Alternative Method to Estimate Alkali-Silica Reactivity of Active-Chert Aggregates

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ABSTRACT

An alternative method for estimation of Alkali-Silica Reaction (ASR) of reactive chert aggregates is proposed. The ASR reactivity of chert aggregates (including Yoro and Seto) was studied with alkalinity under accelerated conditions at 60, 70 and 80°C and compared the results with normal sand. At different temperatures, the activation energy ($E_a$) value of aggregates was calculated by Arrhenius equation. The activation energy values were approximately 19.81 kJ/mol for Yoro-chert, 41.40 kJ/mol for Seto-chert and 112.52 kJ/mol for Normal-sand, respectively. The lower $E_a$ value indicates the higher ASR reactivity of aggregates. For hydrated products, the investigation employed Coupled Plasma Atomic Emission Spectrometry (ICP-AES), X-Ray Diffraction (XRD), and $^{29}$Si-Nuclear Magnetic Resonance ($^{29}$Si-NMR) analysis. A reduction in total dissolved silica was observed and was shown to be due to the presence of the Ca(OH)$_2$ that was involved in the formation of ASR products, such as calcium alkali silicate hydrate (C-Na-S-H) and calcium silicate hydrate (C-S-H). After Ca(OH)$_2$ was almost consumed, the Q\textsuperscript{3} peaks at -92.3 ppm appeared and indicated a defect in comparison with the tobermorite structure of C-S-H that had been assigned at low Ca/Si ratio.

INTRODUCTION

One of the chemical issues in deteriorated concrete is alkali-silica reaction or ASR. ASR is the chemical reaction between reactive Si and alkali (Na, K and Ca) remaining in pore solution, forming ASR gel. This gel can adsorb water to cause swelling, and cracking in concrete structure, leading to the severity of concrete expansion. Based on visual inspection, the map cracking and cracks with an opaque white coating on the surface of concrete dam damaged by ASR were found [Ahmad and Jack 2006]. It has also been shown that the ASR problem decrease the service-life of concrete structure and the reaction is difficult to control.

Many researchers have suggested ways of reducing ASR problem without affecting the quality of concrete structures such as the use of supplementary cementitious materials and the limitation of alkali content in concrete mix design [Fernandez et al., 2007; Michael 2011; Seyed et al., 2013]. It is generally accepted that the quality of aggregate considered to use is the effective to ASR mitigation. Much research in recent years has pointed on the quality of aggregate using the ASTM standards such as ASTM C289, C227, C1260 and C1293 [Farny and Kerkhoff, 2007; Chatterji, 2005; Seyed et al, 2013]. For example, the
mortar-bar method conforming to JIS A1146 (similar to ASTM C227) was demonstrated by [Eiji and Keiji, 2008]. Their investigation revealed a possible cause for the expansion of mortars containing Yo-chert (Yo) or Seto-chert (Se) due to ASR. Additional attempts focused on identifying the minerals of sedimentary rocks (Yo and Se) under polarizing microscope. The minerals of microcrystalline quartz and chalcedony were found in these two cherts [Table 2], confirming Yo-chert (Yo) or Seto-chert (Se) has been shown to ASR problem. The studies on ASR reactive minerals of aggregates were reported in reference [J.M. Ponce and Batic, 2006] and supported the fact that sedimentary rocks containing microcrystalline quartz and chalcedony minerals can be grouped as rapid-reacting aggregate. However, the mortar-bar method can be time-consuming and the identification of minerals of sedimentary rocks under polarizing microscope are often technically difficult to perform.

New correlations were developed with excellent results of past study [Eiji and Keiji, 2008], the approach we have used in this study aims to introduce an alternative method to examine the ASR reactivity of aggregate by considering the activation energy (E_a) value of aggregates (Yo-chert, Se-chert and normal-sand). Depending on temperatures, the calculation of E_a using Arrhenius equation is presented in Eq. 1. The E_a value of each aggregate will help us to prove without a doubt that the aggregate is deleterious, which is prone to ASR-affected concrete structures, or truly innocuous for concrete production. Moreover, the chemical structures of hydrated product with and without Ca(OH)_2 solid under temperature of 70°C are also described in this paper in order to insight the reaction sequence of ASR formation.

\[
\ln k = \ln A - \frac{E_a}{RT}
\]

where  
- \( k \) is the rate constant
- \( E_a \) is the activation energy (kJ/mol)
- \( R \) is the gas constant (8.314 J/mol-K)
- \( T \) is temperature in kelvin (K)
- \( A \) is pre-exponential factor or Arrhenius factor

**EXPERIMENTAL INVESTIGATION**

**Materials and Methods with Active Aggregates.** The material used in this part was crushed into particle sizes (150 to 500 µm): a non-reactive sand (Silica sand, Ns) and the reactive chert aggregate (Yoro, Yo and Seto, SE). Two reactive aggregates used in this experiment including Yoro-chert (Yo) and Seto-chert (Se) taken from different locations in Japan. The ASR behavior of aggregates was tested with the method of JIS A1145, as shown in Table 1 [Eiji and Keiji, 2008]. This method confirmed that both cherts are deleterious aggregates. In this paper, the experimental procedure adapted from our previous work [Lalita et al., 2015], aggregate (150 to 500 µm) was mixed with and without Ca(OH)_2 solid “CH” at different temperatures. In the absence of CH, 1 M-NaOH solution was added to 5.0 g of aggregate sample (Yo, Se or Ns) in the ratio of 0.25 (aggregate/solution) and suddenly mixed well for 3 h by magnetic stirrer. The samples were divided into polyethylene tubes and placed in the vacuum dry ovens. The experiments were conducted at constant temperatures of 60, 70 and 80°C. The reaction was stopped at 1, 3, 5, 7, 10, 14, 20 and 24 days for the mixtures by filtration through a 0.45µm filter and washing the solid with acetone solution to stop the reactions. Solids were placed in a vacuum drying chamber at 40°C until they were dehydrated. According to [Lalita et al., 2015], it has been known that Si can be dissolved from reactive chert aggregate. Then this dissolved Si mixed with Ca ions, leading to formation of calcium silicate hydrate, C-S-H, of inconstant composition depending on the activity of the ions. To investigate the chemical compositions and structures, 5.0 g of aggregate samples (Yo or Se) were mixed with CH by magnetic stirrer and then NH solution for 1 h and 3 h, respectively. The samples were kept at 70°C as the same method as mentioned earlier.
Sample Examination. The investigation employed ICP-AES, XRD and $^{29}$Si-NMR. After filtration, liquid samples were provided for ICP-AES 9000 with Ar gas. Standard method (concentration range: 10 ppb to 10 ppm) was chosen. For dissolved Si in the liquid samples, the initial concentration was supposed to be 500 mmol/L, and then diluted to be 5 ppm for ICP-AES analysis. The XRD investigated (fine powder of solid samples) was carried out using a rigaku instrument with CuKα radiation ranging from 5 to 70°2θ at a scanning rate of 1°2θ per min and a step size of 0.02°2θ. The $^{29}$Si-NMR was executed and recorded from a MSL 400 9.4 T BRUKER operating with frequencies of 79.486 MHz for $^{29}$Si at room temperature to show the structure of produced ASR in the solids. The conditions were as follows; a 90° pulse length of 5μs for $^{29}$Si, recycling delay of 60 seconds and 480 scans. The Q₈M₈ (Si(CH₃)₈Si₈O₂) at 12.4 ppm was used as an external standard for the $^{29}$Si-NMR chemical shifts. The NMR data were transferred to a PC and further explored by NUTS [Acorn, 1997].

Table 1. JIS A1145 results of the two chert aggregates here [Eiji and Keiji, 2008]

<table>
<thead>
<tr>
<th>Aggregates</th>
<th>Prefectures</th>
<th>Minerals</th>
<th>Results of JIS A1145 (mmol/L)</th>
<th>S_c/R_c</th>
<th>Interpretation of chosen aggregates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yo-chert</td>
<td>Gifu</td>
<td>Chalcedony and Cryptocrystalline quartz</td>
<td>329</td>
<td>130</td>
<td>2.53</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>391</td>
<td>88</td>
<td>4.44</td>
</tr>
<tr>
<td>Se-chert</td>
<td>Aichi</td>
<td>Chalcedony and Cryptocrystalline quartz</td>
<td>116</td>
<td>58</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>316</td>
<td>128</td>
<td>2.47</td>
</tr>
</tbody>
</table>

Table 2. Chemical compositions of chert by X-ray fluorescence

<table>
<thead>
<tr>
<th>Compositions</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>P₂O₅</th>
<th>MnO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yo</td>
<td>93.33</td>
<td>4.61</td>
<td>0.65</td>
<td>0.10</td>
<td>0.71</td>
<td>0.10</td>
<td>0.15</td>
<td>0.04</td>
<td>0.25</td>
<td>0.05</td>
</tr>
<tr>
<td>Se</td>
<td>93.19</td>
<td>5.17</td>
<td>0.34</td>
<td>0.09</td>
<td>0.54</td>
<td>0.07</td>
<td>0.19</td>
<td>0.16</td>
<td>0.25</td>
<td>0.01</td>
</tr>
<tr>
<td>Ns</td>
<td>86.93</td>
<td>11.78</td>
<td>0.06</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.16</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

RESULTS AND DISCUSSIONS

Experimental Results without CH. When reactive aggregate is in contact with highly alkaline solution, the silica mineral can be converted to a silanol group (Si-OH) due to the OH⁻ ions, acting as reactive silica. Reactive chert was immersed in the NH solution at varying temperatures of 60, 70 and 80°C, contributing to the free Si ions dissolved in the liquid samples. Data obtained from liquid samples can be used to calculate the Ea value of chert aggregates on the basis of Arrhenius law.

Si concentration determined by ICP-AES. ICP-AES results for dissolution degree (Si concentration in unit of moles/liter, M) of the mixtures of Ns+NH, Yo+NH and Se+NH are shown in Figures 1 and 2. It is obvious that the rate of Si dissolution significantly increased with increasing of temperature. This was because high temperature accelerated the dissolution reaction of Si from reactive aggregates during contacting with NH solution. For the content of Na⁺ ions (0.8 M) was almost the same as initial concentration of NH solution but very low amount of Ca ions (lower than 0.02 M) was observed in all liquid samples with CH. In Figure 1 (Normal-sand), the Si concentrations of Ns+NH (60°C), Ns+NH (70°C) and Ns+NH (80°C) were 0.06, 0.25, and 0.54 M, respectively. Si concentration of Yo+NH (see Figure 2), sharply rose up, which were 0.54 M for Yo+NH (60°C), 0.69 M for Yo+NH (70°C) and 0.87 M for Yo+NH (80°C). Comparing Yo and Se, Si degree dissolution for three temperatures of Yo-chert
(Yo+NH) was greater than Se-chert (Se+NH). The amount of Si at 576 h of Se+NH (60°C), Se+NH (70°C) and Se+NH (80°C) increased to 0.34 M, 0.65 M and 0.81 M, respectively. As temperature increases, Si dissolution occurs faster. This contributes to the high amount of dissolve Si in liquid solution, in particular the high reactive materials such as Yo-chert and Se-chert.

Figure 1. Si Dissolution of Ns+NH

Figure 2. Si Dissolution of Yo+NH and Se+NH
The $E_a$ value estimated by Arrhenius equation. Data obtained from previous section showed the contents of Si from Yo-chert, Se-chert or Silica-sand when they were mixed with NH solution. Considering the rate of Si dissolution at any temperatures, the $E_a$ value of aggregate can be calculated on the basis of Arrhenius law. For Ns+NH, the highest $E_a$ value was 112.52 kJ/mol. The $E_a$ value of Yo+NH was approximately 19.81 kJ/mol, which was lower than that of Se+NH (41.40 kJ/mol). The minimum $E_a$ energy means to the Yo-aggregate has a high potential to proceed the chemical reaction by OH- attack, yielding the more contents of dissolved Si in the system. The greater Si contents might react with alkali in pore solution of cement matrix to induce the cracks of concrete due to ASR. This is consistent with results obtained in the past work on reference [Eiji and Keiji, 2008], showing the mortar mixtures made with Yo-chert showed higher expansion than the mortar mixtures Se-chert. In case of normal-sand ($E_a$ = 112.52 kJ/mol), the amount of Si was slowly increase. Generally, the $E_a$ and A parameters are temperature dependence. Addition to the linear equations of temperature at 80°C, it was significantly noticed that the ln A factors of Yo+NH (80°C) and Se+NH (80°C) were positive, while the ln A of Ns+NH (80°C) was negative. This negative factor of normal-sand (Ns) indicated that the rupture of siloxane bond by OH- attack slowly occurred and then the contents of Si was not sufficient for ASR reaction. Regarding the expansion data, we observed that the mortars containing Ns conforming the method of ASTM C227 showed a little expansion that was interpreted as innocuous aggregate (data not shown in this paper). For this reason, it can be concluded that Normal-sand (Ns) has a low potential to cause ASR.

The solids analyzed by XRD and $^{29}$Si-NMR. In this part, the fine powder of Yo- or Se-chert after contacting with NH solution under temperature of 70°C was investigated by XRD and $^{29}$Si-NMR. No identical XRD peaks of ASR were found in both Yo+NH and Se+NH (data shown in Figure 3). According to Figure 4 ($^{29}$Si-NMR), only the spectra of Q$^3$ site (-95 to -98 ppm) was dominant in Yo+NH and Se+NH. This seems to imply that the appearance of Q$^3$ sites means to the Si site tetrahedron has three bridging oxygens and one non-bridging oxygen. The non-bridging oxygen could be bonded to either OH- or other low-charge cations, like in the Na group, which has been suggested in some types of ASR gel, like kanemite (Na/K-S-H). In case of kanemite gel, this product is difficult to detect by XRD since it is a soluble product that is commonly lost during acetone washing [Cong and Kirkpatrick, 1993].

![Figure 3. XRD results of Yo+NH (70°C) and Se+NH (70°C)](image)

Experimental Results with CH. It has been known that mixing CH and silica in water contributes to the formation of calcium silicate hydrate, C-S-H of different compositions. In ASR, dissolved Si from reactive aggregate can react with alkali (K or Na ion) or Ca ions to form products, such as alkali silicate hydrate (Na/K-S-H), calcium silicate hydrate C-S-H, and calcium alkali silicate hydrate (C-Na/K-S-H). In this paper, reactive chert aggregates mixed with CH solid were added with NH solution and placed in the
oven of 60, 70 and 80°C. The consequences on the composition and structure of ASR incorporated with Ca ions are discussed by considering the XRD and $^{29}$Si-NMR results after reacted at 70°C.

**Si concentration determined by ICP-AES**. Similar results were found in Yo+NH+CH and Se+NH+CH, showing the content of dissolved Si was exceptionally low but tended to increase later (see Figure 5). After 240 h of reaction, the amount of Si that remained in Yo+NH+CH was even higher than that of Se+NH+CH. However, the correlation between the temperatures and the contents of Si was somewhat less in case of the presence of CH. It is clear that the $E_a$ values of liquid samples with CH could not be examined in this study. As detailed in Figure 5, Si concentrations at 576 h were as follows: 0.03 M for Yo+NH+CH (60°C); 0.06 M for Yo+NH+CH (80°C); 0.08 M for Yo+NH+CH (70°C). Additionally, Si contents were 0.02 M of Se+NH+CH (60°C), 0.05 M of Se+NH+CH (70°C) and 0.03 M of Se+NH+CH (80°C), respectively. It can be noted that the Si concentration of liquid samples mixed with CH was quite different to the mixtures without CH (see Figure 2) that noticeably increased with increasing reaction time. Therefore, CH may affect the content of Si remained in the solution.

**The solids analyzed by XRD and $^{29}$Si-NMR**. The XRD patterns of powder Yo+NH+CH (70°C) and Se+NH+CH (70°C) exhibit the similar positions at 29.4 °20 that became sharply at 336 h of reaction (see Figure 6). The peaks also show diffractions at 7.2 °20 that are ordinarily observed for amorphous or disordered crystalline silicate. These peak locations are related to the basal peak patterns of layer structure of clay minerals, tobermorite and alkali disilicates, indicating the existence of ASR, like C-S-H, when Ca ions are available [Xiaoqiang et al., 2004 and 2005]. In contrast to the ASR product, the intensities of portlandite peaks located at 18.0 °20 and 34.2 °20 seem to decrease with increasing reaction time. For Yo+NH+CH (70°C) and Se+NH+CH (70°C), the $^{29}$Si-NMR spectra of solids with CH display the relationship between the C-S-H and alkali silicate gels, containing Si on sites with Q$^1$ (-62 to -83), Q$^2$ (-79 to -89) Q$^3$ (-91 to -103) and Q$^4$(-103 to -115) [Cong and Kirkpatrick, 1993; Andreas et al., 2010]. As detailed in Figure 7, the main peaks at -79.6 ppm (the end chain tetrahedral Q$^1$) and -85.03 ppm (nonbridging tetrahedral Q$^2$) were found in Yo+NH+CH (70°C) whereas the small intensity peak at -82.3 ppm (bridging tetrahedral with one hydroxide and water molecule) and peak at -89.3 ppm (the Q$^3$ site nearly to Q$^3$) were also detected. The observed peaks in this paper are similar to a previous study on the formation of ASR products in NaOH solution [Andreas et al., 2010]. Furthermore, it is noticed that the chemical shift of signal was initially dominated by Q$^1$ under the presence of Ca$^{2+}$ ions. These results agree well with those observed in the $^{29}$Si-NMR of synthetic C-S-H with 0.5 M KOH and indicated the formation of C-Na-S-H [Barbara and Andrel, 2015]. With reaction time increase, the intensity of Q$^2$ became predominantly (the Q$^1$/Q$^2$ ratio decreased) associated with the action of available Ca$^{2+}$ ions which can be assigned to a more polymerized structure of C-S-H. At the end of 576 h, the spectrum of Q$^3$ located at -92.3 ppm was visible. This Q$^3$ site links two silicate chains of two adjacent layers which is defect in comparison with the tobermorite structure at low Ca/Si ratio [Brunet et al., 2004; Andreas et al., 2010]. The spectra of products hydrated in Yo+NH+CH (70°C) and Se+NH+CH (70°C) are similar, although for Se+NH+CH (70°C), the main peaks at -79.6 ppm (the end chain tetrahedra Q$^1$) and -84.3 ppm (nonbridging tetrahedra Q$^2$) were detected after 168 h of reaction and subsequently the Q$^3$ site at -93.1 ppm appeared.

Our current findings are in good agreement with the chemical structures of produced ASR with 1M NaOH under temperature at 80°C and expand the sequence of ASR formation [Lalita et al., 2015]. To highlight the step of ASR reaction, Na/K-S-H is supposed to be the first product. In the presence of Ca ions, this contributes to the incorporation of Ca into ASR, forming C-Na/K-S-H (broad XRD peak at 29°20 and Si in Q$^1$ position dominantly). Excessive Ca$^{2+}$ ions are intrinsically involved in the precipitation of ASR gel, likely to the more polymerized structure of C-S-H (dominated by the Q$^2$ site). With a small amount of Ca, the Q$^3$ sites can be detected and ultimately, the occurrence of Na/K-S-H could be attributed to the consumption of CH.
CONCLUSION

The alternative method for considering the ASR reactivity of the aggregates was proposed. We have developed the chemical experiment for accelerating the dissolution of Si and showed that the reaction begins when OH ions present and the high temperature distributes the Si-O-Si bond more liable to rupture, yielding high concentration of Si observed in liquid solution. Under different temperatures, the $E_a$ values of each aggregate can be calculated by the Arrhenius equation. For reactive cherts, the low $E_a$ values were approximately 20-40 kJ/mol, whereas 112.52 kJ/mol of normal-sand was determined. The resulting of low $E_a$ is consistent with the great expansion of mortars containing Yo or Se which occurred.
during the experiment conducted by [Eiji and Keiji, 2008]. This result provides the exact $E_a$ value for reactive chert aggregates, which is prone to ASR-affected concrete structures. Additionally, we identify dramatically different structures in ASR products and the sequence of reaction.

Figure 6. XRD results of Yo+NH+CH (70°C) and Se+NH+CH (70°C)

Figure 7. $^{29}$Si-NMR results of solids with CH

REFERENCES


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