1 **The role of activating solution concentration on alkali-silica reaction in** 2 **alkali-activated fly ash concrete**

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8 **Abstract**

9 To enable commercial use of alkali-activated fly ash concrete, its durability must be better
10 understood. Alkali-silica reaction is a primary concern since highly alkaline solutions are
11 generally used for activation. This study investigated the effect of NaOH activating solution
12 concentration on pore solution alkalinity and subsequent alkali-silica reaction in alkali-
13 activated fly ash concrete. It was found that pore solution alkalinity increased with increasing
14 activating solution NaOH concentration, and this effect was amplified at concentrations
15 above an optimum, defined as the concentration that resulted in the highest mortar
16 compressive strength. Expansion of concrete prisms containing highly reactive fine aggregate
17 and activating solution concentrations above the optimum concentration were approximately
18 three times that of concrete with optimum activating solution concentrations, but only about
19 5% of the expansion observed in the ordinary portland cement control. The low expansion
20 may be attributed to the low calcium levels in the alkali-activated fly ash concrete.

21
22 **Keywords:** *Geopolymers, Alkali-Activated Cement (D), Alkali-Aggregate Reaction (C),*
23 *Durability (C), Pore Solution (B)*

1 Introduction

Alkali-activated fly ash (AAFA) is a class of materials with cementitious properties synthesized by the activation of the aluminosilicate phases in fly ash by a highly alkaline aqueous solution [1]. The general process of fly ash alkali-activation involves dissolution of the initial solid particles by alkaline hydrolysis followed by condensation, reorganization, and polymerization of the hydrolyzed silicate and aluminate species [2]. AAFA is becoming an attractive alternative concrete binder because the solids are comprised entirely of industrial byproducts, in contrast to ordinary portland cement (OPC), which is extremely energy and carbon intensive to produce. A lack of understanding of durability is one of the key factors limiting the use of AAFA concrete [3,4]. Alkali-silica reaction (ASR) is one of the primary durability issues in OPC concrete and occurs when the hydroxyl ions in concrete pore solution attack reactive silica in aggregates [5]. Since AAFA uses alkaline solutions for activation, it is possible that these solutions could trigger ASR if AAFA is used with reactive aggregate.

Material factors unique to AAFA may influence the extent of ASR in these systems. It is well established, for example, that the compressive strength of AAFA is dependent on curing temperature, the activating solution concentration [6], and fly ash material properties. For a given fly ash, compressive strength generally increases with curing temperature and

activating solution concentration, but only to a point, beyond which there is often little or no strength gain and sometimes a loss in strength. This is thought to occur because once the dissolution and reaction product formation are maximized, any remaining alkalis are unused [6,7]. If this is this case, there may be potential for these unused alkalis to react with the silica of reactive aggregate and lead to detrimental expansion [8].

Previous tests for ASR in AAFA concrete reported in the literature [8–10] studied mixtures designed with activating solution concentrations aimed at maximizing compressive strength, but the potential effect of varying activating solution concentrations on the parameters relevant to ASR has not yet been investigated. The study presented here strived to quantify the relationship between initial activating solution concentration and resulting AAFA pore solution alkalinity in hardened specimens and to determine whether increasing the activating solution concentration above an “optimum” for strength results in high residual pore solution alkalis. Finally, the study endeavored to determine whether there is potential for high pore solution alkalinity to lead to expansive ASR in AAFA concrete.

ASR testing of AAFA reported in the literature [8–10] has relied on ASTM C1260 [11], the accelerated mortar bar test (AMBT), which was designed to measure the ASR susceptibility of a given aggregate in OPC mortars by submerging the samples in a 1M NaOH solution. Since the source of alkalis in

the AMBT is external to the mortar, the availability of alkalis to react with siliceous aggregate and cause expansion is dependent on the transport of these alkalis through the material's pore network [12]. The rate and mechanisms of alkali transport are different in AAFA compared to OPC since the pore structure and connectivity differ [13], therefore the AMBT time-dependent expansion limits for OPC mortars may not be directly applicable to AAFA mortars. Further, in AAFA, the source of internal alkalis is very high (from the activating solution), with, in fact, a higher initial concentration than the storage solution used in the AMBT, putting into question the applicability of this test. ASTM C1293 [14], the concrete prism test (CPT), does not rely on the transport of external alkalis and may be a more appropriate test for AAFA. Additionally, the CPT more closely represents actual field conditions since temperatures are closer to ambient temperatures and specimens aren't submerged in sodium hydroxide solution [15].

In this study, compressive strength was first measured for mortar cubes prepared using activating solutions of varying concentrations to determine the "optimum" concentration for maximum strength. Pore solution was then extracted from the broken specimens and analyzed for alkali content to determine whether the mortar prepared with a more concentrated activating solution had higher pore solution alkalinity. Next, AAFA concrete prisms were prepared for the CPT using the optimum activating solution concentration (i.e. concentration that produced the highest mortar compressive

strength), and with activating solutions at above optimum concentrations, to investigate whether a higher pore solution hydroxyl ion concentration in the latter could lead to ASR expansion.

2 Experimental

2.1 Materials

2.1.1 Mortar Cubes

Fly ash with bulk CaO content of 14.14% from Texas, USA was used in this study. The chemical composition of the fly ash was determined by x-ray florescence and is shown in Table 1. Alumina and silica constitute 18.43% and 48.36%, respectively, of the fly ash by mass, giving a $\text{SiO}_2/\text{Al}_2\text{O}_3$ mass ratio of 2.6. Aughenbaugh et al. [16] previously described this fly ash (labeled BBR) as a highly reactive source for AAFA (based on AAFA compressive strength) compared with seven other fly ashes examined. For the activating solution, 50 wt% sodium hydroxide was diluted with Milli-Q water to the desired activating solution concentrations. The fine aggregate was reactive chert aggregate from El Paso, Texas in saturated surface-dry condition. This aggregate was used previously by Ideker et al. [15] (labeled F1), where it showed severe expansion in the CPT.

2.1.2 Concrete Prisms

For AAFA concrete prisms, the fly ash, activating solution, and fine aggregate were the same as for the mortar cubes. Type I portland cement with an $\text{Na}_2\text{O}_{\text{equiv}}$ of 0.76% (increased to 1.25% using a NaOH solution) was used in the control OPC concrete prisms. Both the AAFA and OPC concrete prisms used non-reactive crushed limestone from San Antonio, Texas, USA as the coarse aggregate.

2.2 Methods

2.2.1 Mortar Compressive Strength

Alkali-activated fly ash mortar cubes were prepared and tested for compressive strength using a modified procedure based on the requirements of ASTM C109 [17]. Mortar cubes measuring 50 mm x 50 mm x 50 mm were prepared using 4M, 6M, 7M, 8M, 9M, 10M, and 11M NaOH activating solutions with the following mixture proportions (per six mortar cubes): 500 g fly ash, 1375 g sand, 176 mL NaOH activating solution. The volume of activating solution was held constant for all concentrations to minimize changes in workability between activating solution concentrations and to preserve the direct relationship between solution concentration and total NaOH in the mixture. The mixing procedure was in accordance with the

requirements in ASTM C305 [18], the only exception being that fly ash was substituted for cement and activating solution was substituted for mixing water. Six mortar cubes were cast for each mixture; three were tested at 7 days and three at 28 days. The average of the three compressive strengths is reported for each activating solution concentration.

The compression specimen curing regime consisted of storage at 60°C for the first 24 hours after casting followed by storage at 38°C until the time of the compression tests, which were performed at 7 days and 28 days. This curing scheme was based on a study by Hardjito et al. [19], which concluded that curing at elevated temperatures for the first 24 hours substantially increased polymerization but that increasing the temperature above 60°C had little effect on compressive strength. The 38°C temperature was chosen to parallel the conditions of the CPT so that the rate of reaction of the mortar cubes would be similar to that in the CPT concrete prisms. To prevent moisture loss, the specimens were stored over water in sealed plastic containers for the first 24 hours and subsequently stored in sealed, plastic bags until the 28-day strength tests.

2.2.2 Pore solution Chemistry

Pore solution was extracted and its Na⁺ and K⁺ concentrations measured for a selection of the broken mortar compression specimens. The pore solution

extraction followed the method described by Barneyback et al. [20] using the device described by Giannini [21]. The mortar fragments were stored in sealed, plastic freezer bags and frozen at -20°C from the time of compression testing until pore solution extraction to prevent further polymerization from occurring. After removal from the freezer, the mortar samples were crushed and a representative sample was placed inside the pressure chamber. A pressure of approximately 900 MPa was then applied to the samples to express the pore solution. After extraction, pore solution samples were stored in sealed polypropylene vials at room temperature until Na^+ and K^+ concentrations were determined using a Cole-Parmer model 2655-10 flame photometer. Prior to testing, the samples were diluted to between 1:2,000 and 3:10,000 so that the Na^+ and K^+ concentrations would fall within flame photometry detection limits. For each concentration analyzed, only one pore solution sample was extracted and examined due to the difficulty and danger associated with high-pressure extraction.

2.2.3 Concrete Prism Test

AAFA concrete prisms measuring 76 x 76 x 280 mm were prepared following a modified procedure based on the requirements of ASTM C1293 [14]. Prisms were prepared using 8M and 10M NaOH activating solution with the proportions specified in ASTM C1293, with the only exception being that fly ash was substituted for cement and activating solution was substituted for

186 mixing water. The volume of 8M NaOH solution required to obtain a ratio of
187 activating solution to fly ash powder (s/p ratio) of 0.45, by weight, was
188 determined and this volume of NaOH solution was used in both the 8M and
189 10M NaOH concrete mixtures (i.e. the volume of NaOH solution was fixed
190 between mixtures rather than fixing the s/p ratio). While alkali-activators
191 often contain dissolved silicates to control AAFA composition, only NaOH
192 activators were considered in this study for simplicity. After casting, the
193 specimens were immediately stored over water in sealed plastic containers and
194 placed in a 60°C oven for 24 hours. After 24 hours of heat curing, the AAFA
195 concrete prisms were de-molded and stored over water in a sealed 23 L bucket
196 with absorbent material covering the sides in a room kept at 38°C as specified
197 in ASTM C1293. Expansion measurements were taken at 7, 28, and 56 days
198 as well as at 3, 6, 9, 12, 18, and 24 months. For the AAFA CPT, two replicate
199 mixtures of four prisms each were made for each mixture.

200
201 For comparison, OPC concrete prisms were prepared following the
202 requirements of ASTM C1293. The alkali content of the OPC was increased
203 to 1.25 %Na₂O_{equiv} by adding 50 wt% NaOH solution to the mixing water.
204 The prisms were covered with wet burlap immediately after mixing and stored
205 at room temperature for the first 24 hours. Following 24 hours of curing, the
206 prisms were de-molded and stored at 38°C over water in a sealed 23 L bucket
207 with absorbent material covering the sides. Expansion measurements were
208 taken at 7, 28, and 56 days as well as at 3, 6, 9, 12, 18, and 24 months. For the

OPC CPT, three prisms were cast and measured and the average of the three expansion readings is reported.

2.2.4 Scanning Electron Microscopy

Backscatter scanning electron microscopy (SEM) analysis was carried out on samples taken from the 8M and 10M CPT concrete prisms. Samples were removed from the prisms immediately after the 24-month expansion measurements were conducted. A 75 x 25 x 25 mm section was cut from the center of one each of the 8M and 10M concrete prisms using a masonry saw. A section measuring 25 x 25 x 6 mm was then removed from the center of the larger section with a precision sectioning saw with using isopropanol as a lubricant, and the specimens were dried under vacuum for at least 72 hours, then epoxy mounted under vacuum.

To achieve a microscopically flat surface, samples were progressively ground with silicon carbide paper (#180, #600, #1200) and then polished using a polishing wheel rotating at 100 rpm with diamond paste polishing compound (6 μm , 3 μm , 1 μm , $\frac{1}{4}$ μm fineness, Ted Pella, Redding, CA) applied to a dry twill polishing cloth that was secured to the rotating wheel. Isopropanol was used as a lubricant during polishing and specimens were cleaned with isopropanol between each stage of polishing and grinding. A light microscope

was used to ensure that sufficient smoothness was achieved before progressing to the next stage.

Finally, the samples were gold-coated to prevent charging, and imaging was conducted using an FEI Quanta 650 SEM operating at 20.0 kV with a backscatter electron detector. One section was cut and examined from one 8M AAFA prism and one section was cut and examined from one 10M AAFA prism.

3 Results

3.1 Mortar Compressive Strength

Average compressive strengths of the three mortar cubes prepared for each activating solution concentration are shown in Figure 1. The compressive strength of the 9M NaOH AAFA mortar was not measured at 28 days because all three specimens were damaged upon removal from the mold due to insufficient form oil applied to the mold. The error bars show the range of the measured compressive strength data. The mortar prepared with 8M NaOH showed the highest strength at both 7 and 28 days while an increase in NaOH concentration above 8M showed a decrease in compressive strength. This decrease in compressive strength above an intermediate activator concentration is consistent with findings of Abdullah et al. [6] and Mustafa Al

Bakri et al. [22]; both of these studies showed lower strengths with activator concentrations above 12M. The difference in peak concentrations of 8M and 12M between studies can be attributed the difference in source materials and mixture proportions.

The increase in compressive strength observed as activating solution concentration increases has previously been attributed to more rapid dissolution of fly ash glassy phases at high pH and to the fact that a certain amount of sodium is required to charge balance aluminum tetrahedra [2,7,22,23]. The decrease in strength at higher activator concentrations has been previously attributed to the viscous nature of more concentrated solutions, which limits leaching of silica and alumina, and to the formation of sodium carbonate by the reaction of excess sodium with atmospheric CO₂ [7,22,24]. No obvious difference in efflorescence was observed on the surface of samples prepared with different activator concentrations, which, if present, would indicate sodium carbonate precipitation. The theories regarding mechanisms of strength loss at high activator content were not tested in the work presented here, but the associated effects on pore solution composition are relevant to the present study and are discussed in detail next.

3.2 Pore Solution Chemistry

The alkali concentrations of pore solution extracted from the AAFA mortar cubes (after compression tests, stored at -20°C in sealed plastic bags from time of compression testing until pore water extraction) prepared with equal volumes of 6M, 8M, and 10M NaOH activating solution are shown in Table 2. The concentration of sodium consumed (or leached) over the first 7 days is also shown and was calculated by subtracting the 7-day pore solution sodium concentration from the initial activating solution sodium concentration. Here, the initial activating solution sodium concentrations were assumed based on the extent of dilution of the 50 wt% NaOH solution.

Pore solution sodium concentrations increased with activator concentration and ranged from 1,550 to 2,190 mmol/L. Roughly 75% of the initial sodium was consumed after 7 days in each mortar. It is noted that the sodium concentration likely continued to decrease after 7 days due to further consumption and/or leaching, but this could not be verified since no pore solution could be extracted from older specimens. If it were feasible, longer term pore solution monitoring would be useful to elucidate the extent to which the alkali content continues to decrease. Although sodium was the dominant alkali cation since the NaOH activating solution was the primary alkali source, minor levels of K^+ were detected and originated from fly ash, which contained a small amount of K_2O (Table 1).

Of particular interest is the amplified effect of increasing activating solution concentration from 8M to 10M NaOH when compared to increasing activating solution concentration from 6M to 8M. The pore solution sodium concentration rose 170 mmol/L (11.0%) with an increase in activating solution concentration from 6M to 8M compared to a 470 mmol/L (27.3%) increase in pore solution sodium concentration between 8M and 10M activating solution. Therefore, the effect of increasing pore solution with activating solution concentration appears to be magnified at concentrations above optimum.

As described earlier, the AMBT has been the primary test used to study ASR in AAFA previously. In the AMBT, mortar bars are submerged in 1M NaOH and expansion is measured over a period of 14 days. The test relies on the high hydroxyl ion concentration (as well as elevated temperature) in the bath to accelerate expansion to obtain results in the short duration of the test. It is therefore relevant to point out that the pore solution alkalinity measured at 7-days in the AAFA mortars of this study ranged from about 1.5 to 2.2 times to amount specified for the AMBT, meaning that submerging the mortar bars in 1M NaOH will not increase pore solution alkalinity and therefore is not an effective means of accelerating expansion.

As previously mentioned, pore solution was only extracted from one sample for each activator concentration. The possibility for experimental or

measurement error exists, and while the magnitude of these errors is uncertain, the sample to sample error is estimated to be less than 14% based on work by Cyr et al. [25]. This error estimate implies that the 27% difference between sodium concentrations in the pore solutions of mortars activated with 8M and 10M is statistically significant. While the 11% difference between sodium concentrations in pore water extracted from the 6M and 8M is less than the estimated error, the data do suggest the likelihood of an increasing trend in pore solution sodium as activator concentration increases. The observation of a stronger effect of activator solution above an optimum concentration is not statistically significant based on the estimated error, but again, the possibility of this trend exists. These trends should be scrutinized further in future work.

3.3 *Concrete Prism Test*

Average expansions from the concrete prism test (CPT) for the AAFA concrete and OPC concrete are shown in Figure 2 (a). Figure 2 (b) shows expansion results for both AAFA concretes in more detail, with error bars showing the range of data for measurements taken at 3 months and beyond. Dashed lines represent the ASTM C1293 limit for acceptable expansion at one year of 0.04%. For the AAFA specimens, the average expansion of all prisms from both replicate mixes is shown, and for the OPC mixes the average expansion of all prisms from the single mix is shown. The OPC concrete

prisms expanded substantially, nearly reaching the one-year expansion limit in 28 days and expanding to ten times the expansion limit in 6 months. The observed severe expansion was expected, as similar expansion was observed previously with the same aggregate [15]. The AAFA concrete prisms prepared with 8M NaOH, conversely, showed no signs of expansion in the first 12 months and only 0.006% expansion after 24 months. The AAFA concrete prisms made with 10M NaOH expanded an average of 0.02% at 24 months, or half the ASTM C1293 expansion limit and approximately 5% of the expansion measured in the OPC concrete after 24 months. As mentioned previously, silicate activators were not tested in this study, but is expected that adding silica to the activator would not impact the expansion levels since the chert aggregate used in this study already contribute significant levels of soluble silica.

3.4 Scanning Electron Microscopy

Backscatter electron micrographs of samples removed from the 8M CPT prisms after two years are shown in Figures 3 and 4. The 10M prisms were also observed using backscatter SEM, but no noticeable differences were observed between the 8M and 10M samples. From Figure 3b, one can observe that the reactive fine aggregate is deteriorated from the outside to a depth of roughly 15 μm . Similar deterioration was observed in some other aggregates, but the majority of aggregates did not show obvious signs of deterioration. A

small gap is visible around the outside of the aggregate, and an epoxy-filled crack extends away from the aggregate. Similar gaps were observed around the aggregates throughout the sections that were analyzed. Epoxy is present in these gaps, suggesting that they were not initially filled with ASR gel that was subsequently removed during polishing. It is likely that these cracks formed as a result of shrinkage during vacuum desiccation. In Figure 4, there is a brighter area immediately surrounding a crack protruding from the aggregate, indicating a difference in composition in this area; however, no difference in composition could be identified between the regions of different brightness using SEM-EDS. This same brightness is observable surrounding the aggregate itself, suggesting that a substance is either dissolving away from the aggregate and migrating through the crack or migrating from the paste toward the crack. However, after careful observation of SEM-EDS spectra, no discernable difference was detected in the composition in these regions, and no obvious ASR gel was located by SEM imaging.

4 Discussion

Increasing the NaOH activating solution concentration from 6M to 8M (below “optimum” to “optimum”) resulted in an 11.0% increase in pore solution alkalis, while increasing NaOH concentration from 8M to 10M (“optimum” to above “optimum”) resulted in a 27.3% increase in pore solution alkalis. Thus, increasing the activating solution concentration does increase the pore

solution alkalinity. Furthermore, this effect is greater in the range of concentrations above an optimum point defined as the concentration that leads to AAFA with the highest strength. The primary role of hydroxyl ions in the AAFA activating solution is to promote the liberation of silicates and aluminates, while the alkali cations balance the negative charges of the tetrahedral alumina and become an integral part of the alkali aluminosilicate gel that constitutes the final binder [2,26,27]. Presumably, additional alkalis beyond what are required for complete polymerization of the available aluminates and silicates end up in the pore solution [27] where they are charge-balanced by hydroxyl ions.

A certain minimum pore solution pH is required in order for aggregates to be attacked to a degree that will cause significant ASR expansion [28,29], and a range of minimum pore solution hydroxyl ion concentrations has been suggested for ASR to occur in OPC concrete. Duchesne et al. [30] established a minimum value for pore solution hydroxyl ion concentration of 650 mmol/L, while others have suggested values between 200 and 300 mmol/L [31,32]. In the current study, the pore solution alkali contents of the AAFA prepared with 8M NaOH and 10M NaOH were 1745 and 2224 mmol/L (Table 2), respectively; these values are roughly three to four times higher than the upper value of the previously suggested expansion thresholds for OPC concrete.

Despite the high pore solution alkali contents, essentially no expansion was observed in the optimum (i.e., 8M) activator concentration concrete prisms, and very little expansion (about half of the ASTM C1293 one-year limit) was observed in the 10M activator concentration concrete prisms. While the results are consistent with previous studies [8–10] that found little if any expansion in AAFA prepared with “optimum” NaOH concentrations, those studies relied on the AMBT that relies on an exterior source of alkalis. Additionally, pore solution composition was not examined in those studies to verify that pore solution alkalinity was at levels high enough to cause expansion in OPC concrete. Furthermore, those studies relied on submerging mortar samples in 1M NaOH to accelerate ASR, but the current study found that pore solution alkali contents were greater than 1M after 7 days (Table 2). Submerging mortar with pore solution alkali concentrations above 1M in 1M NaOH would dilute the alkali concentration rather than accelerate the test. Because the CPT does not rely on external alkalis, measures expansion over two years, and uses larger test specimens with closer to ambient temperatures, it is a more appropriate test compared to the AMBT that has been used predominantly to evaluate AAFA concrete [8–10]. The long-term resistance to ASR observed in the current study despite the presence of high pore solution alkalinity and very reactive fine aggregate is an important step in our understanding of AAFA durability.

435 Interestingly, an increased expansion was observed in the AAFA concrete
436 prepared with 10M NaOH compared to that prepared with 8M NaOH. The
437 total pore solution alkali concentration of the 10M NaOH mortar was
438 significantly higher than that of the 8M NaOH mortar at just over 2200
439 mmol/L in the former, compared to about 1750 mmol/L in the latter. It
440 appears that the higher level of pore solution alkalis in the 10M NaOH
441 concrete was enough to cause expansion, albeit still less after one year than
442 half the limit allowed by ASTM C1293. For this particular fly ash, then, the
443 ASR expansion of AAFA concrete made with highly reactive aggregate
444 depends on the pore solution alkali concentration, which is a function of
445 activating solution concentration.

446
447 A discussion of the small expansion levels despite the high pore solution
448 alkalis and aggregate in the concrete of this study is warranted and contributes
449 not only to the conversation about AAFA durability, but also to the general
450 understanding of ASR as it applies to OPC concrete. The relative absence of
451 calcium is perhaps the most likely reason that no substantial expansion was
452 observed. Calcium plays an important role in the expansion of alkali-silica gel
453 in OPC concrete [28,33] and the scarcity of calcium in AAFA concrete has
454 been cited previously as the primary reason for its resistance to ASR [8–
455 10,34,35]. The calcium content of the fly ash studied here, 14.14%, is low
456 compared to OPC (typically around 65% calcium), whose composition is

dominated by calcium silicates, but moderate in comparison to some other fly ashes which can have up to 30% calcium.

Calcium can affect ASR expansion by either (1) freeing up alkalis and associated OH^- ions from the ASR gel through a process called “alkali recycling”, whereby calcium ions in solution exchange with alkalis in the ASR gel, or (2) modifying the chemical and physical properties of the gel itself [28]. Indeed, it has also been suggested that without calcium, no gel is formed at all, and any dissolved silica remains in solution [36]. Alkali recycling is more likely to play a significant role if alkali concentration is a limiting factor, i.e. in a concrete with pore solution in the range of 200-300 mmol/L as discussed earlier. In AAFA concrete, there is a no shortage of alkalis, so it is more plausible that calcium’s direct impact on the gel’s properties is the controlling factor here. One possibility is that a low-viscosity, more fluid gel was formed, which is known to occur in the presence of low calcium levels [35]. This less viscous gel could more easily disperse through the pore structure of the AAFA, thus alleviating internal stresses that would otherwise lead to expansion. This possibility is supported by the backscatter SEM images presented in Section 3.4, where, despite the resemblance of the cracking pattern to typical ASR cracking patterns, no gel was observed. It is thus plausible that sufficient ASR gel formed to cause cracking, but dispersed before substantial cracking was observed.

In addition to the shortage of calcium, a reduction in pore solution alkali content after 7 days could have contributed to the small levels of expansion. As noted previously, the very high pore solution alkali concentrations reported were measured after 7 days. During this period, alkali concentrations of the 8M activating solution mortar dropped from 8000 mmol/L (the initial activating solution concentration) to roughly 2000 mmol/L. The drop in concentration is attributed primarily to incorporation into the aluminosilicate gel (charge balancing aluminum tetrahedra), and may have been furthered by alkali leaching. The decrease in alkalis was likely partially offset by the dissolution of fly ash alkalis, although the relative amount would have been minor for this fly ash. As time progressed past 7 days, it is reasonable to assume that alkali levels would continue to drop over the two years during which expansion measurements were carried out, with leaching being the dominant driver after the binder is mature. Thus, the alkali concentrations measured at 7 days are not necessarily indicative of the concentrations at the time of the two-year expansion measurements and the decrease in pore solution alkalinity after 7 days could have contributed to the lack of expansion observed from the later measurements.

A pessimum effect has been observed in OPC systems for fast reacting aggregates such as chert (the aggregate used in this study), where ASR-induced expansion increases with reactive aggregate dosage only to a point, above which little or no expansion occurs [5]. The pessimum effect has been

attributed to the fact that there is an optimum $\text{SiO}_2/\text{Na}_2\text{O}$ ratio where maximum dissolved silica exists in solution [5,37]. Dent Glasser & Kataoka [37] attributed this maximum in dissolved silica to the fact that higher $\text{SiO}_2/\text{Na}_2\text{O}$ ratios, Si-OH groups at the surface of the reactive silica react with the OH^- in solution to form Si-O^- groups, reducing the solution pH as OH^- is consumed. The result is a decrease in silica solubility, since silica solubility increases rapidly with pH [38]. At low $\text{SiO}_2/\text{Na}_2\text{O}$ ratios, dissolved silica concentrations may not reach the solubility limit [37], so any dissolved silica would remain in solution rather than form expansive gel. In the present study, sodium concentrations were so high, that exceeding the pessimum $\text{SiO}_2/\text{Na}_2\text{O}$ level is unlikely. It is possible, however, that the silica solubility limit was so high due to the highly alkaline conditions, that insufficient silica from the aggregate was dissolved to precipitate ASR gel (i.e. the $\text{SiO}_2/\text{Na}_2\text{O}$ ratio was below the pessimum level.

5 Conclusions

This study suggests that AAFA concrete shows promising performance with regards to ASR compared to OPC concrete. The pore solution analysis confirms that despite high pore solution alkali concentration, it is possible to create AAFA concrete with highly reactive aggregate that is resistant to ASR-induced expansion. Specific findings of this study are summarized as follows:

1. For the fly ash tested in this study, an optimum compressive strength was achieved by activation with an 8M sodium hydroxide solution; higher activating solutions led to a decrease in strength.

2. Increasing activating solution concentrations were correlated with higher pore solution alkali content; this effect was magnified for activating solution concentrations beyond “optimum” (i.e. concentrations higher than 8M).

3. Expansion for both concretes fell well below the ASTM C1293 limit; slightly more expansion was observed in the CPT for prisms prepared with activating solution concentration “higher than optimum” (and thus having even higher concentrations of pore-water alkalis).

4. The AMBT test used predominantly in previous research to study ASR in AAFA is not an appropriate test for AAFA because it depends on external alkalis to accelerate the attack; furthermore, the concentration of the external alkalis specified in the AMBT is lower than the pore solution alkali concentrations measured in the current study.

5. Cracking patterns resembled those of ASR affected OPC concrete, but no gel was observed using SEM. This could be because of insufficient calcium in the system. It is possible that a low-viscosity gel formed and dispersed

through the pore structure and did not cause internal stresses sufficient to drive substantial expansion.

While this study is in agreement with other studies that found little to no ASR-induced expansion in AAFA, there is still insufficient data to make a blanket statement that AAFA concrete is not susceptible to deleterious ASR. The chemical and physical properties of AAFA synthesized with a wide range of source materials with numerous curing regimes vary greatly. Until a better understanding of the nature of ASR in AAFA systems is achieved, caution is advised in using reactive aggregate in AAFA without first testing a given set of source materials and curing conditions. Moreover, more realistic and longer-term tests, such as the concrete prism test, should be used in lieu of the accelerated mortar bar test.

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Figure Captions

Figure 1. AAFA Compressive Strength vs. Activating Solution Concentration (for mortar).

Figure 2. Concrete Prism ASR Expansion for (a) OPC, 8M AAFA, 10M AAFA and (b) 8M, 10M AAFA with a reduced y-axis.

Figure 3. Backscatter electron micrographs of deteriorating reactive fine aggregate particle in specimen removed from 2-year 8M AAFA concrete prism sample.

Figure 4. Backscatter electron micrograph showing representative cracking in specimen removed from 2-year 8M AAFA concrete prism sample.

Table 1. Chemical composition of fly ash (% of mass).

Al₂O₃	SiO₂	CaO	Fe₂O₃	K₂O	MgO	Na₂O	SO₃	TiO₂
18.43	48.36	14.14	7.97	1.14	2.16	0.64	0.40	1.18

Table 2. Pore solution chemistry of 7-day AAFA mortar cubes (values are in mmol/L).

Activator	Initial			Na⁺
Concentration	Na⁺	Na⁺	K⁺	Consumed
6 M	6,000	1,550	20.5	4,450
8 M	8,000	1,720	25.6	6,280
10 M	10,000	2,190	34.1	7,810

Figure 1

Figure 2a

Figure 2b

Figure 3a

Figure 3b

Figure 4