Investigation of ASR Reactivity through Slurry Dissolution Tests

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Abstract
The Alkali silica reaction (ASR) is investigated through the dissolution and determination of the concentration of elemental species, Na, K, Ca and Si in the supernatant fluid of GP cement, aggregate and fly ash slurries. The aggregates selected for investigation were a reactive greywacke and a non-reactive micro-diorite both of which contain quartz. Alkali ions were primarily delivered to solution by the cement, although lower concentrations were released by both aggregates and fly ash which may be of concern in the delayed deleterious ASR. Silica was released in to solution according to aggregate reactivity. Rapid local release of silica can yield an expansive ASR gel for reactive aggregates. Fly ash was also observed to release silica rapidly indicating that the primary action of the fly ash is through a competitive reaction for the formation of silica gel thus mitigating deleterious ASR. Quartz content as determined by x-ray diffraction analysis indicated that this phase was the source of solution silica for the reactive aggregate.

Keywords: ASR, silica and alkali dissolution, mitigation, reactive and non-reactive aggregate, fly ash

Introduction
The alkali silica reaction (ASR) is a potentially deleterious reaction between hydroxide ions and reactive silica present in aggregates [1]. The reaction results in the dissolution of reactive silica followed by solution polymerisation and subsequently precipitation of an expansive silica gel (the ASR gel) which has the potential to cause cracking in concrete [2]. The process is a two-step process where the first step necessitates the formation of the ASR gel through chemical means followed by a second step in the mechanism where the ASR gel acts on the concrete resulting in cracking if the hydrostatic stresses are great enough [2-3].

The reaction is accelerated by elevated pore solution pH and is associated with the dissolution of alkali ions into the pore solution [4]. As alkali content (sodium oxide equivalent, Na_2O_e) influences the pH of the mortar or concrete pore solution promoting the potential for ASR, many standards attempt to mitigate the risk of ASR in construction materials by limiting alkali content [c.f. 5]. Cement is the primary source of the alkali ions in the pore solution; however, there is concern that aggregates as well as supplementary cementitious materials (SCMs) also contribute alkali ions to the pore solution [6-8]. Alternative sources of alkalis have an impact on ASR as they have the potential to replenish the pore solution with alkali ions as the silica gel is formed (a process which depletes the solution of alkali ions [2]) thus maintaining pH and rate of reaction.

ASR is initiated by the dissolution of reactive silica at elevated pH [1]. The solubility of silica increases significantly above pH 10 [9]. As the pore water pH is usually in excess of this pH, reactive silicas present will release silica to the pore solution, but the rate of release is dependent on the pH and thus at lower pH the rate is reduced and a corresponding reduction in the rate of formation of ASR gel occurs. This phenomenon is observed in the expansion of mortar and concrete specimens in accelerated tests where reduction in alkali content in the presence of reactive aggregates results in a reduction in the observed expansion in the test [8]. As the alkali-silica reaction is ongoing even at reduced pH, the reduction in observed expansion is likely to be due to a combination of the reduction of the rate of release of silica and the properties of the ASR gel produced [2]. Reactivity of the silica is important in initiating the process, however deleterious ASR does not occur until the ASR gel physically acts on the mortar or concrete matrix. Mitigation of ASR can therefore be carried out by inhibiting the formation of the ASR gel or by inhibiting its action on the concrete matrix.

Table 1. XRF analysis of the materials used in slurry tests.

Oxide wt.%	GP Cement	Micro-diorite	Greywacke	Fly ash
SiO2	19.66	62.29	66.85	62.71
TiO2	0.26	0.92	0.65	1.00
Al2O3	5.11	15.55	14.24	24.98
Fe2O3	3.04	5.26	3.8	2.72
Mn3O4	0.07	0.11	0.09	0.08
MgO	1.14	1.82	1.58	0.49
CaO	62.78	4.05	1.94	2.25
Na2O	0.24	4.81	4.25	0.87
K2O	0.43	2.43	3.11	1.49
P2O5	0.12	0.21	0.14	0.23
SO3	2.68	0.04	0.19	0.13

SCMs such as fly ash (FA) are known to mitigate deleterious ASR [11]. The mechanism of mitigation is associated with the reduction in pore water pH through the removal of alkali ions from the pore solution [10]. The mechanism of mitigation is through a similar reaction to ASR where the dissolution of the reactive silica occurs followed by polymerisation and precipitation of a silica gel which incorporates alkali ions thus reducing the pore water concentration. The reaction is a competitive reaction and therefore SCMs should rapidly release silica to the pore water solution.

As the mechanism of ASR is a two-step process of chemical reaction followed by the mechanical action of the gel on the concrete, the first step in investigating the role of alkali in the reaction is to follow the dissolution of the species involved in the reaction. This paper investigates the dissolution of the reaction species; Ca, Si, Na and K ions, through concentration measurement in slurries containing cement and aggregates of known reactivity as assessed by AS-1141.60.1 and 2 [12-13]. As supplementary cementitious materials, in particular, FA are known to mitigate ASR, FA is also investigated.

Materials and Methods

Materials:

GP Cement, aggregates micro-diorite (M) and greywacke (G) and low calcium fly ash (FA) were supplied by Cement, Concrete and Aggregates Australia (CCAA). Oxide composition (wt%) are listed in Table 1. The aggregates M and G have been classified according to AS1141.60.1 (AMBT) [12] as: slowly reactive (M) and reactive (G), and according to AS1141.60.2 (CPT) [13]: non-reactive (M) and reactive (G). The as-received aggregates were ground in a RockLab ring grinder for 5 min and stored in resealable plastic bags in a desiccator until required. The GP cement, fly ash and slag were used as received.

MP-AES

Slurry tests were carried out by mixing 1.00 ± 0.01 g of test material in HDPE centrifuge tubes with 10 mL of water or 1.0 M of sodium hydroxide. The tubes were sealed and shaken and then placed in an 80°C oven for 7, 14, 21 and 28 days. The supernatant fluids were extracted and filtered prior to dilution with 1% nitric acid. Microwave plasma atomic emission spectroscopy (MP-AES) was used to determine the elemental compositions of the supernatant liquid.

X-ray Diffraction (XRD):

Samples of Aggregates M and G (1g) were place in HDPE tubes and shaken with 10 mL of 0.6, 0.8, 1.0 and 1.25 M NaOH before placing in an 80°C oven for 28 days. The solids were recovered by filtration, dried, ground and stored in a vacuum oven at 50°C until required for XRD analysis. XRD data was collected using a Bruker Discovery D8 XRD using Cu Kα radiation in the range 5° to 75° with a step increment of 0.04 °2θ. Phase identification was carried out using the International Centre for Diffraction Data (ICDD) ICDD Products - PDF-4+ database.
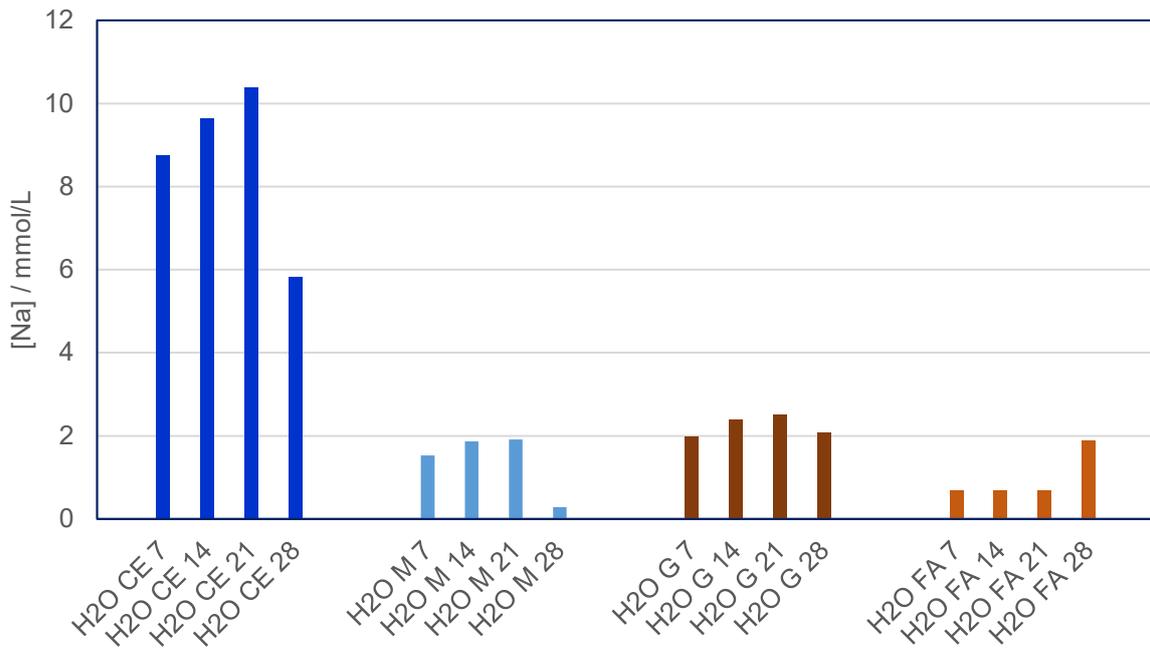
Figure 1 Sodium concentrations in the supernatant fluid at 7, 14, 21 and 28 days for GP cement, aggregates M and G and SCMs FA and slag in ultrapure water.
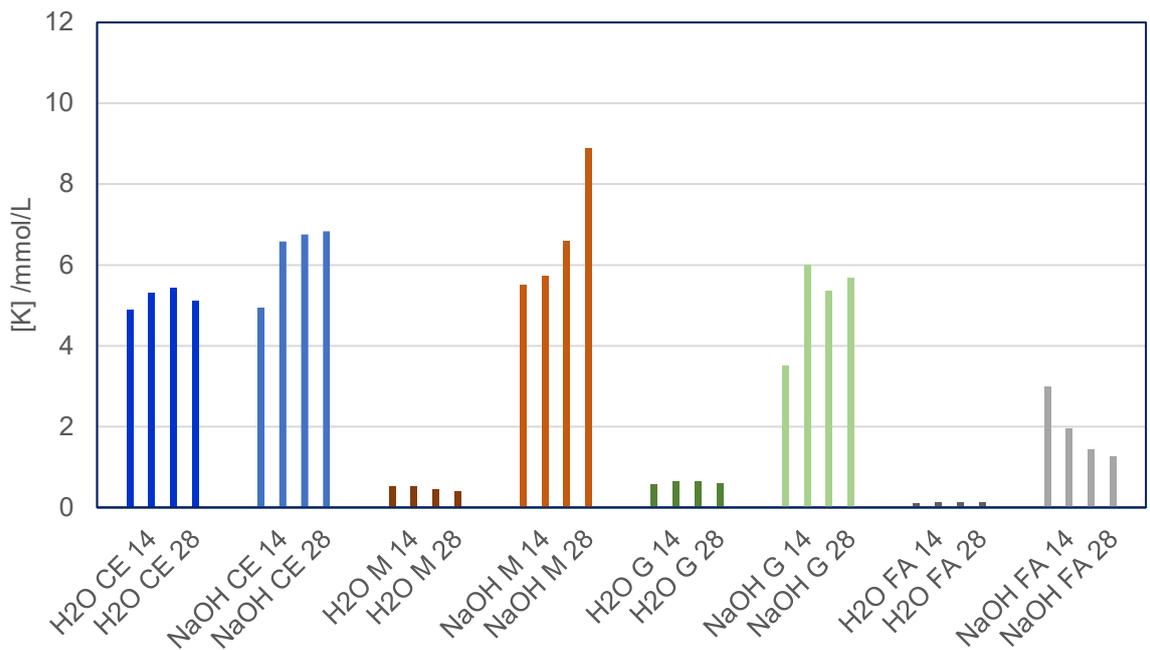

Figure 2 Potassium concentrations in the supernatant fluid at 7, 14, 21 and 28 days for GP cement, aggregates M and G and SCMs FA and slag in ultrapure water and 1 M NaOH.

Results and Discussion

Elemental concentrations for the supernatant fluid for the cement, Aggregates M and G and FA are shown in Figures 1 to 4. The sodium concentrations are shown in Figure 1. As the alkali used to elevate the pH was NaOH, the sodium concentration for dissolution is shown for only the ultrapure water dissolution test. Significant concentrations of sodium are released by the cement. For the Aggregates M and G and FA, although sodium ions are observed in solution, the concentrations observed are significantly lower. The concentration of sodium ions observed is indicative that the primary source of alkali ions on hydration is the cement [4].
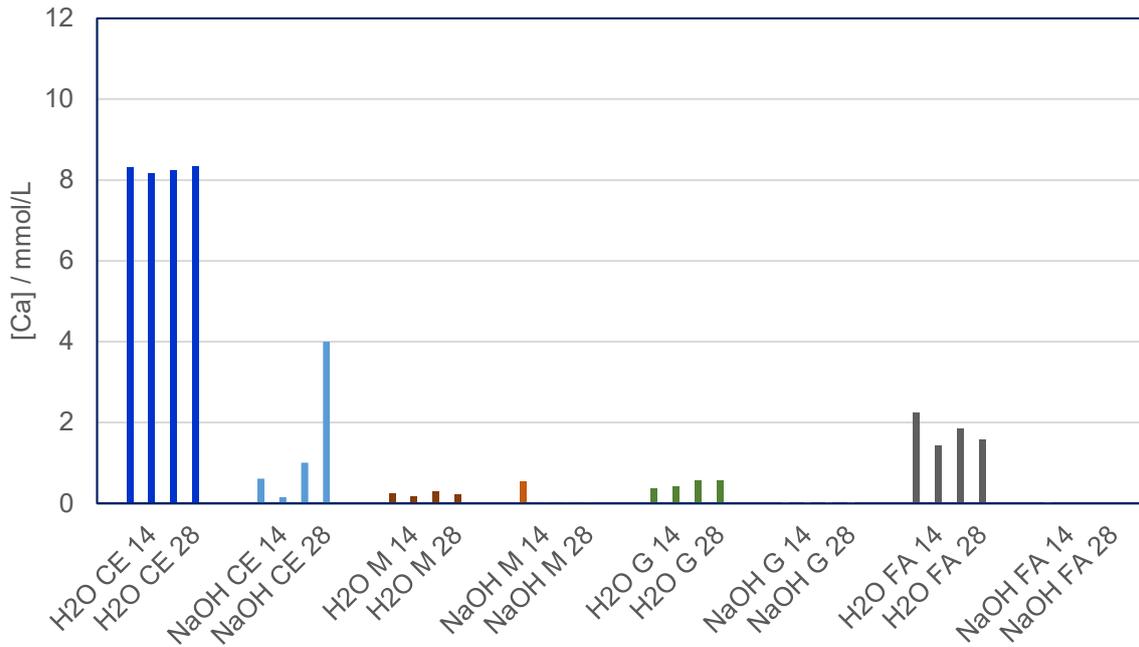
Figure 3 Calcium ion concentrations in the supernatant fluid at 7, 14, 21 and 28 days for GP cement, aggregates M and G and SCMs FA and slag in ultrapure water and 1 M NaOH.
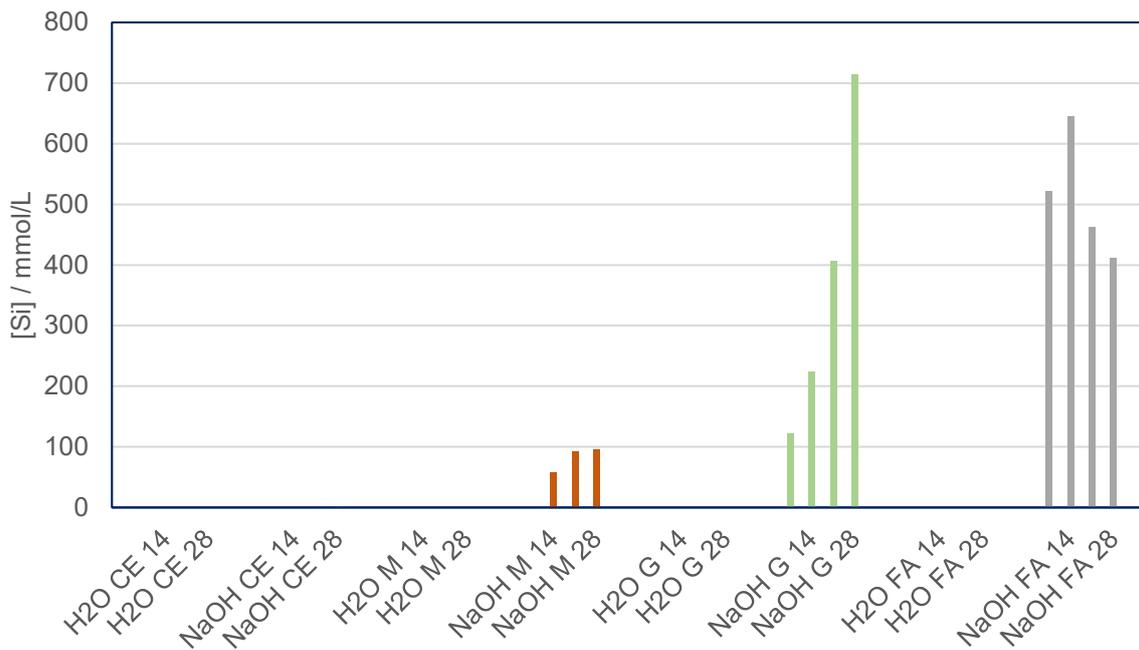

Figure 4 Silicon concentrations in the supernatant fluid at 7, 14, 21 and 28 days for GP cement, aggregates M and G and SCMs FA and slag in ultrapure water and 1 M NaOH.

Potassium ion concentrations in the supernatant fluid are shown in Figure 2. For ultrapure water, potassium is only observed in significant concentrations for the cement slurry indicating that cement is again the primary source of dissolved alkalis which is consistent with the sodium ion concentration data. In NaOH solution, potassium ions are released by both aggregates and to a lesser extent by FA indicating that at higher pH aggregates as well as supplementary cementitious materials may be an additional source of alkali ions in solution. There is concern that aggregates and SCMs may contribute to the pore solution alkali content increasing the potential risk of ASR [6-8]. The elevated potassium ion concentrations for elevated pH dissolution suggest that this may be an issue where release of alkali ions from the aggregate or SCM may replenish the alkali ion concentration in the pore solution as the solution is depleted by the formation of the ASR gel which contains alkali as well as calcium ions.

The calcium dissolution data is shown in Figure 3. The dissolution of calcium ions to the solution is only expected in significant quantities for cement as the aggregates and FA are relatively low in CaO content (Table 1). The calcium ion concentration in the NaOH solution is significantly depressed as is expected as the solubility of calcium ions decreases significantly with increasing pH [14].

The silicon solution concentrations are shown in Figure 4. These data show that there is little dissolution of silica in ultrapure water. Amorphous silica has a solubility of circa 10^{-3} mmol/L at pH 7 and therefore strained quartz or even more reactive silica phases would not be expected to release silica to the solution at neutral pH [9]. The solubility of silica in alkaline media rises with pH and significant silicon solution concentrations are observed for G and FA and to a much lesser extent M in 1 M NaOH solutions. G is a reactive aggregate (based on AMBT and CPT expansion tests) and is expected to release silica to the solution especially at 80°C. The fact that M does not release significant concentrations of silicon to the solution is consistent with its classification as slowly reactive in the AMBT (note it is classified as non-reactive by CPT).

The FA is also observed to rapidly release significant concentrations of silicon to the solution with concentrations at similar levels to G. This release of silica is important in ASR mitigation. From the context of the concrete pore solution, the rapid release of silicon species to the solution from the FA provides solution silica for precipitation throughout the binder matrix. This precipitation is a competing reaction to the deleterious ASR reaction associated with aggregate silica dissolution. The processes are similar in that reactive aggregate releases silicon to the solution in a similar manner to FA and the elevated concentration of silicon in solution results polymerisation of the silica and ultimately precipitation of a silica gel, however, for the reactive aggregate this precipitation process is a localised process where the silica gel can accumulate and expand to exert hydrostatic stresses which may cause cracking of the concrete. The silica gel precipitated by the dissolution of silica from the FA on the other hand is widely dispersed and no localised accumulation of silica gel occurs and hence any silica gel produced is likely to be non-deleterious.

Both aggregates M and G contain silica in the form of quartz. The reactivity of the quartz in these silicas can be easily differentiated by following the relative intensities of the (101) diffraction peak at 26.64°2θ (Cu K_α). Figure 5 shows the normalised (101) peak intensity as a function of NaOH concentration. Increasing the pH increases the reactivity of the medium and increased quartz dissolution is observed. The relative degree of dissolution corresponds with the reactivity of the aggregates. Aggregate G is categorised as reactive and correspondingly, the quartz content is observed to decrease significantly. The CPT non-reactive Aggregate M shows little change even at elevated NaOH concentrations and despite the elevated temperature (80°) in which the reaction has occurred.

Summary and Conclusions

Deleterious ASR is a two-step process: (i) dissolution and precipitation of reactive silica in the alkaline pore water solution to form the expansive silica gel and (ii) the physical action of the gel on the concrete matrix resulting in cracking. In this study the initial stage (dissolution) of the first step has been investigated through the determination of the solution concentrations of slurries of cement, a CPT non-reactive aggregate (M), a CPT reactive aggregate (G) and a SCM (FA).

In alkaline conditions, both aggregates and to a lesser extent the FA release alkali into the solution. The release of alkali is some cause for concern as there is a potential for ASR associated with the raised pH as pH is a function of alkali solution concentration in the cement pore water. Corresponding with the reactivity of the aggregates, the release of quartz to the solution was significantly greater for the reactive aggregate. The observation of some dissolution for the CPT non-reactive aggregate M is consistent with its categorisation as slowly reactive in the AMBT as these tests were carried out at 80°C in 1 M NaOH.

The high concentrations of silica released into solution by the FA in alkaline conditions indicates that FA has significant reactivity. The reactivity of FA is consistent with its potential for mitigating ASR. The mitigation is not just in its reactivity, but through the manner in which FA reacts in the formation of a competitive silica gel. FA in blended cement is finely divided and is therefore dispersed through the cement matrix. Any silica gel produced will therefore be also distributed throughout the matrix reducing the potential of this silica gel to accumulate and hence cause deleterious cracking. In contrast, the ASR
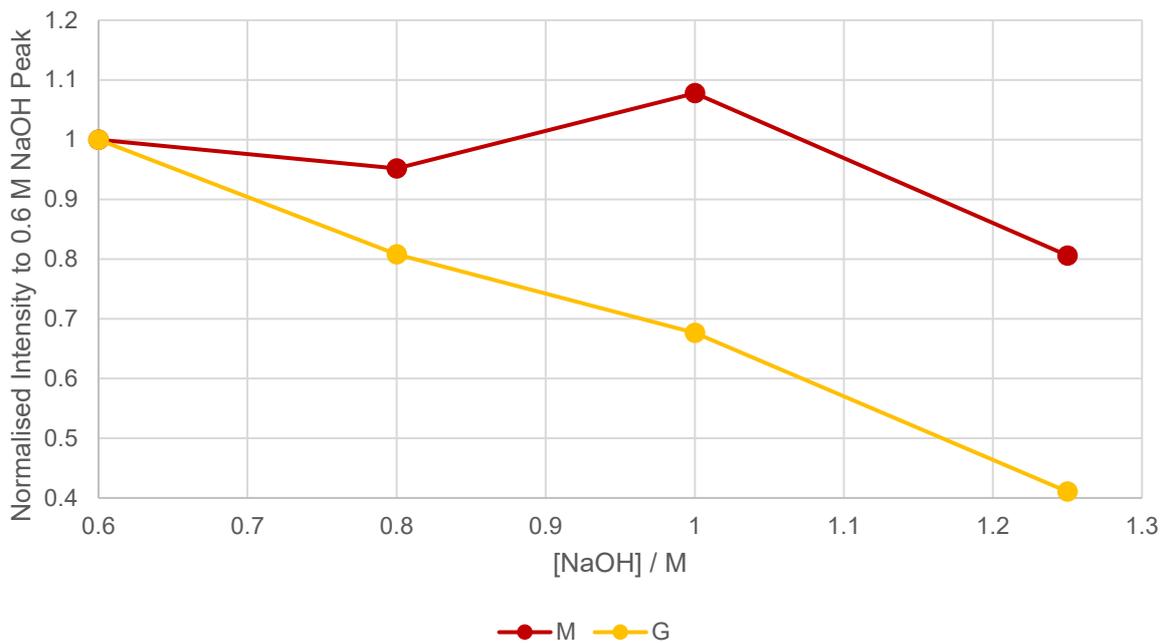
Figure 5 XRD data of the quartz (101) peak normalised to the intensity of the 0.6 M NaOH solution specimen.

gel produced by the dissolution of aggregate silica is localised and has the potential to accumulate leading a potential for cracking through the second step of the two-step process where expansive stresses are transferred to the concrete resulting in cracking.

The elemental solution concentrations determined in this study are indicative of the chemical part of the mechanism for ASR. The high concentrations of silica for the FA suggest that FA provides silica to the pore solution in a competing reaction in the presence of reactive aggregates in ASR mitigation. The necessary realisation that deleterious ASR is not just a chemical process, however, provides an approach to mitigation that can be attained based on the inhibition of the mechanical action of the ASR gel through the control of the chemical part of the deleterious ASR mechanism. Further investigation into the role of the reactants and their action will be part of future investigation into the overall mechanism and potential solutions for deleterious ASR mitigation.

Acknowledgements

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