Effect of Alkali Silica Reaction (ASR) in Geopolymer Concrete

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ABSTRACT

Alkali silica reaction (ASR) occurs due to chemical reaction between hydroxyl ions in the pore water within the concrete matrix and certain forms of silica. This reaction could lead to strength loss, cracking, volume expansion and potentially failure of the structure. This manuscript reports findings of an experimental investigation of the inter-particle bonding between the reactive aggregates and the geopolymer matrix. Specimens were prepared using two Class F and one Class C fly ash stockpiles. Mechanical testing included the potential reactivity of aggregate and length change measurements as per ASTM standards. Petrographic analysis was conducted using Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR). The results suggest that the extent of ASR reactions due to the presence of reactive aggregates in fly ash-based geopolymer concrete is substantially lower than in the case of OPC based concrete, and well below the ASTM specified threshold. The ability to utilize ASR-vulnerable aggregates in the production of geopolymer concrete products would increase the economic and sustainability appeal of this technology, potentially resulting in significant cost savings and reduce carbon footprint by eliminating the need to transport large volumes of high quality aggregates across the country.

INTRODUCTION

Durability of normal Portland cement is of a major issue in the civil infrastructure industry. Alkali silica reaction (ASR) occurs due to the chemical reaction between hydroxyl ions in the pore water within the concrete matrix and certain forms of silica. This reaction could lead to strength loss, cracking, volume expansion and potentially failure of the structure. Figure 1 provides a schematic diagram of the ASR process in Ordinary Portland Cement (OPC) based concrete. Studies have shown that ASR is a multistage process. ASR initiates by the chemical reaction between alkaline solution hydroxyl ions and the aggregate at its interface. The hydroxyl ions attack the silanol groups (Si-OH) and the Si-O-Si (siloxane bonds). The second stage consists of the formation of expansion products. Depending on gel formation generated, an internal pressure is created within the cement matrix, triggering macroscopic expansion, and subsequently degradation of the concrete matrix.
Diamond reviewed various reactive aggregates that caused ASR expansion as shown in Table 1. Opaline and Chalcedonic silica are non-crystalline or poorly-crystalline forms of silica that can be found in cherts, flints, sandstones, limestone and dolomites. Tridymite and cristobalite (silicon dioxide) are other reactive forms of silica found in volcanic rocks that lead to ASR expansion. Low alkali cements used to prevent ASR often contain fly ash and granulated blast furnace slag (GGBFS). Class F and C fly ash pozzolans are effective in mitigating ASR when 30% of the Portland cement is replaced by mass. Natural pozzolans and small amounts of silica fume were also found to be effective in inhibiting ASR expansion.

Davidovits first introduced the term geopolymers to class F fly ash forming 3D silico-aluminate materials. A detailed study regarding the chemistry of geopolymer was conducted by Davidovits. Geopolymers belong to a family of inorganic binders and are similar to zeolite materials with amorphous microstructure. The polymerization process involves a rapid reaction under alkaline conditions of silicon-aluminum minerals. These result in a 3D polymeric chain and a structure of Si-O-Al-O bonds.

The two main ingredients of geopolymer are alkaline liquids and source materials such as kaolinite, fly ash etc. Alkaline liquids frequently used are sodium hydroxide (NaOH) or Potassium Hydroxide (KOH) in combination with sodium silicate (Na$_2$SiO$_3$). Geopolymer mortars made from activated fly ash contain high alkali content with minimal calcium content.
Table 1. Physical and chemical character of deleterious rocks²

<table>
<thead>
<tr>
<th>Reactive substance</th>
<th>Chemical Composition</th>
<th>Physical character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Opal</td>
<td>SiO₂nH₂O</td>
<td>Amorphous</td>
</tr>
<tr>
<td>Chalcedony</td>
<td>SiO₂</td>
<td>Microcrystalline to cryptocrystalline commonly fibrous</td>
</tr>
<tr>
<td>Certain forms of quartz</td>
<td>SiO₂</td>
<td>Microcrystalline to cryptocrystalline, Crystalline but intensely fractured strained or inclusion-filled</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>SiO₂</td>
<td>Crystalline</td>
</tr>
<tr>
<td>Tridymite</td>
<td>SiO₂</td>
<td>Crystalline</td>
</tr>
<tr>
<td>Rhyolitic, dactic, latitic,</td>
<td>SiO₂</td>
<td>Glass or cryptocrystalline material as the matrix of volcanic rocks or fragments in tuffs</td>
</tr>
<tr>
<td>cryptocrystalline devitrification</td>
<td>Siliceous with lesser proportions of Al₂O₃,Fe₂O₃, alkaline earths, and alkalies</td>
<td></td>
</tr>
<tr>
<td>products</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synthetic siliceous glasses</td>
<td>Siliceous with less proportions of alkalies, alumina and other substances</td>
<td>Glass</td>
</tr>
</tbody>
</table>

The potential for ASR in geopolymer concrete is considered minimal as a dense bond is already formed in the vicinity of the aggregates after the initial reaction.⁷,⁹ Experimental studies demonstrated that geopolymer-based fly ash mortars are activated with an alkali solution and expand less than 0.1% after almost two weeks. ASR was not detected on these samples. The alkalis in geopolymer concrete are involved in the chemical reaction. While the alkalis are taken up by the amorphous component in the fly ash and converted into cementitious binders and zeolite crystals. The unutilized alkali attack the reactive aggregates. Due to lack of calcium in the geopolymer, the silica gel (alkali aggregate product) was found not expansive. The ASR reaction is initiated while the material is still in a gel like form. These reactions are helpful in providing a strong bond at the paste-aggregate interface, thus enhancing the tensile strength of geopolymer concretes.

EXPERIMENTAL PROCEDURE

This section presents an experimental investigation developed for evaluating the extent of ASR in geopolymer concrete (GPC) manufactured from Class F and C fly ash stockpiles. The testing program, summarized in Figure 2, utilized specimens prepared using reactive aggregates known to initiate ASR reaction. These specimens were prepared as per ASTM C 490.¹¹ Aggregates utilized in the testing program include quartz, sandstone and limestone. Accelerated motor bar method and length change measurements were conducted as per ASTM C-1260¹¹. Fragmented GPC specimens underwent a petrographic analysis including scanning electron microscopy (SEM), X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR).
The dimensions of the specimens were 254 mm in length and 51 mm in breadth and height, as shown in Figure 3. The GPC specimens were prepared using three types of aggregates, namely quartz, limestone and sandstone. Class F fly ashes were obtained from Dolet Hills power station, in Mansfield, Louisiana and Avon Lake power station in Ohio, and were designated ‘Dolet Hills’ and ‘Ohio’, respectively. Class C fly ash was obtained from the Monticello power station located at Mount Pleasant, TX, and was designated ‘Monticello’.

The GPC specimens were prepared using an activator solution (a blend of sodium silicate and 14 M sodium hydroxide), which was mixed with the designated fly ash, fine aggregates and coarse aggregates. Four specimens were prepared for each combination of binder (i.e., fly ash stockpile or OPC) and reactive aggregate (i.e., limestone, sandstone and quartz), for a total of 48 specimens. All the specimens were immersed in 1 M NaOH and placed in oven at 80°C. Length change measurements
were conducted as per ASTM C490-07 as shown in Figure 4. The percent length change was calculated using the following expression:

\[
L = \frac{L_x - L_i}{G} \times 100
\]  

[1]  

where \( L = \) change in length at an age of ‘x’ days (%), \( L_x = \) comparator reading of specimen at age ‘x’ minus comparator reading of the reference bar at age ‘x’ (mm), \( L_i = \) initial comparator reading of the specimen minus the initial comparator reading of the reference bar (mm); \( G = \) nominal gauge length (250 mm).

Petrographic analysis was conducted using scanning electron microscopy (SEM), X-Ray Diffraction (XRD) and Fourier Transform Infra-Red Spectroscopy (FTIR). SEM analysis was conducted using a Hitachi S-4800 field emission scanning electron microscope (FE SEM) manufacture by Hitachi, Pleasanton, CA. XRD was performed on powdered samples using a Bruker AXS Inc, Billerica, MI. FTIR spectra analysis was conducted using a Nicolet 6700 manufactured by Thermo-Scientific, West Palm Beach, FL.

![Figure 4. Experimental setup of ASTM C 1260](image)

RESULTS AND DISCUSSION

The results from bar specimen tested as per ASTM C 1260 are shown in Figure 5. The OPC concrete made from quartz, limestone and sandstone exhibited an expansion of 0.18%, 0.12% and 0.16% after 34 days. After 21 days of exposure these specimens showed expansions of 0.13 % (OPC-sandstone), 0.081 % (OPC-limestone) and 0.09 % (OPC-quartz). OPC specimens made with sandstone, quartz and limestone
exceeded the ASTM threshold (0.1%) for expansion after 14, 27 and 34 days, respectively. The GPC specimens made from Dolet Hills, Monticello and Ohio ash stockpiles showed an average expansion of 0.076%, 0.037% and 0.008% after 14 days and 0.024%, 0.021% and 0.031%, respectively, following a 34 days exposure to sodium hydroxide solution. None of the GPC specimens exceeded the ASTM threshold, and most appeared to be stable at the 34 day mark. On average OPC specimens exhibited six times greater expansion than their GPC counterparts after 34 days of exposure to NaOH.

Figure 5. Results of ASTM C 1260 Experiments on GPC and OPC specimens

Visual observation of the OPC specimens revealed signs of leaching, while the GPC specimens did not show any indication of leaching as shown in Figure 6. The percent expansion and leaching effect on OPC samples indicate possible alkali silica reactivity after 21 days of sodium hydroxide exposure. ASR reactivity is often found in coexistence with leaching mechanism. The NaOH solution penetrated through the OPC matrix and initiated the ion exchange process by augmenting the partial dissolution of the aggregate, resulting in the leaching of alkali.
The GPC specimens were also immersed in 1 M NaOH solution but exhibited no signs of leaching. The specimens were subjected to 1 M sodium hydroxide, as studies have shown that exposure to higher concentrations in the range of (5-8M) NaOH could cause disruption of the geopolymer gel matrix.

A SEM image of OPC concrete indicating ASR gel expansion and microcracking is shown in Figure 7. ASR expansive gel was observed around the vicinity of the aggregate-cement matrix of the OPC specimens after 21 days of NaOH exposure (Refer to Figure 7A). The ASR gel formation was observed due to the chemical reaction between alkalis from Portland cement, hydroxyl ions, and siliceous constituents from the aggregate. During the NaOH exposure, the hydroxyl ions from the cement paste depolymerized the silica in the aggregate along with alkali-metal ions, generating analkali-silica gel. This silica gel caused volumetric expansion co-related to the data presented in Figure 5. This expansion caused micro-cracking at the matrix-aggregate interface, the expansion pressure exceeded the tensile capacity of the matrix, as shown in Figure 7B.
The SEM microscopy image of GPC concrete made with Dolet Hills and Ohio fly ash is shown in Figure 8. The aggregate-cement matrix interface of the GPC samples did not exhibit any indication of cracking nor ASR gel formation. The spherical morphology observed in the images can be attributed to the fly ash. During mixing the fly ash was activated by the NaOH and Na$_2$SiO$_3$, resulting in a sodium-silicate gel giving rise to a cementitious matrix. Some unreacted fly ash particles co-exist in the amorphous geopolymer matrix as shown in Figure 9 (A and B). The darker spherical zones indicate Ca-alumuniosilicate particles, and suggest that calcium was formed due to reaction between the calcium based aggregates and glassy fly ash particles (Si and Al) along with the alkaline solution. 

![Figure 7. Scanning electron microscopy (SEM) images of OPC samples](image)

![Figure 8. SEM analysis of GPC samples made from dollet hill (A) and ohio fly ash (B)](image)
Figure 9. Cement and fly ash matrix after geopolymerization using Dollit Hill (A) and Ohio Fly ash (B)

The results of a X-ray diffraction study of the GPC and OPC specimens is shown in Figure 10. The OPC specimen exhibits peaks of syngenite \([K_2Ca(SO_4)_2 \cdot (H_2O)]\) at 16°, 22°, and 32° 2θ. Peaks of thenardite are observed at 22°, 48°, 49° and 59° 2θ. The potassium and sodium in Portland cement are present as sulfate phases, and due to the NaOH exposure and elevated temperature conditions the OPC specimens exhibited additional formation of syngenite. Syngenite forms when the OPC is immersed in high alkaline hydroxide solutions like NaOH. Presence of syngenite could act as a precursor for the growth of ettringite. Thenardite occurred due to reaction between Na⁺ ions from the NaOH solution with sulfate ions (SO₄²⁻), leading to the formation of sodium sulfate decahydrate \(Na_2SO_4 \cdot 10H_2O\) as shown in Equ. 2. Repeated crystallization of sodium sulfate decahydrate causes thenardite (refer to Equ. 3). Thenardite could also lead to external sulfate attack via delayed ettringite formation (DEF).

\[
2Na^+ + SO_4^{2-} \rightarrow Na_2SO_4 \cdot 10H_2O \quad [2]
\]

\[
Na_2SO_4 \cdot 10H_2O \leftrightarrow Na_2 SO_4 \quad [3]
\]

XRD analysis of the GPC specimens showed the presence of quartz, analcime, anorthite, mullite, jadeite and albite. The presence of the anorthite phase indicates that calcium from the aggregate is reacting with the Na-poly(sialate-siloxo) along with alumino-silicate forming Ca-poly(sialate) anorthite and albite [Na(Si₃AlO₈)]. Albite can be associated with the strength enhancement region of the geopolymer matrix. Studies have shown that the compressive strength increases from 20 MPa to 90 MPa with 40~50% addition of albite. The analcime phase belongs to the zeolite (hydrated alumino-silicates) group. This analcime is formed when fly ash is mixed with NaOH, and acts as a precursor for geopolymerization. The GPC specimens made with Monticello fly ash showed the presence of jadeite (NaAlSi₂O₆) which belongs to the family of aluminosilicates. The mullite phase is partially involved in the zeolitization process and less reactive compared to other aluminosilicates.
The FTIR analysis of fly ash and GPC is shown in Figure 11. The aluminosilicates assigned to Al-O are detected in the range of 950-1250 cm\(^{-1}\). The unreacted fly ash showed Si-O bonds in the range of 1088-1100 cm\(^{-1}\). GPC samples shifted to lower number (960 cm\(^{-1}\)) due to geopolymerization of the fly ash. This shows the presence of Si:Al composition from the geopolymerization network.\(^7\) Carbonation in terms of CO\(_3^{2-}\) bonds were detected in the GPC specimens due to excess sodium which may not have been involved in the reaction.\(^9\) The OPC specimen showed the presence of SO\(_4^{2-}\) ions which can be involved in the formation of ettringite at a later stage.

Figure 10. XRD Analysis of Geopolymer Concrete (GPC) and Ordinary Portland Cement (OPC)
CONCLUSION

OPC concrete exhibited higher average expansion by a factor of 6 as compared to GPC samples after 34 days of exposure to NaOH. OPC specimens made with sandstone, quartz and limestone aggregates exceeded the permissible threshold (0.1%) for expansion as specified by ASTM, thus exhibiting signs of potential alkali silica reactivity of the aggregates. Visual observation of the OPC specimens showed signs of leaching, which was not observed in the GPC specimens. SEM and XRD analyses indicate the presence of formation of calcium based geopolymer network in addition to the silico-aluminosilicate formation. The formation of Ca-based geopolymer network suggest possible strength increase at the aggregate-matrix interface, an observation supported by the fact that during compressive strength tests the authors rarely observed a ‘pull-out’ failure of an aggregate. The observations reported in this study support the notions that fly ash based geopolymer concrete is significantly less vulnerable to ASR compared with OPC-based concrete. Considering that nearly 85% of a concrete matrix by weight consists of aggregates, lower sensitivity to reactive aggregates provide geopolymer concrete with significant economic advantage in areas where high quality deposits of aggregates are been rapidly depleted.

Figure 11. Fourier Transform Infra-red Spectroscopy (FTIR) of fly ash and geopolymer concrete
REFERENCES


