THE INEFFECTIVENESS OF SODIUM BASED SURFACE TREATMENT ON THE MITIGATION OF ALKALI SILICA REACTION

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ABSTRACT
Crack injection and surface treatment method were being used in Japan for repairing damaged concrete due to Alkali Silica Reaction (ASR) since 1988. In the case of surface treatment method, the sodium based surface treatment is commonly used for repairing damaged concrete due to ASR. The first part of this paper discusses the investigation results from repaired concrete bridge structures in Japan using sodium based surface treatment. The second part presents the experiments results regarding some surface treatment materials for repairing damaged concrete structure due to ASR. The experiment results of accelerated mortar bar tests according to modified ASTM C1260 test method show the ineffectiveness of sodium based treatments on ASR mitigation. Expansions were observed for mortar bars immersed in sodium solution. In the other hand, the results of mortar bar tests show the ASR mitigation effects of lithium based surface treatment, especially lithium silicate, on mitigating ASR in concrete.

KEYWORDS: Alkali Silica Reaction, Concrete Repair Method, Sodium and Lithium Based Surface Treatment

I. INTRODUCTION

Sodium silicate (Na$_2$SiO$_3$) has been used in the concrete industry mainly as cement admixtures or sealants, to reduce the porosity and permeability of concrete, thus increasing its overall durability. This silicate-based compound in concrete reacts with excess calcium hydroxide (CH), a by-product of cement hydration. By reducing the amount of available calcium hydroxide, it further improves the acid and sulphate resistance of concrete. Calcium hydroxide tends to crystallize as hexagonal platelets near the cement paste/aggregate interface, resulting in poorly packed and weak areas and has high propensity to chemical attack. Thus, its consumption by sodium silicate is not only beneficial in terms of filling in porosity and cracks with calcium silicate hydrate (CSH) gel, reducing the permeability, increasing the hardness and strength of concrete, but also increasing the concrete resistance to acid and other chemical attacks.

In addition to the initial chemical reaction, the CSH gels will also physically absorb the water, preventing it from being transported through the concrete [1]. The reaction of this silicate-based compound in concrete can be described by following chemical equations [2]:

\[ \text{Na}_2\text{SiO}_3 + y\text{H}_2\text{O} + x\text{Ca(OH)}_2 \rightarrow x\text{CaO-SiO}_2-y\text{H}_2\text{O} + 2\text{NaOH} \]  

The exact mechanism by which the silicates act to improve the performance of concretes is unclear [2]. McGettigan states that the silicates are effective sealers as the result of SiO precipitating in the pores [3]. While Higgins report that the silicates react with excess calcium present in the near surface district of the concrete to form relatively insoluble calcium-silicate hydrates [4]. A third theory is that the silicates form an expansive gel similar to that formed in alkali silica reaction that fills the pores in the concrete by swelling [2]. The second theory is currently the most accepted. In this way, theoretically, the pore blockers are products composed by silicate, which penetrate the superficial pores of the concrete and react with portlandite forming CSH gel [5].
Only few research works conducted regarding Sodium silicate as a surface treatment. Medeiros, et al investigate the effectiveness of 25% sodium silicate [5]. The results indicated that the surface treatment using sodium silicate reduced the chloride diffusion coefficient and the immersion water absorption of the concrete. In addition, when compared with other groups of treatment (hydroporphic pore liner and surface coatings), the treatment with sodium silicate can increase the service life in the same way as silane/siloxane pore liner and to an acrylic coating; however, the protection with polyurethane coating was more efficient than that with sodium silicate.

Despite of these advantages of sodium silicate, the report by NZ Transport Agency stated that in regard to alkali silica reaction, the silicate-based treatments must not be based on sodium or potassium, which these agents may exacerbate ASR [1]. There has been a lack of awareness that the formation of sodium hydroxide (NaOH) from the reaction between sodium silicate and water inside the concrete may raise the alkalinity of the pore solution, which in turn, might lead to alkali silica reaction in case there are reactive aggregates available in the concrete.

Beside sodium based surface treatments, recently lithium silicate (Li$_2$SiO$_3$) was also being used in the concrete industry as cement admixtures or sealants. The works by McCoy and Caldwell reported that lithium silicate is one of the most effective agents to mitigate ASR expansion in mortars besides LiCl, Li$_2$CO$_3$, LiF, LiNO$_3$ and Li$_2$SO$_4$ [6]. Similar to Na$_2$SiO$_3$, The reaction of Li$_2$SiO$_3$ can be described by following chemical equations:

$$\text{Li}_2\text{SiO}_3 + y\text{H}_2\text{O} + x\text{Ca(OH)}_2 \rightarrow x\text{CaO-SiO}_2 \cdot y\text{H}_2\text{O} + 2\text{LiOH}$$ (2)

In accordance with this concern, the main purpose of this paper is to investigate the use of sodium based surface treatment for repairing damaged concrete due to ASR and also to propose more effective material for construction or rehabilitation of deteriorated concrete structures. This paper will be divided into two parts. The first part of this paper will discuss the investigation results from repaired concrete bridge structures in Japan using sodium based surface treatment, which is stated in the section II. As for the second part, the experiments results regarding some surface treatment materials for repairing damaged concrete structure due to ASR will be presented. This part will be highlighted in the section III with detailed information of the experiment stated at the subsection 3.1 until 3.6. Furthermore, the discussion of the future works regarding of this topic could be found in section IV. Finally, this paper will be closed with main concluding remarks in section V.

II. THE APPLICATION OF SODIUM SILICATE BASED SURFACE TREATMENT

In Hokuriku district, Japan, the crack injection and surface coating methods were being used for repairing damaged concrete due to ASR since 1988. However, cracks and blisters on surface coating occurred again within 5 years after repairing [7]. In addition, as shown in Figure 1, a concrete surge tank of water power station subsequently re-damaged by ASR after treated with sodium silicate. A lot of cracks filled with ASR gel can be seen on the surface of the structure.

The sodium silicate material that used for repairing the concrete structure in Japan is mainly an industrial products manufactured from the reaction between sodium carbonate (Na$_2$CO$_3$) and silicon dioxide (SiO$_2$) heated in a reflection furnace (around 300 °C), as can be describe by following chemical equations:

$$\text{Na}_2\text{CO}_3 + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{CO}_2$$ (3)

Regarding this matter, the investigations report of the Japan Highway Public Corporation in Hokuriku Branch, which is now becoming Central Nippon Expressway Company Limited, had revealed interesting facts about the most commonly sodium silicate compound (xypex) used in Japan [8]. Based on the chemical analysis results, this type of sodium silicate has a high content of sodium as can be seen on Table 1. Moreover, based on the X-ray diffraction analysis, sodium carbonate (Na$_2$CO$_3$) was also detected in this type of sodium silicate compound (eg, Na$_2$SiO$_3$, 5~9 H$_2$O).

There is a concern that the remaining sodium carbonate inside the sodium silicate could also produce sodium hydroxide when react with water, as shown by this chemical equation:

$$\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{NaHCO}_3 + \text{NaOH}$$ (4)

Moreover, due to high temperature, the sodium hydrogen carbonate NaHCO$_3$ could gradually decomposes into sodium hydroxide (NaOH) and carbon dioxide (CO$_2$), as can be seen on the following equation:

$$\text{NaHCO}_3 \rightarrow \text{CO}_2 + \text{NaOH}$$ (5)
Based on the Eq. (1), (4) and (5), sodium hydroxide not only produced by the reaction from the sodium silicate itself with water but also can be produced by the reaction of water with the possible remaining sodium carbonate inside the sodium silicate. Thus, the use of this type of penetrating sealer (sodium silicate compound) has a high possibility to significantly raise the alkalinity of the pore solution. Furthermore, the present of Na$_2$CO$_3$ in concrete will reduce the concrete strength and increased the total porosity which will make the ASR process become easier to be occurred. The excess of CO$_3^{2-}$ ions from Na$_2$CO$_3$ retards the Ca(OH)$_2$ development and enables an intensive rise and growth of CaCO$_3$ crystals in hydrated cement that can cause loss in binding capability due to preferential CaCO$_3$ formation at the early stage of cement hydration [9].

In addition, EPMA analysis of sample cores drilled from Shogawa bridge in Toyama prefecture are shown in Figures 2, 3 and 4, respectively. The presence of sodium, silica and calcium inside the crack width of approximately 0.5 mm that occurred from the surface could not be found. These results are confirming that the surface treatment of sodium silicate solution has not been able to fill out the cracks even after 17 years of repair. In accordance with that, Dai et al also reported that the penetration depth of this silicate based treatment is very low [10]. It seems that sodium silicate has no water repellent properties as silicate gels are formed after chemical reaction with the concrete with the involvement of CO$_2$. Dai et al also found that sodium silicate is not water resistance since it was closely related to penetration depth. This adds another concern of using sodium silicate beside the fact that it may exacerbate ASR.

Figure 1. Surge tank of water power station treated with sodium silicate and subsequently re-damaged by ASR

Table 1. Chemical compositions of Na$_2$SiO$_3$ from xypex industries [8]

<table>
<thead>
<tr>
<th>Bulk</th>
<th>Ig. Loss</th>
<th>Insol.</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>SO$_3$</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>TiO$_2$</th>
<th>P$_2$O$_5$</th>
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<td>15.89</td>
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<td>7.43</td>
<td>1.94</td>
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<td>31.51</td>
<td>4.30</td>
<td>1.05</td>
<td>5.02</td>
<td>0.19</td>
<td>0.10</td>
<td>0.04</td>
<td>99.84</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Insol.</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>Total</th>
<th>Ca(OH)$_2$</th>
<th>CO$_2$</th>
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<td>83.98</td>
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<td>1.89</td>
<td>2.30</td>
<td>96.38</td>
<td>3.03</td>
<td>3.60</td>
</tr>
</tbody>
</table>
Figure 2. Mapping imagery of sodium (Na) inside sample core drilled from Shogawa bridge in Toyama prefecture by EPMA analysis

Figure 3. Mapping imagery of silicate (Si) inside sample core drilled from Shogawa bridge in Toyama prefecture by EPMA analysis

Figure 4. Mapping imagery of calcium (Ca) inside sample core drilled from Shogawa bridge in Toyama prefecture by EPMA analysis

III. EXPERIMENTS RESULTS OF MORTAR BARS IMMersed IN SODIUM AND LITHIUM SOLUTIONS

Previous research works were conducted to investigate the ASR mitigation effect of sodium and lithium solutions [11]. Two sodium electrolytes sources and one lithium electrolytes sources were selected, which are sodium nitrite (NaNO3), sodium silicate (Na2SiO3) and lithium silicate (Li2SiO3). The experiments were conducted using accelerated mortar bar test method according to modified ASTM C1260 method.

3.1. Materials, Mix Proportions, and Method

Crushed calcined flint produced from industrial raw materials in England was used as reactive aggregate, with the grain size ranging from 0.6mm to 2.5mm, and cristobalite as the only reactive component. Regarding the chemical method, in accordance to JIS A1145-2007, the dissolved silica content (Sc) and the reduction in alkaline concentration (Rc) were 1063 mmol/L and 70 mmol/L, respectively. Crushed limestone sand with 0.15mm to 5.0mm particle size was used as non-reactive aggregate and considering the pessimum mixing ratio to this calcined flint, the mass ratio of calcined flint and crushed limestone sand was set at 25%:75% [12]. Ordinary Portland cement (T Corporation, Ltd., density: 3.16 g/cm³, Blaine specific surface area: 3300 cm²/g) was used. The alkali content of the cement was 0.42%. The mortar bar specimens were prepared with dimension 25 x 25 x 280 mm. In order to assess the effects of sodium and lithium solutions on suppression of ASR expansion, the accelerated mortar bar test, in accordance to modified ASTM C1260 method, were conducted for specimens immersed in a low (0.5 mol/L) and high (2.5 mol/L) concentrated Na2SiO3 and Li2SiO3 solutions and also for specimens immersed in a low (1 mol/L) concentrated NaNO3.
3.2. Expansion Ratio of Mortar Bars Immersed In Sodium and Lithium Solutions

As shown in Figure 5, regardless of concentrations, the specimens immersed in Li$_2$SiO$_3$ solution did not expand at all, which suggests no ASR occurrence. One of the interesting properties of lithium ions (Li$^+$) is that they tend to be incorporated into the cement hydrates to much greater extent than sodium (Na$^+$) and potassium (K$^+$) [13]. Moreover, lithium silicate compound (Li$_2$SiO$_3$) crystal and a Li-bearing (low Ca silica gel) could serve as a diffusion barrier and protective layer to prevent the reactive silica from further attack by alkalis [14].

In addition, a very interesting phenomenon occurred in sodium solution. Specimens immersed in 0.5 mol/L Na$_2$SiO$_3$ solution exceeded 0.2% at 14 days and surpassed 0.4% after 28 days period. As for specimens immersed in 1 mol/L NaNO$_3$, although there was no expansion until 14 days, the specimen expands and surpassed 0.3% after 28 days period. On the contrary, for specimens immersed in 2.5 mol/L Na$_2$SiO$_3$ solution, only an early small expansion was observed and over curing time this expansion vanished. Furthermore, unlike the 0.5 mol/L Na$_2$SiO$_3$ solution, which at 80°C is in the liquid state, 2.5 mol/L Na$_2$SiO$_3$ solution revealed a very high viscosity and remained in paste-like state up to 14 days.

It is likely that, at the early stages, the ability of this high-concentrated water-glass solution to penetrate the specimens is compromised, while at the presence of highly reactive flint aggregates, the hydrolysis reaction of sodium solution and water to produce NaOH is raising the alkalinity in pore solution, which also increases the OH$^-$ in the solution, thus triggers the occurrence of ASR. However, continuing supplied by high concentration of Na$_2$SiO$_3$ from the outside make the reaction between Na$_2$SiO$_3$ and Ca(OH)$_2$ take place and surpasses the pace of alkali-silica reaction. The overwhelming amount of CSH gel produced engulfs and surrounds the ASR-gel previous produced, and the ASR-induced expansion is suppressed. This phenomenon is different to that observed in the presence of sodium solutions, because the highly reactive lithium prevents ASR occurrence in the first place.

3.3. Differential Scanning Calorimetry Analysis (DSC) of Mortar Bars Immersed in Sodium and Lithium Silicate Solution

Figures 6 and 7 show the DSC curves of mortar bars immersed in 0.5 mol/L and 2.5 mol/L Na$_2$SiO$_3$ and Li$_2$SiO$_3$ solutions respectively. Around 450°C, a CH peak was observed. At about 800°C decarbonation of calcite, which is present in the limestone aggregates, was observed. However, ettringite peaks (Ett) were not detected due to thermal curing in the solutions at 80°C for 28 days. In the case of Li$_2$SiO$_3$ solution, the residual amount of CH tends to more and directly proportional to solution concentration.

This may be evidence that lithium ions (Li$^+$) exchanged calcium ions (Ca$^{2+}$) from the CSH gels and the released calcium ions precipitated into calcium hydroxide (CH), thus leading to more residual CH in the cement pastes. The DSC analysis of mortar bars immersed in 2.5mol/L Na$_2$SiO$_3$ solution was divided in two parts. The residual CH peak area in the “outer” curve was similar to that observed in the specimens immersed in 0.5 mol/L Na$_2$SiO$_3$ solution. Both curves were less than the one in the “inner” curve. This could be an indication that ASR occurred to a greater extent in the former than in the latter.

3.4. X-ray Diffraction Analysis (XRD) of Mortar Bars Immersed in Sodium Silicate Solution

XRD patterns of mortar bars immersed in 0.5 mol/L and 2.5 mol/L Na$_2$SiO$_3$ solutions is shown in Figure 8. Overall, XRD patterns are showing the same result as DSC curves. Residual calcium hydroxide (CH) was confirmed by sharp peaks at 18º and 34º. No ettringite peaks (Ett) were detected. In addition, sharp peaks believed to be α-quartz were observed at 22º. This believes as the reactive aggregate used in the mortar bar tests, and may have ended mixed up with the portions of cement pastes selected for the XRD analysis.
3.5. **Electron Probe Micro-Analysis (EPMA) of Mortar Bars Immersed in Sodium Silicate Solution**

The mapping imagery of sodium (Na) and silica (Si) in mortar bars immersed in 0.5 mol/L and 2.5 mol/L Na$_2$SiO$_3$ solutions obtained by Electron probe microscope analysis (EPMA) are shown in Figures 9 and 10, respectively. EPMA of thin sections was conducted to obtain more understanding in the occurrence of ASR in specimens immersed in 0.5 mol/L and 2.5 mol/L Na$_2$SiO$_3$ solution. EPMA results confirmed that ASR indeed occurred in both specimens, but was later suppressed in the outer-section of mortar bars immersed in 2.5 mol/L Na$_2$SiO$_3$ solutions. In the case of 0.5 mol/L Na$_2$SiO$_3$ solution, although ASR-gel was observed covering the entire section, the amount of Na is quite low and is similar to the one observed in the inner-section of mortar bars immersed in 2.5 mol/L Na$_2$SiO$_3$ solution. However, the reflections of Na in the outer-section were far more, which combined with the low silica (Si) content in this part, suggests that ASR occurred, although ASR-gel could not be detected by uranyl acetate fluorescence method. High silica content in the inner-section of specimens immersed in 2.5 mol/L solution is indicative of un-reacted flint particles. These findings, confirmed...
the underlying ASR mitigation mechanism of $\text{Na}_2\text{SiO}_3$ solution.

3.6. ASR Gel Formation in Mortar Bars Immersed in Sodium and Lithium Silicate Solutions

Uranyl acetate fluorescence method of coloring area was carried out to measure. The image of ASR gel observations in mortar bars immersed in sodium and lithium solutions by uranyl acetate fluorescence method are shown in Figure 11. The ASR gel shows a greenish-yellow coloration area on the cutting surface of the specimens. The results show that no ASR gel could be found in $\text{Li}_2\text{SiO}_3$ concentration, regardless of its concentrations. This result is suggesting again that no ASR gel occurs in $\text{Li}_2\text{SiO}_3$ specimens. In the case of specimens immersed in 0.5 mol/L $\text{Na}_2\text{SiO}_3$ and 1 mol/L $\text{NaNO}_3$ solution, the whole cross-section is covered by dense spots of ASR gel. As for mortar bar immersed in 2.5 mol/L $\text{Na}_2\text{SiO}_3$ solution, ASR gel was only observed in the inner-section of the mortar bars. It confirmed that ASR indeed occurred in this specimen, but it was later suppressed in the outer-section of mortar bars immersed in 2.5 mol/L $\text{Na}_2\text{SiO}_3$ solutions. Due to huge amount of CSH gel produced that could sink the ASR gel.

![Figure 9](image1.png)

(a) specimen with 0.5 mol/L $\text{Na}_2\text{SiO}_3$  
(b) specimen with 2.5 mol/L $\text{Na}_2\text{SiO}_3$

**Figure 9.** Mapping imagery of sodium (Na) in mortar bars immersed in 0.5 mol/L and 2.5 mol/L $\text{Na}_2\text{SiO}_3$ solutions obtained by EPMA analysis (observed area: 25 mm x 25 mm)

![Figure 10](image2.png)

(a) specimen with 0.5 mol/L $\text{Na}_2\text{SiO}_3$  
(b) specimen with 2.5 mol/L $\text{Na}_2\text{SiO}_3$

**Figure 10.** Mapping imagery of silica (Si) in mortar bars immersed in 0.5 mol/L and 2.5 mol/L $\text{Na}_2\text{SiO}_3$ solutions obtained by EPMA analysis (observed area: 25 mm x 25 mm)
IV. FURTHER RESEARCH WORK

The effectiveness of Li₂SiO₃ solution as repair material had been proved from the experimental works. However, there is an economic concern regarding lithium. Due to the global demand for lithium use, especially in batteries, lithium prices have been increased sharply since 1999. As in Japan, in the past only one supplier of lithium-based compounds exists. Thus, this has driven the whole concrete industry into the usage of the highly expensive lithium nitrite (LiNO₂) for both, ASR mitigation and control of reinforcing steel bar corrosion [15]. Therefore, experimental works of Li₂SiO₃ solution with concentration lower than 0.5 mol/L should be carried out. This experiment could help to determine the minimum use of this solution and to investigate the effect of Li₂SiO₃ with lower concentrations. In addition, the experimental results also revealed that higher concentration of Na₂SiO₃ solution were also effective enough to suppress the ASR. Thus, the further research works should also conducted regarding the Na₂SiO₃ solution with concentration higher than 2.5 mol/L. This research is valuable due to the inexpensiveness of Na₂SiO₃ solution compared to Li₂SiO₃ solution.

Moreover, for a better understanding on the silicate-based surface treatment as the repair method of ASR deteriorated concrete structure, it is also important to evaluate the binding capacity of this surface treatment to the cement paste by assessing the diffusivity of Na₂SiO₃ and Li₂SiO₃ solutions through cement paste. Post analysis such as Electron Probe Micro-Analysis (EPMA) should also be conducted to backup the diffusivity test result.

V. CONCLUSIONS

The main concluding remarks drawn from this study are as follows:
The investigation results of repaired concrete structures in Japan show that the use of sodium based surface treatment is not effective for suppressing ASR progress in ASR-affected structures.

The use of sodium silicate based surface treatments in the concrete structures may exacerbate ASR, in case there are reactive aggregates available in the concrete. This is due to the use of this type of surface treatments have a high possibility to significantly raise the alkalinity of the pore solution.

Regardless of Li$_2$SiO$_3$ concentration, the mortar bar expansion tests show that the specimens did not expand at all, this suggests no ASR occurrence. Thus, it can be recommended for the mitigation of ASR-induced expansion in deteriorated concrete structures.

Instead of using sodium based surface treatments, lithium based surface treatments (lithium silicate) can be more effective for repairing ASR-affected concrete structures.

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AUTHOR BIOGRAPHY

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