solubility and thermodynamic and kinetic data for silicates such as anorthite. However, the results indicate that CO_2 trapping in calcite could occur during CO_2 migration (Fig. 6). Depending on the injection conditions, trapping could be substantial. Consequently, the approach merits further consideration.

References

Ueda, A., Ajima, S., and Yamamoto, M.: Isotopic study of carbonate minerals from the Sumikawa geothermal area and its application to water movement, J. Geotherm. Res. Soc. Japan, 23, 181–196, 2001.