

Water Softening Property of Layered Sodium Silicate

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Abstract

Layered sodium silicate (δ - $\text{Na}_2\text{Si}_2\text{O}_5$) was compared in detail with the currently used zeolite 4A and ion exchange resin in terms of the water softening power. The silicate showed better performance in hard water softening than zeolite 4A and ion exchange resin provided it is applied in alkaline aqueous medium. Since the silicate even exchanged with calcium and magnesium ions is gradually depolymerized into soluble water-glass fragments, it is expected as an environmentally benign detergent builder with high water softening efficiency.

Keywords: Detergent, Builder, Water softening, Layered sodium silicate, Zeolite 4A, Ion exchange resin.

1. Introduction

Builders are an essential component of detergents and as such have to meet a wide range of requirements to be obtained in terms of wash performance, cost efficiency and in particular environmental friendliness.¹⁾ They must soften the water to enhance the effectiveness of surfactants and hence protect the machine and the laundry from lime deposits. Builder substances should also provide the necessary alkalinity for the washing process and should ensure a stable pH.

For years, sodium tripolyphosphate was used as a builder and had very good properties. However, concerns about the possible eutrophication of rivers and lakes by phosphates have led to a decline in the use of this builder. An insoluble aluminosilicate, zeolite 4A,²⁾ is now used as a phosphate substitute. Zeolite 4A effectively softens the water by ion exchange, but it has now posed a serious problem that it deposits as a mass of mud in the city drains. A new type of washing machines equipped with cation exchange resin as a built-in builder has recently been developed. The resin builder, however, must be frequently regenerated with aqueous sodium chloride. Very recently, a certain type of layered sodium silicate³⁾⁻⁵⁾ (soluble) has been developed as a new generation of builder in detergent formulations.

In the present paper, layered sodium silicate was compared in detail with the currently used zeolite 4A and ion exchange resin in terms of the water softening power.

2. Experimental

2.1. Builder materials

Commercially available synthetic zeolite 4A (powder) and cation exchange resin (Dowex 50W-X8, Na-form) were employed. The resin was dried at 60 °C for 8 h prior to use. Layered sodium silicate (δ - $\text{Na}_2\text{Si}_2\text{O}_5$, powder) was kindly supplied from Clariant Tokuyama Limited. The layered sodium silicate is similar to the widely used substance water glass but is anhydrous and crystalline. The structure of this compound shown in Fig. 1 is virtually identical to that of the natural substance natrosilite. Owing to its polymeric character, this compound dissolves in water only slowly. The calcium and magnesium ions are bound to the crystalline layered silicate in an ion exchange process. This exchange process takes place more rapidly than the dissolution of the layered silicate.

2.2. Estimation of water softening power

An aqueous solution of CaCl_2 or MgCl_2 (500 ml) was added to a beaker (1000 ml). A thimble supported by a wire cage was dipped in the solution (Fig. 2). A builder sample (1.0 g) was added to the hard water and the resultant suspension was well agitated. The Ca^{2+} or Mg^{2+} in the filtrate collected in the thimble was determined by means of EDTA chelete titration.

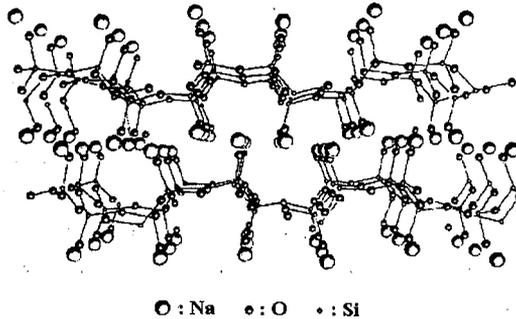


Fig. 1 Structure of layered sodium silicate δ - $\text{Na}_2\text{Si}_2\text{O}_5$

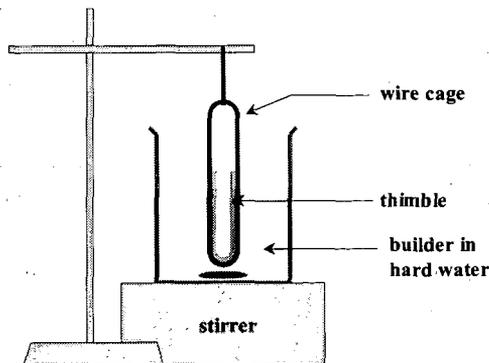


Fig. 2 Experimental apparatus

3. Results and Discussion

3.1. $\text{Ca}^{2+}/\text{Mg}^{2+}$ binding capability

The water softening power of layered sodium silicate was evaluated in aqueous solutions of calcium chloride (hardness 1000 ppm) and magnesium chloride (hardness 600 ppm) at 25 °C, in comparison with zeolite 4A and ion exchange resin. $\text{Ca}^{2+}/\text{Mg}^{2+}$ binding capability of the three builders is shown in Figs. 3 and 4, respectively. The initial pH of the layered sodium silicate suspension was in the range between 10 and 11 since the silicate is an alkaline compound.

The layered sodium silicate showed better $\text{Ca}^{2+}/\text{Mg}^{2+}$ binding than zeolite 4A and ion exchange resin in terms of both the binding rate and the binding capacity per unit weight of builder. As for the Mg^{2+} binding, zeolite 4A was little effective, because the openings of zeolite 4A are too narrow to accept large hydrated Mg^{2+} ions inside the pores of the zeolite while smaller hydrated Ca^{2+} ions pass freely through the openings.

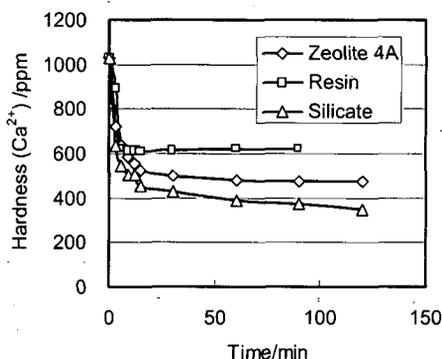


Fig. 3 Ca^{2+} binding capability at 25 °C

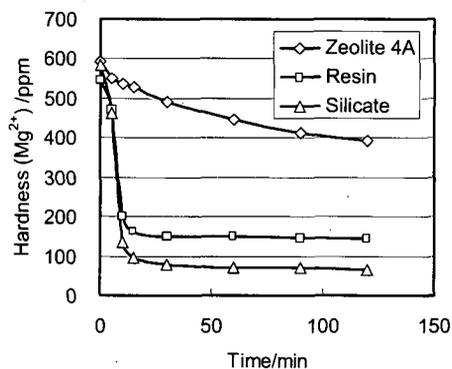


Fig. 4 Mg^{2+} binding capability at 25 °C

3.2. Effect of sodium sulfate on $\text{Ca}^{2+}/\text{Mg}^{2+}$ binding

In order to enhance wash performance, a large amount of sodium sulfate is usually contained in detergents. An excess of Na^+ ions may disturb the $\text{Ca}^{2+}/\text{Mg}^{2+}$ binding of builder. Addition of sodium sulfate to the suspension (0.5–2.0 g/500 ml) generally decreased the $\text{Ca}^{2+}/\text{Mg}^{2+}$ binding capacity of builder. The binding power of the layered sodium silicate was least affected on addition of sodium sulfate (85 to 94% of the binding capacity in the absence of sodium sulfate was maintained).

3.3. Effect of suspension pH on $\text{Ca}^{2+}/\text{Mg}^{2+}$ binding

The pH of hard water containing the layered sodium silicate or zeolite 4A remarkably influenced $\text{Ca}^{2+}/\text{Mg}^{2+}$ binding power (Figs. 5 and 6). The pH of suspension was adjusted by adding NaOH or H_2SO_4 . The $\text{Ca}^{2+}/\text{Mg}^{2+}$ binding capacity of the layered sodium silicate decreased with decreasing pH, and showed almost no binding at a pH below 7.1. The reason is that the silicate is readily broken down (depolymerized) at a low pH into smaller fragments (the known water glass) which have no binding with Ca^{2+} and Mg^{2+} ions. On the other hand, the silicate is stable in alkaline aqueous

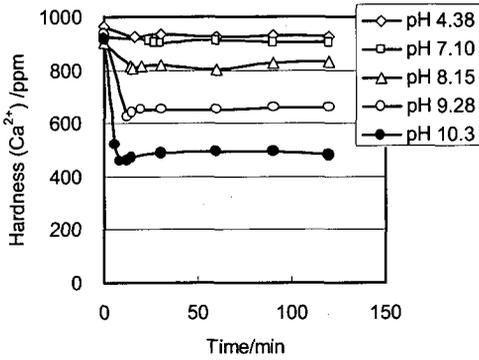


Fig. 5 Effect of pH on Ca²⁺ binding capability of layered silicate at 25 °C

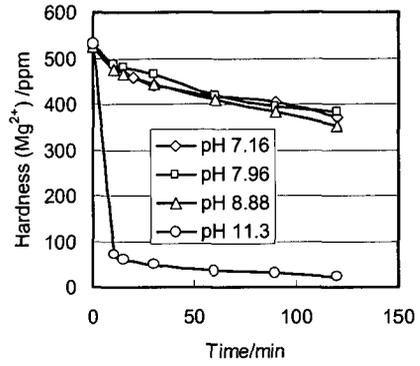


Fig. 6 Effect of pH on Ca²⁺ binding capability of Zeolite 4A at 25 °C

solutions, and the silicate network is more stabilized when the sodium ions of the silicate are replaced by Ca²⁺ and Mg²⁺ ions which cause the water hardness.

A sudden decrease in hardness (Mg²⁺) observed with zeolite 4A at a pH 11.3 shown in Fig. 6 was caused by the precipitation of Mg(OH)₂; the filtrate collected in the thimble apparently became very soft.

3.4. Effect of suspension temperature on Ca²⁺/Mg²⁺ binding

The Ca²⁺ binding capacity of zeolite 4A appeared somewhat to increase when the temperature of the suspension was raised to 40 °C (Fig. 7). Interestingly, its Mg²⁺ binding capacity notably increased above 40 °C (Fig. 8). This increase may be due to enlargement of the openings of zeolite 4A at higher temperatures to be able to accept large magnesium hydrated ions.

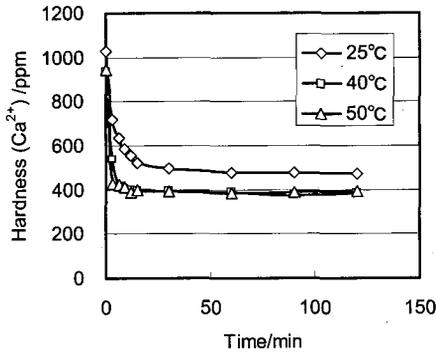


Fig. 7 Effect of suspension temperature on Ca²⁺ binding capability of Zeolite 4A

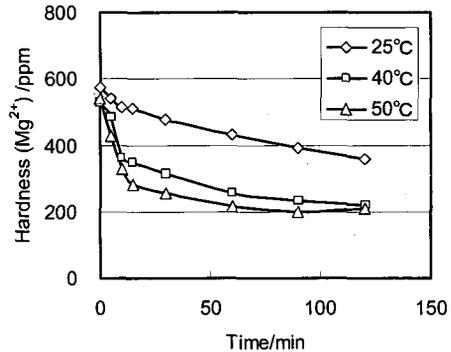


Fig. 8 Effect of suspension temperature on Mg²⁺ binding capability of Zeolite 4A

3.5. Binding capability in Ca²⁺/Mg²⁺ binary systems

Figures 9 and 10 denote the Ca²⁺/Mg²⁺ binding of zeolite 4A, ion exchange resin and layered sodium silicate builders for Ca²⁺ (350 ppm)-Mg²⁺ (50 ppm) and Mg²⁺ (350 ppm)-Ca²⁺ (50 ppm)

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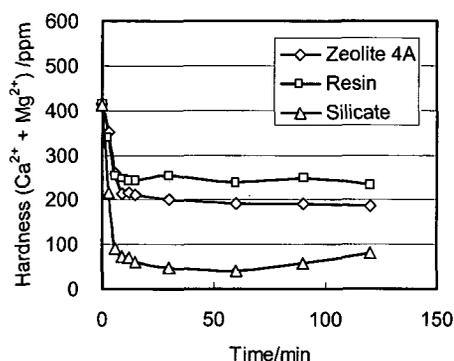


Fig. 9 Binding capability for Ca^{2+} (350 ppm) - Mg^{2+} (50 ppm) binary metal ion system at 25 °C

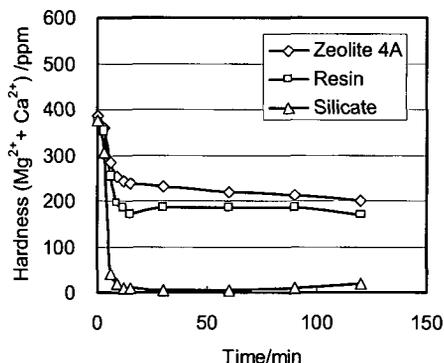


Fig. 10 Binding capability for Mg^{2+} (350 ppm) - Ca^{2+} (50 ppm) binary metal ion system at 25 °C

binary systems.

The layered sodium silicate also showed highest binding power in these binary systems, which means the silicate is better than zeolite 4A and ion exchange resin as a practical detergent builder.

4. Conclusion

Recently developed layered sodium silicate showed better performance in hard water softening than the currently used builders of zeolite 4A and ion exchange resin provided it is applied in alkaline washing liquors. Since the silicate even exchanged with calcium and magnesium ions is gradually depolymerized into soluble fragments, it is expected as an environmentally friendly detergent builder with high water softening efficiency.

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