FORMATION CONDITION OF SMECTITE IN SILICA SCALE: ROLE OF MAGNESIUM

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SUMMARY – To elucidate the formation mechanism of smectite contained in silica scale formed in the pipeline at geothermal power plants, seven silica scale samples were characterized by chemical analysis, powder X-ray diffraction, and ^{27}Al MAS NMR. Smectite was present in silica scale samples whose magnesium content was higher than 10 % as MgO, and aluminium content was lower than ca. 10 % as Al_2O_3. The peak assigned to 6-coordinated Al was observed in the 27Al MAS NMR spectra for magnesium-rich samples, while, no peak due to 6-coordinated Al appeared in magnesium-poor samples. From the comparison between the ^{27}Al MAS NMR spectra for synthesized precipitates of Al_2O_3 and Al_2O_3-MgO, the half-width of peak for 6-coordinated Al of the Al_2O_3-MgO was narrower than that of Al_2O_3, suggesting that magnesium may stabilize the octahedral sheet (AlO_6) in smectite.

1. INTRODUCTION

In many geothermal fields, silica scale deposits in a pipeline and in re-injection wells cause a decrease in re-injection capacity and in electricity generated, and a poor heat exchange performance. Scale inhibition control methods employed in geothermal fields have generally been specific with respect to brine chemistry and process conditions. Many methods have been applied to prevent silica deposition including hot brine re-injection, pH adjustment and dilution with condensed water. However, no single or simple solution to depositional problems is available so far.

In some geothermal power plants, silica scale containing smectite (silica-smectite scale) has been forming for several years after being absent in the early operation of these plants. Recently, number of production wells at geothermal power plants has increased. From the detailed observation in geothermal power plants, silica-smectite scale seems to be formed where neutral geothermal water (Mg concentration: below detection limit) and acidic geothermal water with magnesium (Mg vonventration: for example 8 ppm) mixed. Therefore, it is important to investigate the formation mechanism of the silica-smectite scales because the saturation temperature of smectite is higher than that of silica. There is the possibility that more silica-smectite scale will precipitate in the near future.

The purpose of this study is to examine the formation condition of silica-smectite scale by characterization of silica-smectite scales collected in the pipeline at a geothermal power plant and synthesized precipitates consisting of Al_2O_3, Al_2O_3-MgO, and Al_2O_3-SiO_2-MgO.

2. EXPERIMENTAL

2.1 Collection of Silica Scale Samples

Silica scale samples were collected from the pipeline at geothermal power plant.

2.2 Preparation of Sample Solutions for Model Experiments

All of the reagents used were of analytical regent grade. An aluminum stock solution (Al concentration; 1 mol dm^{-3}) was prepared by dissolving crystalline $AlCl_3 \cdot 6H_2O$ in diluted hydrochloric acid (1 mol dm^{-3}). A magnesium stock solution (Mg concentration; 1 mol dm^{-3}) was prepared by dissolving crystalline $MgCl_2 \cdot 6H_2O$ in diluted hydrochloric acid (1 mol dm^{-3}). The silica solution (Si concentration; 6.67 mmol dm^{-3}) was prepared by dissolving silica gel powder in NaOH solution (1 mol dm^{-3}). The $AlCl_3 \cdot 6H_2O$, $MgCl_2 \cdot 6H_2O$ and silica gel were commercially obtained from Wako Pure Chemical Industries Ltd.

2.3 Synthesis of Silica Precipitates

The aluminum and magnesium stock solutions were added into the silica solutions with various Al/Mg ratio and pH, and stirred for 24 h. The pH of the solutions was adjusted by adding a sodium hydroxide solution and/or hydrochloric acid. The precipitates were filtered with 0.45 μm membrane filter, and air-dried at room temperature for several days.

2.4 ^{27}Al Magic Angle Spinning (MAS) NMR Measurements

The ^{27}Al MAS NMR spectra were recorded on a CMX300 Infinity plus spectrometer operating at 78.1 MHz (acquisition time, 10.24 msec.; repetition time, 2 sec.; 2000 – 4000 transients). Samples were taken in 4 mm NMR tubes made of ZrO_2. The spinning rate of the sample tube was 12 KHz. All the chemical shifts are relative to external $[Al(H_2O)_6]^{3+}$ as reference. The NMR measurements were carried out at ambient temperature.

3. RESULTS AND DISCUSSION

3.1 Chemical Properties of Silica Scale Samples

Table 1 represents the mineralogical composition of silica scale samples. The composition was determined from powder X-ray diffractograms for samples. All samples except for the SU-1 contain quartz. The samples SU-1, 3, and 4 showed a broad peak around 2θ=20˚, showing the existence of amorphous silica. Weak peaks were assigned to magnetite, pyrite, and pyrrhotite, and clay minerals, smectite, chlorite, and illite are present. Smectite was absent in samples containing iron minerals.

Table 1. Mineralogical composition of silica scales

	Su-1	Su-2	Su-3	Su-4	Su-5	Su-6	Su-7
smectite				x	x	x	x
chlorite	x	x	x				
illite		x					
quartz		x	x	x	x	x	x
pyrite	x	x	x				
magnetite		x	x				
pyrrhotite		x					
am SiO2	x		x	x			

Table 2 represents the chemical composition of silica scale samples. SiO_2 content ranged from 51.11 to 67.28 % and Al_2O_3 content from 6.59 to 11.72 %. MgO content was poor in samples SU-1–3, while was rich in samples SU-4 – 7. It should be emphasized that samples with less amount of aluminum (Samples SU-4 – 7) contain large amount of magnesium and smectite is found only in these samples. It suggests that the octahedral sheet of smectite consists of magnesium in addition to aluminum.

Table 2. Chemical composition of silica scale samples. unit: wt%

	SU-1	SU-2	SU-3	SU-4	SU-5	SU-6	SU-7
SiO_2	67.28	60.20	62.90	51.11	55.43	52.14	54.42
Al_2O_3	11.52	11.72	9.84	6.59	7.72	7.30	7.58
MgO	0.39	0.70	0.02	14.80	11.13	13.83	11.61
Fe_2O_3	0.61	7.40	7.53	3.97	2.19	1.82	2.04
MnO	0.12	0.05	0.05	1.67	1.20	1.28	1.22
CaO	3.82	2.54	3.03	1.82	1.74	1.62	1.66
Na_2O	1.33	0.88	0.95	0.26	0.61	0.62	0.68
K_2O	1.94	2.11	1.43	0.62	1.04	0.87	1.02
TiO_2	0.04	0.23	0.10	0.06	0.06	0.07	0.07
S	0.30	3.10	2.20	0.91	0.54	0.25	0.30
Al/Si atomic ratio	0.20	0.23	0.18	0.15	0.16	0.16	0.16
Mg/Si atomic ratio	0.01	0.02	0.00	0.43	0.30	0.39	0.32

3.2 Coordination Structure of Aluminum in Silica Scale Samples

Figures 1(a) and 1(b) show the ^{27}Al MAS NMR spectra of aluminum in silica scale samples (a: SU-1 and b: SU-7) collected from the pipeline of a geothermal power plant. In general, ^{27}Al MAS NMR spectrum gives the information on the coordination number of aluminum. It is based on the chemical shift (in ppm) relative to the signal for $[Al(H_2O)_6]^{3+}$ used as an external standard. The chemical shift ranges from –10 ppm to 30 ppm for 6-coordinated aluminum (AlO_6, Al(6)), from 30 to 40 ppm for 5-coordinated aluminum (AlO_5, Al(5)), and from 40 to 80 ppm for 4-coordinated aluminum (AlO_4, Al(4)) (Engelhaldt and Michel, 1987). In Fig. 1(a), the peak around 50 ppm is due to Al(4) and other peaks were not observed. In Fig. 1(b), the peak around 50 ppm is due to Al(4) and the peak around 10 ppm is due to Al(6). This fact indicates that aluminum in SU-1 was present as only Al(4) and that in SU-7 was present as Al(4) and Al(6).

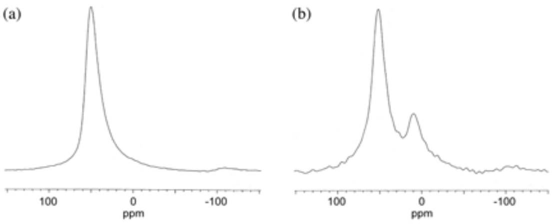

Fig. 1. ^{27}Al MAS NMR spectra of silica scale samples collected at geothermal power plant. (a) SU-1; (b) SU-7

According to Komarneni et al. (1986), in the inorganic coprecipitation of silicic acid and aluminum, the population of Al(4) ([Al(4)]/[total

Al] atomic ratio) depends on the Al/Si atomic ratio of the resulting precipitate because of formation of Al(4) due to substitution with Si in silica, that is, with decreasing Al/Si atomic ratio of precipitate the population of Al(4) increase. According to Table 2, the Al/Si atomic ratio of the SU-1 was slightly larger than that of the SU-7. However, opposite phenomena were observed in their ^{27}Al MAS NMR spectra in spite of the Al/Si atomic ratio of samples. Al(6) was absent in the SU-1, however, Al(6) was present in the SU-7. Not only the SU-7 but also the SU-4, 5, and 6 containing much magnesium showed the existence of Al(6). These suggest that magnesium can stabilize the Al(6).

3.3 Effect of Magnesium on ^{27}Al MAS NMR spectra

Only Al_2O_3 and Al_2O_3-MgO precipitates were synthesized at pH 7 – 9 to examine the effect of magnesium on the chemical state of aluminum in the precipitates as described in the experimental section. Figure 2 shows the ^{27}Al MAS NMR spectra of these samples. Only a peak due to Al(6) was observed in all spectra. The half width of the Al(6) peak was different depending on whether magnesium is present or not. The half width of the Al_2O_3-MgO precipitate was significantly narrower than that of the Al_2O_3 precipitate. This indicates that the symmetry of Al(6) become better by addition of magnesium, suggesting that magnesium may control the formation of the octahedral sheet in smectite. The difference in half width of Al(6) peak decreases with increasing pH.

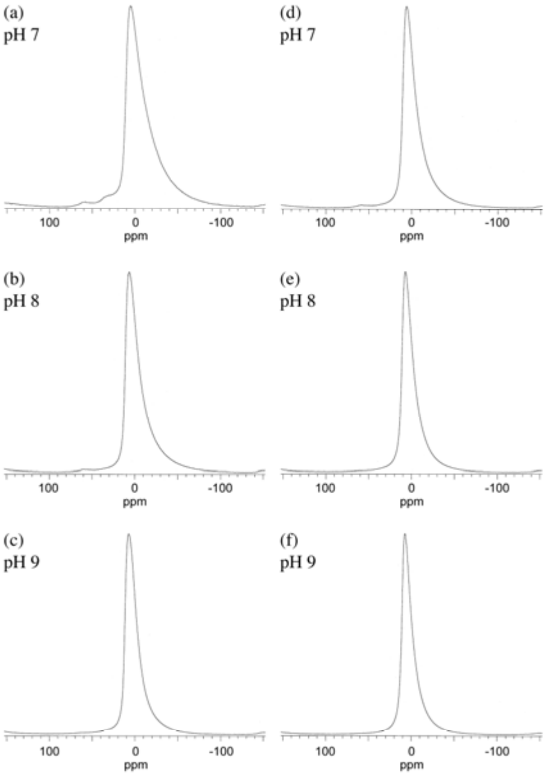

Fig. 2. ^{27}Al MAS NMR spectra of synthesized precipitates. (a)–(c) Al_2O_3-precipitates; and (d)–(f) Al_2O_3-MgO-precipitates (Al/Mg atomic ratio = 1).

Subsequently, one Al_2O_3-SiO_2 and two Al_2O_3-SiO_2-MgO precipitates were synthesized at pH 8 in the presence of silica. The Si/Al atomic ratio was constant 20 and the Mg/Al atomic ratio was 0, 1, and 3. Figures 3(a), 3(b), and 3(c) show three ^{27}Al MAS NMR spectra corresponding to the precipitates with Mg/Al atomic of 0, 1, and 3. In Fig. 3(a), a large peak around 50 ppm due to Al(4) and a small peak around 0 ppm to Al(6) exist. This spectrum shows that most of aluminium was substituted with Si atom as the Al(4) and a small amount of aluminium was present as Al(6). In Fig. 3(b) the peak intensity of Al(6) in the precipitate with Mg/Al atomic ratio of 1 is strong compared with that in the

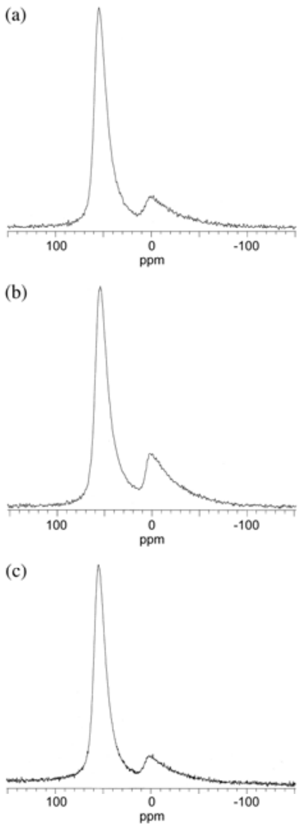

Fig. 3. ^{27}Al MAS NMR spectra of Al_2O_3-SiO_2 or Al_2O_3-SiO_2-MgO synthesized precipitates. (a) Mg/Al = 0; (b) Mg/Al = 1; (c) Mg/Al = 4

precipitate with Mg/Al of 0. In Fig. 3(c) the peak intensity due to Al(6) decreases, suggesting that magnesium may stabilize Al(6) in the presence of a lot of silica by retardation of the substitution.

The facts shown in Figs. 2 and 3 suggest that magnesium may control the formation of octahedral sheet of smectite in geothermal water.

4. CONCLUSION

From the mineralogical, chemical and ^{27}Al MAS NMR analysis for silica scale samples collected in the pipeline at geothermal power plant, it was reasonably considered that most of magnesium in silica scale samples consists of octahedral sheet in addition to aluminum. From ^{27}Al MAS NMR analysis for synthesized precipitates consisting of only Al_2O_3, Al_2O_3-MgO, and Al_2O_3-SiO_2-MgO, it was found that the symmetry of Al(6) become better in the presence of adequate amount of magnesium. The result of this study show that magnesium may stabilize Al(6) during the formation of the octahedral sheet of smectite in geothermal water.

References

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