

# Solubility of Layered Sodium Silicate in Aqueous Solutions

Yusuke IZUMI

## Abstract

In order to estimate environmental adaptability of layered sodium silicate as a detergent builder, its solubility in water was investigated in detail in the presence of polyvalent metal cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Zn}^{2+}$  normally existing in drainage.

The layered sodium silicate was easily dissolved in water, and could be completely soluble with excess water. The polyvalent metal cations, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Zn}^{2+}$ , generally retarded dissolution of the silicate owing to the formation of insoluble silicates. Particularly,  $\text{Al}^{3+}$  drastically reduced solubility of the silicate when  $\text{Al}^{3+}$  concentration exceeded 50ppm. Since the concentration of  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Zn}^{2+}$  ions contained in usual city drainage is much less than 50ppm, it is expected that the layered sodium silicate after discarded into drainage could eventually dissolved to soluble silicate fragments. The layered sodium silicate is, therefore, an efficient and environmentally benign detergent builder.

*Keywords:* detergent builder, layered sodium silicate, solubility

## 1. Introduction

Currently used zeolite 4A<sup>1)</sup> as a detergent builder effectively softens hard water by its ion exchange capability. The zeolite, however, has posed a serious problem that it is piled up in the city drains to form a layer of mud. A new type of washing machines equipped with cation exchange resin as a *built-in* builder has recently been commercialized. The resin builder has a drawback that it must frequently be regenerated with aqueous sodium chloride. A certain type of layered sodium silicate of  $\delta\text{-Na}_2\text{Si}_2\text{O}_5$  has been offered as a new type of builder in detergent formulations.<sup>2)-5)</sup>

The author has recently reported<sup>6)</sup> that the layered silicate shows much better performance in softening of hard water than zeolite 4A and ion exchange resin when it is applied for washing in alkaline solutions. The layered silicate is expected as an environmentally benign detergent builder with high water softening efficiency because it appears to be decomposed eventually into soluble water-glass fragments in drainage even exchanged with calcium and magnesium ions.

In order to estimate the environmental adaptability of layered sodium silicate as a detergent builder, its dissolution behavior in water was investigated in detail in the presence of polyvalent metal cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Zn}^{2+}$  normally existing in drainage.

## 2. Experimental

### 2.1. Material

Layered sodium silicate ( $\delta\text{-Na}_2\text{Si}_2\text{O}_5$ , powder) was kindly supplied from Clariant Tokuyama Limited. The layered silicate is similar to a widely used water glass in terms of chemical composition, but the layered silicate is anhydrous and crystalline. The structure of the layered silicate shown in Fig. 1 is virtually identical to that of a natural substance of natrosilite. Owing to its polymeric character, the layered silicate dissolves in water only slowly. The calcium and magnesium ions are bound to the layered silicate through ion exchange. This exchange process takes place much more rapidly than the dissolution process of the layered silicate.

### 2.2. Measurement of solubility

One liter of an aqueous solution containing metal cations was added to a beaker (2000ml). A thimble supported by a wire cage was dipped in the solution (Fig. 2). The layered silicate (1.0 g) was

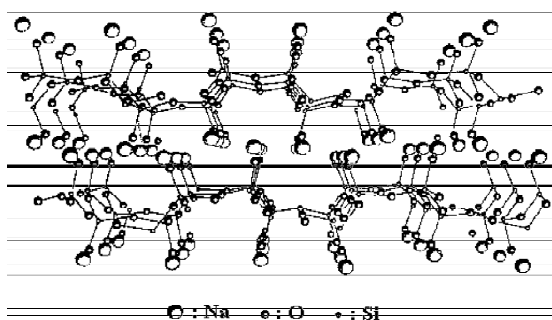


Fig. 1 Structure of layered sodium silicate  $\delta\text{-Na}_2\text{Si}_2\text{O}_5$

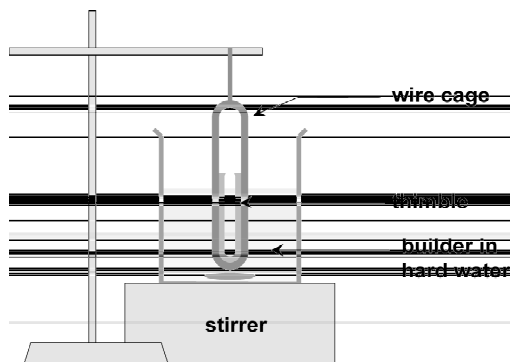


Fig. 2 Experimental apparatus

added to the solution, and the resultant suspension was well agitated at 296K. The solution collected through the thimble was periodically taken out, and the soluble silicate in the solution was determined by means of absorptiometry: the silicate solution was added by ammonium molybdate to form yellow molybdosilicate ions having a maximum absorption at 380 nm.

### 3. Results and Discussion

#### 3.1. Solubility of layered silicate in single metal cation systems

The changes in solubility of layered sodium silicate with the time elapsed are illustrated in Figs. 3 to 9 for the aqueous solutions of various kinds of metal cations with different concentrations (50ppm, 150ppm, and 300ppm as hardness).

Figure 3 denotes the solubility change in distilled water. The layered sodium silicate was easily dissolved in water, and the solution was saturated with the soluble silicate (600ppm) 2 hours after: about 60% of the silicate dissolved. The layered sodium silicate per se, therefore, could be completely soluble with excess water. Potassium ions gave no retardation effect on dissolution of the silicate (Fig. 4).

The solubility of the layered sodium silicate was decreased with increasing concentration of  $\text{Ca}^{2+}$  (Fig. 5), but 24 hours after around 55% of the silicate dissolved (550ppm). The calcium ions exchanged with sodium ions presumably could form insoluble networks in the layered silicate structure. The silicate dissolved in the  $\text{Ca}^{2+}$  system much more slowly than in distilled water. The rates of dissolution were decreased with increasing  $\text{Ca}^{2+}$  concentration. A similar tendency in solubility of the silicate was observed for  $\text{Mg}^{2+}$  system, except for slower initial rates of dissolution and somewhat higher saturation solubility than in the calcium system (Fig. 6).

Concerning iron, aluminum, and zinc ions, remarkable effects on dissolution of the silicate were observed (Figs. 7, 8, 9). Particularly,  $\text{Al}^{3+}$  drastically retarded the dissolution even at a low  $\text{Al}^{3+}$  concentration of 50ppm. This suggests rapid formation of insoluble aluminosilicate species in the

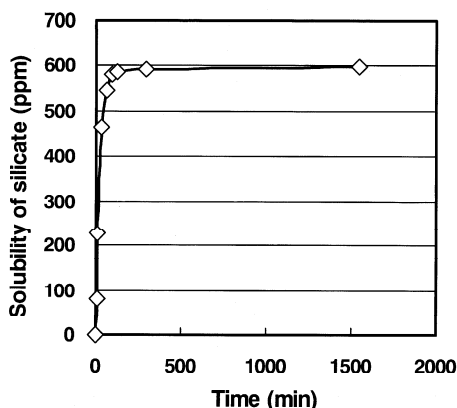


Fig. 3 Solubility of silicate in distilled water at 25 °C

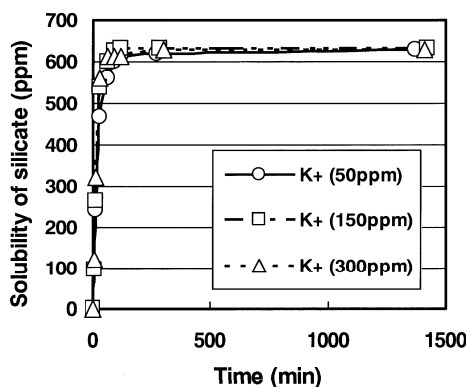


Fig. 4 Solubility of silicate in aqueous  $\text{K}^{+}$  at 25 °C

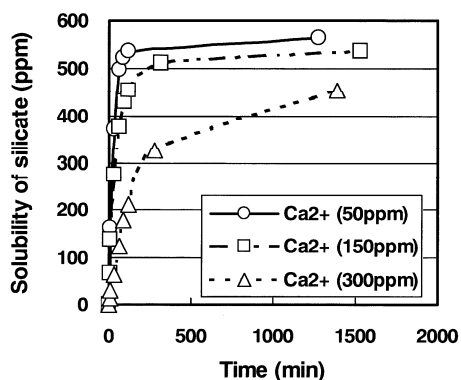


Fig. 5 Solubility of silicate in aqueous  $\text{Ca}^{2+}$  at 25 °C

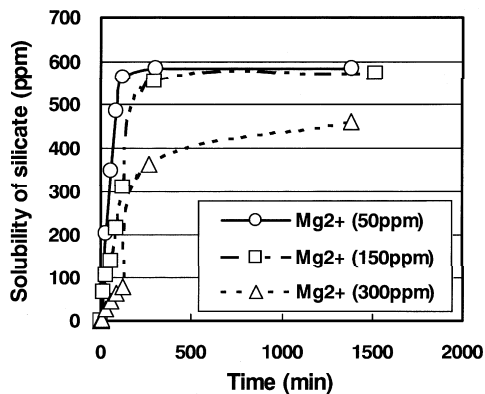


Fig. 6 Solubility of silicate in aqueous  $\text{Mg}^{2+}$  at 25 °C

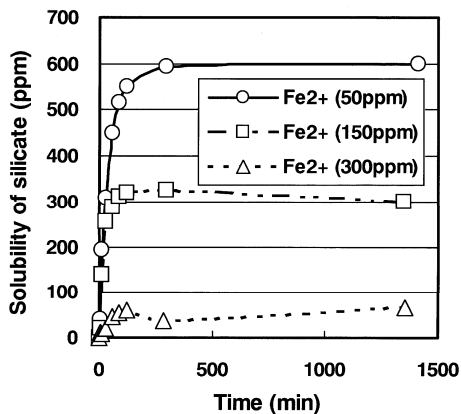


Fig. 7 Solubility of silicate in aqueous  $\text{Fe}^{2+}$  at 25 °C

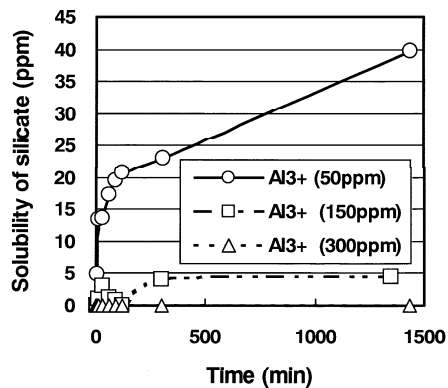


Fig. 8 Solubility of silicate in aqueous  $\text{Al}^{3+}$  at 25 °C

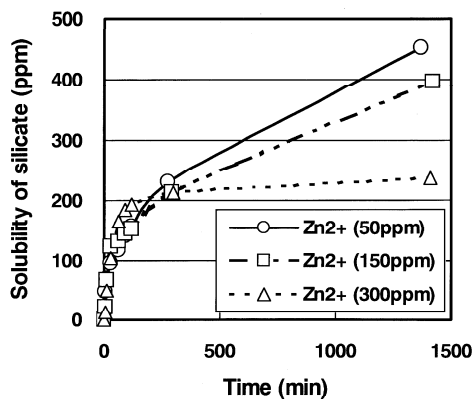


Fig. 9 Solubility of silicate in aqueous  $\text{Zn}^{2+}$  at 25 °C

presence of  $\text{Al}^{3+}$ . Iron and zinc ions at a concentration of more than 150ppm and 300ppm, respectively, were both unfavorable to dissolution of the silicate.

### 3.2. Solubility of layered silicate in binary metal cation systems

The changes in solubility of layered sodium silicate were examined in three binary metal cation systems for  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Al}^{3+}$  typically existing in drainage.

The solubility of the silicate in the  $\text{Ca}^{2+}$  (300ppm)- $\text{K}^+$  (50–150ppm) system was almost identical with that observed in the  $\text{Ca}^{2+}$  single system. Potassium ions, therefore, have no effect on the dissolution of the silicate (Fig. 10). The silicate dissolved more slowly in the  $\text{Ca}^{2+}$  (300ppm)- $\text{Mg}^{2+}$  (50–150ppm) system than in the single cation systems of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  (Fig. 11). The initial rate of dissolution was also reduced. This appears to be due to faster formation of insoluble network structure of the layered silicate in the presence of  $\text{Mg}^{2+}$ . Except for a binary system of  $\text{Ca}^{2+}$

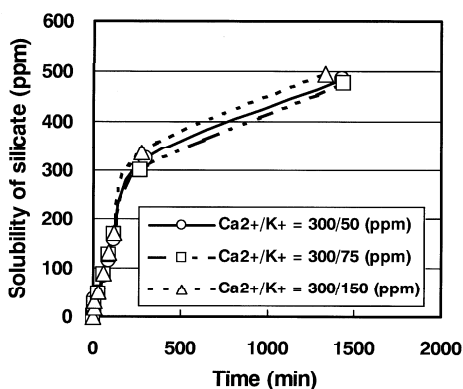


Fig. 10 Solubility of silicate in aqueous  $\text{Ca}^{2+}$ - $\text{K}^+$  at 25 °C

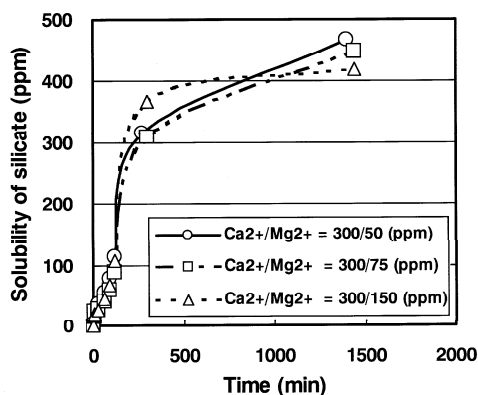


Fig. 11 Solubility of silicate in aqueous  $\text{Ca}^{2+}$ - $\text{Mg}^{2+}$  at 25 °C

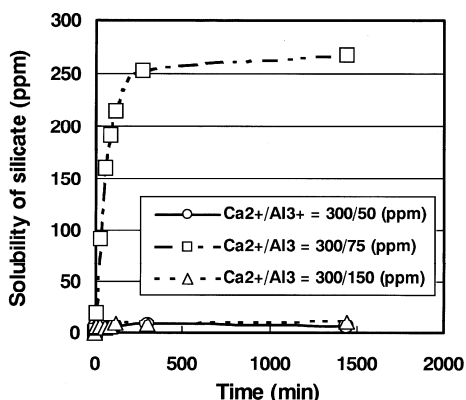


Fig. 12 Solubility of silicate in aqueous  $\text{Ca}^{2+}$ - $\text{Al}^{3+}$  at 25 °C

(300ppm)- $\text{Al}^{3+}$  (75ppm), the existence of aluminum ions completely retarded the dissolution of the silicate, resulting in the formation of insoluble aluminosilicate (Fig. 12). Similar peculiar behavior for dissolution of the silicate was confirmed with a binary system of  $\text{Mg}^{2+}$  (300ppm)- $\text{Al}^{3+}$  (75ppm) separately tested: the formation of the corresponding aluminosilicate may be extremely slow.

### 3.3. Solubility of layered silicate in hard water

Figure 13 depicts the change in solubility of layered sodium silicate detergent builder in a commercially available mineral water “Evian®” which contains  $\text{Ca}^{2+}$  (200ppm) and  $\text{Mg}^{2+}$  (100ppm). The dissolution behavior was quite similar to that obtained with the binary system of  $\text{Ca}^{2+}$  (300ppm)- $\text{Mg}^{2+}$  (150ppm) above mentioned.

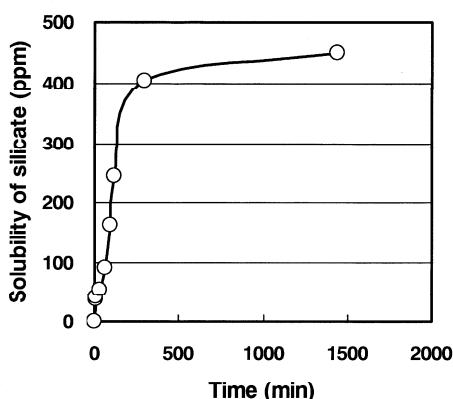


Fig. 13 Solubility of silicate in mineral water at 25 °C

## 4. Conclusion

The layered sodium silicate builder was easily dissolved in water, and could be completely soluble with excess water. The polyvalent metal cations possibly existing in drainage, such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Zn}^{2+}$ , generally retarded dissolution of the silicate owing to the formation of insoluble silicates. Particularly,  $\text{Al}^{3+}$  drastically reduced the dissolution of the silicate when  $\text{Al}^{3+}$  concentration exceeded 50ppm.

It is expected that the layered sodium silicate builder could eventually dissolved into soluble silicate fragments when discarded in drainage, since the concentration of  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ , and  $\text{Zn}^{2+}$  ions contained in usual city drainage is much less than 50ppm. The layered sodium silicate, therefore, is efficient and environmentally benign detergent builder.

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### References

- 1) Bruce, D. W. and O'Hare, D. eds., *Inorganic Materials*, 296p. (John Wiley & Sons, 1992).
- 2) Pant, A. K. and Cruickshank, D. W., The Crystal Structure of  $\alpha$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, *Acta Cryst.*, Vol. 24, 13–19 (1968).
- 3) Pant, A. K., The Crystal Structure of  $\beta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, *Acta Cryst.*, Vol. 24, 1077–1083 (1968).
- 4) Coker, Eric N. and Rees, Lovat V. C., *J. Mater. Chem.*, Vol. 3, 523–529 (1993).
- 5) Katada, M., Status on development of inorganic builder and their applications, *Fragrance Journal*, No. 11, pp. 43–48 (1995).
- 6) Izumi, Y., Water Softening Property of Layered Sodium Silicate, *Journal of Sugiyama Jogakuen University (Natural Sciences)*, No. 32, pp. 67–71 (2001).

(生活科学部 生活環境学科)