Proceedings World Geothermal Congress 2020+1
Reykjavik, Iceland, April - October 2021

Chemical State of Aluminum in Geothermal Water

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Keywords: aluminum, chemical state, geothermal water, silica scaling.

ABSTRACT

It was found that the chemical state of trace aluminum in geothermal water can be examined by the measurement of ^{27}Al MAS NMR spectra for aluminum adsorbed and concentrated to ion exchange resins. In an acidic geothermal water of pH 2.8, aluminum was present as $[Al(H_2O)_6]^{3+}$. On the other hand, in weak alkaline geothermal waters (pH: 8.7 and 9.2), aluminum existed as aluminosilicate complex anions with a high Si/Al atomic ratio judging from the chemical shift values. In this method, however, only ionic aluminum species can be detected, but non-ionic aluminum species cannot be detected in principle. Therefore, an adsorption experiment of aluminum in geothermal water to silica gel powder, which is a model compound of previously deposited silica scale, was performed at the same time. Based on results from the ^{27}Al MAS NMR measurements and adsorption experiments, the chemical state of dissolved aluminum in geothermal waters was deduced. In addition, the formation mechanism of silica scale, in which aluminum participates, was discussed.

1. INTRODUCTION

In geothermal power plants of the liquid dominated type, deposition of silica scaling from near neutral and neutral geothermal water has been a serious problem for a long period. A solution of the silica scaling problem would be of great socially benefit. However, a technique that prevents silica scaling has yet to be developed. To solve the problem, the detailed formation mechanism of silica scales should be elucidated. Although many studies on the formation of silica scales have been performed, no accurate formation mechanism has been made clear yet. As one of the reasons, it should be emphasized that researchers have regarded silica scales as pure amorphous silica. Yokoyama et al. (1993) reported both chemical compositions of silica scales formed in geothermal power plants in Kyushu, Japan and chemical compositions of geothermal waters from which silica scales were precipitated. From the results, they reported that aluminum is concentrated from geothermal water to silica scales during the formation of silica scales. Gallup (1997 and 1998) defined silica scales as amorphous aluminosilicate scale and measured the solubility. He found that the solubility of aluminosilicate scale is lower than that of pure amorphous silica. These results strongly suggest that silica scale is not pure amorphous silica but aluminosilicate, and aluminum participates in the precipitation of silicic acid from geothermal water (silica scaling). Carroll et al. (1998) conducted a column experiments using a sodium silicate solution and geothermal water, whose silicic acid concentrations were the same. They passed the fluids through columns packed with zirconia ceramic balls and the change in the permeability with time was compared. The permeability when geothermal water was passed decreased more quickly than that when the sodium silicate solution was passed. They concluded that trace aluminum in geothermal water may accelerate the precipitation of silicic acid. As aluminum is concentrated from geothermal water to silica scale, the characterization of the aluminum was performed using infrared spectroscopy and ^{27}Al magic angle nuclear magnetic resonance (MAS NMR) by Gallup (1997) and Yokoyama et al. (1993 and 1999). However, no characterization has been performed for aluminum species in geothermal water because of extremely low concentrations (0.n ~ 1.0 ppm). In order to elucidate the formation mechanism of silica scale, it is essential to elucidate the chemical state of aluminum in geothermal water.

The purpose of this work is to propose a method to determine the chemical state of aluminum species in geothermal water. This characterization method is based on the concentration of aluminum in geothermal water to cation or anion exchange resins and detection of the aluminum by ^{27}Al MAS NMR. In addition, adsorption behavior of aluminum in geothermal water on silica gel powder, which is a model compound of silica scales previously deposited, was examined. In this paper, the adsorption mechanism of aluminum species is deduced from the results of the ^{27}Al MAS NMR and the adsorption experiments.

2. EXPERIMENTAL

2.1 Characterization of Aluminum Species in Geothermal Water

The cation exchange resin (1.0 g, Dowex TM C-10, 200-400 mesh, Na type)) or anion exchange resin (1.0 g, Dowex TM-1×8, 200-400 mesh, Cl type) was added into geothermal water (0.8 L) and shaken at 90°C for 30 min. The ion exchange resin was filtered with a 0.45μm membrane filter and was air-dried at room temperature. The ^{27}Al MAS NMR (^{27}Al magic angle spinning nuclear magnetic resonance) spectra for aluminum species adsorbed to ion exchange resins were measured by a JEOL ECA 400 NMR spectrometer. The observation frequency was 104.17 MHz. A zirconia rotor (4 mm diameter) was used and the spinning rate was 15 kHz. The acquisition time and the relaxation delay were 5.12 msec and 0.5 sec, respectively. The chemical shift was relative to a $[Al(H_2O)_6]^{3+}$. The measurement was carried out at ambient temperature.

2.2 Adsorption Experiment of Aluminum Species in Geothermal Water to Silica Gel Powder

Silica gel powder (1.0 g) was added into geothermal water (1.0 L) and was shaken for 30 min at 90℃. An aliquot of the suspended solution was taken out at given intervals (5, 10, 15, 20, 30, 40, 50 and 60 min). Total silicic acid and monosilicic acid concentrations in filtrates were spectrophotometrically determined. After the adsorption reaction, the remaining silica gel powder was filtered with a 0.45 membrane filter and was air-dried at room temperature. The ^{27}Al MAS NMR spectra for aluminum species adsorbed on the surface of the silica gel powder were measured as described above. The silica gel powder (D-50-1000 AW) was purchased from a chemical company (AGC Si tech, Japan). The specific surface area was 28 m^2/g because the specific surface area of siliceous deposits at the Hatchobaru geothermal plant in Japan was lower than the detection limit (10 m^2/g) (Yokoyama et al., 2002).

3. RESULTS

3.1 ^{27}Al MAS NMR Spectra for Aluminum Adsorbed to Ion Exchange Resins from Geothermal Waters

Table 1 represents the analytical result of three geothermal waters used in this study (from production wells in the Hatchobaru and Takigami geothermal power plants in Kyushu, Japan). Geothermal water A is acidic (pH: 2.8) and iron concentration is relatively high (6.8 ppm (Fe)) but aluminum concentration was low (0.5 ppm (Al)). Total silicic acid concentration is 736 ppm (SiO_2). Geothermal waters B and C are weak alkaline (pH: 8.7 and 9.2). Aluminum concentrations of both geothermal waters are lower than that of geothermal water A and almost the same (0.35 and 0.38 ppm). Total silicic acid concentration of the geothermal waters were 714 and 619 ppm, respectively. Geothermal waters A and B are produced in the same geothermal area but geothermal water C is from different geothermal area. Origin of the three geothermal waters is meteoric water (Hirowatari, 1991).

Table 1: Analytical results for geothermal waters (A, B and C) (mg / L).

Element	A	B	C
Na	1030	1060	572
K	192	168	76.7
Ca	28.3	5.78	10.9
Mg	9.40	0.731	0.007
Cl	1390	1560	780
SO4	890	289	120
HCO3	nd	60.0	55.0
SiO2*	736	714	619
Al	0.50	0.35	0.38
Fe	6.80	0.05	<0.004
Temperature (℃)	97	97	97
pH (25°C)	2.8	8.7	9.2

*Total silicic acid. nd: not detected

Figure 1 shows ^{27}Al MAS NMR spectra for aluminum species adsorbed to cation and anion ion exchange resins in geothermal waters A, B and C. When the coordination atom for the aluminum ion (Al^{3+}) is oxygen, Al^{3+} shows one of the following coordination numbers: 4-coordinated (AlO_4, tetrahedral), 5-coordinated (AlO_5, trigonal bipyramid) and 6-coordinated (AlO_6, octahedral). These coordination structures can be determined based on the range of chemical shifts relative to $[Al(H_2O)_6]^{3+}$. The 6-coordinated aluminum shows the chemical shift range of 0 ~ 30 ppm, 5-coordinated aluminum 30 ~ 40 ppm and 4-coordinated aluminum 40 ~ 80 ppm (Engelhaldt and Michel, 1987). In Figure 1, the ^{27}Al MAS NMR spectra show a sharp peak on a broad peak (from 100 to -50 ppm). Due to a small amount of aluminum adsorbed to ion exchange resins, weak noise signals from materials of the NMR probe may be accumulated. They may cause the broad background peak. The sharp peaks are real peaks due to aluminum adsorbed to ion exchange resins from geothermal water. In Figure 1, only the spectra where a sharp peak appeared are shown.

The chemical state of species is considered to be maintained even after the ion exchange reaction with an ion exchange resin because of a simple electrostatic adsorption. Etou et al. (2009) and Etou et al. (2012) found that even when aluminum tridecamer, which consists of one 4-coordinated aluminum ion and twelve 6-coordinated aluminum ions, is adsorbed to chelate resin, the chemical structure was maintained. The adsorption occurred by a simple ion exchange reaction with Na^+ on carboxyl groups. The ^{27}Al MAS NMR spectra for aluminum adsorbed to chelate resin and ion exchange resins is considered to reflect the chemical states in aqueous solution.

A sharp peak due to aluminum species adsorbed from geothermal water A (a) appeared around 0 ppm, indicating that cationic 6-coodinated species is present in the geothermal water A. In the acidic geothermal water A, aluminum species were adsorbed to the cation exchange resin but the adsorption to the anion exchange resin was not detected, suggesting that no anionic aluminum species existed. In the weak alkaline geothermal waters B (b) and C (c), aluminum species were adsorbed to the anion exchange resin but was not adsorbed to the cation exchange resin. The facts suggest that anionic aluminum species are present in the geothermal waters B and C. Only ionic aluminum species with electric charges can be adsorbed to ion exchange resins by an ion exchange reaction. Information about non-ionic aluminum species cannot be obtained in principle by this method, if they exist.

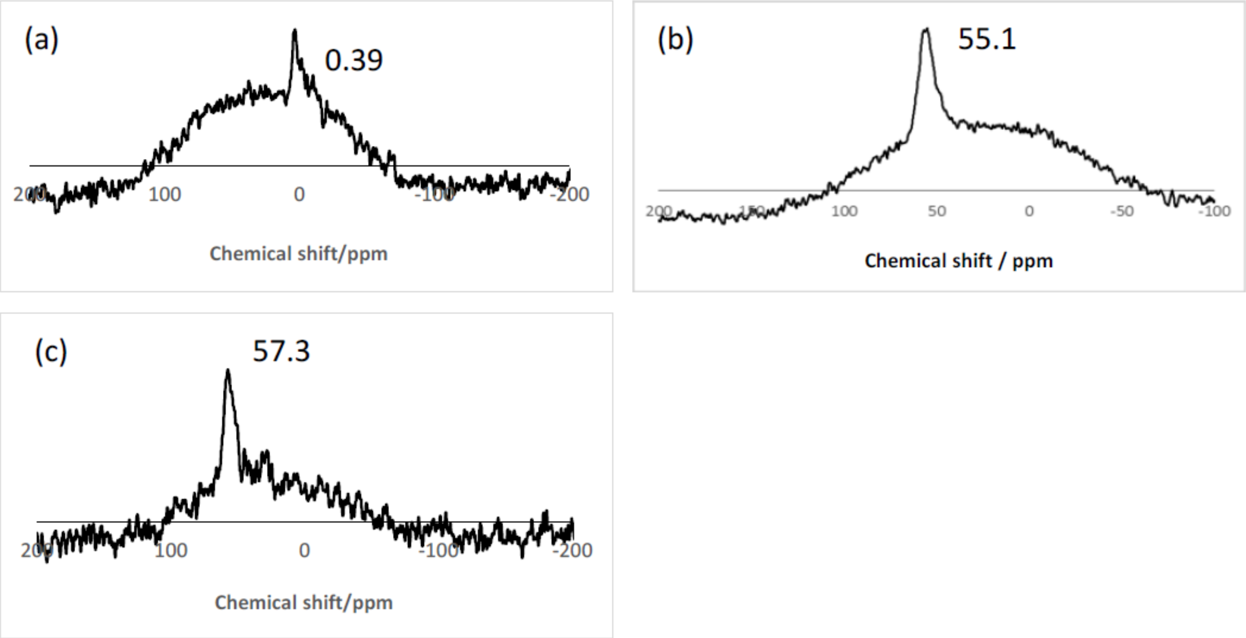

Figure 1: ^{27}Al MAS NMR spectra for aluminum adsorbed to cation or anion exchange resins. Geothermal water A, cation exchange resin. (b) Geothermal water B, anion exchange resin. (c) Geothermal water C, anion exchange resin.

3.2 ^{27}Al MAS NMR Spectra for Aluminum Adsorbed to Silica Gel Powder from Geothermal Waters

Silica gel powder used in this study has a narrow specific surface area (28 m^2/g). The specific surface area of the silica scales deposited from geothermal water is also small as described above. Consequently, the silica gel powder is regarded as a model compound of silica scales previously deposited from geothermal water. The ^{27}Al MAS NMR spectrum for aluminum adsorbed to the silica gel powder from the geothermal water A showed only a background broad peak (see Figure 1a). It suggests that no aluminum species was adsorbed on the silica gel powder from the acidic geothermal water A. This fact suggests that adsorption of aluminum species was difficult around pH 3 depending on the chemical state.

On the other hand, the ^{27}Al MAS NMR spectra for aluminum adsorbed on the surface of the silica gel powder from geothermal waters B and C showed the same sharp peak as those adsorbed to the anion exchange resin (the chemical shift values were also the same), suggesting that the anionic aluminum species was adsorbed as it was in the geothermal waters (see Figures 1b and 1c).

4. DISCUSSION

4.1 Existing State of Low Concentration Aluminum Ion in Geothermal Water

Aluminum ion and its hydrolytic species are highly toxic to living things in ecosystems. While, if the aluminum coordinates with various ligands, the toxicity considerably lowers (Sposito, 1996). Since silicic acid, which originates from chemical weathering of rocks, is included in natural waters, the interaction between aluminum ion and silicic acid was investigated. Exley et al. (2002) reported the formation of "hydroxyaluminosilicate (HAS)" by the reaction of aluminum with silicic acid in an acidic solution. Beardmore et al. (2016) examined the formation mechanism of the HAS by theoretical calculation. Yokoyama et al. (1987, 1988) and Pokrovski et al. (1998) reported quantitatively the formation of aluminosilicate complexes in neutral to basic solutions. As a result, trace aluminum in a silicic acid solution is considered to be present as an aluminosilicate complex depending on given conditions such as pH, aluminum concentration and silicic acid concentration.

In Figure 1a, for aluminum species adsorbed to the cation exchange resin from geothermal water A, the ^{27}Al MAS NMR peak appeared around 0 ppm, showing that the aluminum existed as a 6-coordinated species. Based on the formation constant of $[AlOSi(OH)_3]^{2+}$ in an acidic solution (Farmer and Lumsdon, 1994), aluminum cannot form the aluminosilicate complex around pH 3. Therefore, aluminum probably existed as $[Al(H_2O)_6]^{3+}$ in the acidic geothermal water A (pH=2.8). In case of the geothermal waters B and C (see Figures 1b and 1c), both ^{27}Al MAS NMR peaks appeared at 55.1 and 57.3 ppm, respectively, indicating that the aluminums existed as 4-coordinated species. The chemical shift for the aluminate ion ($[Al(OH)_4]^-$) adsorbed to the anion exchange resin is around 80 ppm, according to our measurements. On the other hand, according to the result by Pokrovski et al. (1998), the ^{27}Al NMR peaks due to $[(OH)_3SiOAl(OH)_3]^-$(Al:Si=1:1 complex) and $[(OH)_3SiOAl(OH)_2OSi(OH)_3]^-$ (Al:Si=1:2 complex) in a basic aqueous solution appeared at 74 and 69.5 ppm, respectively. As the Si/Al ratio in aluminosilicate complexes increases, the ^{27}Al NMR peak up-field shifts. Consequently, aluminums are considered to be present as 4-coordinate aluminosilicate complex anions with larger Si/Al atomic ratio in geothermal waters B and C.

4.2 A Proposed Sorption Mechanism of Aluminum Species from Geothermal Water to Silica Gel

In an acidic geothermal water A, aluminum existed as $[Al(H_2O)_6]^{3+}$. Most of the aluminum did not adsorb on the surface of the silica gel powder, suggesting that adsorption of aluminum occurs by the condensation reaction between the aluminol group (Al-OH) and the silanol group (Si-OH). Here, as the specific surface area of the silica gel was small (number of Si-OH group was small), the adsorption of aluminum may depend on the formation of the Al-OH group. With increasing pH under acidic conditions above pH 3, hydrolysis of $[Al(H_2O)_6]^{3+}$ proceeded to form its aqueous hydrolytic species such as $AlOH^{2+}$, $Al(OH)_2^+$ and $Al(OH)_3^{0+}$ and the 6-coordinated HAS may be formed as described above. In Table 2, adsorption proportions of aluminum to the cation and anion exchange resins and to the silica gel from each geothermal water are shown.

Table 2: Adsorption proportion (%) of aluminum to ion exchange resins and silica gel after 60 min. Cation and Anion: cation and anion exchange resins. *Proportion: per exchange capacity of ion exchange resins. **Proportion: per initial aluminum concentration in geothermal water.

Geothermal water	Proportion (%)		
	Cation*	Anion*	**Silica gel
A	32	0	6.8
B	0	68	3.1
C	0	100	99.5

In the weak alkaline geothermal waters B and C, aluminum existed as 4-coordinated aluminosilicate complex anions. The adsorption proportion (%) of aluminum was significantly different between geothermal waters B and C. The adsorption proportions to anion exchange resin were 68% and 100%. This fact suggests that a part of aluminum may be present as a non-ionic species and/or a species with small selectivity against the anion exchange resin in geothermal water B, but all of the aluminum existed as ionic species with the high selectivity in the geothermal water C. Moreover, the adsorption proportions to silica gel powder were considerably different at 3.1% and 99.5%, respectively. Houston et al. (2008) studied the association of dissolved aluminum with amorphous silica and proposed that reaction of dissolved aluminum with amorphous silica consists of at least three reactions: sorption of the dissolved aluminum, surface-enhanced precipitation of aluminum hydroxide and bulk precipitation of tetrahedral aluminosilicate. These reactions strongly depend on pH. According to Houston et al., aluminum can adsorb to silanol groups (Si-OH group) but does not adsorb to the dissociated group ($Si\text{-}O^-$). The Si-OH groups decrease with increasing pH due to dissociation of H^+ from the Si-OH group. Therefore, the amount of aluminum species adsorbed to silica gel decreases with increasing pH in the pH range from 5 to 9. Judging from that viewpoint, aluminosilicate complex anions may be hard to adsorb in geothermal water B due to electrostatic repulsion between the negative charge of the complex anion and $Si\text{-}O^-$ groups on the surface of the silica gel powder. On the other hand, the precipitation of tetrahedral aluminosilicate may proceed more vigorously with increasing pH, especially higher than pH 9. Yokoyama et al. (1991) reported that zeolitic compounds may be formed on the surface of polysilicic acid at pH 9. Consequently, it is suggested that all of the 4-coordinated aluminosilicate complex precipitated to the surface of the silica gel powder from geothermal water C of pH 9.2. Although the adsorption mechanism of aluminum species depends on the property of geothermal water, the adsorbed aluminum species probably accelerates the deposition of supersaturated silicic acid from geothermal water, because the deposited aluminum acts as the adsorption sites of silicic acid.

5. CONCLUSION

In this investigation, it was confirmed that dissolved aluminum species in geothermal water can be characterized from ^{27}Al MAS NMR measurements for aluminum adsorbed to ion exchange resins by a simple ion exchange reaction. In acidic geothermal water (pH 2.8), the dissolved aluminum existed as $[Al(H_2O)_6]^{3+}$. In weak alkaline geothermal waters (pH 8.7 and 9.2), the dissolved aluminum existed as 4-coodinated aluminosilicate complex anions. Since the two aluminosilicate complex anions showed similar chemical shift values, the chemical state of aluminums is possibly similar. However, the adsorption behavior to the surface of silica gel powder considerably different, that is, the adsorption proportions were 3.1 and 99.5 %. What causes the different adsorption behavior? The elucidation of the difference is important future work.

ACKNOWLEDGEMENT

This work was conducted as part of the New Energy and Industrial Technology Development Organization's (NEDO) project (2018-2020): Research and development of geothermal power generation technology/Development technology for advanced use of geothermal energy/Development of chemical processing systems in order to properly utilize acid brine.

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