Concept of the development of scale inhibitors

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ABSTRACT

Referring the inhibition effect of polyacrylic acid (PAA) against the formation of calcium carbonate scale, a concept for search of silica scale inhibitor was tried to build up. To elucidate the inhibition mechanism of PAA, the interaction between calcium ion (Ca^{2+}) and PAA was investigated. It was found that only slight complexation of Ca^{2+} to carboxyl groups (COOH) occurred, suggesting that the inhibition may possibly be caused by inhibition of growth of nuclei due to adsorption of PAA on its surface. For the formation of silica scale, two models for the nuclei of silica scale were designed: (1) aluminum hydroxide ($Al(OH)_3$) with positive surface charges and (2) silica containing the trace amount of Al with negative surface charges. According the properties of nuclei of silica scale, two polymer reagents (acumer 5000 and tiron type DADMAC) were selected as silica scale inhibitors.

1. INTRODUCTION

Since beginning of the commercial operation of geothermal power plants in the world, the formation of scales such as calcium carbonate and silica has often prevented the stable operation. For the calcium carbonate scale in production wells, the formation has been retarded by introducing sodium polyacrylate solution as an inhibitor through a tube in deeper position than the boiling point of the geothermal water. However, the retardation mechanism has still been unclear. On the other hand, no valid inhibitor which can retard the formation of silica scale has been found yet (Gallup, 2002, Ikeda et al., 2017). Recently, we have started a research about the design of silica scale inhibitors based on the interaction between inhibitors and silicic acid in geothermal water or nuclei of silica scale on the surface of solid. In this study, first, the interaction between calcium ion (Ca^{2+}) and polyacrylic acid, which has been used as a calcium carbonate inhibitor in Japan, was investigated and the inhibition mechanism was discussed. Second, we describe the ideas for inhibition mechanism of silica scale inhibitor by referring the inhibition mechanism of calcium carbonate scales. Moreover, the effect of tiron (4,5-dihydroxy 1,3-benzenedisulfonate disodium) and accumer 5000 on the silica scale formation is described.

2. Inhibition mechanism of calcium carbonate ($CaCO_3$) scale by a polyacrylic acid (PAA)

2.1 Possible inhibition mechanisms of the PAA

As general idea of the inhibition mechanism of $CaCO_3$ scale from geothermal water by the PAA in production wells at geothermal power plants, there are two ideas: (1) deactivation of Ca^{2+} ions by complexation of Ca^{2+} with carboxyl groups in the PAA and (2) prevention of nucleus and crystal growth of $CaCO_3$ as shown in Fig. 1.

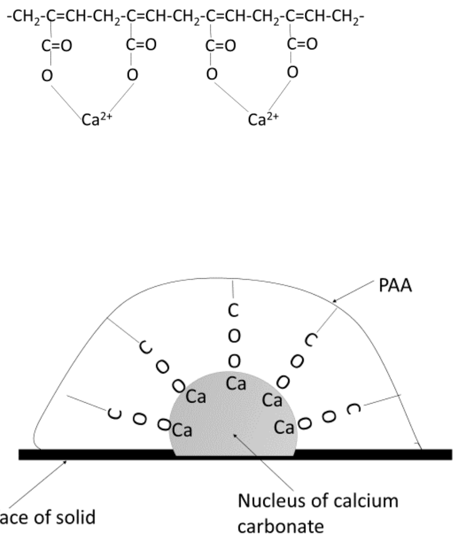


Fig. 1. Images of complexation of Ca^{2+} with PAA (upper) and a nucleus of $CaCO_3$ covered by PAA (bottom).

2.2 Interaction between Ca^{2+} and PAA in geothermal water

2.2.1 Experimental procedure

A 50 mL of geothermal water was put in a 100 mL volumetric flask. A 10 mL of 1 mol dm^{-3} KCl solution for adjustment of ionic strength and 10 mL of 1 mol dm^{-3} NH_3 -NH_4Cl buffer solution were added to the geothermal water. Moreover, 0 ~ 16 mL of 10000 ppm of PAA solution was added. Finally, the mixed solution was diluted to 100 mL. The Ca^{2+} concentration (activity) in the solution was determined by a calcium ion selective electrode.

2.2.2 Variation of free Ca^{2+} concentration with PAA concentration

Polyacrylate has been used as an inhibitor of $CaCO_3$ scale at geothermal power plants (Masunaga et al., 2017). However, the inhibition mechanism has been uncertain for a long time. Therefore, the interaction between Ca^{2+} and PAA in geothermal water was first examined using a calcium ion selective electrode to confirm which mechanisms in Fig. 1

work. The analytical result of a geothermal water used in this study was as follows: Na 1610, K 205, Mg 0.201, Ca 32.0, Cl 2660, SO_4 262, HCO_3 49.0, Si(T) 528 (concentration/ppm). Si(T) indicates the total silicic acid concentration as SiO_2. The temperature was 96℃. From the comparison of the analytical results between total calcium concentration by ICP-AES and calcium ion activity by calcium ion selective electrode, most of calcium ion existed as free Ca^{2+} in the geothermal water. PAA was added in the geothermal water. Figure 2 shows a relationship between PAA concentration and free Ca^{2+} concentration. The Ca^{2+} concentration decreased with increasing the PAA concentration, indicating that a part of the Ca^{2+} coordinates to carboxyl groups (COO^-) in PAA molecules.

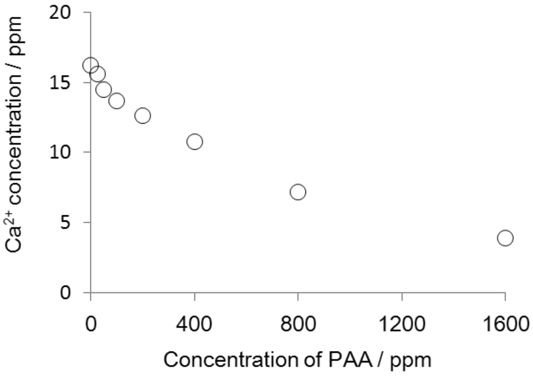


Fig. 2. Variation of free Ca^{2+} concentration with PAA concentration added in the geothermal water

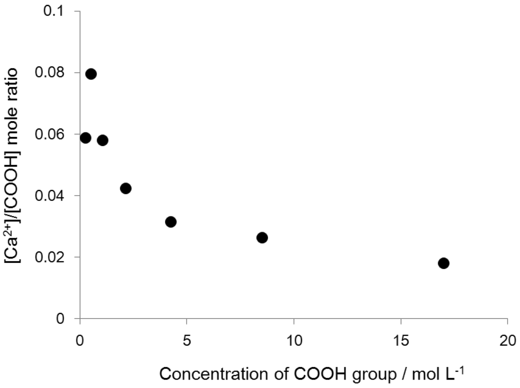


Fig. 3. Variation of $[Ca^{2+}]/[COOH]$ mole ratio with COOH group concentration of PAA added in geothermal water.

2.2.3 Coordination degree of Ca^{2+} to COOH group in PAA

Figure 3 shows a relationship between COOH group concentration of PAA and coordination degree of Ca^{2+} to COOH group ($[Ca^{2+}]/[COOH]$ mole ratio). The coordination degree corresponds to an average number of Ca^{2+} combined to one COO^- group. At 2.67×10^{-4} mol/L of COOH group, the $[Ca^{2+}]/[COOH]$ mole ratio was 0,06 and the mole ratio shows a maximum of 0.08 at 5.32×10^{-4} mol/L. Above the COOH concentration of 1.06×10^{-3} mol/L the $[Ca^{2+}]/[COOH]$ mole ratio decreased gradually. This result indicates that the interaction between Ca^{2+} and PAA is extremely weak. As a result, slight amount of Ca^{2+} in geothermal water coordinates with COOH group of PAA. On the other hand, the formation of $CaCO_3$ scale can be retarded by addition of only about 10 ppm of PAA. The fact suggests that the retardation of $CaCO_3$ scale may be due to prevention of growth of nuclei and crystal of $CaCO_3$ on the solid surface by PAA as shown in Fig. 1. Goto (1986) carried out a similar laboratory experiment (they did not use geothermal water) and described the same idea.

3 Search of silica scale inhibitors

3.1 A complex formation of silicic acid with tiron

Bai et al. (2011) first found that tiron (4,5-dihydroxy 1,3-benzensulfonate disodium) can form a stable 1:3 complex with monosilicic acid (one silicic acid and three tiron) in aqueous solution. Figures 4 and 5 show the molecular structure of tiron and the structure of a tiron-silicic acid complex.

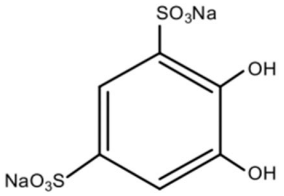


Fig.4 The molecular structure of tiron

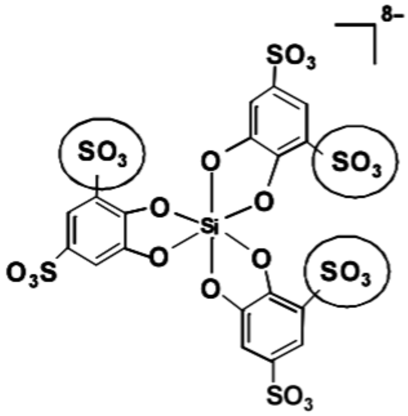


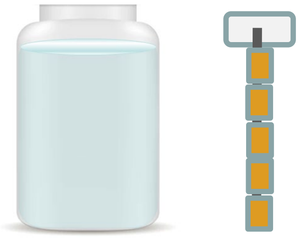
Fig. 5 The molecular structure of a silicic acid-tiron complex

3.2 Evaluation of tiron as a silica scale inhibitor

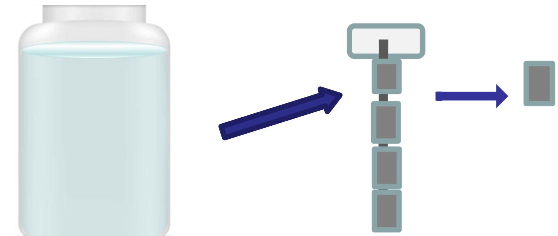
3.2.1 Evaluation method of scale inhibitors

For the evaluation of the formation silica scale, as it forms on the surface of pipes and ground facilities from geothermal water, adsorption rate of each element consisting of the silica scale on the surface of metal plate from geothermal water was measured through a quantitative analysis of elements adsorbed on the metal surface. For this method, we have already reported in the previous New Zealand Geothermal Workshop (2024). For the evaluation of scale inhibitors, the retarding effect of reagents on adsorption of the elements from geothermal water was examined by above method. In this experiment, necessary amount of tiron was put in a 1 L polyethylene bottle in advance, and a 1 L of geothermal water was poured in the bottle. Five copper plates were simultaneously immersed in the geothermal water containing tiron. After 1 h, a metal plate was taken from the geothermal water, as shown in Fig. 6. When one metal plate was taken, the geothermal water was exchanged to a fresh geothermal water containing tiron. Every one hour, a copper plate immersed was taken and the geothermal water was exchanged to fresh one. Elements adsorbed on the surface were analyzed by a laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) because of the trace amount of the element. From the analytical data, variation of concentration of each element adsorbed on the surface of metal plate with time was made clear. From change in the concentration of the elements with time, the power of tiron as a silica scale inhibitor can be evaluated.

(1) Geothermal water in a bottle and five copper plates connected vertically. The copper plates were immersed in the geothermal water.



(2) After 1 h, one copper plate was taken for the LA-ICP-MS measurement.



(3) The geothermal water containing tiron was exchanged to a fresh one. The remaining four copper plates were immersed in the fresh geothermal water again.

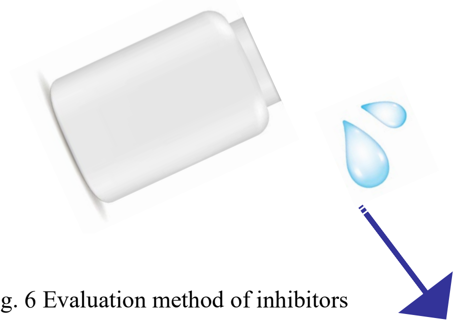


Fig. 6 Evaluation method of inhibitors

The analytical result of a geothermal water in this experiment was as follows. Na 353, K 40, Mg 0.007, Ca 14.9, Cl 428, SO$_4$ 224, Si(T) 486 (concentration/ppm). The temperature was 90℃.

3.2.2 Silica scale formation in presence and absence of tiron

As tiron can form the silicic acid-tiron complex, it is expected to work as a silica scale inhibitor. Figure 7 shows

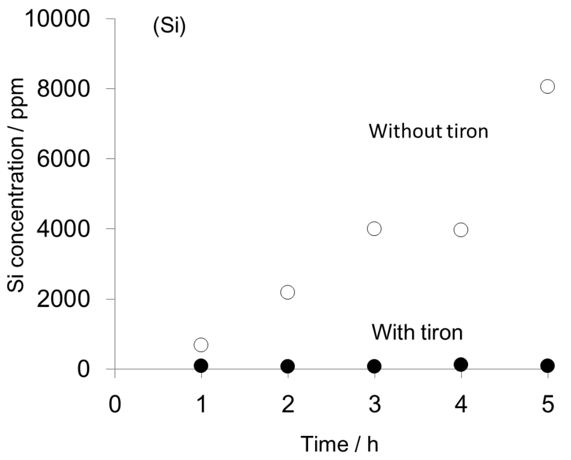


Fig. 7 Variation of Si concentration adsorbed on the surface of copper plate with immersion time.

○ Raw geothermal water, ● Geothermal water containing tiron (600 ppm).

the relationship between immersion time of copper plate and Si concentration adsorbed on the surface of the copper plate. In case of raw geothermal water, the Si concentration increased rapidly with increasing immersion time. The Si concentration was 8049 ppm (Si) at 5 h of the immersion time. On the other hand, in the presence of tiron, silicic acid was not adsorbed. The Si concentration ranged 61.9 ppm to 116 ppm. If all of the tiron formed the silicic acid-tiron complex, the concentration of free silicic acid was estimated to be 223 ppm (SiO$_2$) which is lower than the solubility of amorphous silica or the solubility of the silica scale. The stable silicic acid-tiron complex in aqueous solution cannot participate to the formation of silica scales. Therefore, no nuclei of silica scale occurs. Although the Si is the most abundant element in silica scale, the other elements such as aluminum (Al), potassium (K) and calcium (Ca) are included as constructive elements of silica scale. Figures 8 – 10 show the comparison of adsorption behavior for Al, K and Ca between in the absence and presence of tiron. The Al, K and Ca also did almost not adsorb. The Al^{3+} can also form a stable complex with tiron (Yokoyama et al., 1997). It is considered that the complexation between tiron and silicic acid and Al may inhibit the formation of nuclei of silica scale. As described previously (Yonezu et al., 2024), the electrostatic adsorption of K and Ca to nuclei of silica scale may be retarded. Consequently, tiron adequately worked as a silica scale inhibitor when the concentration was 600 ppm. The concentration of tiron added should be decided based on the stoichiometric complexation of tiron with silicic acid.

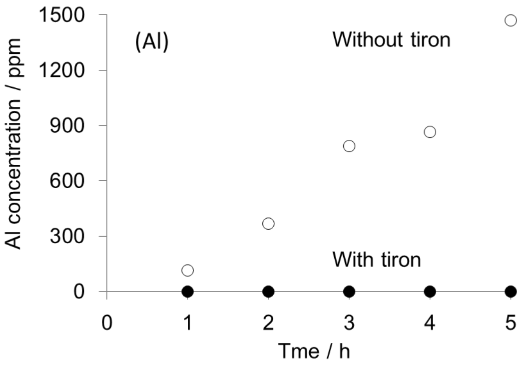


Fig. 8 Variation of Al concentration adsorbed on the surface of copper plate with immersion time.

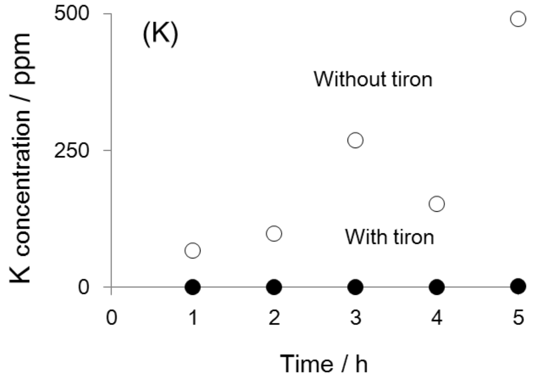


Fig. 9 Variation of K concentration adsorbed on the surface of copper plate with immersion time.

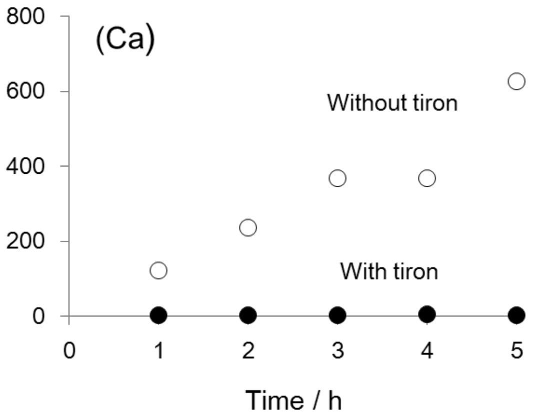


Fig. 9 Variation of Ca concentration adsorbed on the surface of copper plate with immersion time.

3.3 Nuclei of silica scale

As described above, tiron inhibits the formation of silica scale by deactivating oversaturated silicic acid through the complexation. If polysilicic acid exists, the complexation of tiron and silicic acid proceeds by decomposition of the polysilicic acid to monosilicic acid (Bai et al., 2009). Therefore, the stoichiometric concentration of tiron is required. On the other hand, the PAA, which is an organic polymer, can inhibit the formation of $CaCO_3$ scale even by addition of small amount of PAA (1 ~ 10 ppm). To prevent growth of nuclei of $CaCO_3$, it is essential to cover the surface of the nuclei. To sufficiently cover surface of nuclei of scales, organic polymers are considered to be favorable. As the surface of nuclei may be highly reactive, the combination possibility of inhibitor molecule to its surface is high. Considering the combination, what is the nuclei is important. Accordingly, how do we consider interactions between the surface of nuclei and functional groups may be a keypoint.

3.3.1 Aluminum hydroxide

As a formation mechanism of silica scale from neutral to weak alkaline geothermal water, Yokoyama et al. (1993) and Nishida et al. (2009) proposed that first aluminum hydroxide ($Al(OH)_3$) deposits on the solid surface and it acts vigorously adsorption site of silicic acid. Figure 11 shows an image of nuclei of $Al(OH)_3$. As the isoelectric point of $Al(OH)_3$ is around pH 10, the surface of $Al(OH)_3$ nuclei has positive charge under the neutral condition. Based on the facts, Nishida et al. (2010 and 2011) reported the prevention mechanism of silica scales in the cooling water by organic polymers with carboxyl groups as a functional group. By the interaction between carboxyl group (COOH) in the polymer and Al^{3+} on the surface of the $Al(OH)_3$ nuclei, the surface of the nuclei is covered by the polymer. In the interaction, the complexation of COOH groups to Al^{3+} is included in addition with the electrostatic interaction. In this study, we also examined the effect of "Acumer 5000 (commercial name)" on inhibition of silica scale from a geothermal water. Fig. 12 shows the structure of the Acumer 5000 which is a polymer whose monomeric units are sodium acrylate (AA), 2-acrylamide-2-methylpropanesulfonic acid (AMPS) and N-tert-Butylacrylamide (tBuAAM).

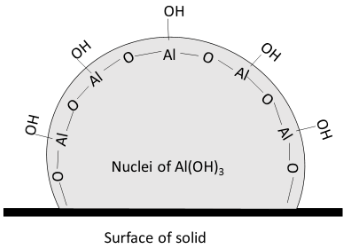


Fig. 11 Image of nuclei of $Al(OH)_3$

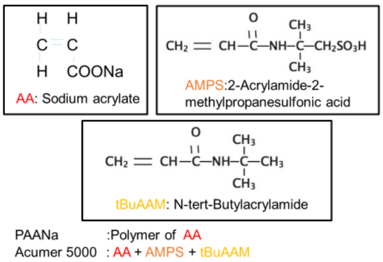


Fig.12 Structure of Acumer 5000

Figures. 13 to 16 show the comparison for adsorption of Si, Al, K and Ca in the absence and presence of Acumer 5000. The concentration of Acumer was only 10 ppm.

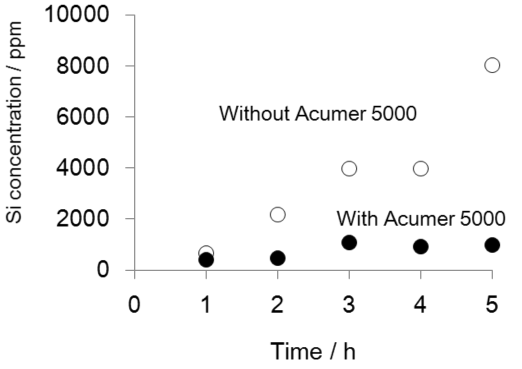


Fig. 13 Variation of Si concentration adsorbed on the surface of copper plate with immersion time.

○ Raw geothermal water, ● Geothermal water containing Acumer 5000 (10 ppm).

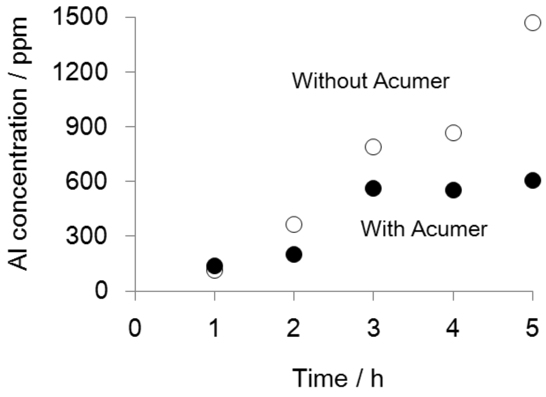


Fig. 14 Variation of Al concentration adsorbed on the surface of copper plate with immersion time.

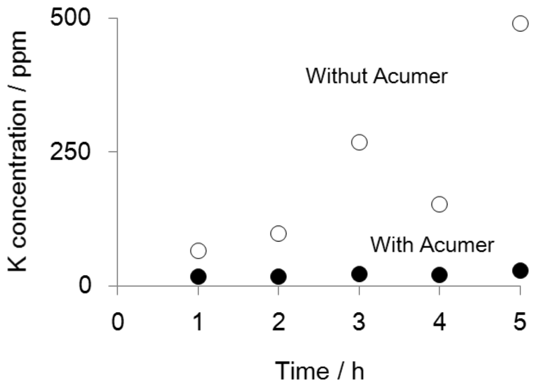


Fig. 15 Variation of K concentration adsorbed on the surface of copper plate with immersion time.

In Figs. 13 to 16, adsorption of Si, Al, K and Ca was considerably retarded, suggesting that the Acumer 5000 can sufficiently work as the silica scale inhibitor in case of the geothermal water used in this study. Especially, the adsorption of Si and K was retarded greatly. On the other hand, the adsorption of Al was not inhibited strongly. It suggests that the nuclei of the silica scale might be $Al(OH)_3$.

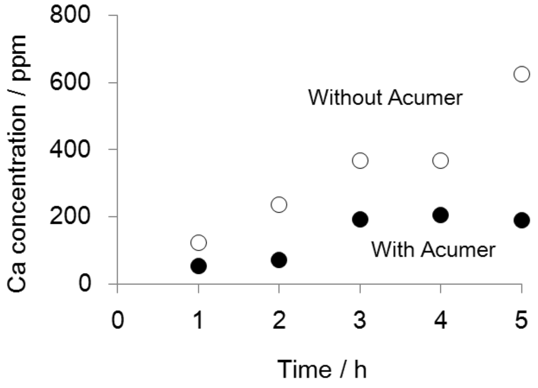


Fig. 16 Variation of Ca concentration adsorbed on the surface of copper plate with immersion time.

3.3.2 Silica containing the trace amount of Al

Aluminum in neutral to weak alkaline geothermal water exists as an aluminosilicate complex. If the nuclei is $Al(OH)_3$, it may be generated by the surface hydrolysis of Al^{3+} in the aluminosilicate complex. However, the composition of nuclei is also considered to be possibly close to that of the silica scale. The silica scales precipitated from neutral to weak alkaline geothermal water often consists of SiO_2 as main constituent and Al_2O_3 as minor element. Based on the fact, the nuclei of the silica scale is possibly silica containing the small amount of Al. Figure 17 shows an image of the nuclei.

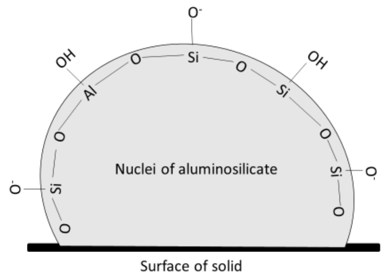


Fig. 17 An image of nuclei of silica scale consisting silica containing the trace amount of Al

The nuclei has negative charges on the surface because of dissociation of silanol group (Si-OH → Si-O$^-$) and a permanent negative charge generated by the isomorphous substitution of Al^{3+} with Si^{4+} in silica. In this case, a polymer with positive charges is a candidate as a silica scale inhibitor. Here, DADMAC (dimethyl diarylammonium chloride) was selected as a polymer with positive charges because it was used to precipitate polysilicic acid formed in a geothermal water (Hanajima and Ueda, 2017), indicating that DADMAC can interact with polysilicic acid. It deduces that DADMAC is possibly cover the surface of nuclei shown in Fig. 17. Figure 18 shows the structure of DADMAC.

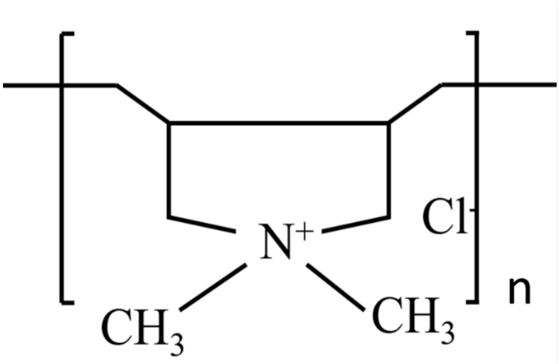


Fig. 18 Structure of DADMAC

However, if DADMAC precipitates polysilicic acid, the precipitation may cause the formation of silica scales. The precipitation of polysilicic acid occurs by electrostatic interaction between negative charges on the polysilicic acid and positive charges in DADMAC. If the positive charges can be reduced, the DADMAC may interact with only the surface of nuclei of silica scale. From an experiment using chloride ion selective electrode, it was confirmed that most of the chloride ions are dissociated in aqueous solution. Therefore, if a compound with negative charges can tightly combine with the positive charges in DADMAC, the electrostatic force of positive charge can be reduced. We try to react between DADMAC and tiron. Figure 19 shows variation of zeta potential of DADMAC with [tiron]/[N+ of DADMAC] ratio. The zeta potential of DADMAC was positive. While, the zeta potential reduced with increasing the amount of tiron added. The fact indicate that we can control the zeta potential of DADMAC by addition of tiron. We call this new species “tiron type DADMAC”.

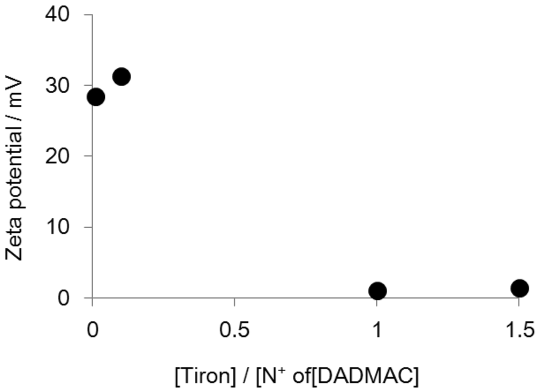


Fig. 19 Variation of zeta potential with concentration ratio of tiron and DADMAC

Figure 20 shows an image of the tiron type DADMAC. In near future, we will examine the effect of the tiron type DADMAC on the formation of silica scales, especially the effect of [tiron]/ [N$^+$ of DADMAC] ratio.

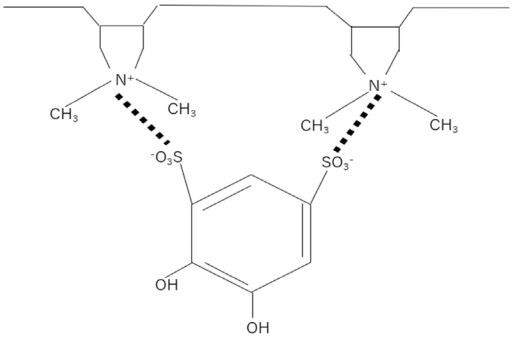


Fig. 20 An image of a structure of the tiron type DADMAC

3. CONCLUSION

As a concept to search the silica scale inhibitors used at geothermal power plants, it is important to predict the nuclei of silica scale. Based on the properties of the nuclei silica scale, polymer compound should be searched. For the formation of silica scales at a limited position such as heat exchanger of the binary system, the complexation reagents such as catechol derivatives including tiron may be useful.

4. ACKNOWLEDGEMENTS

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