Short Communication

Formation of a silicato complex of zinc in aqueous solution and its accelerating effect on the formation of silica scales in cooling water systems

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ABSTRACT

This study elucidates the effect of zinc (Zn), which is an anticorrosive water additive, on the formation of silica scales from cooling water. In these experiments, the silica scales were analyzed by EPMA, and the results indicate that Zn is sorbed into the silica scales during formation. Measurements of the solubility of $Zn(OH)_2$ at various concentrations of silicic acid demonstrate that Zn is present as a silicato complex of Zn (SCZ) in cooling water. From adsorption experiments of the SCZ on silica and alumina, which are major components of the silica scales, it can be concluded that the SCZ accelerates the formation of silica scales from cooling water.

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1. Introduction

A significant quantity of industrial water is used as cooling water in Japan. The industrial water is mainly groundwater or river water that contains silicic acid in the concentration range of 5–25 mg dm^{-3} (as Si). In addition, an aluminum compound is often added into the industrial water as a coagulant to remove turbidity, however, some of the aluminum remains in the industrial water due to an extremely slow precipitation rate [1]. When industrial water is used repeatedly as cooling water because of insufficient water resources, the dissolved components are gradually concentrated due to water evaporation. Siliceous deposits (silica scales) may begin to form when aluminum and silicic acid concentrations exceed certain levels. In the cases of geothermal power plants or hot spring water, some reports suggest that aluminum may play an important role in silica scale formation [2–5]. Recently, Nishida et al. [6] reported the characterization of silica scales, which formed from cooling water, and proposed a mechanism for their formation, in which aluminum participates. As zinc (Zn) compounds are also added into cooling water as an anticorrosive [7], the sorption of Zn into silica scales during their formation is possible [8].

In this study, the distribution of Zn in silica scales from cooling water was examined by EPMA. The state of the Zn present in the cooling water was determined by measuring the solubility of $Zn(OH)_2$ in silicic acid solution at pH 9, which is similar to the pH of the cooling water. The adsorption behavior of Zn on the surface of silica and alumina was then examined to estimate the effect of Zn on the formation of silica scales from the cooling water.

2. Experimental

2.1. Sample solutions and reagents

All reagents used were of analytical reagent grade. A stock solution of sodium silicate was prepared by dissolving sodium metasilicate ($Na_2SiO_3 \cdot 9H_2O$, Wako Pure Chemicals) into 0.1 mol dm^{-3} NaOH solution. The Si concentration was determined using inductively coupled plasma atomic emission spectrometry (ICP-AES). As a stock solution of $Zn(NO_3)_2$, the standard solution for atomic absorption spectrometry (1000 mg dm^{-3} (as Zn) in 0.1 mol dm^{-3} HNO$_3$, Wako Pure Chemicals) was used. Silica gel (Wakogel C-200, specific surface area 450 m^2/g, Wako Pure Chemicals) and alumina gel (MP Alumina N-Super I, specific surface area 200 m^2/g, MP Biomedicals) were used as adsorbents. All solutions were prepared with ultrapure water (Milli-Q SP system, Millipore).

2.2. Measurement of $Zn(OH)_2$ solubility

The stock solution of sodium silicate was diluted with water to the desired concentrations, and the pH of each solution was

adjusted to 3 with HNO_3. The desired amount of $Zn(NO_3)_2$ solution was added to the sodium silicate solutions, and the pH of each solution was adjusted to 9 with NaOH solution. The sample solutions were then magnetically stirred. At appropriate intervals, a small volume of the sample solution was collected and filtered with a 0.45-μm membrane filter. The Zn concentration in each filtrate was determined by atomic absorption spectrometry.

2.3. Effect of silicic acid concentration on adsorption of Zn on alumina and silica

Silica (0.5 g) or alumina (0.2 g) gel was added into 200 cm^3 of the Zn and silicic acid solution at pH 9 ([Zn]: 5–15 mg dm^{-3}, [Si]: 50 mg dm^{-3}), and the mixture was stirred magnetically. At appropriate intervals, a small volume of the suspended solution was collected and filtered with 0.45-μm membrane filter. The Zn and Si concentrations in each filtrate were determined by ICP-AES.

2.4. Reaction between ferron and Zn species in silicic acid solution

The degree of polymerization of the dissolved Zn species was examined in the Zn and silicic acid solution at pH 9 by comparing the reaction rate of ferron (8-hydroxy-7-iodoquinoline-5-sulfonic acid) and the Zn species with that of ferron and free Zn^{2+} in water. This method is frequently used to examine the degree of polymerization of aluminum hydrolytic species in aqueous solution [9].

3. Results and discussion

3.1. Distribution of zinc in silica scales and its concentration factor

Fig. 1 shows a backscattered electron image of a silica scale from cooling water, which was investigated by Nishida et al. [6], and the qualitative analytical results for zinc (Zn) that were deter-

mined using EPMA are shown for three points on the backscattered electron image.

A qualitative analysis for Zn in the silica scale indicates that Zn was sorbed into the silica scale to a significant extent during the formation. The same cooling water and silica scales were analyzed by chemical analysis [6]. Based on the bulk analytical results of the cooling water and silica scales, the concentration factor (CF) of Zn into the silica scales from the cooling water (CF = $[Zn/Si]_{silica\ scale}/[Zn/Si]_{cooling\ water}$) is in the range of 12–16 (Supplementary material). These results indicate that Zn is concentrated into the silica scales and distributed throughout the scale. Therefore, elucidating whether Zn affects the formation of silica scales is important.

3.2. Effect of silicic acid concentration on the solubility of Zn(OH)₂

The solubility product of $Zn(OH)_2$ is 2×10^{-15} (mol $dm^{-3})^3$, which yields an equilibrium Zn^{2+} concentration of approximately 1.3 mg dm^{-3} in water at pH 9. As shown in Fig. 2a, Zn^{2+} precipitated as $Zn(OH)_2$ in the absence of silicic acid and the concentration was nearly consistent with the above theoretical estimation. The effect of the silicic acid concentration on the solubility of $Zn(OH)_2$ was then measured under a constant concentration of Zn^{2+} (2 mg dm^{-3}). When the Si concentration was 2 mg dm^{-3}, the precipitation of $Zn(OH)_2$ decreased to 80%. Above a silicic acid concentration of 5 mg dm^{-3} (as Si), $Zn(OH)_2$ precipitation did not occur. In a related experiment, the solubility of $Zn(OH)_2$ was measured at various Zn concentrations under a constant concentration of silicic acid (50 mg dm^{-3} as Si), and, as shown in Fig. 2b, $Zn(OH)_2$ precipitation did not occur below 15 mg dm^{-3} of Zn. These results suggest that silicato complexes of Zn (SCZ) with Zn–O–Si bonds were formed. Based on the concentrations of Si (50 mg dm^{-3}) and Zn (2 mg dm^{-3}) in the cooling water (Supplementary material), the majority of the Zn is considered to be present as SCZ.
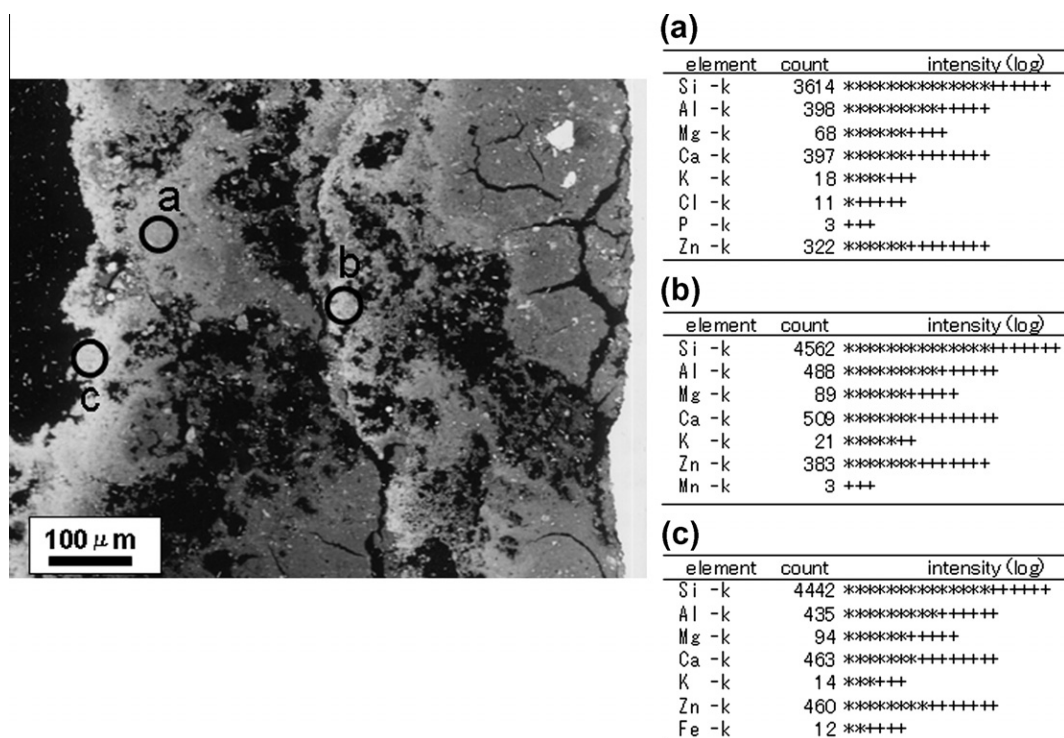

Fig. 1. A backscattered electron image of a silica scale and the qualitative analytical results of zinc by EPMA at three points (a–c) on the backscattered electron image, (*background intensity, + real intensity).
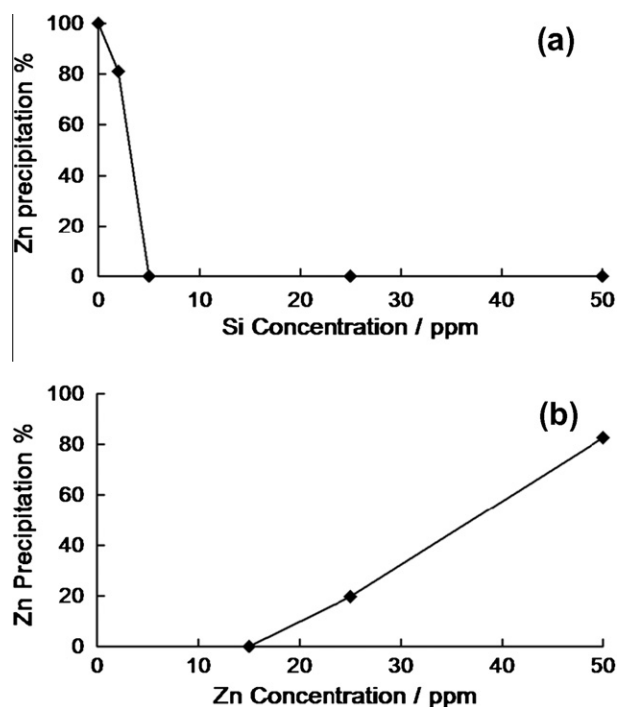
Fig. 2. The variation of percentage of zinc precipitated with silicic acid concentration ([Zn] = 2 mg dm^{-3}) (a) and with zinc concentration ([Si] = 50 mg dm^{-3}) (b) at pH 9.

To examine the degree of polymerization of the dissolved Zn species, the reaction rate between ferron and SCZ was compared with that between ferron and free Zn^{2+}. Ferron, a chelating ligand for Al^{3+}, is generally used to estimate the degree of polymerization for hydrolytic species of Al^{3+} [9]. In this method, the reaction rate between ferron and mononuclear hydrolytic species of Al^{3+} and free Al^{3+} is very rapid, whereas the reaction rate between ferron and multinuclear hydrolytic species, such as the dimer, tetramer, and tridecamer, is slower than that of free Al^{3+}. Based on this difference in the reaction rate with ferron, the degree of polymerization for hydrolytic species of Al^{3+} can be estimated. In this study, the reaction rate between SCZ and ferron was very rapid, which is consistent with the rate observed for ferron with free Zn^{2+} (pH 5), suggesting that hydrolytic Zn^{2+} species may be present in the mononuclear state in the SCZ. According to the thermodynamic considerations, Zn^{2+} is present as tetrahedral species at pH 9. Consequently, the SCZ structure may be [Zn(–OSi(OH)$_3$)$_n$]$^{2-n}$ (n = 1–4), which is an analogue of complexes that were detected only in strong alkaline solutions by Anseau et al. [10].

3.3. Effect of SCZ on dissolution of silica

Because Zn is strongly concentrated into silica scales formed from the cooling waters, the effect of SCZ on the formation of silica scales was investigated. An adsorption experiment is a suitable method for examining this effect due to its simplicity. The main constituent of silica scales formed from the cooling water is silica. Therefore, the adsorption of SCZ on silica was measured. As shown in Fig. 3a, the amount of Zn adsorbed increased as the Zn/Si atomic ratio in the initial solution increased. Fig. 3b shows the variation in silicic acid concentration over time during the adsorption of SCZ, which is depicted in Fig. 3a. The silicic acid concentration was almost constant in the presence of SCZ, whereas it increased gradually with time in the absence of SCZ. Based on the results in Fig. 3b, the solubility of silica at pH 9 (25 °C) in this study is considered to be 70 mg dm^{-3} (as Si), and this value is quite close to the value
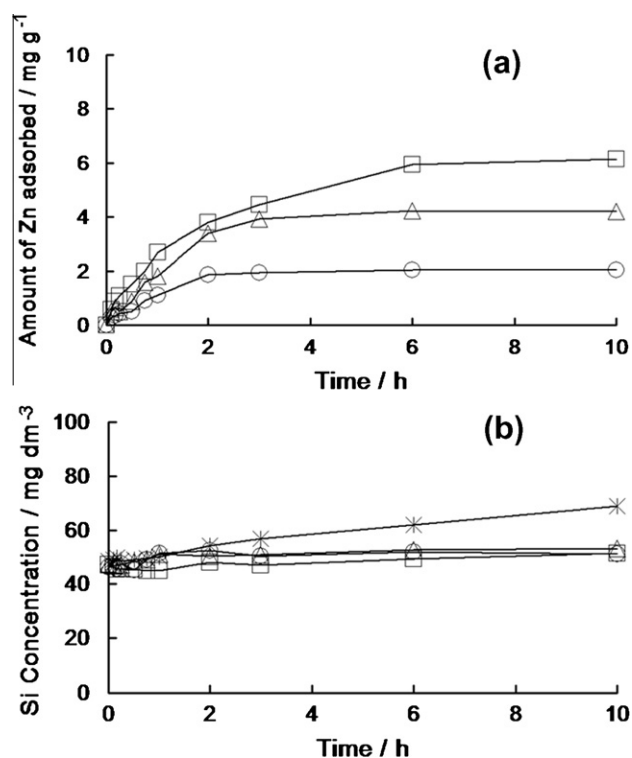

Fig. 3. The variation of the amount of zinc adsorbed on silica with time (a) and the variation of the silicic acid concentration with time (b). Atomic ratio of Zn/Si in the initial solutions before addition of silica: (∗) 0, ([Zn] = 0 and [Si] = 50); (○) 0.04, ([Zn] = 5 and [Si] = 50); (△) 0.09, ([Zn] = 10 and [Si] = 50); (□) 0.13, ([Zn] = 15 and [Si] = 50). [ ] indicates the initial concentration of mg dm^{-3} as a unit.
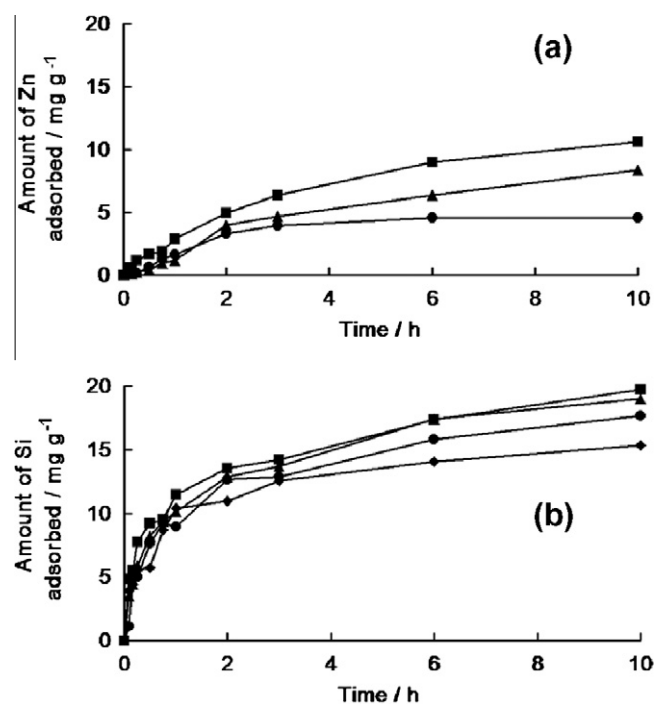

Fig. 4. The variation of the amount of zinc adsorbed on alumina with time (a) and the variation of the amount of silicic acid adsorbed with time. Atomic ratio of Zn/Si in the initial solutions before addition of alumina: (♦) 0, ([Zn] = 0 and [Si] = 50); (●) 0.04, ([Zn] = 5 and [Si] = 50); (▲) 0.09, ([Zn] = 10 and [Si] = 50); (■) 0.13, ([Zn] = 15 and [Si] = 50). [ ] indicates the initial concentration of mg dm^{-3} as a unit.

reported in the literature [11]. These data support the conclusion that insoluble zinc silicates may form on the surface of silica as described in the literature [11–13], and they may prevent the dissolution of silica. Willey and Neumann and Nieden described that zinc silicates may deposit in seawater [12] and a specific plant [13].

3.4. Effect of SCZ on adsorption of silicic acid on alumina

Aluminum is also a major constituent of silica scales, therefore, alumina was selected as an adsorbent. Alumina powder was added into SCZ solutions with various Zn/Si atomic ratios. Fig. 4a shows the variation in amount of Zn adsorbed on alumina over time. As the Zn/Si atomic ratio increased, the amount of adsorbed Zn also increased. The adsorption of silicic acid was measured simultaneously, and Fig. 4b shows the variation in amount of silicic acid adsorbed on alumina over time. The amount of silicic acid adsorbed in the presence of SCZ was higher than that adsorbed in the absence of SCZ.

This result suggests that a surface complex is formed between Zn^{2+} and aluminol groups on the surface of alumina, as described previously by Roberts [14] and Miyazaki et al. [15]. Based on the mechanism for the formation of silica scales from the cooling water proposed previously [6], aluminum hydroxide particles smaller than 0.2 μm act as active sites for the adsorption of silicic acid. As a result, it can be reasonably concluded that SCZ accelerates the adsorption of silicic acid, that is, formation of silica scales from cooling water.

4. Conclusion

Zinc compounds are added into cooling water as an anticorrosive. When this water is used repeatedly, the pH increases to approximately 9. In the presence of silicic acid at pH ~ 9, the Zn in solution is present as silicato complexes of zinc (SCZ) above a certain Zn/Si atomic ratio. The SCZ are concentrated into silica scales formed from cooling water. Because the SCZ accelerate the adsorption of silicic acid on alumina and prevent the dissolution of silica at the same time, we can conclude that SCZ accelerate the formation of silica scales from cooling water.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcis.2010.09.054.

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