The ASR mechanism of reactive aggregates in concrete and its mitigation by fly ash: A critical review

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Abstract

Alkali-silica reaction (ASR) of reactive aggregates is a major durability concern of concrete. The use of fly ash as a supplementary cementing material (SCM) shows a reliable way to control ASR expansion. This paper investigates the recent findings on effects of coal fly ash as a SCM on ASR of reactive aggregates. ASR is the reaction of amorphous silica of aggregates with highly alkaline pore solution in the binder matrix producing an expansive gel. The use of fly ash as cement replacement reduces pH of the pore solution by alkali binding and thus reduces the aggregate dissolution rate and swelling pressure of the ASR gel. The efficiency of fly ash primarily depends on its chemical composition with low calcium fly ash being more effective in mitigation of ASR expansion. Based on the available literature, this paper also analyses the ASR mitigation mechanisms of fly ash and provides some recommendations for future research. The degree of aggregate reactivity measurement, effect of alumina in fly ash, swelling properties of ASR gel in presence of fly ash and the long-term alkali contribution of fly ash on ASR are of particular importance.

Keywords: Aggregate dissolution, alkali binding, alkali-silica reaction, fly ash, pore solution, reactive aggregates.

1. Introduction

Concrete is the most widely used construction material in the world. There are various reasons behind the popularity of concrete as the first choice of building material, such as durability, low relative cost, low maintenance and high fire resistance. However, exposure to an aggressive environmental condition for an extended period of time can cause deterioration of concrete. The lifespan of concrete can be reduced by various factors, such as reinforcement corrosion, alkali-silica reaction (ASR), carbonation and leaching. Among all the concrete damage mechanisms, ASR is one of the severe durability related issues for concrete that may cause extensive damage to concrete structures. Repair works of structures affected by ASR can be very complicated, expensive and time-consuming. In 1940, Stanton [1] pointed out that concrete can suffer deleterious expansion due to the use of reactive aggregates. The author further observed the effectiveness of using pozzolans as partial replacement of cement to reduce ASR [2]. Since then, researchers reported about ASR expansion in concrete structures

in different parts of the world. In 1980, Cole et al. [3] found dams in Australia suffering from deleterious cracking due to a similar phenomenon. Ono [4] noticed concrete structures in Japan showing significant cracking due to deleterious expansion by ASR. Swamy [5] reported the failure of airfield pavements in New Zealand due to ASR expansions. Recently, structural damages due to ASR have been identified in Seabrook nuclear power in the USA [6] and Mactaquac Dam in Canada [7]. Though the fundamental concept of ASR in structural concrete has been known to the scientific community for a few decades, there are still cases of modern structures suffering from severe damage due to this deleterious expansion which proves the complexity of ASR mechanism.

There are several factors that influence this mechanism significantly. Silica is present in amorphous form in reactive aggregates such as opaline silica, chalcedony, cristobalite, tridymite, volcanic glasses, cryptocrystalline quartz, strained quartz etc. and the pore solution of cement binder matrix is highly alkaline [8]. The reaction of amorphous silica of aggregates with alkaline pore solution produces a gel that can cause expansion and cracking of concrete [9]. Thus the alkali content of cement plays a vital role in ASR expansion. It is noted that the higher concentrations of alkali in cement can result in higher expansions due to ASR [10]. The use of low alkali cement has been suggested by different standards to minimise ASR. However, cement with alkali content lower than 0.6% could not reduce the expansion below the limiting value. This is often because of the alkali contribution by aggregates [10, 11]. The amorphous structure of manufactured aggregate such as volcanic glass, unwashed marine sand, feldspar, mica, clay minerals and zeolites can increase the alkalinity of pore solution of concrete, hence caused considerable ASR expansion [12-17]. In addition, applying impermeable coatings into structure was not successful to mitigate the expansion due to moisture ingress from the surrounding environment. Consequently, the alkali of cement and reactive aggregates cause deleterious expansion with the available moisture present in the concrete pore solution [18].

The use of supplementary cementing materials (SCM) has been found to be the most efficient way of ASR mitigation technique based on the available research conducted so far. In this connection, extensive research has been carried out using different types of SCM such as silica fume (SF), fly ash (FA), ground granulated blast furnace slag (GGBFS) and other pozzolans [19-25].

It has been found that SF mixed concrete shows high strength with less porosity than the conventional concrete [19]. Furthermore, SF is able to reduce the hydroxyl ion from pore solution and hence reduce the ASR expansion [20-22]. Aquino et al. [23] tested ASR expansion by accelerated mortar bar test using SF as a 10% replacement of cement and found 50% reduction in expansion as compared to control specimens after 28 days of testing. Similarly, Fournier et al. [24] reported that the use of 7.5% SF as a cement replacement kept the expansion of concrete prisms within the allowable limit even after a testing period of 10 years. In addition, Oberholster [25] showed that 3.5% SF mixed concrete exhibited 0.25% expansion whereas concrete containing 7% SF exhibited 0.07% expansion after a testing period of 7 years. In contrast, Shehata & Thomas [19] pointed out that 5% SF may reduce alkalinity at the early ages with a gradual increase over a period of 2 to 3 years.
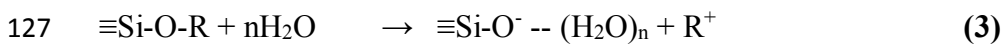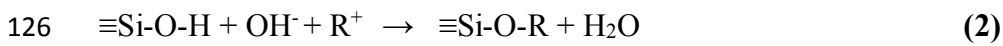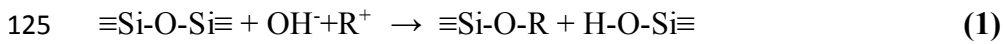
79 GGBFS has been well known to produce concrete with high strength, low permeability,
80 high density, and resistance to chloride ion penetration, sulphate attack and corrosion of
81 reinforcing steel [26-29]. The effectiveness of GGBFS on ASR mitigation was been studied
82 extensively in past decade [26, 30-35]. It is noticed that usually a large volume of cement
83 replacement is required for ASR mitigation by GGBFS. Saha & Sarker [17] showed that 30%
84 replacement of cement by GGBFS was not enough to reduce the ASR expansion ferronickel
85 slag fine aggregate below the allowable limit. On the other hand, Thomas [33] reported that
86 more than 50% cement replacement by GGBFS was required in order to reduce the expansion
87 of concrete prisms below 0.04% after the two years of testing when reactive Spratt fine
88 aggregate was used. The concentration of alkali in pore solution reduced significantly by using
89 50% GGBFS as a cement replacement. As a result, expansion did not exceed the allowable
90 limit [34]. Similarly, according to accelerated mortar bar test results conducted by Choi & Choi
91 on FNS aggregates [31], 60% cement replacement was required to reduce the ASR expansion
92 below the allowable limit.

93 Fly ash (FA) is a well-recognised supplementary cementing material, used in concrete
94 productions in different parts of the world. The use of FA as partial replacement of cement can
95 produce concrete of high strength and improved durability [36-41]. Oner et al. [41] investigated
96 the optimum quantity of FA in concrete and it was suggested that cement can be replaced by
97 FA up to 40%. Concrete incorporated with FA showed high-performance due to its significant
98 pozzolanic reaction where calcium hydroxide produced from cement hydration reacts with the
99 amorphous silica present in FA and forms calcium silicate hydrate (C-S-H), which has
100 excellent binding properties [41]. The use of FA in concrete has also been studied extensively
101 as an ASR mitigation measure during the last decades. Therefore, this paper reviews the latest
102 advancements on the knowledge of ASR mechanism and contribution of the ingredients of
103 concrete on this deleterious expansion. The use of FA in concrete as an ASR mitigation
104 technique has been discussed in details and the needs for further research have been identified.

2. ASR mechanism

106 ASR takes place between the reactive silica of aggregates and the alkaline solutions in
107 micropores of concrete. The primary sources of alkali are the binder, aggregates and the
108 surrounding environment. Alkalis generated from alkali metal ions take part in reactions with
109 water to form soluble alkali hydroxides [42]. The silica present in aggregates in the form of
110 quartz is chemically inert. However, the poorly crystalline silica has the affinity to react with
111 water and generate amorphous hydrous silica. Some examples of poorly crystallised silica are
112 opal, chert, chalcedony and glasses [43]. Portlandite ($Ca(OH)_2$) and calcium silicate hydrate
113 (C-S-H) are produced by the reaction of cement with water in the hydration process. This
114 $Ca(OH)_2$ contributes hydroxyl ions (OH^-) into the pore solution [43]. The ASR mechanism
115 consists of three major stages of chemical reaction as shown by Eqs. 1 to 3. At the initial stage
116 of ASR, the hydroxyl ions undergo reaction with Si-O-Si bonds of amorphous silica to produce
117 silicic acid (Si-OH) and alkali silicate (Si-O-R), where R^+ represents the alkali metal ions. Then
118 the silicic acid reacts with the hydroxyl ions (OH^-) and metal alkali that forms alkali silicate
119 hydrate by liberating water. Finally, the expansion occurs due to hydration of the alkali silicate

3

120   gel [43-46]. Later, the hydrated alkali-silicate gel gets defused from aggregate to cement paste
121   and undergoes reaction with the calcium ions (Ca^{2+}). This generates alkali-calcium-silicate
122   hydrate gel [47-50]. These products absorb moisture from the surroundings and expand in
123   volume. Excessive expansion can cause cracking of aggregate and cement paste to initiate
124   degradation of concrete.

125    $\equiv$Si-O-Si$\equiv$ + OH$^-$+R$^+$ $\rightarrow$ $\equiv$Si-O-R + H-O-Si$\equiv$ **(1)**

126    $\equiv$Si-O-H + OH$^-$ + R$^+$ $\rightarrow$ $\equiv$Si-O-R + H_2O **(2)**

127    $\equiv$Si-O-R + nH_2O $\rightarrow$ $\equiv$Si-O$^-$ -- $(H_2O)_n$ + R$^+$ **(3)**

128   **2.1. Effect of aggregate characteristics**

129   Aggregates play a significant role in ASR expansion. Depending on the reactivity of
130 aggregates, it can be classified into two categories. Aggregates mostly containing amorphous
131 silica are classified as reactive and those containing crystalline silica are classified as non-
132 reactive. The reactive aggregates may also consist of meta-stable crystals, microcrystalline
133 silica and other crystalline forms containing many lattice defects, residual strains, or internal
134 micro-cracks [51]. The reactive aggregates can be found from natural sources as well as from
135 industrial processes as by-products. For instance, obsidian, which is a volcanic glass exhibits
136 deleterious alkali silica reaction. The lava coming out from a volcano cool down very quickly,
137 as a result, the formation of silica is found to be amorphous rather than in crystalline structure
138 [52]. Similar phenomenon can also be observed in reactive industrial by-products. It has been
139 found that rapid cooling of molten Nickle slag by water results in formation of amorphous
140 silica causing susceptibility to ASR, whereas, slowly cooled nickel slag by air flow is found to
141 be less reactive or non-reactive. The slow cooling process leads to formation of crystalline
142 silica, as a result, the aggregate is found to be non-reactive [31]. Similarly, production process
143 of glass also goes through a rapid cooling process. As a result, glass particles contain a
144 significant amount of amorphous silica that causes ASR expansion when used as aggregate
145 [53-54]. Therefore, the amorphous silica content of an aggregate indicates the potential ASR
146 susceptibility of that aggregate. **Table 1** shows the amorphous silica contents of some reactive
147 aggregates used in different studies and the corresponding expansions in accelerated mortar
148 bar tests (AMBT) and concrete prism tests (CPT). A relationship can be seen between
149 expansion and the percentage of amorphous silica present in the aggregates. It can be seen that
150 expansion generally increased with the increase of amorphous silica content in aggregates.
151 However, the correlation is not proportional. For example, three different aggregates such as
152 FNS, glass and sintered silica fume exhibited similar expansion, which is about 0.65% in
153 AMBT even though the reactive silica content was 50%, 73% and 85%, respectively.
154 Furthermore, concrete samples with Chinese limestone containing only 4.6% amorphous silica
155 exhibited ASR expansion of 0.064% CPT which exceeds the allowable limit of 0.03%
156 suggested by the ASTM C1293 standard [61]. Therefore, amorphous silica content of
157 aggregates acts as a governing factor of ASR expansion.

158   Figs. 1(a) to 1(c) show the photos of typical volcanic glass [62], nickel slag [63],
159 recycled glass aggregates [64]. It can be seen that volcanic glass and nickel slag aggregates are
160 similar dark colour [31, 65]. Both of the particles possess a high level of angularity in physical
161 appearance. Some siliceous limestones are found to be alkali-silica reactive due to the presence
162 of amorphous siliceous phase. Siliceous limestone such as kieselkalk, tournaisian and spratt
163 are found to exhibit alkali silica reactions. Generally, kieselkalk is found in Switzerland,
164 tournaisian aggregate is found in Belgium and Spratt aggregate is found in Canada [66-68]. In
165 addition, aggregates found from quarry operations, such as basalt is found as alkali silica
166 reactive when applied in concrete as aggregate [69].

167   The reactivity of an aggregate also depends on its size. Aggregates with smaller
168 particles give higher surface area that increases ASR expansion [1, 70]. However, Poyet et al.
169 [71] found that very small size reactive aggregates could also reduce ASR expansion. This is
170 because very finely ground particles of reactive aggregate may take part in the pozzolanic
171 reaction and reduce alkalinity of the pore solution. In the reaction process, the silicate ion of
172 reactive aggregate is first detached by the hydroxyl ion of pore solution which is then reacted
173 with soduim or potassium ions to form an alkali-silicate gel. Since there is adequate calcium
174 available in concrete at the early ages, the alkali-silicate gel is quickly converted to calcium-
175 silicate-hydrate (C-S-H) in the pozzolanic reaction. On the other hand, for large reactive
176 aggregates, it takes years to occur ASR in concrete. Since there is less calcium available for
177 reaction in matured concrete, the alkali-silicate gel in this case is not quickly converted to C-
178 S-H and absorption of water by the gel causes expansion. Therefore, aggregate containing
179 amorphous silica may contribute to strength by pozzolanic reaction at early ages or may case
180 ASR expansion at matured ages depending on the size.

181   Rajabipour et al. [72] reported that soda lime glass aggregates of size ranging from 1.18
182 mm to 2.36 mm showed maximum expansion. Furthermore, Bažant and Steffens [46]
183 suggested that the swelling pressure of ASR gel depends on particle diameter. The maximum
184 pressure was observed for particles with the size of 2 to 3 mm. However, Maraghechi et al.
185 [73] argued that ASR expansion increases with the increase of particle size because larger
186 particles consist of the greater amount of reactive microcracks. Furthermore, Ichikawa [74]
187 confirmed the effectiveness of excessive amount of reactive aggregates above the pessimum
188 proportion can reduce ASR expansion. According to the author, there were two primary reasons
189 behind this phenomenon. Firstly, calcium hydroxide was consumed by the alkali silicates with
190 the increase of reactive aggregates. As a result, formation of the reaction rims was reduced.
191 Secondly, reduction of alkali hydroxides for individual aggregate particles reduced the
192 reaction. Besides, the pessimum proportion for a different type of aggregate can be very hard
193 to predict. Different researchers suggested different pessimum aggregates size which can
194 exhibit the highest expansion [46, 72]. With the current standard test such as AMBT and CPT
195 it is difficult to correlate the expansion with the pessimum aggregate proportion because both
196 the tests use specific aggregate gradation for testing [59-61]. Therefore, there is a scope of
197 further investigation into the effect of aggregate size on ASR expansion.

198 **2.2. Role of alkali in ASR**

199   The pore solution alkalinity is a governing factor in ASR. Cement hydration contributes
200 to a significantly high alkalinity to the pore solution. Therefore, reducing the alkalinity of pore
201 solution is complicated. In addition, lower alkalinity in pore solution can cause carbonation
202 and corrosion of the reinforcement. Besides, aggregates can also supply alkali to the binder
203 matrix to amplify the alkali silica reaction. It is reported that reactive aggregate such as volcanic
204 aggregates, glass aggregate, and non-reactive aggregates such as granite, mica, zeolites, clay
205 minerals and feldspars can release alkali and increase the pH of pore solution [6, 9, 73, 75-76].
206 Grattan-Bellew [77] pointed out that the alkali released from aggregates can be a significant
207 reason behind the ASR expansion of concrete. The amount of alkali released from an aggregate
208 depends on its mineral structure. The mechanism of alkali dissolution from the aggregates was
209 attributed to the cation exchange with the calcium hydroxide of pore solution [77].
210 Furthermore, Goguel [78] showed that the rapid cooling leads to the poor crystallisation of
211 minerals in an aggregate that can release a high concentration of alkali (1% Na_2O) into the pore
212 solution, whereas well-crystallized minerals released less amount of alkali (0.1% Na_2O).

213   On the other hand, it has been observed that there are different types of supplementary
214 cementing materials (SCM) that contain a significant amount of alkali, often more than 6% by
215 mass which is the allowable limit for OPC [79]. Nevertheless, SCMs can reduce the alkalinity
216 of pore solution by alkali binding [33]. However, this ability of alkali binding depends on the
217 alkali content of a SCM. Shehata and Thomas [80] reported that low calcium fly ash could
218 increase the alkali-binding capacity of C-S-H as compared to high calcium fly ash. Similarly,
219 Bhatty and Greening [81] proved that alkali retention of C-S-H gel is increased by lowering
220 the calcium to silicon (Ca/Si) ratio when fly ash is used as a SCM. Hong and Glasser [82]
221 pointed out that the addition of alumina in C-S-H gel formed C-A-S-H, which improved the
222 alkali binding capacity. Uchikawa et al. [83] showed that the effect of the pozzolanic reaction
223 of fly ash could reduce the alkalinity of the pore solution. Fig. 2 shows the relationships
224 between the available alkalis in pore solution with respect to its chemical composition [80]. It
225 can be seen that a linear correlation exists between the amount of alkali release from the binder
226 with respect to its chemical combination particularly alkali, calcium and silica content (Na_2O_e
227 $\times$ CaO/SiO_2). From Fig. 2, it is noticeable that the available alkali in pore solution gradually
228 decreased with the increment of silica content. As a result, this alkali release phenomenon can
229 lead to the deterioration of concrete due to ASR at the later stages of its service period.
230 According to the study conducted by Ideker et al. [84], a high alkali SCM mixed concrete did
231 not exhibit any sign of expansion for a period of ten years in normal environmental exposure.
232 However, the authors found significant cracking after ten years, though these mix combination
233 did not show any sign of ASR expansion in concrete prism test (CPT).

234   From the above discussion, it can be seen that both aggregate and binder contribute to
235 the pore solution alkalinity, which causes the ASR expansion. On the other hand, a binder with
236 low Ca/Si ratio results in low alkalinity of the pore solution. Therefore, aggregate with low
237 alkali content and binder with high silica content are desirable to reduce the ASR expansions.

238 **2.3. Role of calcium**

The amount of calcium has a noticeable effect on ASR expansion of concrete. Different approaches have been documented to exhibit the dependency of portlandite ($Ca(OH)_2$) in ASR. Earlier, Chatterji [85] described that the presence of high amount of portlandite in pore solution formed a semi-permeable layer around the aggregates, which allowed the hydroxyl ion penetration into the reactive silica grain but prevented the silica diffusion from the reactive site. As a result, cracking and expansion occurred in the test specimens. Then, an experimental work carried out by Wang and Gillott [86] showed that calcium acts as a buffer to maintain the pH of pore solution by releasing hydroxyl ion in pore. In addition, Thomas et al. [87] found that the alkali silicate gel formed due to aggregate dissolution is fluid in nature and has the capability to get dispersed in the binder matrix. However, the addition of calcium replaces the alkali from this gel, which is a more viscous product that has the affinity to expand by absorbing water. In contrast, Powers and Steinour [88] reported that low concentration of portlandite formed expansive alkali silica gel, whereas a high concentration of portlandite formed non-expansive calcium-alkali-silica gel. The chemical composition of ASR products can be different depending on the location of the gel. For instance, a gel located in pores and cracks contains a higher amount of calcium as compared to the gel in the reactive aggregates [50, 89]. Therefore, it is difficult to correlate the chemical composition and the expansion of ASR products. Vayghan et al. [51] found significant expansion for sufficient concentration of the calcium in a binder matrix. The authors explained that viscosity and yield strength of ASR gel increased due to the presence of calcium. As a result, greater stress was caused by the gel expansion. However, Lehmann et al. [90] demonstrated that the water binding capacity of ASR gel not only depends on calcium content but also on calcium to silicon ratio (Ca/Si). According to their study, ASR gel bound water both physically and chemically. Fig. 3 shows the water binding capability of ASR gel with respect to Ca/Si ratio as found by Lehmann et al. [90]. As seen in Fig 3(a), the chemically bound water gradually decreased with the increment of the Ca/Si ratio. The physically bound water of ASR gel was found to be maximum when the Ca/Si was in the range of 0.2 to 0.3, with a decreasing trend when Ca/Si was outside this range, as seen in Fig 3(b).

From the above discussion, it is seen that calcium content of binder plays an important role in ASR expansion. Lowering the portlandite can reduce the ASR expansion significantly; however, concrete mix with too low portlandite might suffer from very slow strength development. Therefore, a balance needs to be established so that deleterious ASR expansion can be mitigated with the minimum compromise with strength properties of concrete.

3. Effect of fly ash

Fly ash is a widely known SCM. Extensive investigation has been conducted on the use fly ash as an ASR mitigation measure. Although use of fly ash has been studied extensively as an ASR mitigation technique, contradictory opinions on its effect can be observed among researchers. Therefore, the mechanism associated with fly ash to mitigate ASR expansion is categorised in the following sections and discussed in details.

3.1. Effect of chemical composition

7

The chemical composition of fly ash plays a vital role on its ASR mitigation mechanism. According to ASTM C618 [91], a fly ash containing low alkali and low calcium is classified as class F and those with high alkali and high calcium content belong to class C. It has been reported in several studies that class F fly ash showed better performance in ASR mitigation as compared to class C fly ash [80, 55, 92-93]. Therefore, chemical analysis of fly ash is considered as an initial step to determine its effectiveness as an ASR mitigation measure. Table 2 compares the effect of fly ash types and replacement level on ASR based on available literature. It can be seen that relatively lower proportions of class F fly ash were found adequate to mitigate the expansion due to ASR in both AMBT and CPT. According to the testing standards, the allowable expansion limit is 0.04 % after two years for CPT [61] and 0.01 % after 16 days for AMBT [59, 60]. However, a higher cement replacement by class C fly ash was required to keep expansion within the allowable limit. The chemical composition of class F fly ash plays a vital role in this regard. Class F fly ash contains high amount of amorphous silica and significantly low amount of lime. As a result, the presence of high amorphous silica consumes the portlandite from pore solution [19]. Consequently, the utilization of portlandite from pore solution causes reduction of its alkalinity [57]. On the other hand, class C fly ash has a higher amount of calcium oxide as compared to class F fly ash that eventually contributes to the generation of portlandite [94]. Furthermore, the amorphous silica of class F fly ash reduces porosity by the product of the pozzolanic reaction. As a result, less voids are available in class F fly ash mixed concrete to accumulate the viscous ASR gels [19, 55].

In addition, the expansions of samples not only depend on the calcium content of fly ash but also on the calcium oxide to silica (CaO/SiO_2) ratio. Fig. 4 shows the relationship between CaO/SiO_2 ratio and expansion as reported by Shehata and Thomas [55]. It can be seen that the fly ashes with higher CaO/SiO_2 ratios showed higher expansions as compared to lower CaO/SiO_2 ratios.

Researchers have been studying to find a correlation between the alumina (Al_2O_3) content in fly ash and ASR expansion. Though the presence of Al_2O_3 is stated to suppress ASR expansion, the available literature is limited to support the statement. Ramlochan et al. [97] reported that Al_2O_3 present in SCM was insufficient and ineffective to mitigate ASR expansion. The authors explained that formation of a large quantity of ettringite replaced the mono-sulphate in pore solution and started to expand. Nevertheless, high alumina fly ash alters the chemical composition of alite phase by providing a significant amount of Al^{3+} in CSH gel. Besides, Warner et al. [98] reported that 18% to 25% high alumina fly ash is more useful to reduce ASR expansion. The authors developed a relationship between expansion and alumina or silica content, as presented in Fig. 5. It can be seen that high alumina and silica fly ash specimens exhibited lower expansion as compared to the low alumina and silica fly ash specimens. As seen in Fig. 5(a), there is an exponential regression relationship between expansion and the total alumina and silica (Al+Si) content with a degree of determinacy of 0.83 for two different type of fly ash FA2 (class C) and FA3 (class F). On the other hand, Fig. 5 (b) shows that expansion gradually decreased with the increment of alumina content. It is also noticeable that a linear trend line has a degree of determinacy of 0.46 which is very low. In another study, Hong and Glasser [99] reported that high alumina fly ash has higher alkali

321 binding capacity as compared to the low alumina fly ash. As a result, high alumina fly ash is
322 stated to be more effective to reduce the alkalinity of the pore solution. Consequently, low
323 expansion was observed by the use of high alumina fly ash.

324   Similarly, Shafaatian [100] attempted to evaluate the impact of alumina on ASR. The
325 author used aluminium hydroxide $Al(OH)_3$ as an admixture in a mortar to study its effect on
326 alkali-silica reactivity. According to microstructural studies as presented in Fig. 6, the author
327 observed that the addition of $Al(OH)_3$ created an aluminosilicate layer around the aggregate
328 surface which protected the aggregates from dissolution by the hydroxyl ions. Therefore, the
329 author concluded that the addition of $Al(OH)_3$ reduced ASR expansion significantly.
330 Furthermore, Chappex and Scrivener [101] concluded that the alumina present in pore solution
331 is absorbed by the silica surface of aggregate and hence reduce the decomposition of silica and
332 retard the ASR expansion.

333   The effect of alkali content of fly ash on ASR expansion was reported by several
334 researchers. Schumacher & Ideker [102] observed that low alkali fly ash based samples
335 exhibited less expansion than the high alkali fly ash based samples in AMBT. Similarly,
336 Duchesne & Bérubé [103] found that low alkali fly ash was more effective than high alkali fly
337 ash to reduce the ASR expansion after more than 10 years of testing period, as shown in Fig.
338 7. It can be seen that both low alkali and high alkali fly ash showed relatively steady expansion
339 up to 2 years of testing. It can be seen that 40% high alkali fly ash samples is completely
340 ineffective against expansion, however, 20% low alkali fly ash samples exhibited expansion
341 within an acceptable limit of the ASTM C1293 Standard [61]. Similarly, Shehata and Thomas
342 [55] illustrated the relationship between alkali content in fly ash and ASR expansion, as shown
343 in Fig. 8. It can be seen that expansion increased gradually with the increment of alkali content.
344 The sample containing a total alkali of 2.85 kg/m^3 showed expansion within the allowable limit,
345 whereas, the other mixes with higher alkali contents exceeded the allowable limit. Thus, the
346 high alkali fly ash was unable to keep expansion within the allowable limit. Therefore, for a
347 similar level of cement replacement, low alkali fly ash is more effective than high alkali fly
348 ash.

349 From the above discussion, it is evident that the chemical composition of fly ash carries a great
350 significance in its ASR mitigation mechanism. High silica and low alkali class F fly ash is
351 found to be the most effective ASR mitigation technique.

3.2 Reduction of aggregate dissolution

353   ASR is initiated with the aggregate dissolution process. At first, the alkali from pore
354 solution attacks the amorphous silica bonds of the aggregate. Then, this generates alkali silicate
355 gel, which absorbs moisture and expands that may cause cracking and reduction of strength
356 [19, 55]. Earlier, Dron & Brivot [47, 48] noticed that aggregate dissolution process was mainly
357 responsible for ASR and the authors linked the dissolution rate with the crystallinity and
358 silanol/siloxane ratio of aggregate. Recently, Hernández-Cruz et al. [104] investigated the
359 aggregate dissolution process by microtomography analysis. Fig. 9 presents the 3D image of

360 ASR affected samples after different curing ages [104]. The authors reported that 1M NaOH
361 solution exposure resulted in numerous micropores and air voids due to aggregate dissolution
362 at the initial stage. D and G indicate the reactive aggregates and pores filled with ASR gel
363 respectively in the figure. Next, these micropores and the air voids were gradually filled by
364 ASR gel that started the expansion. Afterwards, cracks are noticeably filled with ASR gel
365 which are denoted by C. Finally, the specimens suffered from internal stress due to the
366 expansion of these gels and introduced cracking.

367 Fly ash plays a significant role to mitigate this aggregate dissolution. Shafaatian et al.
368 [58] studied the effectiveness of fly ash to mitigate the aggregate dissolution rate. The authors
369 exposed soda-lime glass into 1 M NaOH solution at 80ºC and recorded the mass loss at 7 and
370 14 days. Fig. 10 shows the mass loss of glass aggregates at 7 and 14 days [58]. It can be seen
371 that the mass loss of glass aggregates significantly decreased when 10 g and 20 g fly ash was
372 added into 1M NaOH solution. At 14 days, the mass losses were 0.18 mg/mm^2 0.08 mg/mm^2
373 and 0.06 mg/mm^2 for no fly ash, 10 g fly ash and 20g fly ash, respectively. Therefore, the mass
374 loss of the aggregates significantly decreased with the addition of fly ash. The authors
375 explained that fly ash reduced the alkali concentration at the aggregate surface by providing
376 available silicate surface area which reacted with the available alkali in pore solution. As a
377 result, the aggregate dissolution rate decreased significantly.

3.3. Pore solution chemistry

379 Fly ash has a significant influence on the pore solution to mitigate ASR. Firstly, fly ash
380 reduces the alkalinity of pore solution by alkali binding. Diamond [105] measured the alkali
381 concentration (Na$^+$ and K$^+$) in pore solution of OPC paste and fly ash blended paste (30% fly
382 ash + 70% OPC). Fig. 11 shows the alkali concentration in pore solution of OPC paste and fly
383 ash blended paste after 10 days of curing [105]. It can be seen that alkali concentration
384 decreased considerably with the addition of fly ash. It was shown that inclusion of fly ash
385 engaged the alkali ion from pore solution by providing free silicate surface that reduced the
386 concentration of alkali ion. Although fly ash may contain a significant amount of alkali, some
387 fly ash does not contribute alkali at all and others may provide a small proportion at a very
388 slow rate [105, 106]. Nixon & Page [106] suggested that class F fly ash did not add alkali to
389 the pore solution.

390 Secondly, fly ash consumes alkali from the pore solution by the pozzolanic reaction.
391 As a result, the alkalinity of the pore solution is reduced significantly. Canham et al. [107]
392 pointed out that pozzolanic CSH gel confined the alkali from pore solution, thus minimised the
393 alkalinity of the pore solution. Besides, Hong and Glasser [82] stated that the alkali binding
394 capacity primarily depends on the calcium to silica (C/S) ratio of the CSH gel. Fig. 12 shows
395 the relationship between the C/S ratio of CSH gel and the related alkali (Na and K) binding
396 capacity [82]. It can be seen that low C/S has higher alkali binding capacity as compared to
397 high C/S ratio. The authors concluded that CSH gel with low C/S leads to form acidic silanol
398 (Si-OH) groups, which is neutralised by the reaction of the alkalis (NaOH or KOH). However,
399 Detwiler [108] argued that it may not be possible to mitigate ASR expansion of highly reactive

400 aggregates by fly ash, as there may not be enough time for the pozzolanic reaction to initiate
401 and reduce the alkalinity of the pore solution.

402   Finally, fly ash reduces the calcium (Ca) concentration of pore solution. At the very
403 beginning, Chatterji [85] investigated the role of portlandite in ASR and offered a $CaCl_2$
404 solution to leach out portlandite successfully from concrete to reduce ASR expansion. It was
405 recommended to use a SCM to reduce the portlandite of concrete as an ASR mitigation
406 technique. Then, Wang & Gillott [86] explained that the presence of portlandite increased the
407 alkalinity of pore solution by releasing hydroxyl ions. An experimental program carried out by
408 Bleszynski & Thomas [109] compared the effect of lime ($Ca(OH)_2$) on ASR expansion of OPC
409 and fly ash blended concrete. The expansion results after 24 days obtained from the study are
410 plotted in Fig. 13. It can be seen that both OPC and fly ash blended concrete slowed down
411 expansion when $Ca(OH)_2$ was added. The authors concluded that the presence of calcium in
412 mixture creates a high calcium reaction rim, which acts as a semi-permeable membrane. This
413 reaction rim allows the penetration of alkali hydroxides into the silica particle but prevents the
414 circulation of the aqueous alkali-silica from the silica particle to pore solution [109]. However,
415 the expansion was minimised when fly ash was added.

416   Therefore, pore solution chemistry undoubtedly plays the most significant role to
417 initiate ASR expansion. However, the addition of fly ash changes the scenario of the pore
418 solution chemistry by binding alkali and removing free calcium. As a result, fly ash can reduce
419 the ASR expansion of concrete and mortar.

3.4. Alteration of ASR gel

421   It has been shown in some research that ASR gel is produced in mortar and concrete
422 containing fly ash without considerable expansion. This is because fly ash can change the ASR
423 gel properties by reducing the viscosity, swelling capacity and swelling pressure [74, 109, 110].
424 Struble and Diamond [111] investigated the swelling properties of sodium silicate and sodium
425 calcium silicate gels to identify the basic mechanism of ASR expansion in concrete with
426 sodium hydroxide as a source of potential alkali. It was found that sodium silicate (Na-Si) gel
427 was in a fluid state, whereas sodium calcium silica gel was in a solid state. Bleszynski &
428 Thomas [109] found that alkali-silica gel was formed in low calcium and high alkali fly ash
429 concretes. This gel acted as a fluid and was diffused in the cement paste. On the other hand,
430 for conventional concrete, alkali present in this gel was replaced by calcium and produced a
431 viscous product, which swelled in contact with water. Later, Ichikawa [74] concluded that the
432 alkali silicate is fluid in nature and is also able to diffuse in pores of the paste; however, the
433 presence of calcium (Ca^{++}) replaces alkali from the alkali silicates to create solid calcium alkali
434 silicates, which is expansive in nature. On the other hand, the inclusion of fly ash reduces the
435 calcium content in the mix. Therefore, less amount of calcium alkali silicate is produced.
436 Hence, the deleterious expansion due to ASR is mitigated. Bonakdar et al. [110] suggested that
437 fly ash specimens contained fibrous platelets of Ca-Na-Si-O groups and it formed a non-
438 expansive dense network of scattered distribution. Recently, Gholizadeh-Vayghan and
439 Rajabipour [112] conducted an experiment on synthetic ASR gel of different chemical

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440 compositions. The authors found that swelling pressure and water absorption capacity of ASR
441 gel increased with the increment of Na/Si and K/Si ratios. Furthermore, in another study by
442 Vayghan et al. [51] showed that ASR gel with Ca/Si = 0.2 and Na/Si = 0.85 exhibited the
443 highest expansion and swelling pressure. The measured pH of the synthetic gels with respect
444 to calcium and sodium content at different time intervals are presented in Fig. 14. In this figure,
445 a gel with low Ca/Si and Na/Si is denoted as C-N-, high Ca/Si and Na/Si is denoted as C+N+,
446 low Ca/Si and high Na/Si is denoted as C-N+, and high Ca/Si and low Na/Si is denoted as
447 C+N-. As seen in Fig. 14, C-N+ and C+N- do not have a major influence on the pore solution
448 pH. However, C+N+ significantly increased the pore solution pH. Therefore, the addition of
449 fly ash as a SCM is an effective solution to reduce the alkali-silica ratio as well as calcium
450 silica ratio in ASR gel.

451 In contrast, Powers & Steinour [113] believed that expansion occurs due to swelling of
452 alkali-silica (Na-Si) gel and a non-expansive lime-alkali-silica gel is generated in presence of
453 sufficient lime. Similarly, Monteiro et al. [114] stated that the presence of higher lime/alkali
454 ratio in alkali-silica gel reduces the expansion of the gel. Helmuth et al. [115] also observed
455 the similar trend and reported that the presence of excessive alkali can reduce expansion due
456 to the spontaneous reaction from diffusion of silica to the unconfined sites. Thus high Na/Si
457 ratio reduces the gel viscosity and swelling pressure.

458 Therefore, the presence of fly ash modifies the alkali-silica gel properties, which leads
459 to the reduction of expansion. However, contradictory opinions are found in literature about
460 the chemical composition of ASR gel and its swelling pressure. Moreover, further experimental
461 works can be conducted to evaluate the chemical composition of ASR gel and its swelling
462 pressure comprehensively.

3.5. Reduction of porosity

464 The porosity of concrete plays a vital role in expansion due to ASR. Usually, high
465 porosity of concrete allows moisture from the surrounding to penetrate and trigger ASR.
466 According to the study by Bulteel et al. [116], at first, alkali diffused in the pores between
467 aggregate and the binder matrix and then initiated the aggregate dissolution, and finally started
468 ASR. Similarly, Multon et al. [117] pointed out that ASR gel penetrates through the voids
469 between the aggregate and cement paste. Later, this gel imparts swelling pressure and causes
470 expansion and cracking. Haha et al. [118] also found that highly porous aggregates suffered
471 from greater expansion as compared to the aggregates with lower porosity. Similarly, Shah and
472 Ahmad [119], and Steffens et al. [120] showed that lower porosity increases the ASR resistance
473 of e concrete structures. Furthermore, Moser et al. [57] investigated the relationship between
474 the hydraulic permeability of concrete and ASR expansion. According to the findings reported
475 by the authors, SCM reduced the permeability of concrete that resulted in the reduction of water
476 absorption and expansion of the ASR gel. Fly ash concrete has lower permeability due to two
477 main reasons: firstly, reduction of the transition zone thickness between surrounding
478 aggregates and cement matrix; and secondly, fly ash reduces the pore size of the binder matrix
479 by pozzolanic reaction product and filling effect of the fine unreacted particles [121, 122].

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480 Thus, low permeability of fly ash samples reduces alkali diffusion from the surroundings.
481 Furthermore, the presence of fewer pores in cement paste mitigates the alkali-silica reaction as
482 well as accumulation of alkali-silica gel. As a result, fly ash specimens exhibit less expansion.
483 In contrast, Pandey & Sharma [123] found that use of fly ash as a partial replacement of cement
484 increased the porosity of the mortar samples at the initial stages of curing. Similarly,
485 Chindaprasirt and Jaturapitakkul [124] pointed out that fly ash blended cement paste showed
486 higher porosity when compared to Portland cement paste. The higher porosity of the samples
487 was because of less reaction product or reduced rate of hydration at the early ages due to cement
488 replacement by fly ash. Therefore fly ash concrete exhibited higher porosity at early ages as
489 compared to concrete without fly ash [123, 124].

490 Although the use of fly ash may show higher porosity at the early age of curing, it can
491 reduce the internal pores and prevent the ASR gel accumulation around the aggregates at the
492 later ages. Furthermore, fly ash reduces permeability by pozzolanic reaction and filler effect
493 that can eventually reduce the alkali attack from the surrounding environment.

494 **4. Test methods and their limitations**

495 AMBT and CPT have been adopted in different standards and used by researchers for decades
496 to identify potentially reactive aggregates and evaluate the effectiveness of supplementary
497 cementing materials to mitigate ASR. Yet, in some cases, these two test methods have been
498 unsuccessful to predict the deleterious expansion due to ASR. Shi et al. [125] hold the view
499 that the exposure period of 16 days for AMBT is not sufficient for slowly reactive aggregates.
500 Their experimental study showed expansion of specimens within the allowable limit for 16
501 days of the test with much higher expansions thereafter. Fernández-Jiménez et al. [126] showed
502 that formation of zeolite can lead to a rapid expansion after initial low values during the first
503 16 days of the test. Therefore, Palacios & Puertas [127] recommended to extend the test for up
504 to 6 months. Furthermore, this test condition requires submerging the samples at 80 °C in 1M
505 Sodium hydroxide (NaOH) which is very harsh as compared to field condition. Therefore, this
506 test often exhibited misleading results and identified aggregates as reactive while they showed
507 satisfactory field performance [128]. As a result, CPT has been adopted in addition to AMBT
508 to identify the reactive aggregates which exhibits a more realistic concrete exposure condition.
509 During this testing method, samples are exposed at 38 °C at 95% RH for a period of 1 year
510 [61]. In addition, ASTM C1293 [61] suggests that if an aggregate exhibited expansion
511 exceeding the allowable limit in AMBT but the expansion was lower than the allowable limit
512 in CPT, the aggregate can be used in concrete constructions. However, this test requires one
513 year, which is considered to be long to identify reactive aggregates [125]. In addition, the test
514 specimens suffer from significant alkali leaching during the CPT [129, 130, 131]. For this
515 reason, some researchers suggested to conduct the test for two years in order to have a better
516 understanding of the amount of SCM's required to mitigate ASR expansion [132, 133, 134].
517 Even two years of testing of concrete prisms has shown not enough reliability of results in
518 some cases. Rajabipour et al. [72] pointed out that concrete using high-alkali SCM's exhibited
519 expansion within the allowable limit (≤0.04%) after two years of testing, yet exhibited
520 deleterious expansion after 8 to 10 years. Ideker et al. [84] conducted an experimental program

521 on concrete using high-alkali SCM's and reactive aggregates which was tested for more than
522 10 years. It is reported that the concrete samples started significant cracking only after 10 years
523 due to a steady release of alkali from the SCM's. Furthermore, to overcome the time lag of the
524 reaction, researchers are currently evaluating the effectiveness of CPT [135-137]. During CPT,
525 the samples are exposed to a temperature of 60 ºC for 6 months [137]. However, Ideker et al.
526 [135] found that accelerated testing leads to misleading prediction of aggregate reactivity.
527 Similarly, Islam & Akhtar [136] pointed out that accelerated concrete prism test is unreliable
528 to measure the SCM's requirement to mitigate ASR. Considering the limitations of current
529 test methods establishment of the alternative test method to determine the safe percentage of
530 SCM's in concrete to mitigate ASR is a matter of great importance.

5. Optimum percentage of fly ash to mitigate ASR

532 It is known that both class C and class F fly ash as a SCM has the ability to mitigate ASR in
533 concrete. However, use of an excessive volume of fly ash as cement replacement can
534 significantly reduce the early age strength of concrete which can be a major concern for its
535 commercial application. For example, Supit et al. [139] showed that use of class F fly ash as a
536 SCM replacing 40% OPC in concrete, the 7-day compressive strength was only 61% of its 28-
537 day strength, as compared to 85% for the control concrete. On the other hand, optimising the
538 quantity of fly ash can lead to a noticeable early age strength development. For instance, Saha
539 and Sarker [63] found that for 30% cement replacement by a class F fly ash, the 7-day
540 compressive strength was 78% compared of its 28-day compressive strength. Therefore, it is
541 essential to adopt the optimum amount of fly ash which will control the ASR without
542 compromising much of the early age strength. According to recent studies 30% class F fly ash
543 is optimum to reduce the ASR expansion within the allowable limit in both AMBT and CPT
544 [140-145]. In addition, researchers recommend using at least 50% class C fly ash to mitigate
545 deleterious ASR [142-147]. Furthermore, a recent numerical modelling on ASR by Vayghan
546 et al. [147] recommended using 30% class F fly ash or 50% class C fly ash to mitigate ASR.
547 Besides, replacing cement by fly ash in concrete reduce the rate of hydration which lead to the
548 low early age strength [63, 139]. In order to overcome the issue of low early-age strength due
549 to the use of fly ash, researchers adopted different techniques, such as addition of ultra-fine fly
550 ash or nano-silica blended with fly ash. For instance, Supit et al. [139] experimentally showed
551 that addition of ultra-fine fly ash blended with conventional fly ash can accelerate the heat of
552 hydration and the concrete samples exhibited high early age strength development. According
553 to the experimental findings, after 7 days of curing period, the samples containing 8% ultrafine
554 fly ash with 32% regular fly ash gained 75% of its 28-day compressive strength. Concrete with
555 40% fly ash exhibited only 61% strength at 7 days of curing compared to its 28 day strength.
556 Besides, the application of this blend (ultrafine fly ash and fly ash) to mitigate ASR has not
557 been investigated by researchers. Thus, this ternary blend of ultrafine fly ash, fly ash and OPC
558 can be considered for future research works to evaluate ASR mitigation. Furthermore, Shaikh
559 et al. [149] showed that application of nano-silica blended with fly ash and cement can improve
560 the early age compressive strength of the concrete up to 7% and suggested that 2% nano-silica
561 as the optimum quantity. Similarly, Supit & Shaikh [150] pointed out that addition of 2% nano
562 silica blended with fly ash and OPC increased the density of the microstructure and reduced

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563 the pore size. Furthermore, addition of nano-silica accelerate the pozzolanic reaction and thus
564 exhibits higher strength development as compared to use of fly ash without nano-silica [150].
565 Besides, researchers also evaluated the ASR mitigation measure of nano-silica blended with
566 fly ash. Zeidan and Said [142, 151] showed that nano-silica (3%) blended with fly ash (29%)
567 and cement (68%) was able to reduce the expansion within allowable limit. Similarly,
568 Mukhopadhyay and Liu [152] showed that fly ash and nano-silica blends can reduce the
569 expansion due to ASR. In addition, experimental data showed that addition of nano-silica can
570 reduce the OPC replacement level by fly ash to mitigate ASR. According to the test results
571 35% fly ash was essential to mitigate the ASR but samples containing 1% nano-silica blended
572 with only 25% fly ash exhibited satisfactory performance regarding ASR expansion [152].
573 However, nano-silica is not readily available around the world and can increase the concrete
574 production cost [153, 154]. Therefore, further investigation can be carried out regarding
575 alternative approach to find a suitable quantity of fly ash and without compensating the early
576 age strength of concrete.

577 **6. Effectiveness of fly ash over other SCMs to mitigate ASR**

578 Researchers have studied different SCMs apart from fly ash to mitigate ASR in concrete, such
579 as slag, metakaolin and glass powder. All the SCMs were effective to reduce ASR because they
580 consist of high amount of amorphous silica which consume portlandite and reduce the
581 alkalinity of pore solution. However, the dosage of SCMs can be significantly different
582 depending on the chemical composition [155-159]. It is suggested that more than 50% cement
583 replacement by GGBFS is necessary to control ASR [33, 134, 155]. GGBFS generally consists
584 of 20-30% silica content as compared to 50-70% in class F fly ash. Therefore higher
585 replacement of OPC is required by GGBFS to mitigate ASR [33]. Boháč et al. [160] pointed
586 out that addition of 50% GGBFS significantly reduce the heat of hydration compared to 100%
587 OPC. Specimens with fly ash showed very low early age compressive strength [161]. Similarly,
588 Ustabaş and Kaya [162] showed that samples with 50% slag has SCM has a significantly low
589 compressive strength of 18 MPa whereas OPC samples had a strength of 40 MPa after 7 days
590 of curing. The experimental results also point out that 25% fly ash blends had a compressive
591 strength around 30 MPa. Thus, fly ash has the clear advantage over slag as lower replacement
592 of fly ash can be adopted to mitigate ASR without significant reduction of early age strength.
593 In addition, slag generally need grinding before use as a SCM [163]. Fly ash can be used
594 without any further processing from its source which makes it a more economical option
595 compared to slag [164-166]. Furthermore, metakaolin has been another popular choice among
596 researchers to mitigate ASR. Ramlochan et al. [167] pointed out that 20% dosage of highly
597 reactive metakaolin (HRM) was sufficient to control ASR in both AMBT and CPT for two
598 different types of reactive aggregates such as Spratt and Sudbury. Similarly, Aquino [23]
599 pointed out that, HRM reduce the portlandite content from pore solution thus control ASR. On
600 the contrary, Lee et al [168] pointed out that 20% dosage of metakaolin was unable to reduce
601 the ASR expansion of mortar bars using recycled glass aggregate, however, 20% replacement
602 of OPC by fly ash was successful to reduce the expansion within the allowable limit.
603 Furthermore, waste glass powder has got the attention of researchers as a SCM due to its
604 pozzolanic activity. The recent findings suggested that it improve the durability of concrete

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605 [169, 170]. This leads to its application as an ASR mitigating measure [157, 158, 171-173].
606 Zheng [157] pointed out that replacement of cement by 30% waste glass powder successfully
607 mitigate ASR expansion. The effectiveness of glass powder to mitigate ASR was attributed to
608 two primary reasons. First, glass powder consumes portlandite by pozzolanic reaction. Second,
609 it releases alumina in pore solution which minimized the dissolution of reactive aggregates
610 [157]. Similarly, Afshinnia & Rangaraju [158] showed that application of 30% glass power as
611 SCM can control the ASR within the allowable limit. In addition, authors pointed out that
612 fineness of glass powder as SCM plays a crucial role to prevent ASR. The experimental studies
613 indicated that 17-micron glass particles as a SCM showed lower expansion compared to 70-
614 microns particles for an equal replacement ratio. Furthermore, Guo et al. [171] conducted
615 AMBT for the samples using 30% glass powder as a SCM and found that the expansion was
616 within allowable limit and microstructure studies also indicated the absence of ASR gel in the
617 samples. Even though glass powder was successful to mitigate ASR, for an equal dosage of fly
618 ash and glass powder with similar reactive aggregates the fly ash found to be more effective
619 [173]. In addition, the waste glass requires careful recycling process in order to make it suitable
620 for replacing cement in concrete which can be costly [174]. Therefore, fly ash has a clear
621 advantage over other SCMs considering an economical way to mitigate ASR as well as without
622 excessive reduction of early age strength.

7. Conclusions

624 The following conclusions are drawn based on the extensive literature review on ASR
625 mechanism in concrete and the contribution of fly ash:

626 1. ASR expansion is one of the most severe durability related issues for concrete
627 structures. This expansion can be deleterious depending on its magnitude and may lead to
628 significant cracking and strength loss of concrete. The presence of reactive silica in aggregate
629 and high alkalinity of pore solution are the primary reasons for ASR. The process starts with
630 the disintegration of the reactive silica by alkali attack from pore solution. This forms alkali
631 silicate gel which absorbs moisture from the surroundings and generates swelling pressure in
632 concrete.

633 2. Extensive research has been conducted to explore the effect of fly ash on ASR.
634 Though there is some scientific debate among researchers, most research works clearly
635 demonstrate the positive contribution of fly ash as an ASR mitigation method by the following
636 mechanisms:

637 2.1 Use of class F fly ash as a partial replacement of cement is found to be more
638 effective than class C fly ash in reducing ASR. Fly ash with higher percentages of silica
639 and alumina and lower percentages of alkali and calcium oxides are found to be most
640 effective in reducing ASR.

641 2.2. Fly ash prevents aggregate dissolution due to alkali attack by providing
642 sacrificial amorphous silicate surface area.

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2.3. The addition of fly ash reduces the pH of pore solution by alkali binding and reducing free calcium ions.

2.4. Fly ash modifies the chemical composition of ASR gel and reduces its swelling properties so that the gel can move freely into the voids between aggregate and binder paste.

2.5. Fly ash reduces the porosity of binder matrix that offers resistance against alkali diffusion from the surroundings.

3. Thus, use of class F fly ash as a supplementary cementitious material is considered as an effective and efficient method of ASR mitigation of concrete utilising various reactive aggregates obtained from natural sources and industrial processes as by-products. Utilisation of these aggregates together with fly ash can make a significant contribution towards sustainable concrete production.

8. Recommendations for the further research

Based on the existing research gaps identified in the extensive review, the following recommendations are proposed for further research:

1. Identification of the degree of reactivity is the major drawback in ASR mitigation. The test methods are limited to identify the amount of aggregate dissolution taking place in this process. Therefore, further research on the development of a comprehensive test procedure to determine the degree reactivity of aggregates would be useful to better understand ASR.

2. Usually, fly ash consists of silica, alumina, calcium and alkali oxides. However, it is not clear yet how the alumina influences the ASR mitigation. Therefore, further study is needed in order to understand the role of alumina in ASR. This will help the manufacturing of low alkali cement for use with reactive aggregates.

3. There are some contradictory opinions among researchers about how the chemical composition of ASR gel influences its swelling properties. Further research is needed to enhance the knowledge on swelling behaviour of ASR gel.

4. Fly ash consists of noticeable amount of alkali, often higher than OPC. Therefore standard test needs to be developed to evaluate the long-term effect of this alkali contribution in ASR expansion.

5. It would be useful to have an analytical model based on chemical compositions of the ingredients for determination of the proportions of fly ash, cement and reactive aggregates in a concrete mix design with predicted ASR expansion within the allowable limit.

675   6. Use of 30% class F fly ash as a SCM can be considered adequate to mitigate ASR of
676 reactive aggregates. In contrast, at least 50% class C fly ash may be required for reduction of
677 ASR expansion by the same level.

678   7. Further investigations on the improvement of the reliability of AMBT and CPT
679 results would be useful to identify potential ASR of aggregates with more confidence.

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1138 **Table 1.** Expansion of aggregates with different amorphous silica content.

Type of aggregate	Source	Amorphous silica (%)	Expansion (%)				References
			CPT (1 year)	Allowable limit	AMBT (14 days)	Allowable limit	
Dolomitic limestone	Pittsburgh quarry, Kingston	91.5	0.616		-		Grattan-Bellew et al. [13]
Chinese limestone	China	4.6	0.064		-		Grattan-Bellew et al. [13]
waste glass	Turkey	71	-		0.820		Topçu et al. [14]
Sintered silica fume	-	85	-		0.650		Juenger & Ostertag [15]
FNS	SLN, New Calidonia	50	-	E ≤ 0.04 [ASTM C1293]	0.653	E ≤ 0.1 [ASTM C1567]	Saha & Sarker [17]
Flint	Thames Valley	50	1.482		0.610		Thomas et al. [40]
Spratt	Ottawa	29.7	0.275		0.375		Shehata & Thomas [55]
Opal aggregate	CELITE, S.A.	84	-		0.890		García-Lodeiro et al. [56]
Chert	Texas	71.2	0.420		0.700		Moser et al. [57]
Glass	Canada	73	-		0.631		Shafaatian et al. [58]

1139 **Table 2.** ASR expansions for different cement replacements by fly ash.

Fly ash type	Test type	Cement replacement level (%)										References
		10	15	20	25	30	35	40	45	50	60	
Class F	AMBT	-	-	-	-	0.08	-	-	-	-	-	Saha & Sarker [17]
Class C	CPT	-	-	-	-	0.14	-	-	0.06	-	0.03	Shehata & Thomas [19]
Class F		-	0.08	0.04	-	-	-	-	-	-	-	
Class F	AMBT	0.55	-	0.18	-	0.06	-	-	-	-	-	Choi & Choi [31]
Class C	CPT	-	-	0.123	-	0.10	-	0.068	-	0.042	-	Shehata & Thomas [55]
Class F		-	0.083	0.043	0.03	-	-	-	-	-	-	
Class F	AMBT	-	-	-	-	0.03	-	-	-	-	-	García-Lodeiro et al. [56]
Class C	AMBT	-	-	-	0.485	-	-	-	-	-	-	Moser et al. [57]
Class C	AMBT	-	-	0.41	-	0.38	-	-	-	-	-	Esteves et al. [94]
Class F		-	-	0.38	-	0.33	-	-	-	-	-	
Class C	AMBT	-	-	0.23	-	-	0.11	-	-	-	-	Shon et al. [95]
Class F		-	-	0.27	-	-	0.10	-	-	-	-	
Class F	AMBT	0.15	-	-	-	0.12	-	-	-	0.07	-	Awal & Hussin [96]

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1141 **<u>Figures</u>**
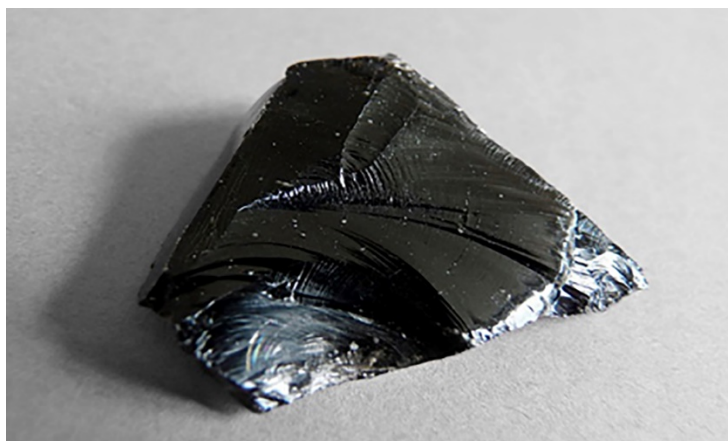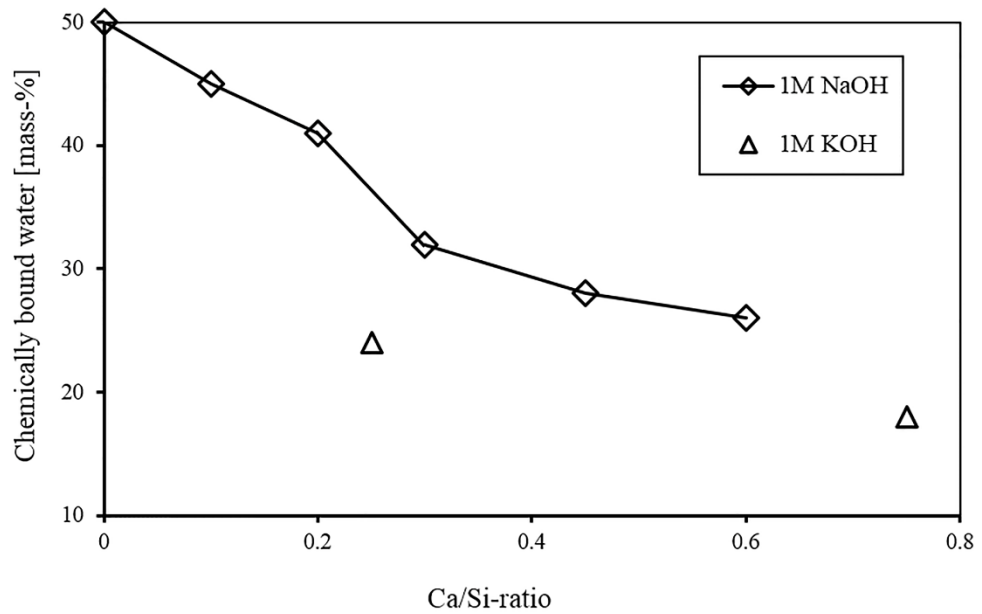
1142 **(a)**

1143 **(b)**
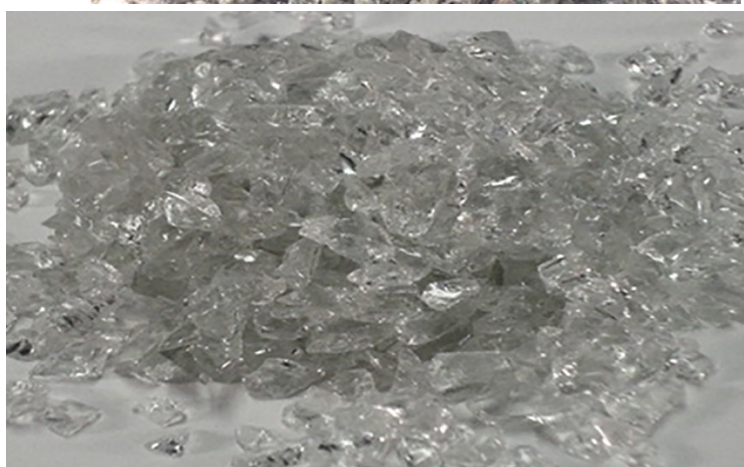
1144 **(c)**

1145 **Fig. 1.** (a) Obsidian, volcanic glass [62] (b) Nickel slag [63] and (c) Waste glass aggregate
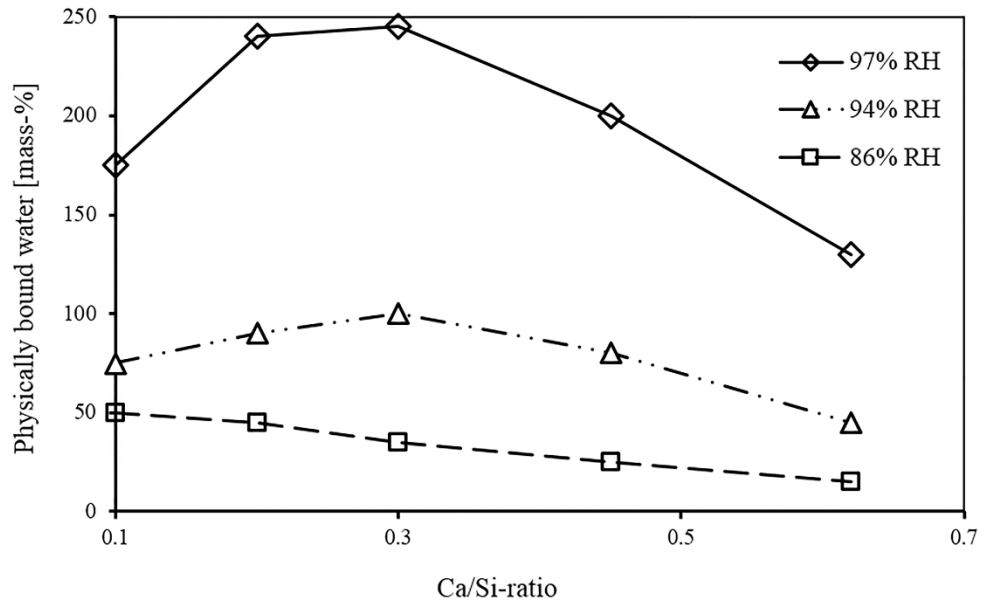1146 [64].
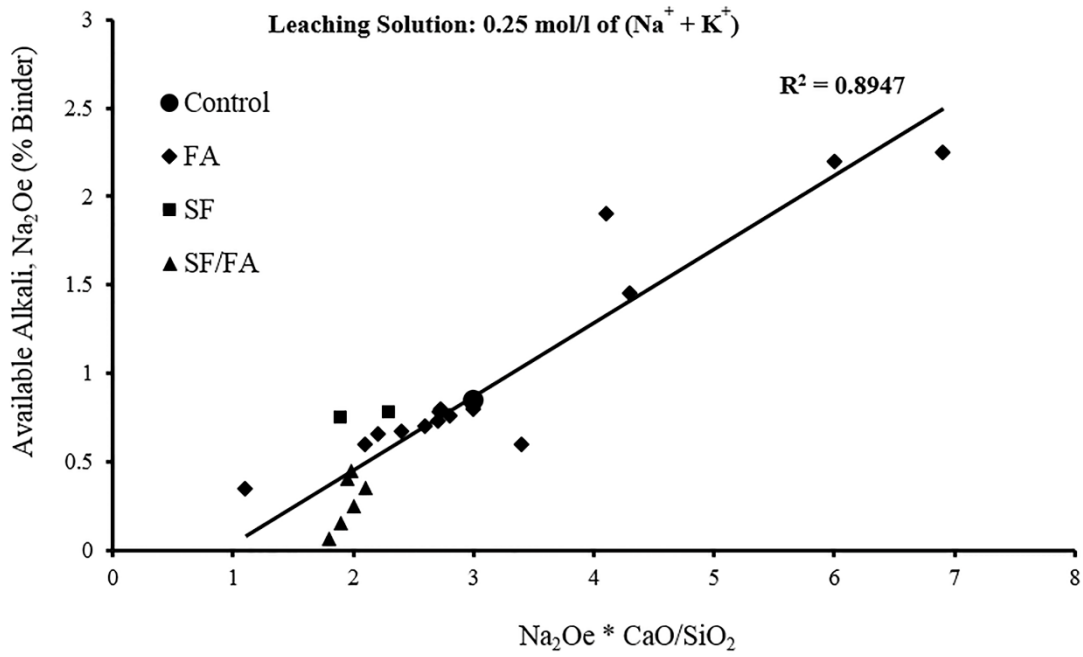
1147

1148   **Fig. 2.** Effect of binder composition on the alkali release in pore solution [80].
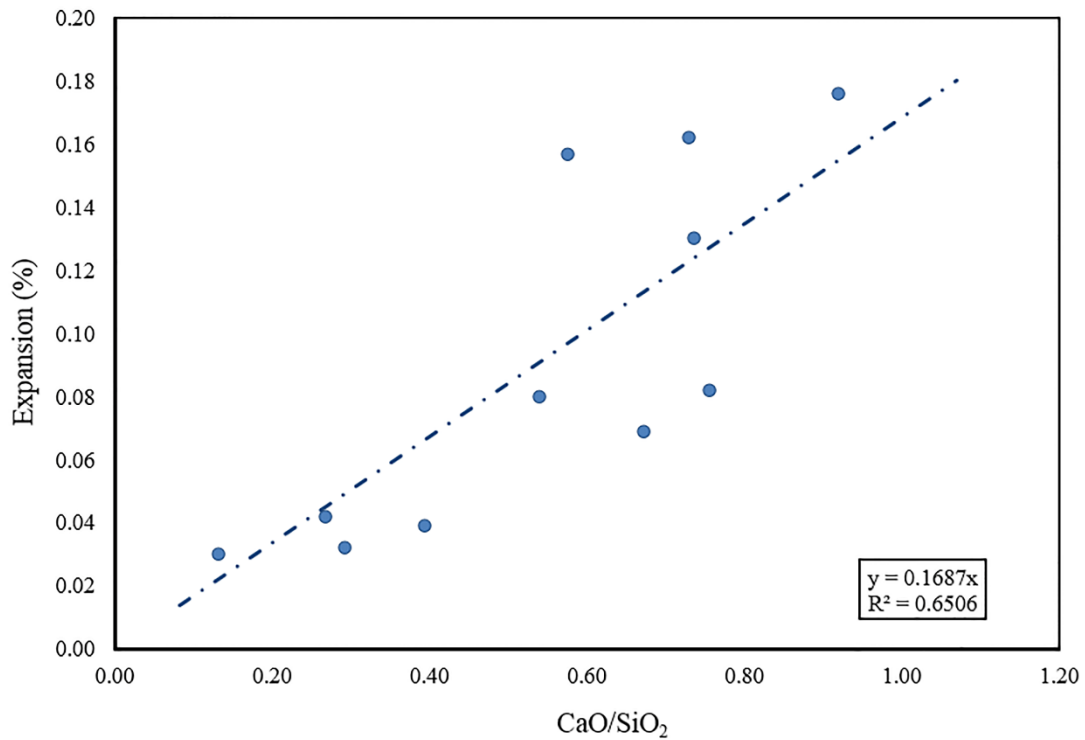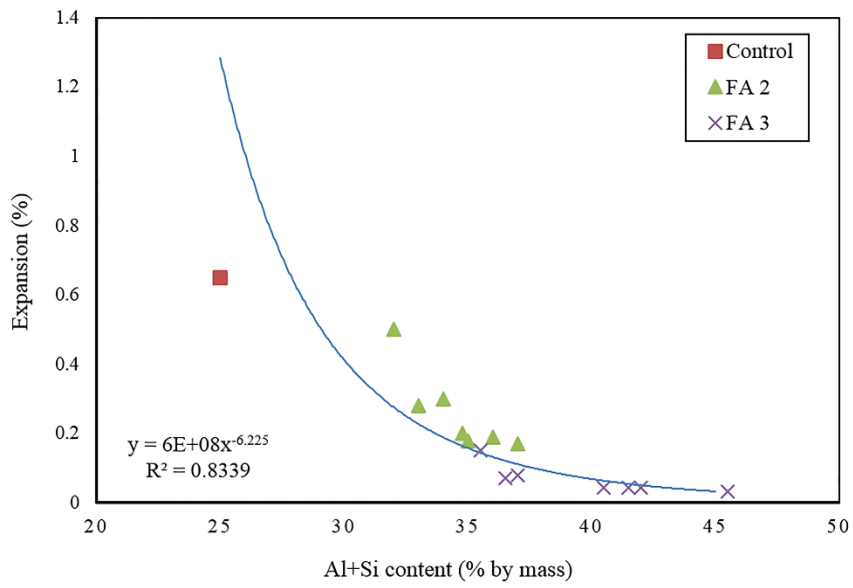

1149   (a)

1150   (b)

1151   **Fig. 3.** Water binding capability by ASR gel with respect to Ca/Si ratio (a) chemically bound
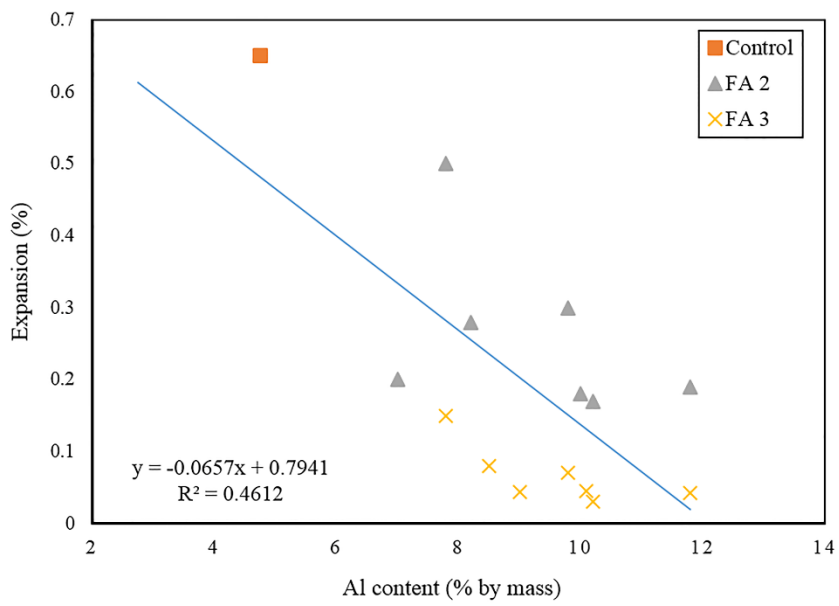
1152   water Vs Ca/Si-ratio and (b) physically bound water Vs Ca/Si-ratio [90].

1153

1154   **Fig. 4.** Correlation between ASR expansion and CaO/SiO_2 of fly ash [55].

1155

1156   (a)

1157   (b)

1158   **Fig. 5.** Relationship between (a) expansion and total Al+Si content and (b) expansion and only
1159   Al content of fly ash [98].

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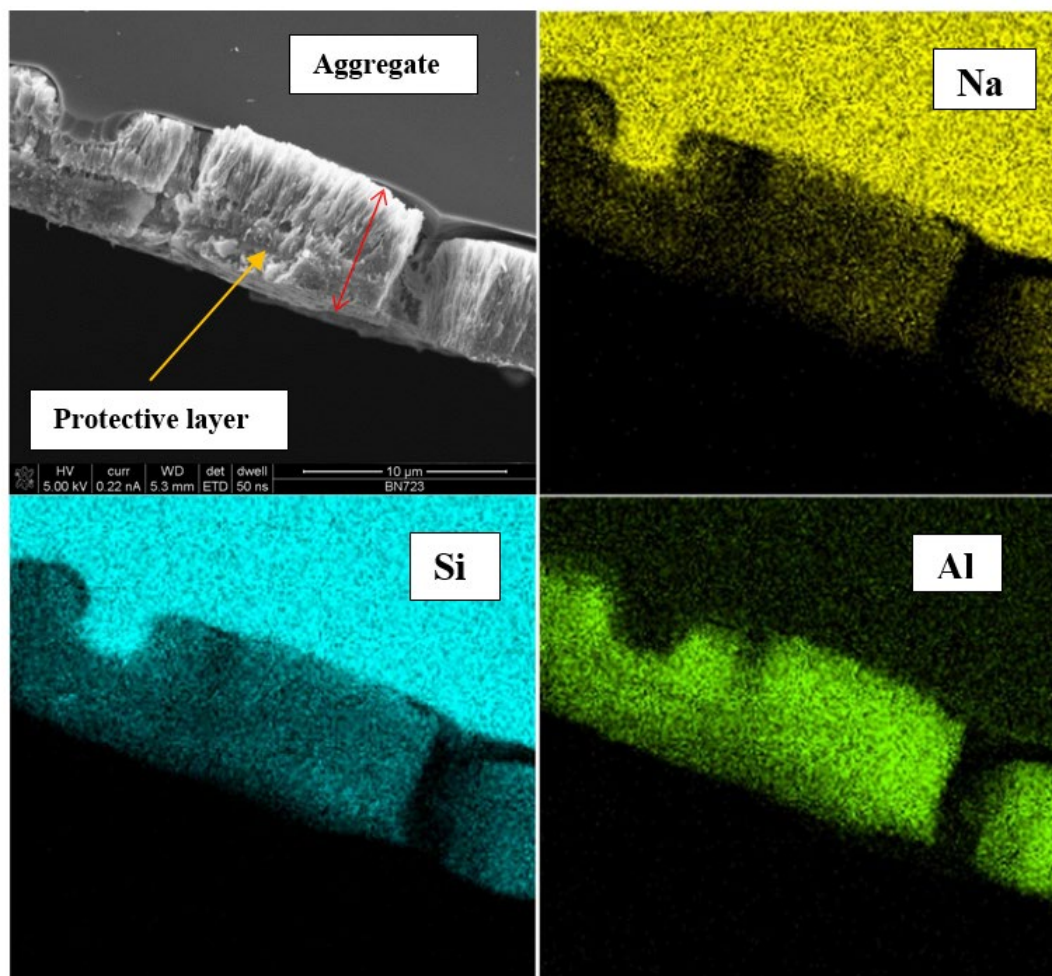
1160

Fig. 6. SEM and EDS mapping of Al, Si and Na elements in the glass slides surface reaction product in presence of $Al(OH)_3$ [100].
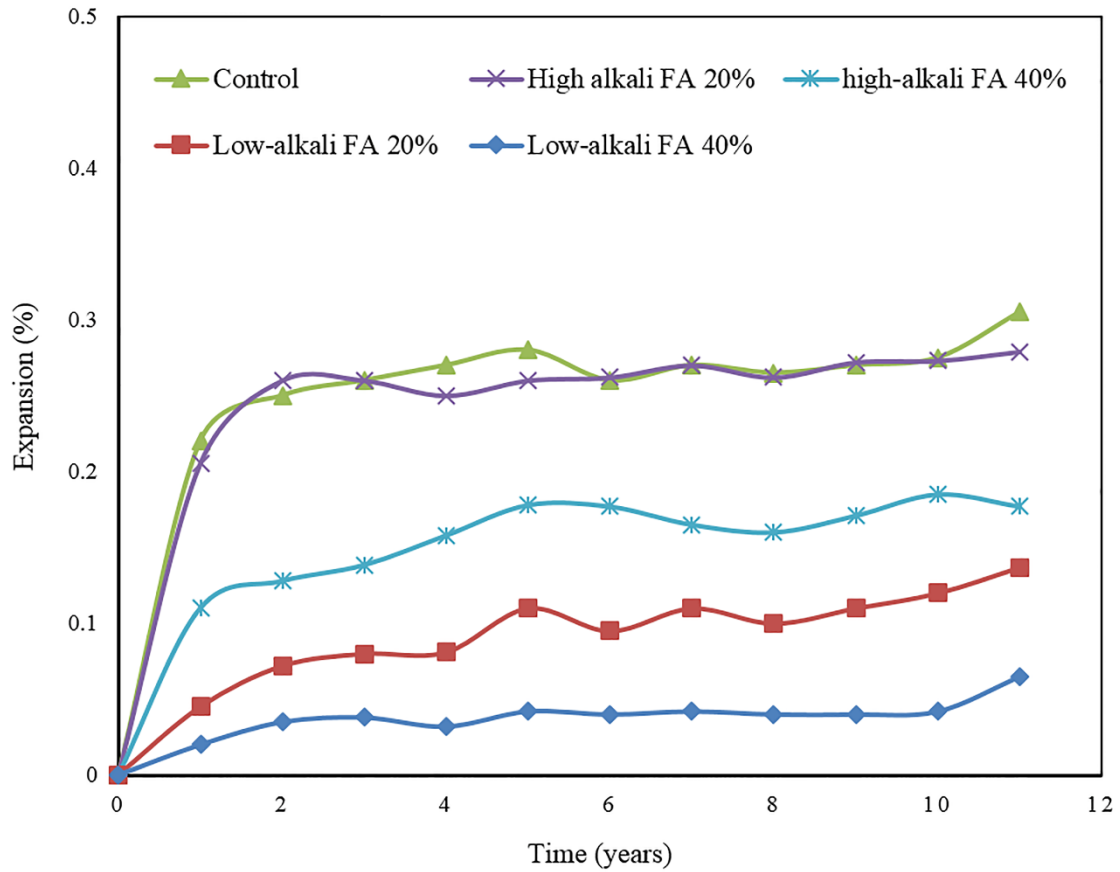
1163

1164   **Fig. 7.** Expansions of fly ash mixed samples cured at 38ºC and 100% RH [103].
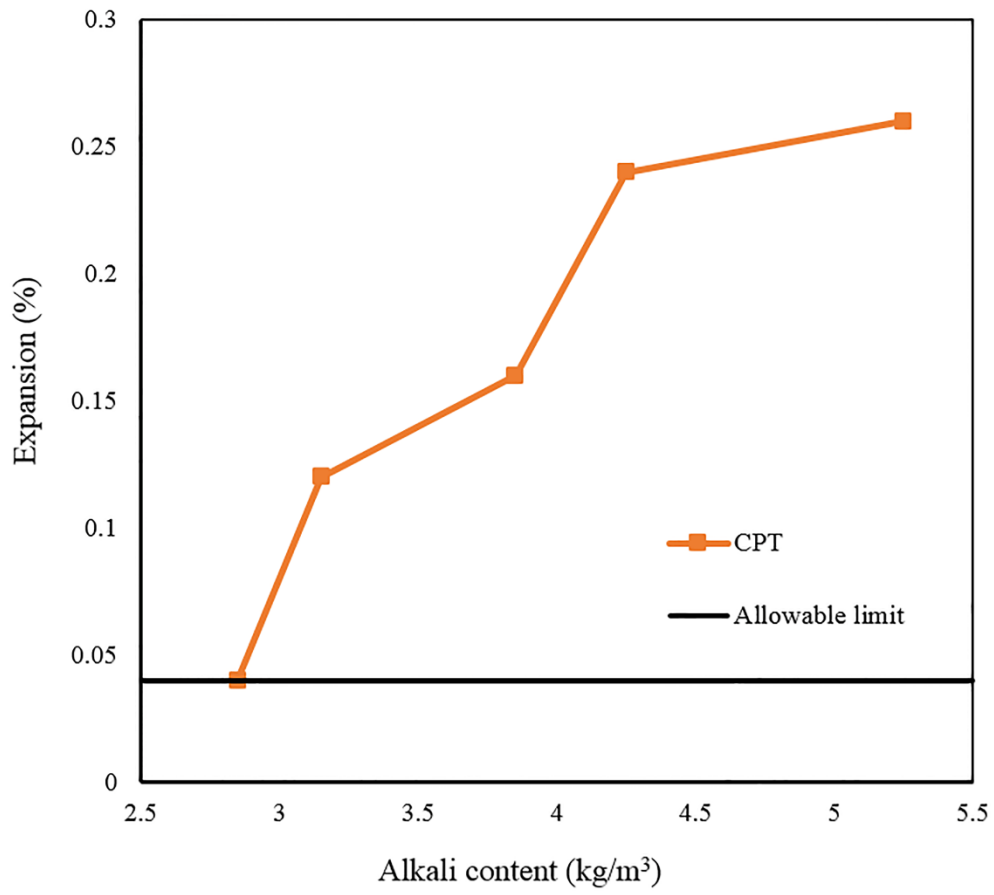
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1166   **Fig. 8.** Effect of alkali content of fly ash on the expansion of concrete after two years of testing
1167   [55].
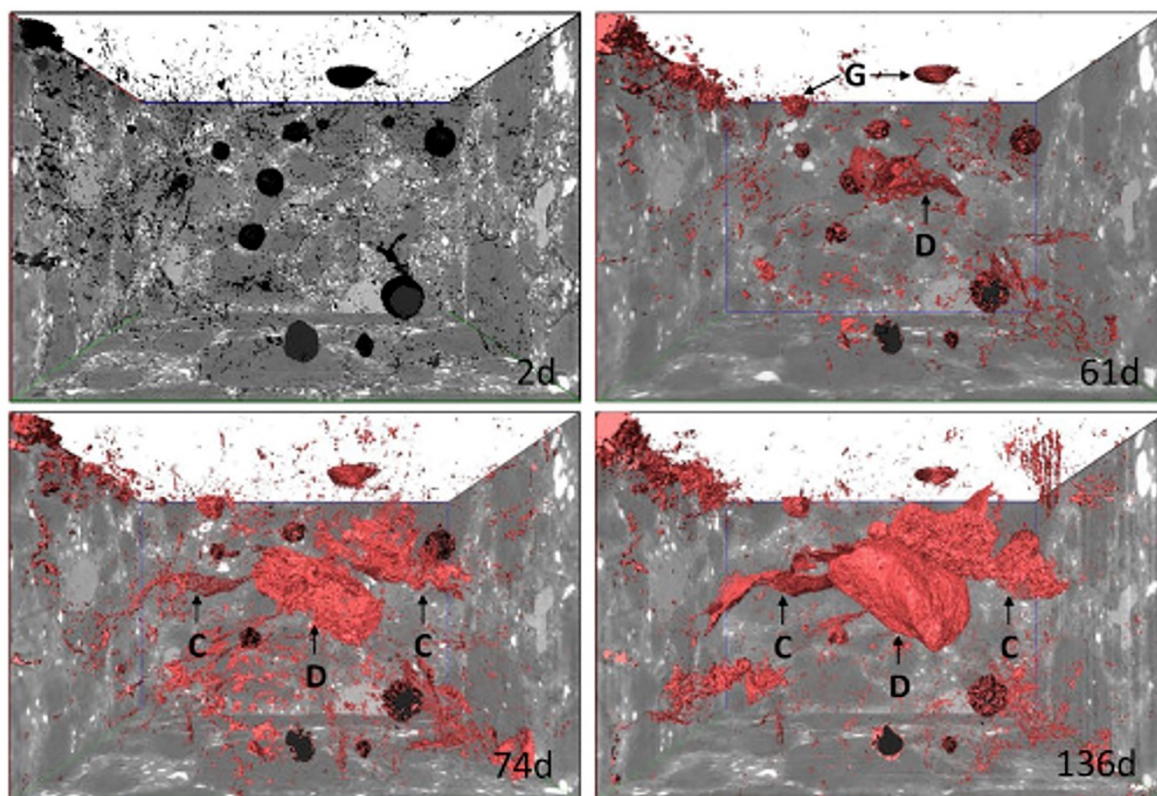
Fig. 9. 3D image of ASR affected samples after 2, 61, 74 and 136 days in 1M NaOH solution at 50 ºC (Initial air gaps are black and the ASR gel is pink) [104].
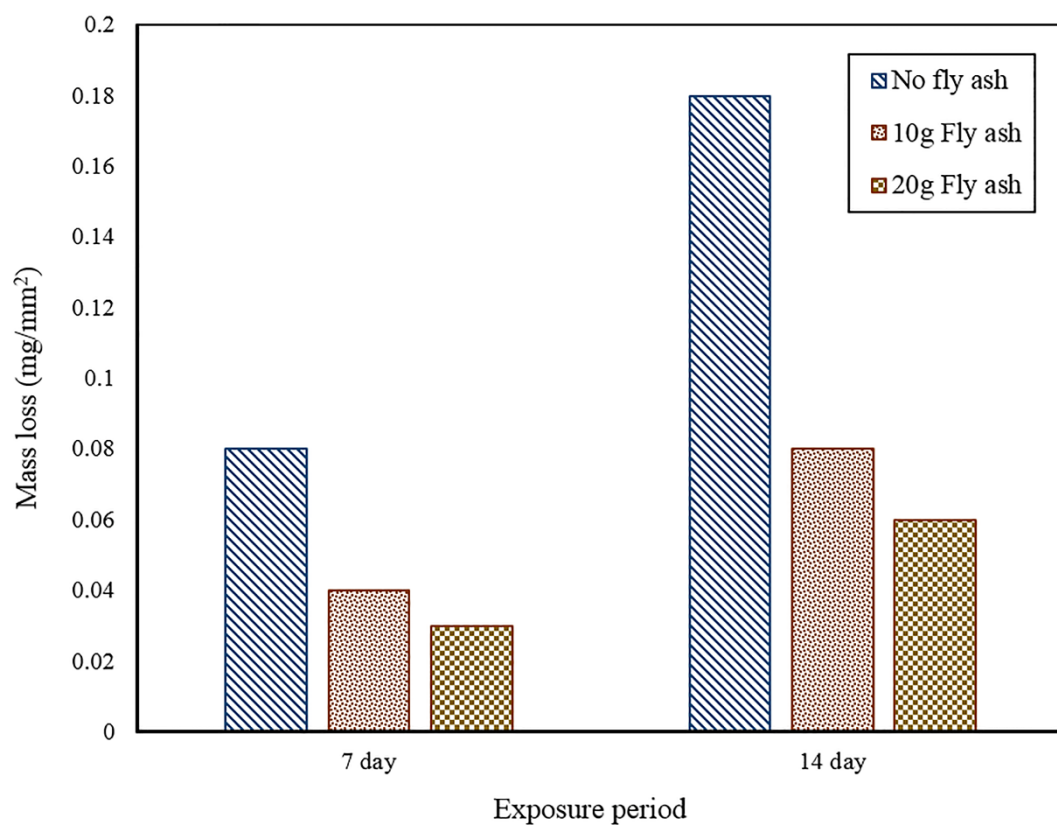
1171

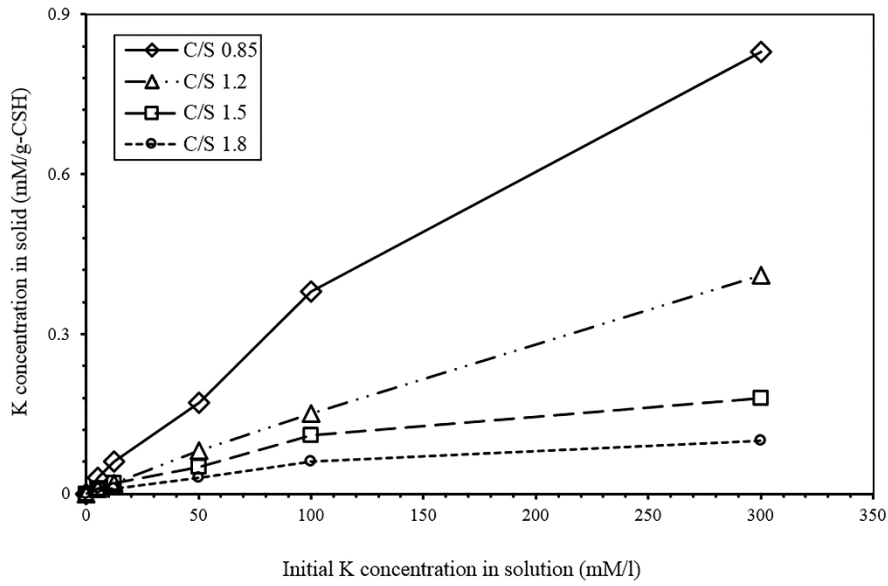1172 **Fig. 10.** Aggregate dissolution by NaOH exposure. [58].
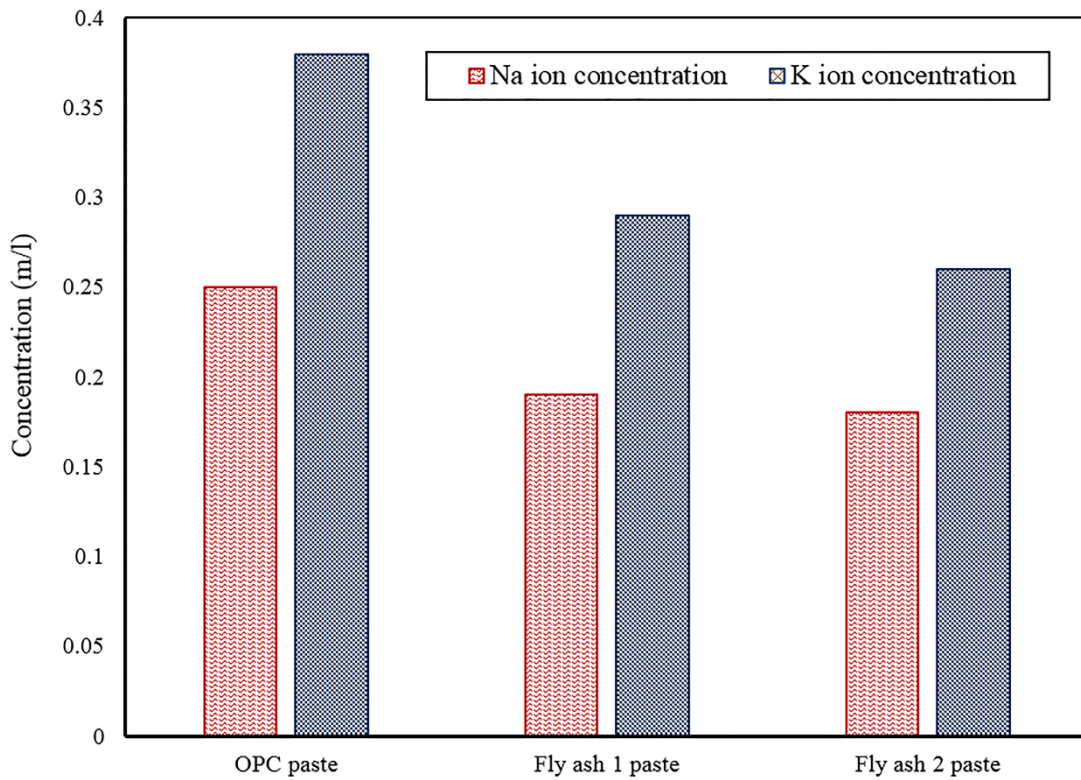
1173

1174   **Fig. 11.** Alkali concentration in pore solution after 10 days of curing [105].
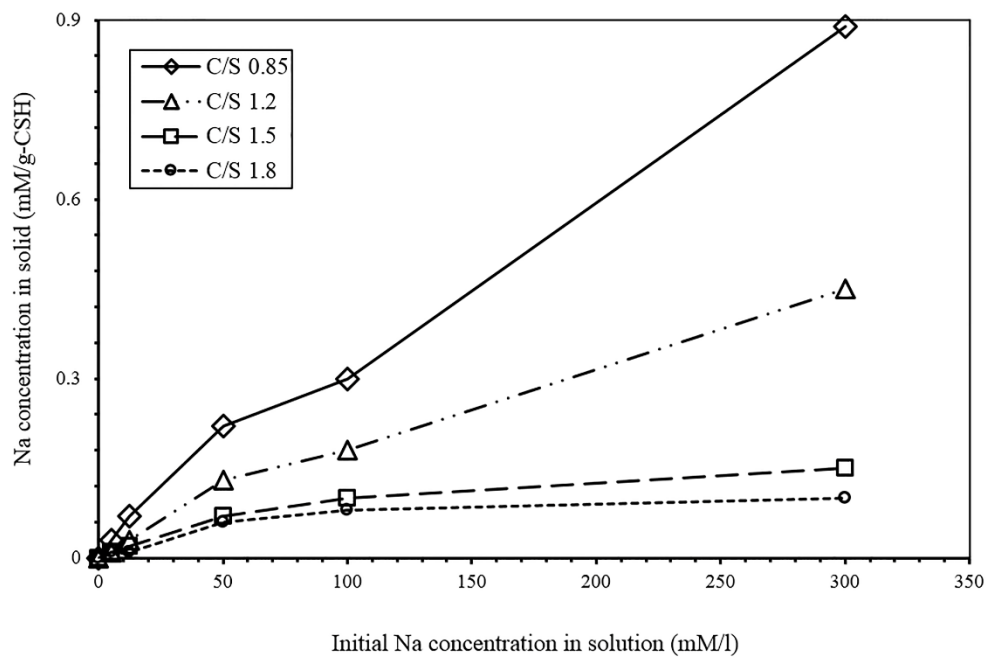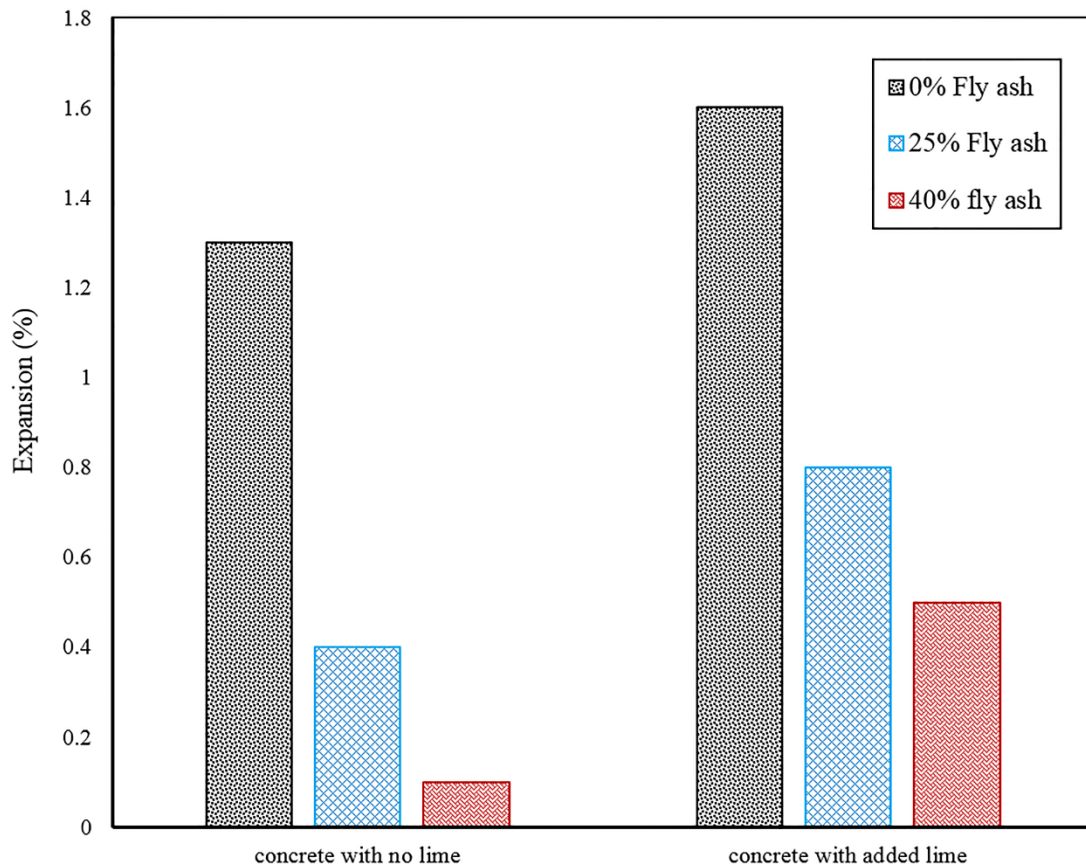

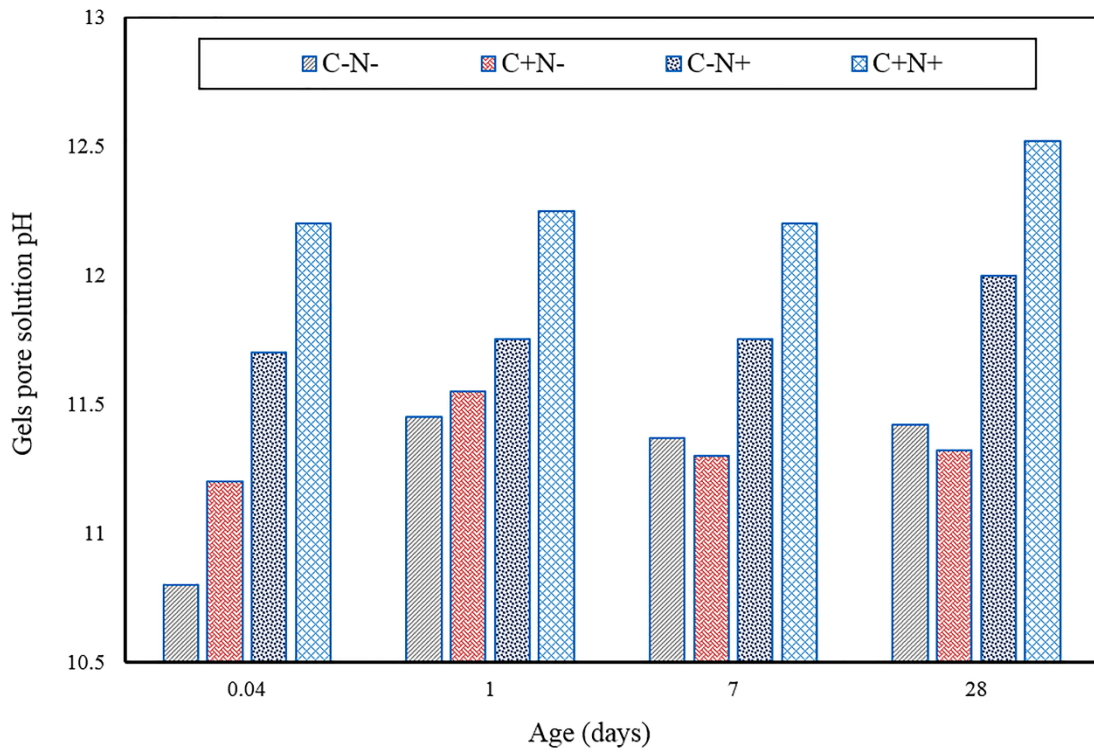1175   (a)

1176   (b)

1177   **Fig. 12.** The concentration of (a) sodium and (b) potassium ion in C-S-H with respect to C/S
1178   [82].

1179

1180   **Fig. 13.** Effect of lime on the expansion of fly ash mixed concrete [109].

1181

1182   **Fig. 14.** pH of the gel pores with respect to calcium and sodium content [51].

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1184