Laboratory and field experiments on carbonate fixation of CO_2 at hydrothermal system;"Georeactor", A case study at Ogachi hot dry rock site, Japan

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ABSTRACT

This paper reports a preliminary result of field experiments of CO_2 sequestration into the Ogachi hot dry rock (HDR) site, where a part of CO_2 will be expected to be fixed as carbonates by interaction with rocks (Georeactor; Ca extraction from rocks and carbonate fixation).

1. INTRODUCTION

In recent years much research has been directed at finding a solution to the problem of global warming caused by anthropogenic CO_2 emissions. Several research programs have focused on the possibility of sequestering such CO_2 underground, where the temperatures of CO_2 reservoirs are less than 100 ℃ and pressures are a few tens to hundreds of bars (Holloway, 1996). Under such conditions, CO_2 is thought to be stable as a supercritical fluid, due to the slow rate at which it reacts with reservoir rocks. Experimental and theoretical investigations of the chemical reaction of CO_2-saturated water and rocks have been reported (Gunter et al, 1996; Perkins and Gunter, 1996; Sorai et al., 2002).

In countries such as Japan, where have many active volcanic areas, one possibility is to sequester CO_2 into hydrothermal regions. The chemical reaction rates between CO2-saturated water and rocks are usually faster than those at room temperature. For example, the following reaction can proceed to the right side at high temperature (Gale and Shane, 1905).

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

Carbonate-rich rock formations can be observed in most Japanese geothermal fields. In the Sumikawa field, Akita, Japan, for example, CO_2-rich ground waters are thought to have reacted with reservoir rocks according to reaction (1), to form a carbonate and kaolinite alteration assemblage (Fig.1). An isotopic investigation of calcites at Sumikawa indicated that the reaction occurred at 100 to 250 °C by interaction of reservoir rocks with meteoric waters (Ueda et al., 2001).

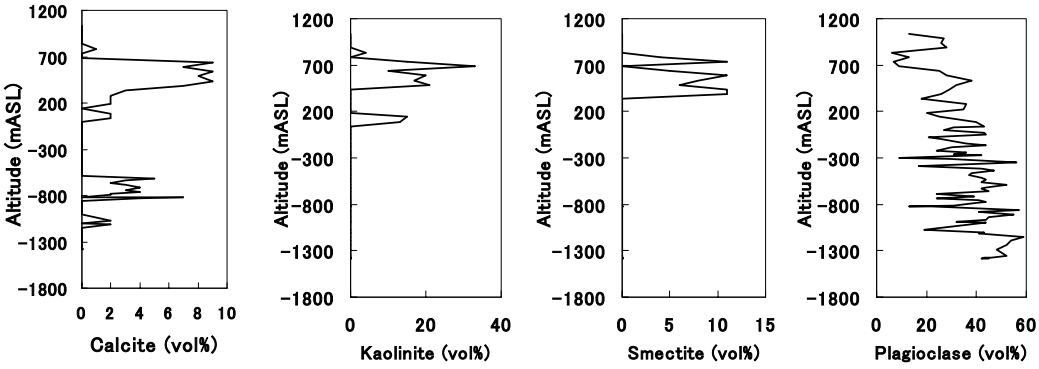

Fig.1 Abundances of calcite, kaolinite, smectite and plagioclase in rocks from Sumikawa geothermal field

2. THE CONCEPT OF "GEOREACTOR"

Reaction (1) moves towards the right side at higher temperature, reflecting the fact that calcite solubility decreases with increasing temperature. The calcite and kaolinite (clay)-rich rock is produced through the reaction and acts as a cap rock for the geothermal reservoir. These considerations, together with the increasing reaction rates as temperatures are elevated and the fact that precipitation of carbonate minerals fixes CO_2 suggest that CO_2 sequestration could be practicable by injection into geothermal fields (Georeactor; Fig.2).

In Japan, total rock volume in high(>150℃) and intermediate (90～150℃) temperature fields are estimated to be 2100 and 2800km^3 respectively. CO_2 storage capacity is calculated to be about 20 billion tons CO_2 (ca. 17 times Japan's total annual CO_2 emissions). The CO_2/(Ca+Mg) mole ratio of typical igneous rocks is 0.012～0.12. If 1～12% of Ca and Mg would be released, CO_2 may be fixed in carbonate minerals (Ohsumi et al., 2005).

In our laboratory experiments, a part of CO_2 can be precipitated as carbonate during interaction with rocks at 100 to 250℃ (Ueda et al., 2005). To examine this phenomena in the field, CO_2 saturated water was injected into the Ogachi HDR site.

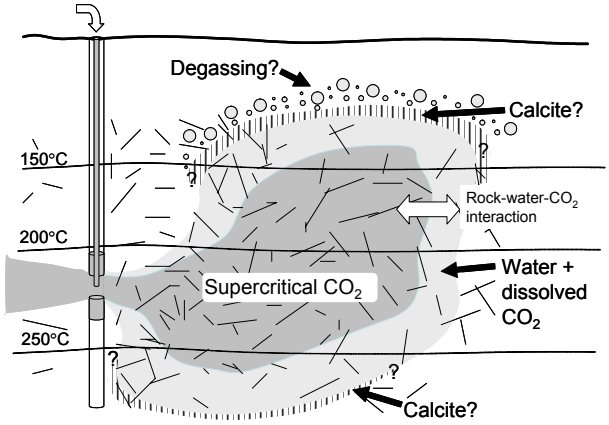

Fig.2 Outline of CO_2 sequestration into geothermal fields

3. FIELD EXPERIMENTS

The Ogachi hot dry rock (HDR) field is situated at the northeast Japan and has been studied to produce geothermal electricity by Central Research Institute of the Electric Power Industry for 20 years. There are two injection/production wells (OGC-1 and -2) and an observation one (OGC-3). Two major feed zones were formed by hydro fracturing at depth of 700m and 1100m, where their temperatures are 170 and 210℃, respectively.

Field experiments of CO_2 sequestration into the Ogachi HDR have been examined for 4 years by our group (Metcalfe et al., 2006; Ueda et al., 2007). In 2006, river waters had been continuously injected (380 L/min, 15 MPa) into an injection

well (OGC-1) and produced (40 L/min) from a prodcution well (OGC-2) during the experiment (2 weeks). After the fluid flow rate became constant, CO_2 dissolved water (0.2 wt%) was injected with tracers (KI; 2kg/200L and uranine; 150g/18m3). The fluids from OGC-2 were geochemically monitored for their isotope and chemical compositions. The final output temperature at the OGC-2 well site is 127.5 ℃. In this field experiment, we could not discuss the fixation rate of CO_2 as carbonate due to the high dilution rate with reservoir fluids as mentioned later.

In 2007, CO_2 dissolved water (river water with dry ice) was directly injected into OGC-2 (Fig.3; Run #1 (from September 2nd to 9th) and Run #2(from September 11th to 16th)). Several tracers were also injected at the same time. Water samples are collected at the depth of ca. 800m by a sampler (500ml in volume) and monitored for their chemical and isotopic compositions (δ D, δ ^{18}O, δ $^{13}C_{CO2}$). During the Run #2 experiment, river water was injected into OGC-1 at 2 days after injection of CO_2 water into OGC-2.

During the field experiments, dissolution or precipitation rates of calcite were determined by using a technique of "in site analyses" (Satoh et al., 2007). Calcite crystals covered with Ti rod or Au film is hold in a crystal cell and set in a crystal sonde. The crystal sonde is then put into OGC-2 and water samples at the certain depth is introduced into the sonde. After 1 hour, the sonde is recovered and the calcite crystal is observed by a newly developed phase shift interferometer (Ueda et al., 2005; Satoh et al., 2008) to analyze the dissolution or precipitation rates of calcite from the reservoir fluids.

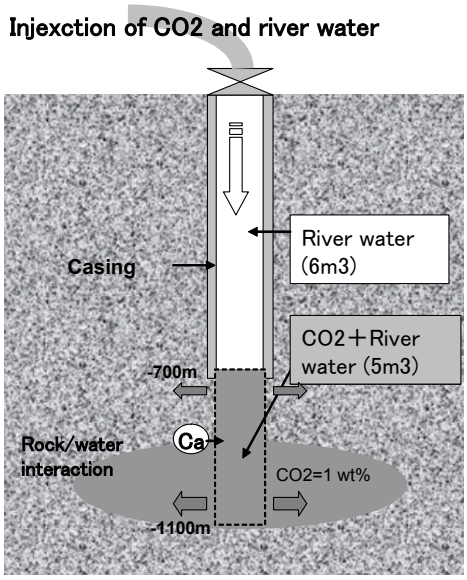

Fig.3 CO_2-water injection test at OGC-2 in 2007

4. RESULTS AND DISCUSSION

Test in 2006

During the experiments in 2006 (flow test), major chemical compositions of fluids collected at the well site of OGC-2 are monitored. The tracers are first detected at 34 hours after the injection and showed the maximum concentration at 67 hours. The dilution rates of the observed to injected concentrations of two tracers (KI and uranine) are calculated to be 6×10^{-5} and 1×10^{-3}, respectively. CO_2 concentrations in the fluids varied from 600 to 200 mg/L with time and showed no correlation with those of the tracers. This is due to the high dilution rate with reservoir fluids. In this field experiment, we could not discuss the fixation rate of CO_2 as carbonate.

Test in 2007

After injection of CO_2 water, the tracer concentrations decrease with the elapsed time (Fig.4). It is noted that the behavior of natural tracers such as Cl, δ D and δ $^{13}CCO_2$ (closed markers in Fig.4) are different from artificially added tracers such as I, Br and fluoresce (opened ones). The reason is not clear so far but one possibility is that river water in the casing pipe could mix with CO_2 water (river water and dry ice).

During the 2007 field experiments, CO_2 concentrations of the water samples under the reservoir pressure could not be correctly monitored due to the broken of the water sampler. This means that water samples were collected around 800m

depth and a part of CO_2 must be degassed during ascending to the surface from the sampler. Therefore, CO_2 concentrations of the reservoir fluids are calculated on the basis of the observed pH and charge balance of each samples (Case 1) and the tracer concentration (Case 2). The Case 2 means that CO_2 in the injected water did not react with rocks. Fig.5 shows the calculated CO_2 concentration with iodine. Iodine concentration decreases from 1000 to 200 μ g/L with the elapsed time. From Fig.4, the fraction of the injected CO_2 water (1 wt%CO_2) is almost zero. This means that the injected water was completely diluted with the reservoir fluid. The calculated CO_2 concentrations vary from 900 to 600 mg/L (Fig.5).

From the chemical compositions of water samples, the saturation index of calcite is calculated as follows;

S.I. (Saturation Index) = Log (Q/K) (2)

, where Q and K are activity and solubility products of calcite, $(Ca^{2+})(CO_3^{2-})$, respectively. If S.I.>0, the fluid is saturated with respect to calcite (calcite precipitation).

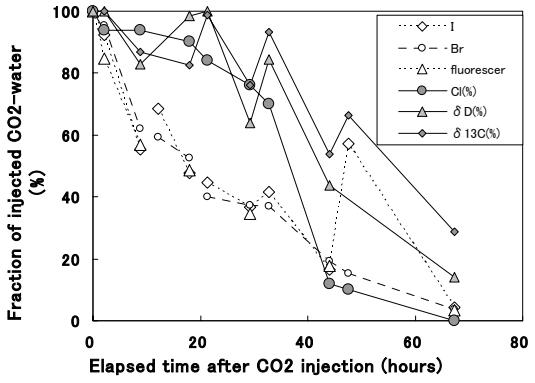

Fig.4 tracer concentrations after CO_2 injection

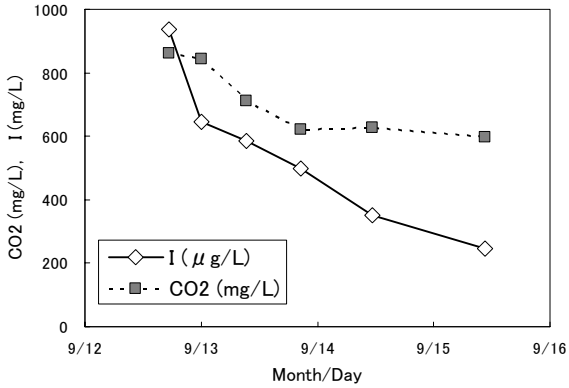

Fig.5 Concentrations of iodine and CO_2

Fig. 6 shows the change of the S.I. during the experiments (Run2). In the case 1, the S.I. is above zero except for the sample collected just after CO_2 injection. In contrast, the S.I. is close to zero in the case 2 implying that the reservoir fluid mixed with the injected CO_2 water is almost in equilibrium with calcite. Fig. 6 also shows the observed dissolution or precipitation rates of calcites which are determined by in site analyses. From these results, the injected CO_2 water is diluted with the reservoir fluid with 3 days and most CO_2 in them might be deposited by interaction with granitic rocks. According to the material balance, only 1 μ m thickness of the granitic rocks is enough to react with the CO_2 water to precipitate as carbonate minerals. In the previous field experiments in 2002 and 2003, Ca concentration in the water samples increased from 10 to 80 mg/L with 1 day and quickly decreased to the background. These results also support the view that CO_2 injected is precipitated as carbonates with few days.

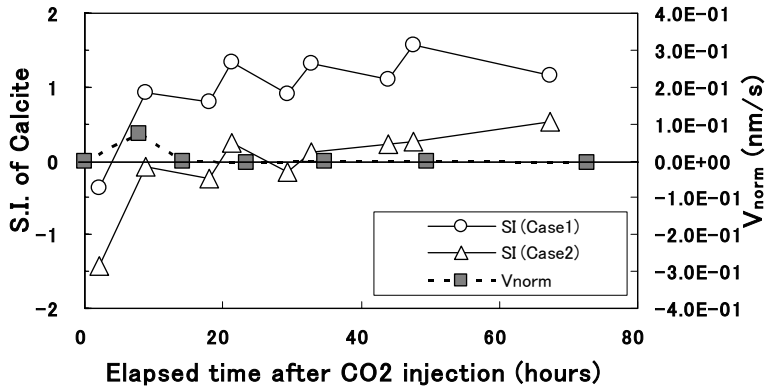

Fig.6 Saturation index of calcite

5. CONCLUSION

The injected CO_2 water is diluted with the reservoir fluid within 3 days. Most CO_2 in them might be deposited as calcite by interaction with granitic rocks. Ca concentration in the water samples increased from 10 to 80 mg/L with 1 day and quickly decreased to the background. These results also support the view that CO_2 injected is precipitated as carbonates within few days.

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