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EXPERIMENTAL STUDIES OF DEEP-GEOTHERMAL FLUIDS AND AMORPHOUS $Mg-SiO_2$ SCALES UP TO 350°C.

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ABSTRACT

Hydrothermal experiments at static and dynamic conditions up to 350°C and pH range from 1 to 7 were conducted to investigate the chemical compositions of deep geothermal fluids and the various types of scales (eg. $Mg-SiO_2$ and silica) that may deposit from the extraction of these fluids. In the static experiments, a $HCl-H_2SO_4$ acid fluid (pH 1 to 3) were interacted with tonalite collected from well WD-1 at 350°C for 15 days. The reacted fluids were found to be enriched in SiO_2, Fe and Mg similar to the deep geothermal fluids observed in the world. The deposited components found are amorphous silica and Mg-silicate, and anhydrite. To study the amorphous $Mg-SiO_2$ components, $MgCl_2$ fluid (1 mMol/kg) and Na_2SiO_3 fluid (1500 mg/kgSiO_2) were mixed and sealed in a quartz glass tube after adjusting each pH from 5 to 9. The tube was packed into a SUS reaction vessel with $4NH_2SO_4$ solution and heated up to 300°C for one day. The reaction product was found to be in amorphous form and the chemical composition is mainly Mg and SiO_2. Thermodynamic calculations showed that the solubility of the amorphous $Mg-SiO_2$ scale decreases with increasing temperature up to 300°C similar to the results (at 120°C) obtained by Hauksson et al. (1991). In the dynamic experiments, $HCl-H_2SO_4$ solution with pH 3 was passed through a 100ml reaction vessel containing tonalite, at 1ml/min for 2 days at 350°C. The concentration of SiO_2 is around 400mg/kg and the pH ranged from 3.1 to 3.5 during the reaction. The total volume of SiO_2 dissolved from the rock is calculated to be 2%.

1. INTRODUCTION

The deep geothermal system is a new target for recent geothermal exploration. The reservoir temperature must be higher than that of shallower geothermal reservoirs, and many chemical components are enriched in deep geothermal fluids. Several types of scales from this deep geothermal system are also expected to be deposited in production and reinjection wells, as well as in surface pipelines of power plants. However, the chemical behavior of the deep geothermal fluids is so far not well understood, and what types of scales deposited should be investigated.

Theoretically, silica (SiO_2) can be a major candidate for deep geothermal scales because of the high solubility of quartz in the reservoir fluids which can produce more than 1000mg/kg of SiO_2 concentration in the produced fluids after flashing at atmospheric condition. The geothermal fluids should be reinjected at around 220°C in order to prevent silica deposition in the surface pipelines and injection wells. Other scales such as $Mg-Fe-SiO_2$, sulfide and anhydrite can also be considered as candidates for deep geothermal scales.

$Mg-SiO_2$ scale has been reported in many geothermal plants as stevensite, smectite and amorphous scales (eg. Hauksson et al.,1991, Kasai et al.,1997). It is generally found in production wells and surface pipelines and commonly caused by the reaction of Mg-rich fluid (e.g. groundwater) and SiO_2-rich geothermal fluid.

In this study, static and dynamic hydrothermal experiments were conducted to investigate the chemical compositions of the deep geothermal fluids and to examine what types of scales are deposited from these fluids. In particular, the occurrence and behavior of $Mg-SiO_2$ scales were examined.

This study was conducted as one of the projects for the development of production technology in deep geothermal exploration by the New Energy Development Organization (NEDO), Japan.

2. EXPERIMENTAL APPARATUS

The experimental apparatus used in the static hydrothermal experiments is shown in Figure 1. A quartz glass tube with 15mm diameter was used as the reaction vessel and was placed into a SUS vessel with 4N H_2SO_4 solution to prevent the dissolution of quartz glass tube. The chemical composition of the deep geothermal fluids were determined by mixing tonalite and $HCl-H_2SO_4$ solution (pH 1 to 3) inside the quartz tube and then heated up to 350°C for 15 days.

The $Mg-SiO_2$ scales were examined by mixing a 1mMol/kg of $MgCl_2$ fluid with 1500mg/kgSiO_2 of Na_2SiO_3 fluid and subsequently sealed in the quartz glass tube after adjusting the pH from 5 to 9.

For the dynamic experiments, rock samples were packed into a reaction vessel tube made of gold. The tube was fitted with an outer reaction vessel using a zirconium packing. By using this two independent reaction vessels, rock samples can be easily handled before and after rock-water interaction. Furthermore, strong acid fluids (pH 1) as well as alkaline fluids can be easily treated. The rate of the fluids was adjusted from 0.1 to 2 ml/min.

3. EXPERIMENTAL PROCEDURES

The rock samples used in this study are cuttings collected from well WD-1 in Kakkonda, Iwate, Japan at a depth of 3550 meters. These cuttings are composed mainly of quartz, plagioclase, K-feldspar and a minor amount of pyroxene (tonalite). Before the experiments, the cuttings were sorted based on their grain sizes (from 1 to 3 mm) and the impurities such as drilling mud and iron chips were repeatedly washed by HCl and distilled water.

Two kinds of solutions were used in this study. The first solution was an equal mole of HCl and H_2SO_4 with pH 1 to 3 which was reacted with the rock samples at 350°C for 15 days in both the static and dynamic experiments. The other solution was a mixture of $MgCl_2$ (1mMol/kg) and Na_2SiO_3 (1500mg/kgSiO_2) with pH 5 to 7 and was reacted at 100 to 300°C for one day.

The two solutions were sealed in a quartz glass tube as mentioned above. The glass tube is packed into a stainless steel reaction vessel with 4N H_2SO_4 solution for preventing the dissolution of the quartz glass in alkaline pH region. The SUS vessel was then heated up to 350°C for one day. The vessel was then cooled using water after the reaction. The reacted solution was filtered through 0.22m filter and was analyzed for their chemical compositions by ICP and AA. The rock samples were then dried in an oven and examined by SEM-EDX and XRD.

4. RESULTS AND DISCUSSION

The results of the hydrothermal experiments are presented in Figures 2 to 5 and summarized in Table 1.

4.1 Deep-geothermal fluids

Table 1 shows the chemical composition of the reacted solutions with the rocks for 15 days for the static condition. The solutions were found to be enriched in SiO_2, Fe, Mg and Al similar to the chemical compositions of the deep geothermal fluids observed in Kakkonda, Japan (Yanagiya et.al.,1997). The final pH is 2.3 to 4.5. The deposited materials found in the reaction glass are composed of amorphous SiO_2, amorphous Mg-SiO_2 and anhydrite. The mineral assemblage of the rock samples did not changed significantly during the reaction.

The chemical compositions of the deep geothermal fluids reported from literature show that the pH ranged from 3 to 5 and the fluids are enriched in SiO_2, Fe, Mg and Al in the range of 100 to 2000mg/kg (Lihir, 1998).

The results of the study show that the concentrations of each chemical component rapidly increased for 5 days and approached unity for about 15 days. In contrast, SO_4 suddenly decreased with increasing pH. Above pH 5, Fe and Mg also decreased. These results show that SO_4, Mg and Fe are deposited during the reaction which is due to the increase of pH. At this time, SiO_2 was also deposited as amorphous scale. In this experiment, the quartz glass vessel is also dissolved in the solution since the dissolution rate of quartz is increased with increasing temperature(eg. Dove,1996). Quartz glass used in this study is in amorphous state and the dissolution rate might be more higher than quartz. However, rock samples studied also contain quartz. Therefore, the concentration of SiO_2 in the reacted solution must be representative of the high temperature fluid.

To investigate the chemical behavior of the deep fluids, water-rock experiments were done at 350°C for 2 days under dynamic conditions mentioned above. The preliminary results show that the solution reacted with rock samples (tonalite and HCl-H_2SO_4 solution) gave a pH of 3.4±0.3 and a concentration of SiO_2 of 450±50 mg/kg (Figure 2). The total volume of SiO_2 dissolved from the rock is calculated to be 2%. The residence time of the solution in the rock is calculated to be 30 minutes. This means that dissolution rate of SiO_2 is quite high under deep geothermal condition.

4.2 Amorphous Mg-SiO_2

Figure 3 shows the experimental results of reaction in a mixture of $MgCl_2$ and Na_2SiO_3 solution. The Mg concentration decreases with increasing pH similar to SiO_2. The deposited materials in the reaction glass was examined by XRD and was found to be composed of amorphous material. The chemical composition was mainly SiO_2. These results shows that amorphous Mg-SiO_2 was deposited.

Mg-SiO_2 scale is observed in the different georthermal systems, for example, as stevensite in the Mori geothermal area, Hokkaido, Japan (Kasai et al.,1997), as amorphous state in the Icelandic geothermal area (Hauksson et al.,1995) and as smectite in other geothermal reservoirs (eg. Reyes and Cardile,1989). The Mg/SiO_2 mole ratios of Mg-SiO_2 scales are 0.17 to 0.47 at Mori (Kasai et al.,1997) and 1.0 to 1.3 at Iceland (Hauksson et al.,1995). In the Icelandic geothermal area, two different fluids are mixed together (Mg-rich groundwater and SiO_2-rich geothermal fluid). Hauksson et al.(1995) experimentally determined the solubility of the amorphous Mg-SiO_2 scale at 60 to 120°C by using the following equation;

$$MgSiO_3 \cdot H_2O + H_2O = Mg^{2+} + H_3SiO_4^- + OH^- \quad (1)$$

$$K = (Mg^{2+})(H_3SiO_4^-)(OH^-)$$

where K is an equilibrium constant and ( ) means activity.

In this study, the solubility of the amorphous Mg-SiO_2 scale was experimentally determined at higher temperature region (100 to 300°C). Figure 4 shows the results where the same calculation was done to compare with the results obtained by Hauksson et al.(1995). The thermodynamic calculations were done by using SOLVEQ (Reed and Spycher,1984). The solubility decreases with increasing temperature similar to the results obtained by Hauksson et al.(1995), where the absolute value in high NaCl solution (0.5mol) is lower than that in low NaCl solution (0.05mol). Around 100°C, the solubility determined by this study is lower than that determined by Hauksson et al.(1995) whose NaCl concentration was 0.02mol. These differences may be due to the different NaCl concentration in the solutions.

Figure 5 shows the saturation index (Q/K) of amorphous silica, talc ($Mg_3Si_4O_{10}(OH)_2$) and chrysotile ($Mg_3Si_2O_5(OH)_4$)), where Q is an activity product of a certain mineral. The results obtained show that the reacted solution was found to be always saturated with respect to amorphous silica but not with respect to chrysotile throughout the range of pH and temperature examined. In contrast, the solution is found to be saturated with respect to talc in the neutral pH region at 100°C and in the more acidic region at higher temperature.

5. CONCLUSIONS

Static and dynamic hydrothermal experiments were conducted to study the chemical compositions of deep geothermal fluids and the associated scales, especially Mg-SiO_2 scales. The synthesized deep geothermal fluids are rich in Fe, Mg, Al and SiO_2 similar to what was observed in the world. The main deposited materials are amorphous SiO_2 and Mg-SiO_2 components, and anhydrite. The Mg-SiO_2 scales were also determined for their solubility up to 300°C. The solubility of amorphous Mg-SiO_2 scale decreases with increasing temperature similar to what is observed in Icelandic geothermal areas and is lower in saline solution than non-saline solution.

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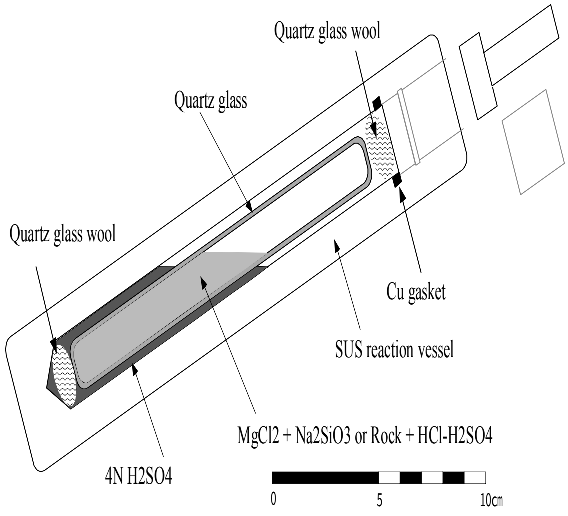

Figure 1 Reaction device for rock-acid solution and for Mg-SiO2 scales.

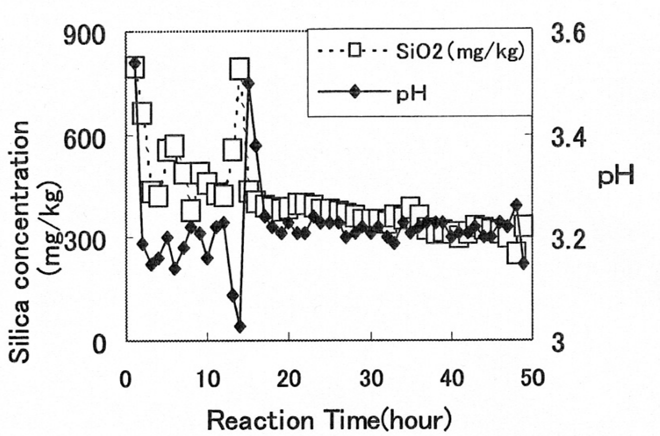

Figure 2 pH and SiO2 in solution after flow type experiments.

Table 1 Chemical compositions of fluids after rock-water experiments (15days).

R/W ratio	pHi	pHf	Na	K	Ca	Mg	Fe	Al	SiO2	Cl	SO4
1:10	1.0	1.2	410	66	330	930	2300	11	1600	9800	4900
1:10	2.0	4.5	290	160	38	3	1	<1	1200	600	150
1:10	3.0	4.6	25	14	8	<1	<1	1	1400	37	38
1:2	1.0	2.6	2400	1400	160	880	2200	3	1500	9900	1800
1:2	2.0	5.3	310	170	70	<1	<1	<1	1200	380	180
1:2	3.0	4.7	28	10	9	<1	<1	2	1200	61	33

pHi : initial pH before reaction,
pHf : final pH after reaction.
R/W ratio : rock/water weight ratio.
Na~SO_4 : mg/kg

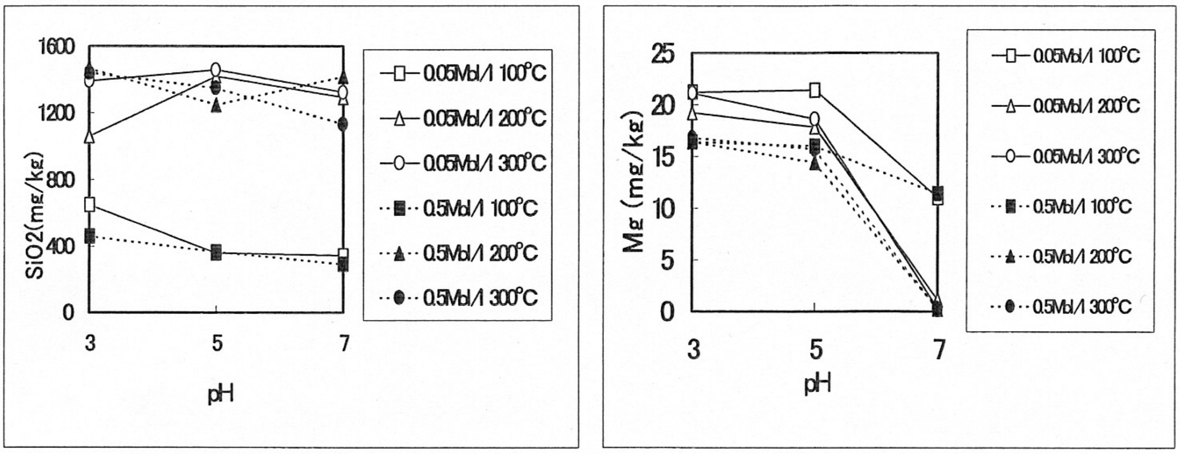

Figure 3 SiO_2 and Mg concentrations in solution after reaction($MgCl_2$-Na_2SiO_3).

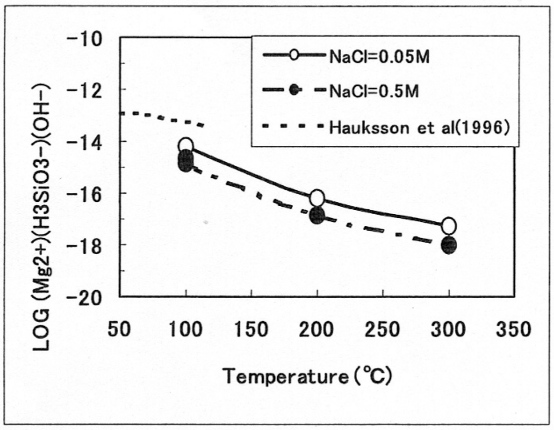

Figure 4 Solubility of Mg-SiO_2 scale.

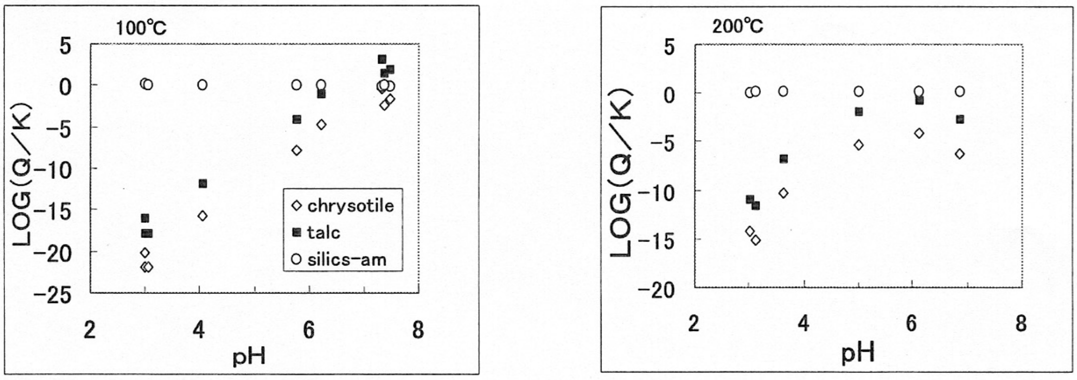

Figure 5 Log(Q/K) of Mg-SiO_2 scales.