Deposition Behavior of Elements Composing of a Silica Scale from a Geothermal Water

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ABSTRACT

Silica scales, which precipitate from geothermal waters, contain some elements such as Al, Na, K, Mg and Ca as major constituents in addition with Si. The movement of the elements from geothermal water to surface of stainless-steel (SUS) plates was examined by the metal plate immersion method. Change in the concentration of the elements deposited on the surface with time was measured by a LA-ICP-MS. From the plot of the concentration of each element against the immersion time of SUS plates in a geothermal water, the followings were made clear: (1) the deposition of Si (silicic acid) correlated with that of Al, suggesting that Al may contribute the deposition of silicic acid, (2) Na, K, and Ca may be incorporated in the silica scale due to neutralization of a permanent negative charge on the 4-coordinated Al.

1 INTRODUCTION

Silica scaling problems at the geothermal power plants has been serious for a long period. Based on the previous investigations, silica scales have been regarded approximately as an amorphous silica. The deposition of the silica scales has been thermodynamically considered from a viewpoint of the solubility of amorphous silica.

On the other hand, silica scales contain some elements such as aluminum (Al), iron (Fe), sodium (Na), potassium (K), magnesium (Mg) and calcium (Ca) as constituents in addition with Si (silica and silicate). However, effect of the elements on the deposition of silica scales has never been investigated. In this study, to examine the deposition behavior of each element composing of a silica scale, four stainless-steel (SUS) plates were simultaneously immersed in a geothermal water, the plates were taken up one by one from the geothermal water every day. First, to qualitatively examine major elements deposited on the SUS plates, the surface was observed by a SEM-EDX. Second, the quantitative analysis of the elements deposited on the surface of the SUS plates was performed by a LA-ICP-MS. In this paper, from the variation of surface concentration of each element with immersion time in the geothermal water, the deposition behavior of Si, Al, Na, K and Ca on the SUS plates was discussed.

2 EXPERIMENTAL

2.1 Procedure of the immersion experiment

Figure 1 shows an image of the stainless-steel (SUS) plates immersed in geothermal water. Immediately after each SUS plate was taken out from the geothermal water, it was rinsed with pure water. The dried SUS plate was preserved in a specific container to keep the state of surface.

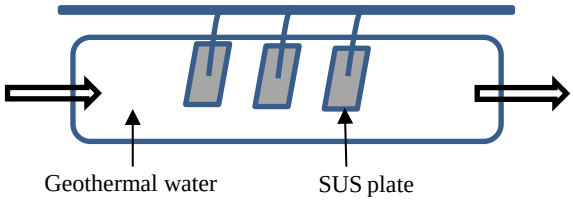

Figure 1 An image of the SUS plates immersed in a geothermal water. Arrow: flow direction of geothermal water

2.2 Analyses of the surface of stainless steel (SUS) plate

The surface of the SUS plates immersed in the geothermal water was observed by a SEM-EDX (Hitachi SU 3500) to obtain the SEM image of the surface and to identify elements deposited on the surface and to make clear their distribution. Moreover, the concentration of each element deposited on the surface of SUS plates was quantitatively measured by a LA-ICP-MS (ESI eximer laser, NWR 193 UC and Agilent Technologies, ICP-MS 7900).

3 RESULTS AND DISCUSSION

3.1 Change in weight of silica scales deposited on the surface of titanium plates with time

Kiyota et al. (2021) measured the change in weight of silica scales deposited on the surface of titanium (Ti) plates from geothermal water with time. They made clear that the increasing rates of weight of silica scales were considerably different depending on the property of geothermal waters. However, this method cannot give us information about the deposition behavior of each element composing of the silica scale deposited from the geothermal water. For the comprehensive understanding of mechanism and kinetics of silica scale deposition from geothermal water, it is important

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to make clear the deposition behavior of each element composing of the silica scale from the geothermal water.

3.2 Identification of elements composing a silica scale by SEM-EDX

The four stainless-steel (SUS) plates were immersed in a Hatchobaru geothermal water at the same time and the SUS plates were taken out one by one every day. The SUS plate was a square with 2.5 cm long and the thickness was 0.5 mm. Aanalytical result of the Hatchoberu geothermal water is represented in Table 1.

Table 1 Analytical result of the Hatchobaru geothermal water used in this study

Constituent	mg/L
Si(T)	970
Si(M)	605
Na	1260
K	223
Mg	0.06
Ca	6.77
Al	1.01
Cl	2160
pH	8.6

Si(T): Total silicic acid concentration (as SiO_2)

Si(M): Monosilicic acid concentration (as SiO_2)

The geothermal water is a weak alkaline and NaCl type containing much silicic acid. At the immersed point of SUS plate, Si(T) and Si(M) were different, indicating that a part of monosilicic acid had already polymerized.

First, the surface of the SUS plate immersed in the Hatchobaru geothermal water was observed by a SEM-EDX. For the comparison of the SEM images between the surface of a fresh SUS plate and the surface of a SUS plate immersed in the geothermal water, the surface of the fresh SUS plate before immersion is relatively uniform and flat, while the surface of the SUS plate after immersion for 4 days was seemed to be rough, suggesting that silica scale may be deposited as a film. The EDX results are shown in Table 2. The unit is atomic %. As the deposit mainly consisted of Si, it was a silica scale including Al, Na, K, Mg and Ca. Fe, Cr and Ni are major constituents of SUS. The contents of Fe, Cr and Ni were large for the fresh SUS, but they decreased with the immersion time in geothermal water, indicating that the change in the contents of Fe, Cr and Ni can be considered to correspond to increase in the thickness of the silica scale film.

Table 2 Analytical result byEDX

Element	Befor immersion atomic %	After immersion atomic %
Si	0.8	96.69
Fe	53.5	0.7
O	7.4	n
Ca	0.26	0.12
Cr	15.39	0.22
Ni	6.08	0.17
C	16.61	n
Na	n	0.77
K	n	0.31
Mg	n	0.41
Al	n	0.89

*n indicates that the element was not detected.

3.3 Quantitative analysis of the elements composing of the silica scale by LA-ICP-MS

The quantitative analysis of elements contained in the silica scale deposited on the surface of SUS plate was performed by a line analysis using a LA-ICP-MS. Under the same analytical condition, a NIST 612 standard material (Pearce et al., 1997) was also analyzed to make a calibration curve for each element. For an example, using the calibration curve of $^{28}Si^{+}$, the Si concentration in the vaporized material (aerosol) including the silica scale deposited on the surface of SUS plate was determined. As the thickness of the silica scale film was thin, the laser beam penetrated the film and attained in the SUS. As a result, the aerosol contained the constituents of the silica scale and the SUS. Consequently, the concentration of each element consisting of the silica scale increased with immersion time of SUS plate in the geothermal water (with increasing the thickness of the silica scale film). As far as the laser beam penetrates the silica scale film and attains the SUS, the element concentration correlates with the amount of the element deposited on the surface of SUS for a given immersion time because the concentration of each element becomes constant after the laser beam cannot attain the SUS due to thickness of the silica scale film. That is, the relationship between the Si concentration and the immersion time corresponds to the deposition rate of Si (silicic acid) from the geothermal water.

3.4 Deposition behavior of elements composing of silica scale

In Table 3, the analytical result of the surface of a fresh SUS plate. Si, Al, Na, K, Mg and Ca, which consist of the silica scale, were analyzed by LA-ICP-MS. The concentrations of the above elements on the surface of the fresh SUS plate were considerably lower than those of the SUS plate immersed in

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the geothermal water except Mg. In this paper, the deposition behavior of Si, Al, Na, K and Ca on the surface of SUS plate from the geothermal water was examined. The examination can predict the interaction among elements which deposit during the formation of silica scale. In geochemistry, it is meaningful to examine the deposition behavior of each element consisting of silica scale from geothermal water. Based on the interaction, the formation mechanism is possible to be quantitatively proposed.

Table 3 Analytical result of elements on the surface of a fresh SUIS plate by LA-ICP-MS

Element	mg/kg
Si	522
Al	2.92
Mg	1.00
Ca	3.60
Na	11.8
K	0.05

3.3.1 Silicic acid and aluminum

In Table 1, although the total silicic acid concentration (as SiO_2) was 970 ppm, the monosilicic acid concentration was 605 ppm, indicating that a part of monosilicic acid polymerized to form polysilicic acid (colloid). The total aluminum concentration (as Al) was 1.01 ppm. Yokoyama et al. (1993), Gallup (1997), Carrol et al. (1998), Spinthaki et al. (2021) and Wanyonyi et al. (2024) demonstrated that Al concentration is considerably lower than that of silicic acid in neutral to weak alkaline geothermal waters, but the Al probably affect the deposition of silica scales. Therefore, it is important to examine the deposition behavior of Al in addition with that of silicic acid (Si).

Figures 2 and 3 show the changes in Si and Al concentrations on the surface of SUS plates with the immersion time in the geothermal water, respectively (●). Even after 1 hour immersion in the geothermal water, Si and Al were sensitively detected on the surface of SUS plate by LA-ICP-MS. The Si and Al concentrations increased with the immersion time. Although Si and Al concentrations on the surface of SUS plates were different, the increasing pattern was similar, suggesting that Al may participate in the deposition of silicic acid.

As described above, we measured previously the change in weight of silica scale deposited on the surface of titanium (Ti) plate from geothermal water with the immersion time, as shown in Fig. 4 (●). The experiment was conducted for 14 days. The change in the curve with immersion time was approximated empirically to exponential (dotted line). In addition, the regression equation and the correlation coefficient are also shown. In the Figs 2 and 3, therefore, the results of the exponential regression analyses for Si and Al are shown together. By using the approximation relationship, the change in concentration of each element consisting of silica scale with time may be possible to predict.

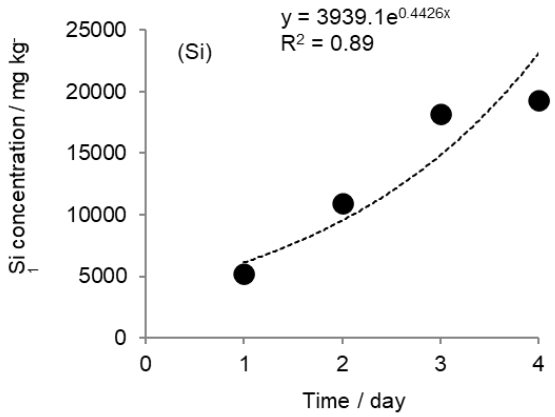

Figure 2 Change in concentration of Si deposited on the surface of SUS with immersion time in the geothermal water. ●: measured concentration by LA-ICP-MS. The dotted line: the exponential regression analysis.

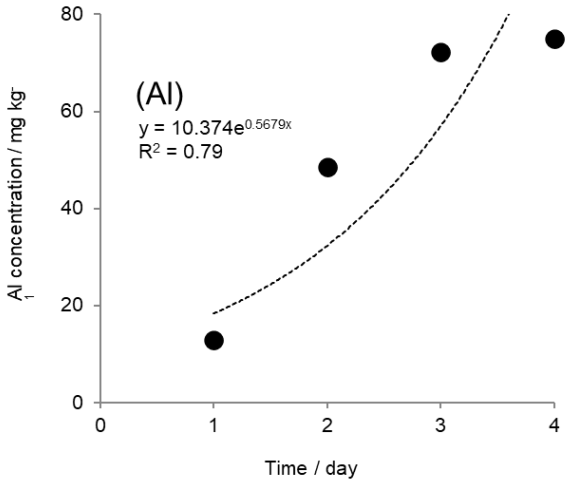

Figure 3 Change in concentration of Al deposited on the surface of SUS with immersion time in the geothermal water. ●: measured concentration by LA-ICP-MS. The dotted line: the exponential regression analysis.

Figure 5 shows a relationship between the mole concentrations of Si and Al shown in Figures 2 and 3. It shows a good linear correlation (R^2 = 0.94) between them,

suggesting a stoichiometric reaction of Al and silicic acid such as coprecipitation of silicic acid with Al and/or adsorption of silicic acid on Al precipitated on ahead. Consequently, Al participates in the deposition of silica scale and an Al averagely precipitates 242 Si from geothermal water in this case. Ichikuni (1970) described that an Al can

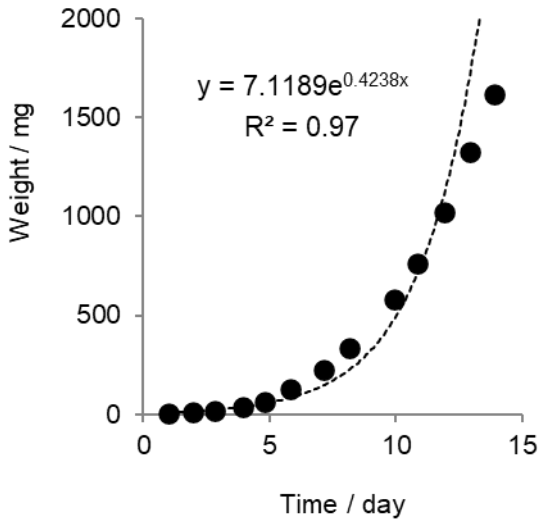

Figure 4 Change in weight (●) of a silica scale deposited on the surface of titanium plate immersed in the geothermal water with immersion time and a result of the exponential regression analysis (dotted line).

precipitate more than 40 Si from geothermal water. At the beginning of the immersion of SUS plate in geothermal water, a part of monosilicic acid had already polymerized, as shown in Table 1. The slight amount of Al significantly reduces the solubility of amorphous silica as demonstrated by Iler (1973). Gallup (1998) reported that the solubility of aluminosilicate scale is significantly lower than that of amorphous silica. During the polymerization, Al is incorporated in polysilicic acid (Yokoyama et al., 1991). Therefore, the concentration of free and mononuclear Al, which participates in the formation of silica scales, was significantly lower than the total Al concentration in Table 1. The Al incorporated in polysilicic acid cannot participate in the formation of silica scale.

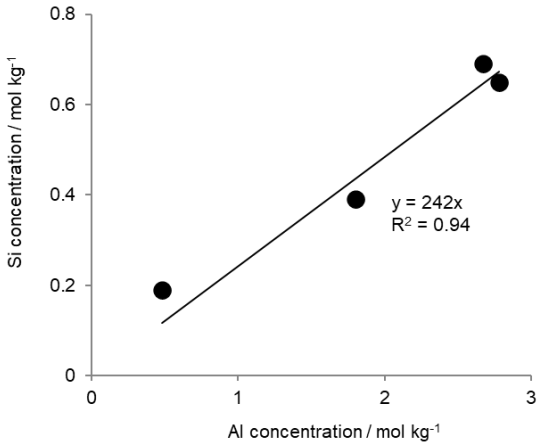

Figure 5 A relationship between the mole concentrations of Si and Al. Al concentration: $\times 10^3$ times.

3.4.2 Na, K and Ca

Figures 6,7 and 8 show the variations of Na, K and Ca concentrations deposited on the surface of SUS plates with the immersion time. The concentrations of Na and K

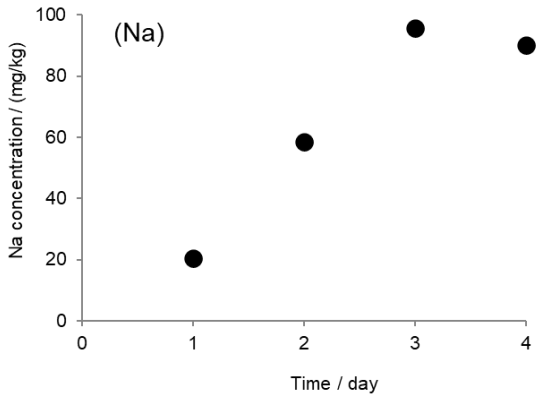

Figure 6 Change in concentration of Na deposited on the surface of SUS with immersion time in the geothermal water.

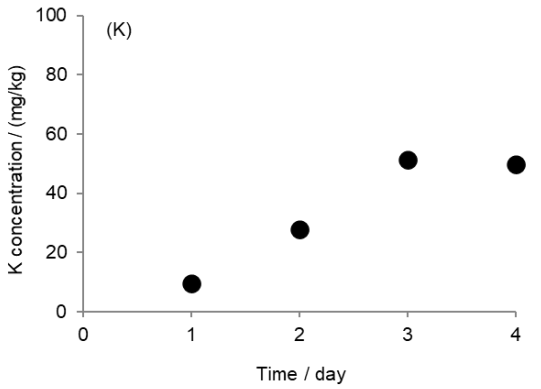

Figure 7 Change in concentration of K deposited on the surface of SUS with immersion time in the geothermal water.

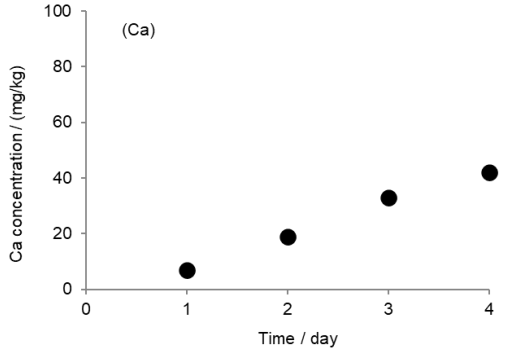

Figure 8 Change in concentration of Ca deposited on the surface of SUS with immersion time.

increased with the immersion time for initial 3 days and the concentrations decreased slightly at 4 day. However, the concentration of Ca increased monotonously for 4 days.

Figures 9, 10 and 11 show the correlation between the concentrations of Al and Na, K and Ca, shown in Figs. 3,6,7 and 8.

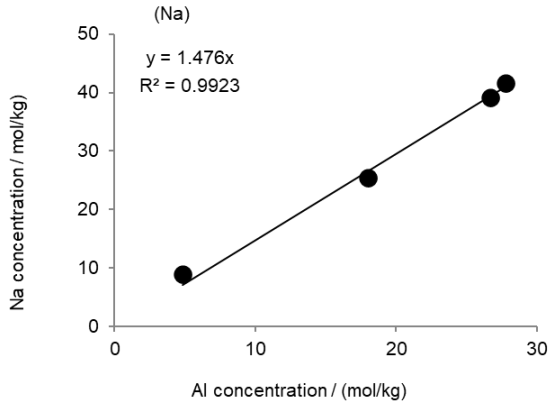

Figure 9 A relationship between Al and Na concentrations deposited on the surface of SUS plates.

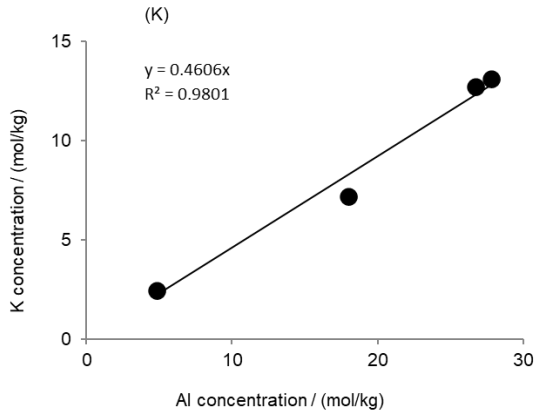

Figure 10 A relationship between Al and K concentrations deposited on the surface of SUS plates.

They show good relationship. Yokoyama et al. (1993), Gallup (1997) and Aramaki et al. (2005) reported that the coordination number of Al in silica scales was both 4 and 6 or only 4. The 4-coordinated Al is generally an Al^{3+} which is substituted with Si^{4+} in silica structure. In the isomorphous substitution, a permanent negative charge is generated on the 4-coordinated Al^{3+} and a cation can neutralize the negative charge. The linear relationship between Al concentration and Na, K and Ca concentrations suggest that Na, K and Ca may be incorporated into silica scale due to electrostatic neutralization of the permanent negative charge on the 4-coordinated Al^{3+}.

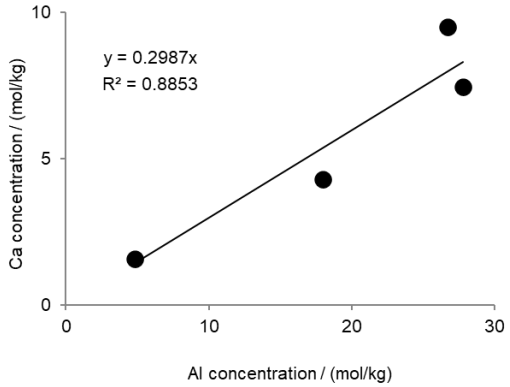

Figure 11 A relationship between Al and Ca concentrations deposited on the surface of SUS plate.

4. CONCLUSION AND IMPLICATION FOR PREDICTION OF SILICA SCALING

By combining the immersion of metal plates such as stainless steel (SUS) in geothermal water and the surface analyses of elements by a SEM-EDX and a LA-ICP-MS, the deposition behavior of elements composing of silica scales can be kinetically detected.

In this study, the geothermal water used was a weakly alkaline and NaCl type with high concentration of silicic acid. As a metal plate, the SUS was selected because of a strong corrosion resistance. Through the analyses of the surface of SUS plates immersed in the geothermal water, the deposition mechanism of silicic acid from the geothermal water and the uptake mechanism of Na, K and Ca into the silica scale were elucidated.

Interestingly, these reactions may be controlled by aluminum (Al) whose concentration in the geothermal water was considerably lower than that of silicic acid. In addition, the deposition rates of silicic acid and Al is possible to predict by the approximation using a function such as exponential. The development of an artificial intelligence (AI) system which can predict silica scaling at geothermal power plants can be expected through the mechanical learning of the relationship between the property of geothermal water and the kinetic data of deposition of elements on the metal plates .

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