THE ALKALI-SILICA REACTION
IN ALKALI-ACTIVATED FLY ASH CONCRETE

A Thesis in
Civil Engineering
by
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ABSTRACT

The global concrete production has grown considerably over the last decades in line with the population growth, industrialization of developing countries, and the need for more infrastructures. In addition to replacing the natural environment by roads and buildings, carbon dioxide emission and depletion of natural resources for manufacturing portland cement, for example, are of major concern. The best approach to minimize the environmental impacts caused by the concrete industry is to build structures that are durable. Another valuable strategy is to manufacture concrete by using industrial by products, such as fly ash, which may fully replace portland cement. The combination of the two approaches is ideal and even more promising towards making concrete a more sustainable man-made material.

This research investigates the risk of alkali-silica reaction (ASR) in alkali-activated fly ash concrete. ASR is a major deterioration mechanism, which shortens the service life of concrete structures. It involves a reaction between metastable (e.g. poorly crystalized) forms of silica in aggregates and the highly alkaline pore solution of concrete. The product of this reaction is formation of an expansive ASR gel, which cracks and damages the concrete structure. Alkali-activated fly ash (AAFA) belongs to a new generation of green concrete binders that fully replace the ordinary portland cement. AAFA binders require a highly alkaline solution to promote hydration of fly ash and strength development, which raises the concern for ASR.

In this research, the concrete prism test (ASTM C1293) was used to evaluate the ASR risk of two structural grade AAFA concretes. Despite their initially high pH and presence of highly reactive aggregate, ASTM C1293 results showed absence of deleterious expansion in these two AAFA concrete mixtures (FA1 and FA2). On the other hand, the control (i.e. OPC-based) mixture, proportioned with the same amount of reactive aggregate, exceeded the expansion threshold early during the test. SEM micrographs were used to assess the extent of aggregate
deterioration and ASR gel formation in the tree mixes. The SEM micrographs reveal that aggregates in FA1 concrete were more preserved than in FA2, where very little ASR gel was detected. Moreover, EDS quantitative analysis detected increased amount of alkalis in residual aggregates with concentrations similar to that found in ASR gel formed in OPC concrete. To understand the mechanism leading to absence of ASR expansion, even though there is aggregate deterioration, microstructural investigation (MIP) and pore solution analysis were performed in AAFA pastes to test four proposed hypotheses. The results suggest that pH drop and abundance of dissolved aluminum decreases the alkaline attack to the aggregates in FA1, while the insufficient calcium prevents polymerization of dissolved silica from aggregates in FA2. In comparison to OPC paste, AAFA pastes had similar or larger porosity and average pore size, despite their significantly lower ASR activity. This rules out a hypothesis that ASR is mitigated in AAFA concrete because of its low permeability. In summary, the mechanisms responsible for absence of ASR in AAFA concretes were (1) pH drop, (2) high concentration of dissolved aluminum, and (3) low concentrations of calcium in the pore solution.
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Chapter 1 - Introduction and Background

1.1 Motivation

Concrete is the second most consumed product by human beings, behind only water (Provis and Deventer, 2014), and it is the most used man-material in the world (Ashby, 2013). To meet such a demand for concrete, the global annual production of portland cement is projected to reach 4 billion tons per year (Schneider et al., 2011). Ordinary portland cement (OPC) is the binder phase of most concrete structures currently in use, including dams, bridges, roads, and buildings (Mindess et al., 2003). Clinker, which constitutes up to 95% of portland cement, consumes high amount of energy during its production and has high carbon footprint. The emission of CO$_2$ in the atmosphere falls in the range of 0.85 to 1.35 kilograms per kilogram of clinker produced, depending on pyroprocessing (Marinshaw and Wallace, 1995). From this huge CO$_2$ emission, 40% is attributed to combustion of fossil fuels, which is used to supply the energy necessary for high temperature production of portland cement, and the remaining 60% to the calcination of limestone (CaCO$_3$ = CaO + CO$_2$) during cement manufacturing (Worrell et al., 2001).

Alternatively to OPC-based concrete, alkali-activated concretes (AAC’s) reduce the environmental impact caused by the concrete industry. Using fly ash as a single binder to produce alkali-activated fly ash (AAFA) concrete reduces up to 80% of CO$_2$ footprint compared to OPC concrete (Duxson et al., 2007). Other positive aspect of using non-OPC binders, including fly ash, blast-furnace slag, rice husk ash, or silica fume, is the beneficial use of the waste from other industries. In addition to decreasing the amount of landfilled by-products, the choice for OPC-free concrete reduces the need for a great amount of raw materials to be quarried, such as limestone. Limestone quarry promote deforestation, deep topography alteration, and soil
depletion, making it very difficult to establish a new vegetation layer (Clemente et al., 2004). Thus, AAC’s can be seen as environmentally friendly alternatives to OPC concrete and may move construction industry towards sustainability. Sustainability is defined as “the capability of an economic or social system to meet its current needs without impairing the ability of future generations to meet their needs” (Oxford English Dictionary, 1989).

Beyond the environmental benefits, other features of AAC’s must be taken into account, including mechanical properties and durability aspects. Specifically, durability with respect to alkali-silica reaction (ASR) is of concern. ASR is a durability issue widely known for compromising the service life of concrete structures and has been documented by more than 50 countries since 1940 (Mindess et al., 2003). The high alkalinity required for activation of AACs could trigger ASR and result in deleterious reaction with aggregates.

In ASR, the alkaline pore solution of concrete dissolves the meta-stable silica that exists in many natural and artificial (e.g. glass) aggregates and generates a hygroscopic gel. The ASR-gel swells and builds up an internal pressure that results in expansion, cracking, and loss of strength of concrete (Fournier and Bérubé, 2000). The simultaneous presence of moisture, reactive aggregates, and sufficient alkalis are three essential factors to trigger ASR. In addition, it has been argued that a source of dissolvable calcium inside concrete is essential for formation and swelling of ASR gel (Rajabipour et al., 2015; Gholizadeh et al., 2016).

The mechanisms of ASR in AACs are unclear, since limited research has been performed in this field. Uncertainties on durability of AAFA concrete, among other factors, have delayed the acceptance of this green concrete by practitioners. As such, understanding the mechanisms that promote or control ASR in AAFA would be a step towards development of guidelines for producing high performance AAFA concrete mixtures. Knowledge about ASR mechanisms also provides benefits towards the development of specific methods for testing AAFA concrete, which incorporate reliability and quality control. The findings of this research is also an important step for deducting whether reactive aggregates may be used in AAFA concretes. The potential of
using ASR-vulnerable aggregates in AAFA concrete make it even more attractive to the construction industry.

1.2 Background on Alkali-Silica Reaction

1.2.1 ASR mechanisms in OPC-based concrete

The crystalline phase of silica mineral is a well-oriented silicon-tetrahedron framework (Prezzi et al., 1997). The interaction between aggregates with the high-pH pore solution of concrete, schematically shown in Figure 1.1-A, leads to network dissolution of metastable silica that may be present within aggregates (Rajabipour et al., 2015). Over time, hydroxyl ions (OH\(^-\)) may depolymerize silica (Table 1.1 - Equation 1), increasing its molecular disorder. As depolymerization progresses the reaction product bind alkalis, which is supplied by the pore solution of concrete (Powers and Steinour, 1955) (Figure 1.1-B).

The mechanism by which alkali binding occurs is through ion exchange. There two ion exchange reactions involved, as shown in Table 1. The first consists in the replacement of one monovalent ion (i.e. H\(^+\)) by another monovalent ion (i.e. Na\(^+\), K\(^+\)) (Equation 2). The second ion-exchange consists of the replacement of two monovalent ions (i.e. Na\(^+\), K\(^+\)) by one single divalent ion (i.e. Ca\(^{2+}\)) (Equation 3) (Rajabipour et al., 2015). The replacement of alkalis by calcium is known as alkali recycling, and will be explained in details on Section 1.2.2 of this manuscript.

The described dissolution-precipitation process generates the so-called ASR gel (Figure 1.1-B), an alkali-alkaline earth-silicate hydrogel, with stoichiometry generally represented by \((\text{SiO}_2)_{(n)}(\text{Na}_2\text{O})_{(a)}(\text{K}_2\text{O})_{(b)}(\text{CaO})_{(c)}\cdot\text{H}_2\text{O}\) (Gholizadeh et al., 2016). Unsatisfied charges within the ASR gel molecule absorbs moisture, which promotes swelling. Over time, the ASR gel gains viscosity and become able to generate such a pressure that exceed the yield tensile strength of concrete. This slow process may take decades to show its symptoms in structures.
FIGURE 1.1 – 2-dimensional representation of the interaction between metastable silica in aggregates and the pore solution of concrete. A) Before ASR takes place. B) After ASR takes place. The ion exchange mechanisms are represented within the circles.
### TABLE 1.1: Summary of ASR steps and their chemical equations

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Chemical Equation</th>
<th>Eq.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Depolymerization of silica</td>
<td>(SiO(_2))(_s) + 2H(_2)O \rightarrow Si(OH)(<em>4)(</em>{aq})</td>
<td>1</td>
</tr>
<tr>
<td>Ion exchange</td>
<td>Na(^+) + (Si(OH)(<em>4))(</em>{aq}) \rightarrow ((OH)(<em>2)SiONa(</em>{aq}) + H(^+)</td>
<td>2</td>
</tr>
<tr>
<td>Alkali recycling</td>
<td>2((OH)(<em>2)SiONa(</em>{aq}) + Ca(^{2+}) \rightarrow (OH)(_2)SiO(^-) - Ca - OSi(OH)(_3) + 2 Na(^+)</td>
<td>3</td>
</tr>
<tr>
<td>Dissolution of portlandite</td>
<td>Ca(OH)(_2) \rightarrow Ca(^{2+}) + 2OH(^-)</td>
<td>4</td>
</tr>
</tbody>
</table>

#### 1.2.2 The role of calcium in ASR

Several researches highlighted the essential role of calcium in promoting the deleteriousness of ASR (Gholizadeh et al., 2016; Rajabipour et al., 2015; Thomas, 2001; Bleszynski and Thomas, 1998; Powers and Steinour, 1955). In OPC-based concrete, the main source of soluble calcium is portlandite (Table 1.1 – Eq. 4), which is one main product of cement hydration. Additionally to being a source of calcium, the dissolution of portlandite increases the concentration of hydroxyl ions in the pore solution, working as a pH buffer.

As mentioned in the previous section, Ca actively participates in the ion exchange (alkali-recycling) mechanism, where one single Ca\(^{2+}\) ion replaces two Na\(^+\) or K\(^+\) ions. This mechanism results in maintaining the alkalinity (i.e. high pH) of concrete pore solution through release of alkalis (Rajabipour et al., 2015). The alkali-recycling mechanism also repolymerizes colloidal silicates dissolved from the aggregates promoting the viscosity gain of ASR gel. Gholizadeh et al. (2016) proposed that there is an optimum concentration of Ca in the gel, among other factors, to promote deleterious expansion. It was found that with too little calcium, silicates remain dissolved in the pore solution without expanding, while too much calcium leads to a non-expansive ASR gel. Thomas (2001) showed that, by incorporating calcium and releasing alkalis, old ASR gels becomes similar in composition to C-S-H, the stable hydration product of cement (Figure 1.2).
FIGURE 1.2: Change in the composition of ASR-gel (Thomas, 2001): with time gel tends to incorporate calcium, release alkalis, and approaches to C-S-H composition.

When the optimum concentration of calcium is reached, the expansion of ASR-gel can exert up to 20 MPa of internal tension in the structure (Krivenko et al., 2014). This process promotes cracking within the aggregates that propagates throughout the cementitious matrix (Figure 1.3- A and B). As it happens simultaneously at many spots within the structure, it leads to the formation of map-like crack, which is ASR’s footprint (Figure 1.3- C and D).
FIGURE 1.3 - Micro and macro structural images showing ASR appearance (A: ASR-gel formation inside Spratt coarse aggregate; B: gel-filled crack bridging two reacted aggregates (Source: fhwa.dot.gov); C: Map cracks in ASR affected concrete (Source: fhwa.dot.gov); D: ASR-damaged structure (www.greensboro-nc.gov)).

1.2.3 The role of aluminum in ASR

A number of studies have shown that the presence of soluble aluminum in the pore solution of concrete decreases the ASR risk. Aluminum may be chemisorbed on the surface of reactive silica, decreasing the rate of aggregate dissolution (Iler, 1985; Oka and Tomozawa, 1980; Iler, 1973) and altering the composition and structure of the silicate gel produced (Chappex and Scrivener, 2012; Chappex and Scrivener, 2013). Several other researches underline the precipitation of a zeolite layer along the surface of dissolved silica (Labrid, 1991; Huenger, 2007; Shafaatian, 2012).
that may also decrease silica dissolution, as soon as the pore solution of concrete is supersaturated with Al (Bickmore et al., 2006). In addition, Hong and Glasser (2002) highlighted the ability of aluminum ions in increasing the alkali-binding capacity of the C-(A)-S-H products, which may decrease pore solution pH.

The three mechanisms described above (i.e., (1) chemisorption of Al by dissolved silica; (2) formation of a protective zeolite layer, and (3) alkali-binding) highlight the positive effect of Al in mitigating aggregate dissolution. As such, dissolved Al in the pore solution of concrete may be seen as a tool to mitigate ASR.

1.2.4 Pore Solution Chemistry of Concrete Undergoing ASR

The progress of ASR affects the pore solution chemistry of concrete. The reaction between silica, from aggregates, and alkalis and OH\(^-\) ions, from concrete pore solution, results in consumption of all these ingredients. Since the consumption of alkalis and hydroxyl continues with ASR progress, Na\(^+\), K\(^+\), and OH\(^-\) concentrations should decrease with time in the pore solution. Moreover, higher temperatures lead to faster ASR and higher consumptions of such ions (Kim et al., 2015). However, if the conditions favor the alkali recycling mechanism (Eq. 3), Na\(^+\), K\(^+\), and OH\(^-\) concentrations are maintained into pore solution of concrete (Rajabipour et al., 2015).

1.2.5 How to prevent ASR in new concrete structures?

The prevention of ASR in new structures has been extensively studied (Fournier et al., 2010; Rajabipour et al., 2015). The ASR expansion mechanism requires access of four prerequisites: (1) reactive silica, (2) high alkalinity (pH), (3) dissolvable calcium, and (4) moisture. By taking off or reducing one of the four prerequisites, it is possible to mitigate ASR. According to AASHTO PP-65 (2013), the following methods can be used to suppress ASR in new (i.e., to be constructed) OPC-based concrete:
• Limiting reactive (silica) aggregates: The approach of using non-reactive aggregate, i.e., the aggregates that showed good field performance (Thomas et al., 2006) or those that pass ASTM C1293 test (ASTM C1293-08b, 2008), can be challenging. Truly non-reactive aggregates are scarce in some regions, for instance in Pennsylvania state, USA. It may involve long-distance transportation of non-reactive aggregates, which considerably raises the cost of concrete production.

• Limiting concrete alkalis: Limiting the amount of Na$_2$O$_{eq}$ (percentage of Na$_2$O + 0.658 x percent K$_2$O) of cement to a maximum of 1.8kg/m$^3$ of concrete is recommended (AASHTO PP 65-11, 2013). However, portland cement is not the only source of alkalis. Aggregates, supplemental cementitious materials, and other admixtures could potentially provide extra alkalis and lead to deleterious ASR (Rajabipour et al., 2015).

• Using of supplementary cementitious materials (SCM): The use of SCMs, including pozzolans (i.e. calcined clays, fly ash) and blast furnace slag, reduces the pore solution pH (Shafaatian et al., 2013; Thomas, 2011). SCMs reduce aggregate dissolution and decrease the availability of calcium, by consuming portlandite. However, if high dosages of SCM are necessary to successfully mitigate ASR, it may negatively impact the setting, compressive strength, and freeze-thaw durability (e.g. scaling) of concrete. If this is the case, the dosage of SCM will be limited and might not be sufficient to mitigate ASR.

• Using lithium admixtures: the presence of lithium in the pore solution of concrete may affect the progress of ASR. In addition to reducing the rate of silica dissolution, Li$^+$ is potentially adsorbed by the reaction product (i.e. ASR gel) altering its mechanical and swelling properties (Rajabipour et al., 2015). However, lithium is a scarce element, which increases the cost of these admixtures and, consequently, affects the overall cost of concrete production.
Since there are challenges related to all preventive measures against ASR, fully preventing the reaction is not achievable in some cases. Thus, ASR continues to be a leading deterioration mechanism in concrete worldwide.

1.2.6 How to mitigate ASR in existing structures?

Suppressing ASR in existing structures has much lower efficacy than preventive measures (Fournier et al., 2010). Two subsets of possible treatments are (i) treating the cause of ASR, and (ii) treating the symptoms of the reaction. Figure 1.3 (Fournier et al., 2010) summarizes the methods available for each of the two subsets.

<table>
<thead>
<tr>
<th>TREAT THE CAUSE</th>
<th>TREAT THE SYMPTOM</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Chemical Treatment/Injection</strong></td>
<td><strong>Crack Filling</strong></td>
</tr>
<tr>
<td>- CO₂</td>
<td>- Aesthetics</td>
</tr>
<tr>
<td>- Lithium Compounds</td>
<td>- Protection (e.g., from Cl⁻ ingress)</td>
</tr>
<tr>
<td><strong>Drying</strong></td>
<td><strong>Restraint</strong></td>
</tr>
<tr>
<td>- Sealants</td>
<td>- Prevent Expansion</td>
</tr>
<tr>
<td>- Cladding</td>
<td>- Strengthen/Stabilize</td>
</tr>
<tr>
<td>- Improved Drainage</td>
<td><strong>Relieve Stress</strong></td>
</tr>
<tr>
<td></td>
<td>- Saw Cutting/Slot Cutting</td>
</tr>
<tr>
<td></td>
<td>(accommodate movement)</td>
</tr>
</tbody>
</table>

**Figure 1.4:** Available methods for mitigating ASR: treatments for cause and for symptoms (Fournier et al., 2010).

The goal of applying treatments for the cause is to disturb directly the ASR reaction mechanisms. In theory, the injection of CO₂ and lithium admixtures in affected concrete may suppress the ASR. However, in practice, neither of the two methods can penetrate deep enough within the structure, even when applied under high pressure. Therefore, they are not effective for mass structures, such as dams (Fournier et al., 2010). On the other hand, the application of sealants, cladding and improved drainage were found to be effective in delaying the progress of
ASR, since the method reduces the penetration of additional moisture within the affected concrete (Fournier et al., 2010).

As opposed to the cause treatments, the symptom treatments (e.g. application of restraint, and relief of stresses) do not act directly against the ASR mechanisms. Instead, they are applied as an attempt to minimize the damage to the concrete and extend the service life of the ASR affected structure (Fournier et al., 2010). Additionally, such methods most of the times are costly major repairs (ACI Committee 364, 2015).

In summary, the application of any kind of ASR treatment extends the service life of affected structure rather than ending the reaction itself (ACI Committee 364, 2015).

1.3 Brief Background on Alkali-Activated Fly Ash Concrete

Alkali-activated fly ash concrete is a subset of geopolymers, a term used to designate low-calcium binder systems among a broader category of alkali-activated materials (AAM) (Provis and Deventer, 2014). Analogously to portland cement, the anhydrous fly ash is mixed up with a liquid phase to produce a solid binder phase. Rather than water, fly ash requires a highly alkaline solution to catalyze its dissolution, as well as the process of hydration and strength gain. This process is known as geopolymerization, a rapid reaction that generates amorphous “-Si-O-Al-O-“ 3D-structure, which is an amorphous zeolite (Fernández-Jiménez et al., 2005; Fernández-Jiménez and Palomo, 2005; García-Lodeiro et al., 2007; Kupwade-patil and Allouche, 2011). When the activating solution supplies sodium to the fresh paste, the Al sites within the 3D aluminosilicate structure incorporate Na. As such, the reaction product is sodium-aluminosilicate hydrate, or N-A-S-H gel in cement chemist notation. Fernández-Jiménez et al. (2005) found that about 50% of reaction to generate N-A-S-H takes place before day-7 (Figure 1.5).
The macrostructure of AAFA concrete is a stable solid comparable to OPC-based concrete. Depending on the composition of the fly ash, activator, and aggregates, as well as their interaction, the overall properties of AAFA vary drastically (Duxson et al., 2007).

1.3.1 The Influence of Activator Composition

The composition of activator has a significant effect on many aspects of AAFA, including, for example, compressive strength and porosity. Both sodium hydroxide solution and a mixture of sodium hydroxide with sodium silicate solutions (Na$_2$O,$n$SiO$_2$,$m$H$_2$O or waterglass) are commonly reported in the literature as activators. The prompt availability of SiO$_2$ provided by waterglass activator boosts geopolymeration and strength gain, producing concretes that may reach up to 90 MPa of compressive strengths (Kazemian et al., 2015; Fernández-Jiménez and Palomo, 2005; Ryu et al., 2013). Simultaneous increase in the activator’s pH and modulus (n), which is the molar ratio [SiO$_2$]/[Na$_2$O], would be ideal for strength improvement in AAFA concretes (Kazemian et al., 2015). But since the two parameters are inversely proportional, increasing pH and n simultaneously is not practical. As opposed to strength, high n and pH has a negative effect in concrete workability (Kazemian et al., 2015), since it leads to activators with
low water content and high viscosity. Additionally, high pH activators showed a negative effect in ASR expansion of AAFA mortar (Shi, 1996; Shi et al., 2014). The selection of the activator, as well as its modulus and pH, for AAFA concrete represents a tradeoff between mechanical and durability properties and should be ultimately tailored to achieve specific requirements.

1.3.2 Curing Method

To enhance dissolution and geopolymerization of fly ash and achieve higher strengths, AAFA concretes must be cured at elevated temperatures (e.g. 60º C) (Kazemian et al., 2015; Xie et al., 2003).

1.4 Research Objectives

The objectives of this research are (1) to properly evaluate the ASR risk in alkali-activated fly ash (AAFA) concrete, and (2) explore the mechanisms of ASR or the reasons for lack of ASR expansion in AAFA concrete. To achieve the first objective, ASTM C1293 concrete prism expansion tests (CPT) were performed on two AAFA concrete mixtures along with a control OPC concrete mixture, all containing the same amount of reactive aggregate. The results of CPT, explained in detail in chapter 2, showed that ASR expansion and damage is absent in AAFA concretes despite their highly alkaline pore solutions.

Since there are four ASR prerequisites ((1) reactive silica, (2) high alkalinity (pH), (3) dissolvable calcium, and (4) moisture, as explained in detail in the previous section), the following hypotheses are proposed to explore the reasons for lack of ASR expansion in AAFA (objective (2)):

1. Despite initially high alkalinity, the [OH\(^-\)] and alkali concentration in AAFA system may decrease over time as a result of reaction with fly ash. The hydroxyl ions are likely to participate in fly ash dissolution, while alkalis will be bond to the main hydration product
of AAFA systems. Lowering the pore solution pH and alkali concentration leads to a significantly milder attack on the aggregates.

2. Aluminum, as mentioned before, could be another factor reducing aggregate dissolution and, consequently, ASR in AAFA concretes. The possibility of having a high supply of dissolved Al in the pore solution of AAFA paste will be investigated and compared to that in OPC paste. The increased supply of Al in class F AAFA systems may also alter the composition of the ASR gel, altering its swelling nature, as well. Pore solution analysis and SEM/EDS investigation will be used to evaluate this hypothesis.

3. The dissolved calcium concentration in AAFA systems might differ significantly from that of OPC. Limited Ca within AAFA concrete may prevent polymerization of dissolved silica (Table 1 – Eq. 3), which potentially impacts the viscosity-gain process of ASR gel. If that is the case, silica will remain dissolved within the pore solution, without damaging the structure.

4. Another relevant factor is the transport of moisture within AAFA matrix. The lower volumetric liquid-to-binder ratio compared to OPC paste, is likely to promote a smaller porosity. As such, the transport of moisture needed to sustain ASR might be hampered in AAFA concrete compared to OPC systems.

Chapter 2 discuss in details the experimental methods, results, and findings of this thesis in a format of a journal paper.

1.5 References


silica reaction: Current understanding of the reaction mechanisms and the knowledge gaps. *Cement and Concrete Research*, 76, 130–146.


Chapter 2 – Exploring the Absence of ASR Expansion in Alkali-Activated Fly Ash Concrete

Abstract

Alkali-activated fly ash (AAFA) is a promising non-portland cement binder for concrete. A potential durability concern in AAFA concrete is that the high alkalinity required for activation of fly ash may result in deleterious alkali-silica reaction (ASR). In this research, the concrete prism test (ASTM C1293) was used to evaluate the ASR risk of two structural grade AAFA concretes containing highly reactive aggregates. The measured expansions of both mixtures were well below the failure threshold, suggesting innocuous ASR performance. The mechanisms responsible for absence of ASR were explored and determined to be: (1) significant reduction in the pH of AAFA pore solution over time, due to reaction with fly ash, (2) the high concentration of Al in the pore solution of AAFA, which mitigates dissolution of silica, and (3) scarcity of Ca in AAFA, which is needed for gelation of silica. It was also determined that low mass transport was not the cause of ASR mitigation in these AAFA mixtures.

2.1 Introduction

The objective of this research was to investigate the risk of alkali-silica reaction (ASR) in class F alkali-activated fly ash (AAFA) concretes. ASR is a leading cause of deterioration in concrete structures and involves a series of deleterious reactions between meta-stable silica (found in many natural aggregates) and the highly alkaline pore solution of concrete (Rajabipour et al., 2015). AAFA is a new generation of concrete materials where the binder phase is fully produced using
pulverized coal fly ash and does not contain any portland cement. As such, AAFA provides significant environmental benefits (e.g., reduced CO2 emission and reduced energy use) in comparison to conventional portland cement concrete (Duxson et al., 2007). However, highly alkaline activators (with pH nominally above 14) are needed to promote fly ash reactivity and produce AAFA concrete with desirable strength (Kazemian et al., 2015). As such, the risk of ASR in AAFA concrete is of concern.

A few publications exist where class F AAFA-based mortars were tested using ASTM C1260 accelerated mortar bar test (AMBT) (Fernández-Jimenez et al., 2007; Kupwade-patil and Allouche, 2011; Li et al., 2006; Xie et al., 2003). In these studies, AAFA binders showed consistently better response to reactive aggregates compared to OPC binders. However, no clear explanation for the lack of ASR was provided. Additionally, AMBT is especially unsuitable for evaluating ASR in AAFA materials since the 1M NaOH (i.e., pH 14) bath used in the test is likely lower than AAFA activator. As such, instead of providing a non-exhausting supply of Na\(^+\) and OH\(^-\) to induce ASR, the bath dilutes the concentrations of these ions within the pore solution of mortars.

A much more suitable laboratory method for testing ASR is the concrete prism test, or CPT, that according to the standard (ASTM C1293) and other authors (Thomas et al., 2006; Rajabipour et al., 2015) provides more reliable results. The CPT test also induces ASR by providing a large supply of moisture and elevated temperature (100% RH and 38 °C). But unlike the accelerated mortar bar test, the CPT continues for at least one year until conclusions can be drawn.

A recent study, which was performed at University of Texas in parallel with the present study (Williamson and Juenger, 2016), has used the CPT to evaluate the propensity of AAFA binder to ASR. Even though the concrete was made with reactive chert fine aggregate and 8M NaOH activating solution, the results showed that the overall expansions were below the threshold limit (0.04% expansion).
The present work also used CPT (ASTM C1293-08b, 2008) to evaluate the ASR performance in two class F AAFA mixtures. If it is proven that deleterious ASR expansion is absent in the two concrete mixtures, the following hypotheses are proposed to explain the lack of ASR:

a. Despite an initially high alkalinity, [OH\(^{-}\)] and alkali concentrations in AAFA pore solution decrease rapidly over time as a result of reaction with fly ash.

b. AAFA pore solution may contain elevated levels of aluminum, and the presence of dissolved Al mitigates dissolution of aggregates even at high pH, as suggested by several researches (Liu et al., 2015; Chappex and Scrivener, 2013; Shafaatian 2012; Chappex and Scrivener, 2012; Huenger, 2007; Bickmore et al., 2006; Labrid, 1991; Iler, 1985; Oka and Tomozawa, 1980). Al may also alter the nature and deleteriousness of ASR gel (Rajabipour et al., 2015).

c. The solid and dissolved calcium concentrations in class F AAFA binders are expected to be low and this might prevent gelation of silica. Even if ASR gel is produced, it may have low yield strength and viscosity (Gholizadeh et al., 2016), and as such, it may be innocuous.

d. Mass transport and water permeability of AAFA binder may be low due to its lower volumetric liquid-to-solid ratio \((L/S)_{\text{binder}}\) compared to OPC paste, resulting in smaller porosity and pore sizes. This could slow down aggregate dissolution, as well as generation and expansion of ASR gel.

The outcomes of this research could provide a step towards better acceptance of AAFA concretes, as the knowledge gained could lead to development of guidelines for durable AAFA concrete mixtures. Moreover, this research moves towards clarifying ARS reaction mechanisms and the role that each element may play, which contribute to developing novel mitigation tools against ASR.
2.2 Materials and Methods

The ASR risk in AAFA concrete was assessed using ASTM C 1293 – Concrete Prism Test (CPT), and compared to a control specimen (i.e., OPC-based concrete). Spratt is a well-researched siliceous limestone and was used as the reactive coarse aggregate to induce ASR in the CPT. The proportion of reactive coarse aggregate was used as a constant parameter in all mixtures, which enabled comparison between AAFA and OPC concrete. The extent of aggregate damage due to ASR was explored through electron microscopy and x-ray energy dispersive spectroscopy in the two AAFA concretes and compared to that in OPC concrete. Pore solution of AAFA pastes were extracted and analyzed over 335-days, to provide a more comprehensive understanding about the binder’s ionic composition. Additionally, mercury porosimetry was performed on AAFA pastes, to enabling characterizing the pore structure of the two AAFA mixtures. All tests performed in this research are compared with the results of a control mixture, in which the binder phase was OPC.

2.2.1 Materials and mixture proportions

Two AAFA concretes and their corresponding pastes (FA1 and FA2) were used in this study along with a control OPC concrete (Table 2.1). Each AAFA concrete and its corresponding paste consisted of the same binder phase. Some of the properties of the two mixtures are provided in Table 2.2.

Earlier research at Penn State (Kazemian et al., 2015) demonstrated that FA1 and FA2 developed 1-day compressive strength of 18.0 MPa and 24.0 MPa and 28-day compressive strength of 32.9 MPa and 41.0 MPa, respectively. As such, both mixtures can be used as structural grade concrete, which is the reason why they were compared with a w/c=0.45 portland cement concrete (control mixture) with similar 28 day strength values. In the study of Kazemian et al. (2015), FA1 and FA2 mixtures were referred to as G1 and G4, respectively.
ASTM C150 (ASTM C150-05, 2011) type I portland cement was used for preparation of the control mixture. Its specific gravity and oxide composition is shown in Table 2.3. The Na$_2$O$_{eq}$ (percent of Na$_2$O + 0.658 times percent of K$_2$O) of the cement was raised to 1.25%, as required by ASTM C1293, through direct addition of NaOH to the mixing water. Class F fly ash was used as the binder phase of AAFA pastes and concrete. Its oxide composition and specific gravity is shown in Table 2.3.

**Table 2.1: Mixture proportions of AAFA and OPC concretes**

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>NaOH (kg/m$^3$)</th>
<th>Water (kg/m$^3$)</th>
<th>Sodium Silicate (kg/m$^3$)</th>
<th>Fly ash (kg/m$^3$)</th>
<th>OPC (Kg/m$^3$)</th>
<th>Non-reactive Oley sand (Kg/m$^3$)</th>
<th>Reactive Spratt coarse agg. (Kg/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA1</td>
<td>58.1**</td>
<td>93.7**</td>
<td>34.1**</td>
<td>479.2</td>
<td>-</td>
<td>659.2*</td>
<td>1047.3*</td>
</tr>
<tr>
<td>FA2</td>
<td>36.9**</td>
<td>59.5**</td>
<td>96.1**</td>
<td>479.2</td>
<td>-</td>
<td>659.2*</td>
<td>1047.3*</td>
</tr>
<tr>
<td>OPC</td>
<td>2.0**</td>
<td>200**</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>420</td>
<td>703.4*</td>
</tr>
</tbody>
</table>

*Values expressed in OD condition
**Values adjusted to account for absorption by aggregates

**Table 2.2: Properties of AAFA and OPC mixtures**

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>(L/S)$_{binder}$* (volumetric)</th>
<th>Activator solution composition</th>
<th>pH</th>
<th>Modulus (n = SiO$_2$/Na$<em>2$O)$</em>{molar}$</th>
<th>Water (mass %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA1</td>
<td>0.8</td>
<td>15</td>
<td>0.21</td>
<td></td>
<td>61.8</td>
</tr>
<tr>
<td>FA2</td>
<td>0.8</td>
<td>14.8</td>
<td>0.76</td>
<td></td>
<td>62.1</td>
</tr>
<tr>
<td>Control (OPC)</td>
<td>1.42**</td>
<td>Neutral</td>
<td>0</td>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>

* Liquid to solid ratio of the binder
** Equivalent to w/c= 0.45 by mass.

**Table 2.3: Oxide composition (mass %) and properties of OPC and fly ash**

<table>
<thead>
<tr>
<th>Oxide</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>SO$_3$</th>
<th>LOI</th>
<th>Specific Gravity</th>
<th>Passing 45µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>19.90</td>
<td>5.44</td>
<td>2.26</td>
<td>62.50</td>
<td>2.31</td>
<td>0.30</td>
<td>0.89</td>
<td>4.93</td>
<td>2.51</td>
<td>3.15</td>
<td>81.0</td>
</tr>
<tr>
<td>Fly ash</td>
<td>46.69</td>
<td>22.44</td>
<td>19.43</td>
<td>4.99</td>
<td>1.04</td>
<td>0.58</td>
<td>1.77</td>
<td>0.76</td>
<td>2.00</td>
<td>2.64</td>
<td>98.4</td>
</tr>
</tbody>
</table>
The activator solutions used in AAFA were a mixture of sodium hydroxide pellets, sodium silicate solution and distilled water. Analytical grade NaOH pellets were dissolved in distilled water to prepare 12M solutions. A commercially available sodium silicate solution (PQ corporation) was used, which was composed of 28.6% of SiO₂, 8.9% Na₂O, 62.5% water, by mass, and had pH=11.3, modulus (SiO₂/Na₂O molar ratio) n=3.24, and specific gravity of 1.39 at 20 ℃. To avoid the test results to be affected by impurities from tap water, specifically Ca²⁺, all the mixtures discussed in this research were prepared with distilled water.

Natural sand (Oley, PA), meeting ASTM C 33 (ASTM C33/C33M-13, 2013) was used as fine non-reactive aggregate in the AAFA and OPC concrete mixtures. It had oven dry specific gravity 2.70, absorption capacity of 0.46% and AMBT expansion of 0.075% at 14 days. The coarse aggregate used was Spratt, a well-known highly reactive siliceous limestone, supplied by the Ministry of Transportation, Ontario, Canada. Spratt had OD specific gravity of 2.64, absorption capacity of 0.74% and AMBT expansion of 0.33% at 14 days.

While the OPC mixture proportions required 2 kg of NaOH per cubic meter of concrete to boost the cement alkalinity to 1.25%, FA1 and FA2 required respectively 58.1 and 36.9 kg of NaOH per cubic meter of concrete to achieve the target activator pH (Table 2.2). ASTM C1293 requires w/cm between 0.42 and 0.45 by mass, which corresponds to liquid-to-solid (L/S)ₜₐ₅ binder by volume in the range of 1.32 to 1.42. However, to produce AAFA concretes with sufficient strength and workability, the liquid-to-solid ratio (L/S)ₜₐ₅ binder had to be decreased to 0.80 (by volume). Master Pozzolith 322 water-reducing admixture was used in FA1 and FA2 at a proportion of 2.5ml per kilogram of fly ash, also to increase workability of AAFA concrete and to avoid false set.

2.2.2. ASTM C 1293 – Concrete Prism Test

AAFA and OPC prisms were prepared according to standard specifications. A pan mixer was used for mixing the concretes. After mixing, the AAFA concrete was poured in molds and cured
at 23 °C, at 100% relative humidity for 24 hours. Next, the AAFA prisms were steam cured at 60 °C for further 24 hours to allow proper strength development. Subsequently, the AAFA concrete prisms were demolded and stored in buckets at 38 °C at 100% relative humidity. The control (OPC) specimens were cured at 23 °C and 100% relative humidity for 24 hours and then demolded and stored in buckets at 38 °C at 100% relative humidity, as specified by ASTM C1293.

24 hours before each periodic length measurement, the buckets containing the specimens were removed from the 38 °C room and cooled down at room temperature. Prism expansions and mass changes were monitored using a digital comparator with accuracy 0.0025mm and a balance with accuracy 0.1g.

2.2.3 SEM/EDS

The purpose of SEM and EDS tests was evaluating the extent of alteration (i.e., change in chemical composition) and damage to the aggregate by ASR in each concrete mixture, as well as determining whether ASR gel is present. Additionally, the evolution of aggregate damage in AAFA concrete was observed by comparing samples from 7- and 12-month-old concrete prisms.

At the age of 7 months, one concrete prism of each AAFA concrete mixture, FA1 and FA2, was sacrificed to obtain specimens for scanning electron microscope (SEM) micrographs. SEM samples were prepared at the age of 7 months and 12 months for AAFA concrete. At this time, the control (OPC) concrete prism was already 21 months old and was sliced at this age to obtain SEM samples. In addition to samples from FA1, FA2 and OPC concretes, Spratt aggregates were independently imaged to determine their microstructure before adding them to concrete. All the concrete samples went through a solvent exchange process (isopropanol alcohol bath) for 7 days, which stopped the geopolymerization and hydration reactions and allowed the drying of the samples with minimal microstructural damage. Afterwards the samples (including the aggregate sample) were dried under vacuum at room temperature for 2 additional days. Next,
each sample was epoxy-impregnated, polished down to 0.05µm, and coated with carbon for SEM and EDS analysis.

The images for compositional analysis were obtained using an ESEM FEI, Quanta 200 scanning electron microscope, equipped with energy dispersive spectroscopy detector. The instrument was operated at high vacuum, 15kV, spot size of 6.8µm, and working distance of 12.5mm, specifically during EDS. Internal standards were implemented on AZTec EDS software to allow truly quantitative analysis. Prior to collecting the EDS spectrums from each specimen, at least three electron beam measurements were performed on copper tape for software optimization. Over 50 spectrums were collected from each phase during EDS analysis for representativeness purposes.

2.2.4 Pore Solution Analysis

Pore solution analysis was used to quantify the ionic composition of the pore solution of FA1, FA2, and OPC pastes over time. Pore solution extractions were performed similarly to the method described by Barneyback and Diamond (1981). Pore solutions of sealed pastes were analyzed, rather than pore solutions of concrete, to exclude the effects of alkali leaching and ASR. This allowed a more comprehensive understanding about the consumption of ions reacting with fly ash, which competes with ASR for OH⁻, alkalis, and likely calcium. Refer to Appendix B for more detailed explanation of pore solution analysis.

The pastes were prepared according to the proportions shown in Tables 2.1 and 2.2, with exception of the OPC pastes, where the alkali content was not raised to 1.25%. The non-addition of NaOH pellets to the mixing water of OPC pastes enables understanding of the evolution of ionic species applicable to a broader range of field concrete, which usually has limited amount of alkalis.

A Hobart mixer was used to prepare the pastes according to ASTM C305-14 (ASTM C305-14, 2014). After mixing, the pastes were poured into cylindrical plastic containers, sealed,
and cured in a similar manner as their corresponding concrete in ASTM C1293 test. After the curing period, the sealed paste containers were stored in buckets at 38 °C and 100% relative humidity until the samples reach the age for pore solution extraction.

Over time, the pastes were taken from the storage buckets, cooled down to room temperature, and then broken into small pieces. The crushed paste was placed inside a steel die specially designed for pore solution extraction, placed inside a compression-testing machine and pressurized up to 1,800kN. This process was replicated until sufficient solution was collected for chemical analysis (ICP-AES) and for acid titration to be performed. Before analysis, pore solution was filtered through 0.2µm filter for removal of remaining colloids and then stored at 4 °C until analyzed.

Solution samples were tested using a Perkin-Elmer Optima 5300 ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectroscopy) to determine their composition. For assessment of the nominal pH of each pore solution, acid titration was performed on 10 times diluted pore solution, which allowed replication of the test. In this stage, 0.1M HCl solution was used as the titrant and phenolphthalein as the indicator.

To quantify the variability between multiple batches, three “identical” FA1 mixes were prepared, all maintained at the same conditions, and solution was extracted at exactly the same age (day-180). The pore solution extractions were all performed at the load of 1,350kN. Afterwards, acid titration was performed and the coefficient of variation (COV) was calculated according to Equation 2.1:

\[
COV = 100 \times \frac{St.Dev. of the sample}{Sample mean} \tag{Eq. 2.1}
\]

Pore solution of 1-year-old AAFA concrete prism (i.e. concrete undergoing CPT) was extracted and analyzed similarly to that of the pastes. The purpose was to compare and contrast
the consumption of ionic species by the binder (AAFA paste) and by the concrete induced to ASR.

2.2.5 Mercury Intrusion Porosimetry (MIP)

Micromeritics AutoPore V 9620 MIP device was used to assess the porosity and pore size distribution of AAFA and OPC pastes. The goal was to evaluate whether the mass transport is likely to be slower in AAFA binder compared to OPC, which would help slow down ASR. The pore sizes of FA1 and FA2 pastes were assessed and compared to OPC paste with w/c ratio of 0.45. The pastes were maintained at the same conditions as their corresponding concrete prism until they reach the age of 100 days, when MIP was performed. Before the test, the samples went through a solvent exchange process (isopropanol alcohol bath) for 7 days, which stopped the geopolymerization reaction and allows drying of the specimens with minimal microstructural damage. The specimens were then dried under vacuum at room temperature for 48 hours.

2.3 Results and Discussion

2.3.1 ASTM C 1293 – Concrete Prism Test

Figure 2.1 shows the ASR expansion of the control (OPC) and AAFA concrete prisms over time. The data shows the OPC (control) specimen, exceeded the 0.04% expansion threshold within two months from the beginning of the test and reached approximately 0.20% of expansion within one year. In contrast, FA1 and FA2 expanded no more than 0.01% and 0.018%, respectively, at approximately 450 days of test, in agreement with William and Juenger (2016). FA1 and FA2 expansions correspond to 20 and 11 times smaller than the expansion of the control, and 4 and 2 times smaller than the standard threshold. It should also be noted that the expansion curves of the two AAFA concretes did not show large variations along the test. As FA1 and FA2 expansions
did not exceed 0.04% at day-365 of test, the remaining of this research focused on explaining the causes of ASR mitigation in AAFA concrete.

2.3.2 SEM/EDS

Figure 2.2 show the SEM micrographs of single spratt aggregate before mixing in concrete. Its chemical composition, obtained via EDS, is shown in Table 2.4. It is mostly composed of limestone (CaCO$_3$), shown as lighter grey, which indicates higher density in the backscattered images (Fig. 2.4). The darker, and therefore less dense, areas are SiO$_2$ intermixed within limestone. Traces of aluminum were also found. As can be noted, the coarse aggregate also contains some porosity. No major difference in composition was observed in the porous region in comparison to the non-porous region.
FIGURE 2.2: Backscattered image of spratt showing the natural heterogeneity in composition and porosity of the material.

TABLE 2.4: Compositional analysis of different phases of spratt, OPC, FA1 and FA2 residual aggregates (ratios expressed as weight %). The results were obtained based on 50 or more spots analyzed per each phase.

<table>
<thead>
<tr>
<th></th>
<th>Spratt aggregate (wt%)</th>
<th>ASR gel in OPC (wt%)</th>
<th>FA1 residual agg (wt%)</th>
<th>FA2 residual agg (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca/Si</td>
<td>6.52</td>
<td>0.45</td>
<td>1.34</td>
<td>2.00</td>
</tr>
<tr>
<td>Strd dev</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.14</td>
</tr>
<tr>
<td>Na/Si</td>
<td>-</td>
<td>0.04</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>Strd dev</td>
<td>-</td>
<td>0.03</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>K/Si</td>
<td>-</td>
<td>0.32</td>
<td>0.03</td>
<td>0.36</td>
</tr>
<tr>
<td>Strd dev</td>
<td>-</td>
<td>0.11</td>
<td>0.07</td>
<td>0.10</td>
</tr>
<tr>
<td>Al/Si</td>
<td>0.07</td>
<td>-</td>
<td>0.07</td>
<td>0.44</td>
</tr>
<tr>
<td>Strd dev</td>
<td>0.02</td>
<td>-</td>
<td>0.04</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Figure 2.3-A to C shows the aggregates in OPC concrete undergoing ASR. As expected, the ASR damage in OPC was huge and most of the coarse aggregates showed high level of
degradation. ASR gel was found within cracks (Fig. 2.3-A) and diffused throughout the cementitious matrix (Fig. 2.3-B). The composition of the ASR gel is shown in Table 2.4. It should be highlighted that the OPC concrete was 21 months old when imaged. However, at the age of 12 months the ASR expansion of OPC concrete was already plateauing at 0.2%. This suggests that at the age of 12 months the ASR in OPC concrete was already in advanced stage. Thus, despite the age difference between OPC and AAFA systems, the OPC concrete could serve as positive control for the AAFA concrete, allowing comparison between residual aggregates and ASR gel.

EDS analysis confirmed that all the wide empty areas within aggregates were filled with epoxy, which assure that it happened prior to epoxy impregnation. It is believed that such voids took place during the vacuum drying process, as explained hereafter. The affected areas consists of fragmented aggregates surrounded by ASR gel, as shown in Figure 2.3-C. When in advanced state, a great fraction of the ASR reaction product is moisture, adsorbed from the concrete pores. Once exposed to vacuum drying, the ASR gel looses its moisture and shrinks considerably, allowing the fragments of aggregates to fall off, leaving empty voids.
FIGURE 2.3-A: Highly degraded spratt aggregate in ASR-affected OPC concrete

FIGURE 2.3-B: ASR-gel path throughout cementitious matrix in OPC concrete
Figure 2.3-C: Optical microscope image of ASR damaged aggregate, showing the fragments surrounded by the reaction product

Figure 2.4-A and B show the aggregates in 7 and 12 months old FA1 concrete, respectively. At the age of 7 months (Fig. 2.4-A), most of the aggregates analyzed in FA1 (expansion<0.01%) seemed intact under SEM. At the age of 12 months, the integrity of the reactive aggregates within FA1 continued to be typically preserved, but some cracks were found. Since no ASR gel was found, EDS was used to determine whether any compositional changes had occurred in the residual aggregates. The composition analysis provided by EDS (Table 2.4) of the 12-month-old FA1 aggregates shows that the concentration of alkalis presented by these aggregates remains negligible, similarly to spratt. The mean Al/Si ratio (by weight %), which was found to be 0.07 in spratt, remains constant in the aggregates within 12-month-old FA1 concrete. The mean Ca/Si ratio, however, was lowered to 1.34, compared to that found in unreacted spratt (6.52). The natural heterogeneity of the materials may be an explanation for such a difference, since limestone is widely known to be stable at high pH and unlikely was consumed by a reaction.
FIGURE 2.4-A: Unreacted spratt aggregate in 7-month-old FA1 concrete

FIGURE 2.4-B: Spratt aggregate presenting some cracks in 12-month-old FA1 concrete
Figure 2.5 A to D shows 7- and 12-month-old aggregates within FA2 concrete. Most of the coarse aggregate is well preserved in FA2 (expansion<0.018) at the age of 7 months (Fig. 2.5-A), with few signs of deterioration on the interfacial transition zone (ITZ) (Fig. 2.5-B). At the age of 12 months, a reasonable increase in aggregate deterioration was observed. The degradation pattern was remarked by cracks (Fig. 2.5-C) and by increased porosity (Fig. 2.5-D), the last resembling aggregate dissolution. Compositional analysis of the residual aggregates within FA2 shows significant alteration at the age of 12 months (Table 2.4). The mean Na/Si and K/Si ratio, which was negligible in the spratt sample, was found to be 0.03 and 0.36, respectively, in the 12-month-old FA2. Indeed, these concentrations are very similar to that found in ASR gel in OPC (Na/Si and K/Si of 0.04 and 0.32, respectively). However, the mean Al/Si ratio was found to be 0.44 in FA2 residual aggregate, while it was 0.07 in spratt and negligible in ASR gel. Like in FA1, the calcium concentration was significantly lower in the residual aggregate of FA2. The mean Ca/Si ratio of 2.0 in 12-month-old FA2 aggregate differs significantly from that in spratt (6.52), but it is also way more than that of ASR gel (0.45). As explained before, natural aggregates are highly heterogeneous materials, which could be the reason of such a difference in calcium concentrations. It should be noted that both cracks and dissolution pattern were more concentrated in aggregates with higher concentrations of silica as opposed to in limestone-rich areas.

Despite considerable aggregate deterioration, little ASR was encountered in FA2 concrete as, as shown in Figure 2.5-E. The composition of the ASR gel found in FA2 had a mean Ca/Si ratio of 0.02, while the deleterious ASR gel in OPC had mean Ca/Si ratio of 0.45. This difference in calcium concentrations emphasizes the lack of soluble calcium in FA2 systems to promote the polymerization (i.e. gelation) of silica. In addition, the concentration of alkalis in FA2 ASR gel was found to be negligible.
FIGURE 2.5-A: Well preserved aggregate within 7-month-old FA2 concrete

FIGURE 2.5-B: Aggregate deterioration on the ITZ of 7-month-old FA2 concrete
FIGURE 2.5-C: Cracked aggregate in 12-month-old FA2 concrete

FIGURE 2.5-D: Silica dissolving in aggregate in 12-month-old FA2 concrete subjected to CPT
2.3.3 Pore Solution Analysis

Figures 2.6 A to F shows the composition of AAFA and OPC paste pore solution over time for up to 335 days of hydration. The final concentrations are also shown on each curve. All day-0 concentrations ([OH]', [Na], and [Si]) in FA1 and FA2 were calculated from the activator composition at the time of mixing and before activator came into contact with fly ash. The other elements (Al, Ca, K) did not exist in the pore solution at day-0, as the activator did not supply them. For OPC paste, as pure distilled water was used for mixing, the concentration of all elements and hydroxyl are negligible at day-0. Since the pore solution analysis was performed on pastes, aggregates and ASR effects on pore solution composition are not reflected. It should be noted that a literature search did not find any publications on the pore solution composition of alkali activated fly ash materials and the present study may be the first attempt to characterize this aspect of AAFA.
- **OH concentration:**

In AAFA pastes, although highly alkaline activators are needed to promote fly ash dissolution and geopolymerization, these reactions rapidly consume OH\(^-\) and reduce the pH of AAFA concrete pore solution over time, as shown in Figure 2.6-A. Indeed, fly ash reactions (dissolution and geopolymerization) compete with ASR in consuming OH\(^-\) from the pore solution. And the higher surface area of fly ash (0.5 – 100 µm in diameter (Fytianos et al., 1998)), compared to that of aggregates, provides fly ash with a significant advantage in such competition.

In concrete FA2, after day-90 the [OH\(^-\)]=0.13M is already below a typically assumed minimum threshold to sustain ASR (approximately 0.25M to 0.30M (Kollek and Varma, 1986). In concrete FA1, [OH\(^-\)] dropped significantly with time, plateauing around 0.95M, and then decreasing to 0.58M at day-335. This is however above the [OH\(^-\)] threshold to sustain ASR. But yet, FA1 showed limited aggregate dissolution, which suggests that other factors beyond pH reduction contributed to ASR mitigation in AAFA concretes. An interesting factor is that the pore solution of concrete undergoing CPT has higher concentration of [OH\(^-\)] than paste (Figure 2.7), despite alkali leaching and consumption of OH\(^-\) due to silica dissolution. This fact underlies existence of additional mitigation mechanisms, other than pH drop.

In contrast to AAFA, the [OH\(^-\)] in OPC paste increases with age (Fig. 2.6-A) due to hydration of cement. Later, [OH\(^-\)] is maintained by dissolution of Ca(OH)\(_2\) (Rajabipour et al., 2008; Taylor, 1990) and become highly available to attack ASR vulnerable aggregates.
FIGURE 2.6: Pore solution composition of AAFA pastes sealed and stored at 38 °C and 100% RH:

A) [OH⁺]; B) [Na⁺]; C) [Si⁺]; D) [Al⁺]; E) [Ca⁺]; F) [K⁺]
Figure 2.7: Comparison between OH\textsuperscript{-} concentration in concrete undergoing CPT and corresponding paste

The variation between three FA1 identical batches was determined, through [OH\textsuperscript{-}], as summarized in Table 2.5. It was found a COV of 7.5%. Since the COV is less than 10%, the variability was found to be acceptable. The COV between FA2 batches is assumed similar to that of FA1.

Table 2.5: Variability between three identical FA1 mixes.

<table>
<thead>
<tr>
<th></th>
<th>FA1-1</th>
<th>FA1-2</th>
<th>FA1-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>[OH\textsuperscript{-}] (M)</td>
<td>1.08±0.09</td>
<td>1.25±0.09</td>
<td>1.21±0.09</td>
</tr>
<tr>
<td>Sample mean</td>
<td>1.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>St. Dev. Sample</td>
<td>0.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>COV (%)</td>
<td>7.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- *Al concentration*:

The pore solution concentration of Al could be very significant with respect to ASR mitigation. In both systems, AAFA and OPC, Al originates from the dissolution of the binder. As it can be seen in Figure 2.6-B, for all the three binders the [Al] increases during young ages, likely over 7 days,
especially in FA1 paste. In FA2, the peak is not so striking likely due to a faster rate of geopolymerization. In both AAFA pastes, a decline is observed afterwards due to generation of N-(C)-A-S-H binder products. Unlike AAFA pastes, the [Al] concentration in OPC does not decline over time. Instead, it is observed a slight increase with age (0.05mM at day-90), since aluminum is not a major component of OPC hydration products (i.e., C-S-H and CH).

For paste FA1, the long-term (335 days) [Al] is 6.65mM. Chappex and Scrivener (2012) suggested that [Al]> 3.9mM in the pore solution of concrete is sufficient to significantly decrease aggregate deterioration even at pH around 14. This matches well with ASR expansion results for concrete FA1, as well as with its SEM and EDS results, which shows absence of high degree of aggregate deterioration. In FA2, the Al concentration (0.09mM at day-335) was lower, possibly due to a lower pH, which reduces the solubility of Al in aqueous solutions. Despite having the lowest pH among the three mixes after day-30, FA2 showed higher degree of aggregate deterioration than FA1. In OPC paste, the Al concentration in the pore solution plateaus around 0.03mM up to day-180, likely due the fraction of Al₂O₃ in OPC binder (5.44% by mass).

In fact, in FA1 and FA2, the concentration of aluminum in the pore solution of concrete is lower than in pore solution of paste, as shown in Figure 2.8. The uptake of Al in concrete undergoing CPT may be attributed to the formation of a passivation layer on the surface of dissolved silica in aggregates. This discrepancy between [Al] in pore solution of concrete and paste is more evident in FA1, which has lower degree of aggregate deterioration.
FIGURE 2.8: Comparison between Al concentrations in concrete undergoing CPT and corresponding paste.

- Ca concentration

The concentration of calcium in the pore solution of concrete (Fig. 2.6-C) is also relevant with respect to ASR. In the three systems [Ca] displays a trend similar to that of [Al]: Ca concentration in AAFA pastes spiked at early ages, especially in FA1 paste, due to dissolution of fly ash. In FA1 paste [Ca] exceeds 11mM at day-7, which in fact surpasses the solubility limit of calcium in OPC-based concrete (0.5mM) (Rajabipour et al., 2015). Afterwards, [Ca] in both FA1 and FA2 pastes decreased and plateaued over time to lower values (1.87mM and 0.57mM respectively). As reported by previous studies (Garcia-Lodeiro et al., 2011), in AAFA systems the N-A-S-H gel tends to bind most Ca from the pore solution rather than forming of solid Ca[OH]$_2$.

In contrast to AAFA, in OPC pastes the calcium concentration increases with age due to availability of solid Ca[OH]$_2$. Ca concentration in OPC systems tends to remains near (and in fact slightly above) the Ca[OH]$_2$ solubility limit (0.5mM). The [Ca] higher than 0.5mM should be due to existing of colloidal Ca-based molecules smaller than 0.2µm, which is the size of the filter used prior to pore solution analysis.
Calcium plays a major role in ASR expansion (Thomas, 2011) and rheological properties of ASR gel (Gholizadeh et al., 2016). A comparison between [Ca] in AAFA paste and concrete undergoing CPT, which is shown in Figure 2.9, suggested a higher uptake of Ca from pore solution of concrete, likely as an attempt to polymerize the dissolved Si. It might be the case that limited amount of soluble Ca (i.e. portlandite) impede higher degree of Si gelation to form an expansive ASR gel. This is clearly evidenced in FA2, which has higher degree of aggregate dissolution, but little ASR gel (Fig. 2.5-E).

![Figure 2.9: Comparison between calcium concentrations in concrete undergoing CPT and corresponding paste](image)

- **Si concentration:**

Si was a major constituent of fly ash and of the activator solution in AAFA systems. Its immediate availability at the time of mixing (i.e., activator supply) plays an essential role in the strength development of AAFA binders (Kazemian et al., 2015). As it can be noted in Figure 2.6-D, the Si concentration in FA2 pore solution, which had the highest modulus (n=0.76), decreased rapidly due to geopolymerization. At day-30, a great amount of the silica had already been consumed, even though fly ash has contributed by releasing more Si to the system. At day-335, only 15mM was left in the pore solution of FA2. On the other hand, the intake of Si in FA1 paste
(n=0.21) took place in a slower fashion, as at day-225 still 487mM was left in the pore solution, followed by an increase to 776mM at day-335. These consumption trends of Si in FA1 and FA2 consistently agree with their strength development (32.9 MPa and 41.0 MPa at day-28, respectively), as reported by Kazemian and coworkers.

As opposed to the two AAFA binders, OPC does not require any extra source of silicon to achieve the desirable strength. As such, the Si in OPC pore solution remains continuously low over time, compared to AAFA systems, achieving a maximum of 0.35mM at day-90.

Recent researches (Belkowitz et al., 2014; Said et al., 2012) reported the ability of colloidal silica in mitigating ASR in OPC-based concrete blended with fly ash. This ability was attributed to the high surface area of the colloidal silica, among other factors. Additionally, it is of common sense that Si in high pH binds [OH\textsuperscript{-}], and in absence of a large supply of soluble calcium Si will remain dissolved in the aqueous solution in the form of SiO\textsubscript{2}(OH)\textsuperscript{2-} (Rajabipour et al., 2015; Leemann et al., 2011). This way, aggregates are more preserved from dissolution as the pore solution approaches to Si solubility limit (Iler, 1985). The ranked Si concentrations of the three systems (776mM, 15mM, and 0.42mM in FA1, FA2 and OPC, respectively) are inversely related to their level of aggregate deterioration. In other words, the more dissolved Si within the pore solution, the milder is the aggregate dissolution. Therefore, the presence of dissolved Si might contributing to ASR mitigation in the two AAFA systems studied in this research.

- **Alkalis concentration:**

The concentration of alkalis in the two AAFA paste pore solutions (Fig. 2.6-E and 2.6-F) showed a declining trend with age, due to fly ash geopolymerization reactions. The formation of N-A-S-H as the main geopolymerization product consumes and binds most of the alkalis from the pore solution. At day-225, yet a high concentration of Na and K can be found in the pore solution of the two AAFA mixes. Williamson and Juenger (2016) also reported a substantial consumption of alkalis in the pore solution of mortar cubes containing reactive aggregate. However, the
respective amounts of alkalis consumed by reaction with fly ash, reaction with silica in aggregates (i.e. ASR), and alkali leaching were not quantified.

In OPC, on the other hand, the alkalis concentration displays an ascending trend, especially the K concentration, which agrees with past research (Diamond, 1983; Lothenbach et al., 2007). Even though the alkali concentration in pore solution of OPC increases with age, its Na$_2$O$_{eq}$ is still lower that found in the pore solution of the AAFA pastes. It suggests that alone, high alkali content in the pore solution is not sufficient to promote deleterious ASR expansions. It should be noted that the alkali content in the pore solution of concrete undergoing ASTM C1293 should be lower than that of sealed pastes, due to alkali leaching.

2.3.4 Mercury Intrusion Porosimetry (MIP)

Figure 2.10 show the pore size distribution of the two AAFA and OPC pastes at age of 100 days. The average pore diameter, critical pore diameter (i.e., steepest point of each curve), threshold pore diameter (i.e., where significant intrusion starts to occur), and the total porosity of each paste were determined and are summarized in Table 5. The threshold diameter is considered to be the widest diameter of interconnected pores that would allow percolation of fluids in a paste (Aligizan, 2006).

Differently from what was expected, the lower (L/S)$_{binder}$ of AAFA (0.80 by volume) did not lead to lower pore sizes, nor to lower total porosity compared to that of OPC (volumetric (L/S)$_{binder}$=1.42). This could be related to the well-defined round shape of AAFA pores (Fig. 2.4 and 2.5), which may ease the percolation of moisture within the cementitious matrix compared to the amorphous and tortuous pores of OPC. It should be noted that, between the two AAFA pastes, FA2 presents the lowest total porosity and smallest pore sizes. This is consistent to the fact that having a larger supply of Si from the activator, AAFA is likely to have lower porosity and smaller pores sizes, as well as higher compressive strength.
Figure 2.10: Pore size distribution of 100 days old AAFA and OPC pastes

Table 2.6: Pore characteristics of AAFA and OPC pastes

<table>
<thead>
<tr>
<th></th>
<th>Critical pore diameter (nm)</th>
<th>Threshold diameter (nm)</th>
<th>Average pore diameter (nm)</th>
<th>Total Porosity (% Vol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA1</td>
<td>678.6</td>
<td>929.2</td>
<td>35.9</td>
<td>26.1</td>
</tr>
<tr>
<td>FA2</td>
<td>111.0</td>
<td>204.2</td>
<td>13.5</td>
<td>22.3</td>
</tr>
<tr>
<td>OPC</td>
<td>21.7</td>
<td>40.2</td>
<td>12.7</td>
<td>23.1</td>
</tr>
</tbody>
</table>

2.4 Conclusions

- Despite containing a highly reactive coarse aggregate and initially high alkalinity, the expansion of the two AAFA concretes studied in this research did not exceed 0.04% threshold of the concrete prism test (ASTM C 1293) passed one year from the beginning of the experiment. Additionally, small length variation was observed in FA1 and FA2.

- One important contributor to ASR mitigation in AAFA concretes is the rapid decline of pore solution alkalinity over time as a result of reactions with fly ash. Results showed that, despite having lower [OH⁻] than FA1 concrete (0.64M at day-365), FA2 concrete
(0.31M at day-365) yet suffered more from aggregate deterioration. This suggests that other factors beyond [OH⁻] drop mitigate ASR in AAFA.

- Dissolved Al is potentially one major contributor against ASR in the FA1 concrete. Despite the high [OH⁻] in FA1 mixture at later ages (0.95M at day-225), its less-deteriorated aggregates are coherent to the Al concentration provided by the pore solution of paste, which is kept at or above 3.9mM up to day-335.

- As expected, low Ca concentration in AAFA is likely a major contributor in mitigating ASR in FA2 concrete. Despite considerable aggregate deterioration, limited amount of soluble calcium in the system prevents the gelation of silica, as such, prevents the formation of an expansive ASR gel.

- Due to the consistency of the results of aggregate dissolution versus Si concentration in FA1 and FA2, it is likely that the high concentration of dissolved silica within the pore solution decreases the rate of aggregate dissolution.

- In comparison to OPC paste, AAFA pastes had similar or larger porosity, as well as similar average pore size, despite their significantly lower ASR activity. This rules out the hypothesis that ASR is mitigated in AAFA concrete because of its low mass transport kinetics (e.g., permeability).

2.5 References


Appendix A – Background information about fly ash

Fly ash is a siliceous or siliceous-aluminous material that is derived from coal combustion. The material is composed primarily of small glassy spheres within the size range of 0.5 – 100 µm in diameter (Fytianos et al., 1998). The variability in fly ash properties results from variations in the composition of coal, combustion conditions, and collection method (Bilodeau et al., 1994; ACI 232.2R). Class C fly ash is defined as high calcium-content, and class F fly ash as low calcium-content (ASTM C618-12a, 2010), being the latest the focus this research.

It is a common practice in concrete industry to partially replace OPC by fly ash. Among other advantages, fly ash positively contributes to the durability of concrete, including resistance to ASR, chloride penetration, and water permeability (Bilodeau et al., 1994). Class F fly ashes also has the ability of consuming most of the portlandite (Ca(OH)$_2$) from the concrete matrix (Mindess et al., 2003), which could serve as pH buffer in OPC concretes. This is also known as pozzolanic effect, where dissolved portlandite is consumed by the silicate phases of fly ash to form C-S-H. Shafaatian and coworkers (2013) reported that fly ash reduces the penetration (i.e. diffusivity) of Na$^+$, lowering the ASR activity.

References


Appendix B – Acid Titration and ICP-AES Sample Preparation

Protocol

The purpose of this section is to explicitly show how pore solutions were handled before ICP-AES, as well as how it was analyzed through acid titration. This section may clarify the steps taken during pore solution analysis, which is essential for replication of the experiments.

General considerations

How much pore solution did I get?

- **5ml or more**: This is often the case for fresh paste, mortar, and concrete. Use a 10ml vial to use in the air extractor device (Figure 1).

- **5ml or less**: This is often the case when extracting pore solution from hardened paste, mortar, or concrete. Use a 5 ml vial in the high-pressure device (Figure 2).

![Figure 1: A) air extractor device and B) 10ml vial](image-url)
Filtering:

Immediately after extracting pore solution, all samples need to be filtered through 0.20µm or 0.45µm filter. The filtering set up is shown in Figure 3.

This step is to eliminate the remaining solid particles and colloidal molecules, which could spoil the pH measurement, as well as the concentration of all elements of interest. It is recommended that you discard the first two drops when filtering and store the remaining solution.
Acid Titration Protocol

Nice tutorial on how to perform titration at:

www.youtube.com/watch?v=sFpFCPTDv2w (part 1/2) (search for “titration – By Carolina Biological” on YouTube. Just don’t get confused by the fact this video uses alkaline solution as titrant (with known molarity) and an acid as analyte (molarity to be determined)).

Terminology:

• **Titrant**: diluted acid with known molarity,

• **Analyte**: concrete pore solution (unknown molarity),

• **pH indicator**: phenolphthalein.

![FIGURE 4: Phenolphthalein](image)

**Working with pipettors:**

Pipettors are the most accurate way to deal with small volumes of solutions. To work with pipettors, you should follow the steps:
a) Choose the pipettor that covers the volume range that you need;

b) Use the disposable pipet tip suitable for the pipettor that you will work with;

c) By spinning around the top of the pipettor, set the volume needed from the liquid sample (Fig. 5);

d) Before placing the pipette tip within the vial with the liquid sample, gently push down the top of the pipettor (do not force it to a second stage);

e) Place the pipet tip within the vial and release the top of the pipettor. Make sure you do not have air bubbles coming into the pipette tip to avoid inaccuracy of volume measurement;

f) To release the solution into another vial, push the top of the pipettor down and this time, you need to force it to a second stage. This second stage applies higher pressure, which will guarantee that no leftovers will be trapped in the pipet tip.

g) The pipet tips are disposable. To eject, push down the side button, as shown in Figure 5. Get another pipet tip every time you begin work with a different solution.

FIGURE 5: Pipettor set up
Preparing 0.1M of HCl solution:

To prepare your diluted HCl solution, use HCl 37%, which has 12M concentration and pH of 0 (Figure 6). Use pipettor to measure the volume of acid and a balance to weight the mass of DI water (Figure 6).

The proportions to get 0.1M HCl are 2.1ml of HCl to 250.9 g of DI water. This will give you about 250ml of 0.1M HCl solution. Keeping the given proportion, you can always multiply both numbers by a factor to have a greater volume of 0.1M HCl solution when necessary.

It is recommended to prepare fresh diluted HCL solution for every day of titration and not storing the leftover for more than a week. So to avoid wasting materials, prepare the amount of diluted acid that you think is sufficient for titrating the amount of samples you have. Discard the leftover HCl solution according to the safety procedures in an appropriate container within the cabinet that is located below the water tank in the chem lab.

FIGURE 6: Carboy containing DI water.
FIGURE 7: Two different HCl 37% (12M) bottles.

Cleaning the burette:

Before initiate acid titration, fill up the burete with 0.1M HCl solution (titrant), open the cock, and allow the titrant to flow through the burette into an empty container to clean up the tube. Discard properly all the HCl used in this step. Then, fill up the burete again and record initial volume of titrant.

Diluting pore solution:

10x dilution: for each 1ml of pore solution, add 9ml of DI water. 10 ml is the minimum amount of analyte to perform titration. Place the diluted pore solution in a clean beaker and titrate immediately.

Titrating:

By adding two drops of phenolphthalein to your diluted pore solution within the beaker, the color will turn into dark pink. Place and turn on the magnetic stirrer under the beaker, that will continuing mix the phases during the titration. Then slightly spin the stopcock and allow the acid to flow slowly until you notice that the solution is turning into a lighter pink.

Depending on the alkalinity of the analyte, it can take a while for the pink color begins to change into lighter pink. This color-changing process (Figure 7) is very sensitive and indicates a
pH range between 10 and 8.3. Keep adding acid little by little (drop by drop!) and stop adding acid as soon as you notice that your solution is completely clear, which means pH equals to 8.3. Remember that a single drop makes all the difference.

Record the final volume of titrant in the burette and subtract the initial volume to calculate how much acid was needed to neutralize the analyte.

![Figure 8: Color changing during acid titration.](image)

To calculate the molarity of your pore solution (or analyte) you need to treat it as simply NaOH solution and apply the formula:

\[ C_{\text{HCl}} \times V_{\text{HCl}} = C_{\text{PS}} \times V_{\text{PS}} \]

where \( C_{\text{HCL}} \) is the concentration of your diluted HCl solution (molarity of 0.1M), \( V_{\text{HCl}} \) is the volume of your HCl solution (the final minus the initial volume of HCl in the burette), and \( V_{\text{PS}} \) is the volume of pore solution (suggested as 10 ml in this protocol). This calculation will give you the concentration of your pore solution (\( C_{\text{PS}} \)).
Remember that you need to multiply the found $C_{ps}$ by 10, since it was diluted 10 times.

The final $C_{ps}$ number corresponds to the $OH^-$ concentration of the sample.

To calculate the nominal pH apply the formula:

$$pH = 14 + \log[OH^-]$$

**ICP-AES Protocol**

After you have filtered your sample, it is needed to dilute your sample in two different manners before sending to ICP-AES analysis. Both samples need to be of 5 ml. The two dilution processes are explained below:

a) **10x dilution in 2% HNO$_3$ solution**: 0.5ml of pore solution + 4.5ml of 2%HNO$_3$ solution.

   To prepare 2% (by volume) HNO$_3$ solution, add 2ml of nitric acid (Figure 9) in 98ml (98g) of DI water. This will give you nearly 100ml of diluted HNO$_3$ solution.

b) **10x dilution in DI water**: 0.5ml of pore solution + 4.5ml of DI water.

The dilution of high pH solutions is necessary to maintain as much as possible the integrity of the ionic species until the samples are analyzed through ICP. The higher the pH of a solution, the more reactive and susceptible to carbonation it is. The dilution in 2% HNO$_3$ solution is works great, except for the fact that silica precipitates in acid. As such, it is needed to prepare two samples.
Multiply by 10 the ICP results, reported as µg/ml (or ppm), for both dilution methods, since the sample was 10 times diluted. The results of the two samples should be very close to each other, except the Si concentrations. For this element, choose the results from the analysis done in that sample diluted with DI water.

_Proper storage of pore solution:_

You have to make sure that you are using a vial compatible to the amount of pore solution you have got. Make sure you use a 5ml vial to store 5ml of sample to avoid carbonation. Do not store solutions in vials that have a volumetric capacity much larger that the amount of solution you have (Figure 10-A) to avoid carbonation. Carbonation lowers the pH of alkaline solutions and this negatively impact pH measurements and ICP results. Ideally, your pore solution should fill in all the volume of the vial without leaving any room for air (Figure 10-B). Store all the samples in the refrigerator that is located across the 60 and 80 ºC ovens. When refrigerated, any chemical reaction in the sample will considerably slow down.
FIGURE 10: Storing solutions. A) bad storage and B) proper storage.

All the containers also need to be properly labeled. The best way to do so is covering the label with a transparent tape (Figure 11). It avoids that the information contained in the label is washed away. Make sure that you include your name, date and sample ID in the label. You are also encouraged to use a rack (Figure 12) if you have multiple samples. Labels and tapes can be found in the chemistry lab.

FIGURE 11: A) labeling with a transparent tape and
FIGURE 12: Rack with multiple samples.

Precautions:

- When preparing acid solutions, always add acid in water and never add water in an acid container.
- Never place flammable solutions (i.e. phenolphthalein) close to acid containers.
- Always store solution (concentrated or diluted) protected from light in a suitable cabinet and shell.
- All samples and solutions must be labeled and it must contain name, date and product ID.
- Discard properly acids and bases leftovers. There are labeled containers in the cabinet under the distilled water tank in the chemistry lab. If you do not find one suitable for disposing your type of solution, use an empty container and label it.
- Wash and rinse well all the glassware used in your experiments.
Appendix C – Library of SEM images

- Spratt Aggregate:
• 21-month-old OPC-based concrete subjected to the concrete prism test (ASTM C1293), showing high degree of aggregate deterioration and ASR gel formation:
- Rosette-like ASR gel found in 21-month-old OPC concrete subjected to CPT:
- Aggregate in 7-month-old FA1 concrete subjected to the concrete prism test (ASTM C1293):
• Aggregate in 12-month-old FA1 concrete subjected to the concrete prism test (ASTM C1293):
• Aggregate in 7-month-old FA2 concrete subjected to the concrete prism test (ASTM C1293):
Early signs of aggregate deterioration in 7-month-old FA2 concrete:
• Aggregate in 12-month-old FA2 concrete subjected to the concrete prism test (ASTM C1293):