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Sent Date: 10/24/2017 3:27:35 PM
Received Date: 10/24/2017 3:28:12 PM
From: Morante, Richard J

Created By: morante@bnl.gov

Recipients:
"Lehman, Bryce" <Bryce.Lehman@nrc.gov>
Tracking Status: None

Post Office: EXMB3.bnl.gov

Files	Size	Date & Time
MESSAGE	175	10/24/2017 3:28:12 PM
Alkali-Silica Reaction 5571e6f008ae7536374c6022.pdf		2107918

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Priority: Standard
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Reply Requested: No
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Expiration Date:
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Alkali–silica reaction: Current understanding of the reaction mechanisms and the knowledge gaps

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ARTICLE INFO

Article history:

Received 15 October 2014

Accepted 19 May 2015

Available online xxxx

Keywords:

Alkali–aggregate reaction (C)

Pore solution (B)

Modeling (E)

ASR gel (–)

Thermodynamic calculations (B)

ABSTRACT

Alkali–silica reaction (ASR) is a major concrete durability problem, resulting in significant maintenance and reconstruction costs to concrete infrastructures all over the world. Despite decades of study, the underlying chemical and physical reaction mechanisms remain poorly understood, especially at molecular to micro-scale levels, and this has resulted in the inability to efficiently assess the risk, predict the service life, and mitigate deterioration in ASR-susceptible structures. This paper intends to summarize the current state of understanding and the existing knowledge gaps with respect to reaction mechanisms and the roles of aggregate properties (e.g., composition, mineralogy, size, and surface characteristics), pore solution composition (e.g., pH, alkalis, calcium, aluminum), and exposure conditions (e.g., temperature, humidity) on the rate and magnitude of ASR. In addition, the current state of computer modeling as an alternative or supplement to physical testing for prediction of ASR performance is discussed.

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1. Introduction

Alkali–silica reaction (ASR) is a deleterious reaction between the alkaline pore solution of concrete and various metastable forms of silica contained in many natural and synthetic aggregates [1,2]. The silica structure is dissolved by the nucleophilic attack of OH[−] ions, and the highly degraded silica structure behaves as a hygroscopic silica gel. Alternatively, the dissolved silica can cross-link (e.g., in presence of Ca ions), coagulate, and form ASR gel. Swelling of this gel leads to stress development and potentially, cracking of concrete. ASR is a major durability problem of concrete, and continues to damage important structures, including dams and hydraulic structures, pavements, bridges, walls, barriers, and nuclear/power plant structures [3–13].

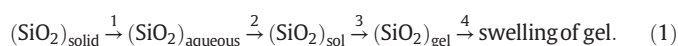
Much has been learned about ASR over the last 70 years, starting from the pioneering work of Stanton [14], who correctly recognized the significance of cement alkali content, availability of moisture, and the effect of pozzolans on the severity of ASR in concrete. Stanton also proposed a test method, which later evolved into the mortar bar test (ASTM C227 [15]), to evaluate the potential reactivity of cement–aggregate combinations. Since the 1940s, research has been primarily focused on (a) understanding the reaction mechanisms [1,16–18],

(b) developing rapid and reliable test methods to identify reactive minerals and aggregates [19–21], (c) predicting the long-term performance of concrete mixtures in service [22–24], and (d) proposing and evaluating effective methods to mitigate ASR in new or existing structures [8,25,26].

This paper further explores items (a) and (d) above, by summarizing the current state of knowledge on the ASR mechanisms and mitigation, and presenting important questions related to the reaction mechanisms and the roles of various species (e.g., OH, Na/K, Li, Ca, and Al) and exposure conditions (e.g., temperature, pressure, humidity) on the rate and magnitude of ASR. In addition, the current state of computer modeling as an alternative or supplement to physical testing for prediction of ASR performance will be discussed.

2. Reaction mechanisms

ASR damage is a result of a number of sequential reactions, including: (1) dissolution of metastable silica, (2) formation of nano-colloidal silica sol, (3) gelation of the sol, and (4) swelling of the gel:



Alternatively, a highly degraded (SiO₂)_{solid} may transform directly into (SiO₂)_{gel}, as long as sufficient but not excessive cross-linking is maintained between silica chains. Among these reactions, silica

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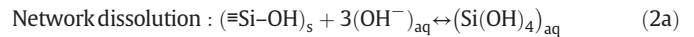
dissolution is often the slowest [27], and as such, primarily controls the rate of ASR in concrete. Factors that accelerate silica dissolution (e.g., higher alkalinity and temperature) are often used to speed up ASR in concrete, for example in accelerated ASR tests. In addition to silica dissolution, swelling of the gel depends on availability of moisture and mass transport properties of concrete, and could limit the rate of ASR damage in dry and dense concrete.

2.1. Dissolution of metastable silica

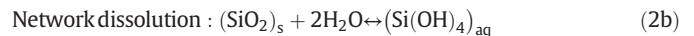
Silicates are the most abundant class of rock-forming minerals on the earth's surface. They are primarily composed of a 3D network of tetrahedral silica (SiO_2) units, with one Si atom in the center, surrounded by four oxygen atoms [28]. The tetrahedral units are connected through oxygen vertices (known as bridging oxygens), which form siloxane (Si-O-Si) bonds. Here, “=” suggests that each Si atom is connected to 3 other oxygen atoms. In addition to pure silica (SiO_2), silica minerals often contain hydrogen or metallic elements (e.g., Na, K, Ca) that are connected to oxygen atoms. The O–Si–O bond angle in silica is fixed at 109° , but the Si–O–Si bond between SiO_2 tetrahedra can vary from 100 to 170° [28]. As a result, a large number of silica structures exist that could be macro-crystalline (Fig. 1a), micro/nano-crystalline, or amorphous (Fig. 1b) [29].

The phenomenon of silica dissolution in water has been studied for over a century, with several hundred articles published, e.g., [30–36]. Most of the existing literature, however, focuses on pure silica and moderate levels of alkalinity ($\text{pH} < 11$). It is well known that in an alkaline

environment, hydroxyl (OH^-) ions progressively attack the (Si-O-) bonds, resulting in network dissolution of silica:



where (Si-OH) represents the silanol groups that are present at the silica–water interface [17]. The dissolving Si(OH)_4 leaves three Si-O^- groups on the solid surface (not shown on the right side of Eq. (2a)), which charge balance the equation. In addition to the mono-silicic Si(OH)_4 , dissolution products can be oligomers of the form $\text{Si}_n\text{O}_a(\text{OH})_b$, where $2a + b = 4n$ [30]. Eq. (2a) can be alternatively written as Eq. (2b), which is easier to describe thermodynamically, but does not convey the actual dissolution mechanism at high pH:



The solubility product of reaction (2b) has been reported by Walther and Helgeson [37] for different polymorphs of $(\text{SiO}_2)_{\text{solid}}$ and at different temperatures. For example, at 25°C , $\log K_{\text{sp}} = -3.999$ and -2.714 has been reported for α -quartz (crystalline and stable) and amorphous silica, respectively. This data can be used to calculate the equilibrium solubility limit of SiO_2 in neutral water as presented in Table 1. It is apparent that the solubility increases with temperature and reduction in silica crystallinity [33].

Table 1 shows that the solubility limit of silica in neutral water is small. While the solubility of non-ionic $(\text{Si(OH)}_4)_{\text{aq}}$ is not significantly

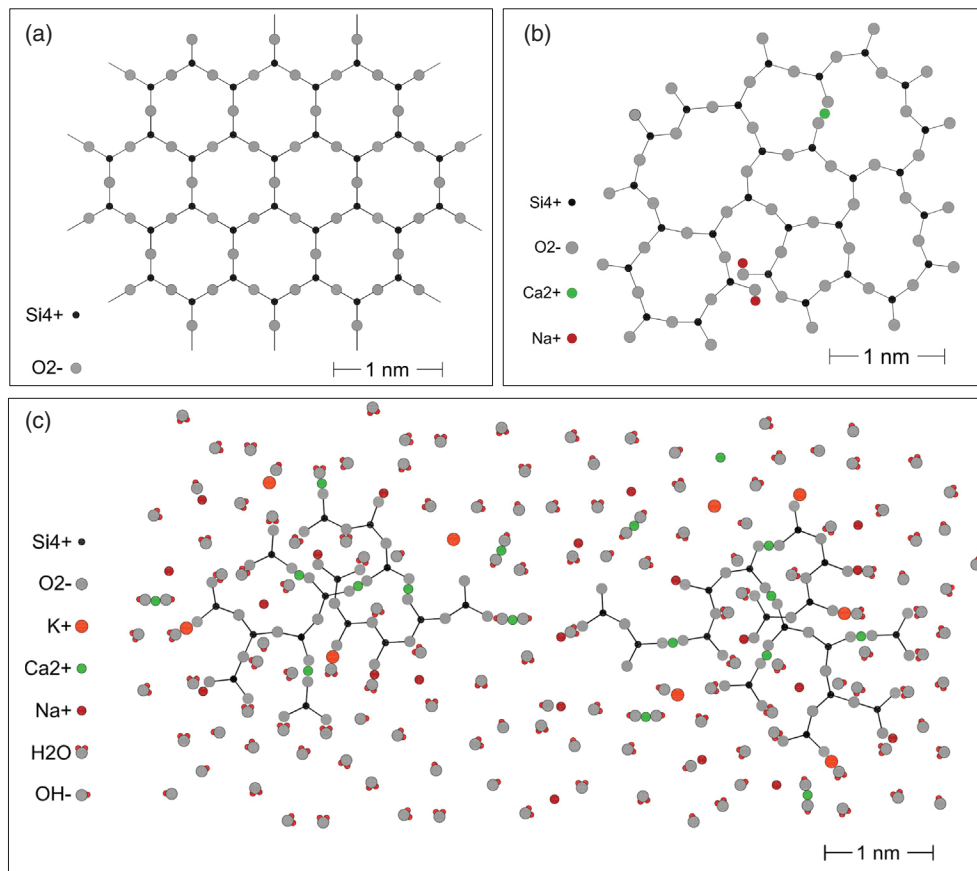


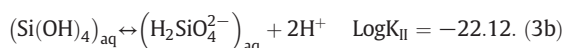
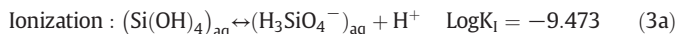
Fig. 1. (a) 2D ball and stick representation of quartz (a common form of crystalline solid SiO_2) composed of uniformly sized silica rings where all oxygens are bridging silicon atoms; (b) amorphous solid SiO_2 , showing non-uniform rings and the contribution of alkalis and Ca in forming non-bridging oxygens; (c) alkali-silica (ASR) gel composed of clustering of colloidal silica particles surrounded by the gel's pore solution; the silica structure is highly degraded with lots of non-bridging oxygens. These models were constructed based on information from Refs. [28,52].

Table 1

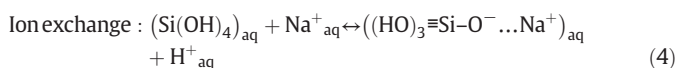
Thermodynamic solubility limit (mM) of various SiO₂ polymorphs in neutral water. Calculated using data from Ref. [37].

T (°C)	α-Quartz	Chalcedony	α-Cristobalite	β-Cristobalite	Amorphous silica
0	0.03	0.06	0.13	0.42	1.01
25	0.10	0.19	0.36	0.99	1.93
50	0.24	0.42	0.74	1.81	3.12
75	0.46	0.79	1.32	2.88	4.57
100	0.80	1.32	2.11	4.22	6.30

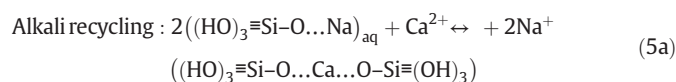
affected by the pH of the solution [30] (as also suggested by Eq. (2b)), at high pH, ionization of Si(OH)₄ occurs, resulting in conversion to highly soluble ions [35]:



Using the solubility products of reactions (3a) and (3b), the equilibrium solubility of silica species in an aqueous solution can be calculated as a function of pH, as shown in Fig. 2. It is observed that at high pH, the apparent solubility of silica increases by several orders of magnitude. In addition, the dominant silica species in the solution are H₃SiO₄[−] and H₂SiO₄^{2−}. Sjöberg [35] reported that at high pH, in addition to monomers, di-, tri-, tetra-, and other poly-meric silicate ions are also present at lower concentrations. It is also important to note that at high pH, reactions (2a), (3a) and (3b) proceed in the direction to reduce the pH. In addition, ion exchange reactions could occur to further decrease the pH; for example:



where O[−]...Na⁺ indicates that the bond is more likely a strong Van der Waals type. These reactions suggest that the pH of concrete pore solution should generally decrease as ASR progresses. As the dissolved silica gels (gelation mechanisms are discussed below), however, some of the alkalis incorporated in silica gel may be replaced by calcium ions, which recycled these alkalis back into concrete pore solution (Eq. (5a)). The resulting calcium deficiency of the pore solution promotes further dissolution of solid portlandite (Eq. (5b)), which results in increasing the pH:



This is further discussed in Section 3.3.

The above discussion is focused on the thermodynamics of silica dissolution. The kinetics are equally important because the rate at which silica dissolves in pore solution can largely control the overall rate of ASR. Literature on this subject is limited and significant knowledge gaps exist with respect to quantifying the dissolution rate as a function of aggregate composition, mineralogy, and surface properties, pore solution composition, temperature and pressure. The few available studies have used batch reactors (e.g., ASTM C1285 [38]) to measure the dissolution rate of silica (e.g., quartz or fused silica glass) in water [39, 40]. A recent study by Maraghechi [41] using soda-lime silica glass shows that the dissolution rate is highly related to the pH and temperature of the system. Up to pH = 14 and at 60 °C, the dissolution rate of glass was found to be a function of [OH[−]]^{0.2}. However, higher pH resulted in smaller dissolution rate. Activation energies in the range 60.9 to 76.6 kJ/mol have been reported for dissolution of crystalline

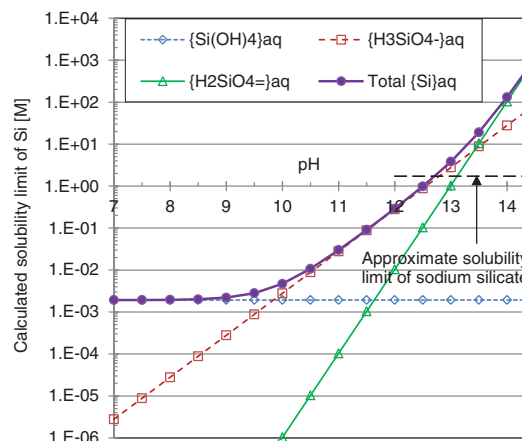
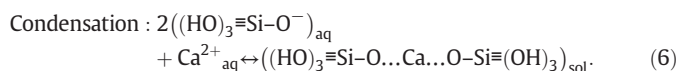


Fig. 2. The calculated solubility limit of amorphous SiO₂ in water as a function of pH (T = 25 °C) (note that to be accurate, y-axis represents Si activity, and the actual molar solubility limit at a given pH is likely to be higher assuming activity coefficient <1). From Ref. [41].

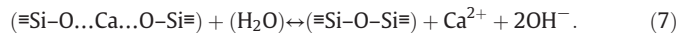
and amorphous silica in deionized water [42,43]. For soda-lime glass at pH = 14, activation energy was measured as 86.2 kJ/mol [41].

2.2. Formation and gelation of colloidal silica

As long as the pH and temperature are maintained to avoid supersaturation with respect to aqueous silica, and in the absence of Ca ions, the dissolved species remain in solution [44]. At high pH, aqueous silica species are negatively charged (Eqs. (3a) and (3b) and Fig. 2), and the resulting electrostatic repulsion prevents gelation. In such a case, aggregate dissolution slows and eventually stops when [Si]_{aq} approaches its solubility limit [45]. This, however, almost never happens in portland cement concrete, since Ca²⁺ (or other polyvalent metal ions; e.g., Al) present in the pore solution, can link silica ions to form poly-metal-silicates [30]; e.g.,:



The compound on the right hand side of Eq. (6) can be alternatively written as H₆CaSi₂O₈ or CS₂H₃ in cement chemistry notation. Gaboriaud et al. [46] suggested that Ca may only serve as a catalyst and could be further ejected, leading to formation of siloxane bonds; although this reaction is not thermodynamically favorable at high pH:



Once a nucleus of critical size is formed, it grows to nano-colloidal silica sol through further condensation [27]. Aggregation of colloidal particles in 2 or 3 dimensions forms larger metal silicate structures, which create either a continuous and space-filling silicate (ASR) gel, or more compact macro-scale precipitates [46–48]. It has been argued that the presence of portlandite (or other soluble sources of calcium) is essential to form ASR gel [18,49–51]; otherwise, silica species remain in the solution (more on this in Section 3.3). Fig. 1c is a schematic representation of the structure of alkali-silica (ASR) gels, which are composed of clustering of colloidal silica particles surrounded by the gel's pore solution. For simplicity and due to space limitation, the figure shows only 2 small colloidal particles. In reality, particles are 10 to 30 nm in size [52]. Further, the distance between the particles is a function of the water content of the gel. Recent work on rheology of ASR gels [53] suggests that they behave as viscous fluids with considerable yield strength up to 85 kPa. This indicates that the particles need to be very close to each other and possibly weakly inter-connected.

2.3. Swelling of the gel

A number of phenomena can be accountable for the significant sorptivity and swelling of ASR gels. The silica gel is porous with a high surface area, bearing many hydrophilic groups (e.g., $-\text{OH}$, $-\text{O}\cdots\text{Na}$, and $-\text{O}^-$) (Fig. 1c) [31]. This results in osmosis, adsorption of water, and swelling of the gel [17]. Additional osmosis could be generated by the Gibbs–Donnan effect [54], where the gel acts as a semi-permeable membrane, allowing small alkali and hydroxyl ions to diffuse into the gel, while the counter diffusion of larger silica ions (e.g., H_3SiO_4^- and $\text{H}_2\text{SiO}_4^{2-}$) to concrete pore solution is prevented [55]. This leads to a higher osmotic pressure and movement of water from the surrounding concrete into the gel. Chatterji et al. [56] argued that the swelling is caused by a differential kinetics of fast inward diffusion of deleterious ions (i.e., Na^+ , Ca^{2+} and OH^-) into the reactive sites and slow outward diffusion of silica ions from these sites. Swelling has also been attributed to the electrical double-layer repulsive forces that form on the charged surface of the gel's solid particles [57,58]. Garcia-Diaz et al. [59] attributed the ASR expansion to the increase in the aggregate pore volume during the $\text{Q}_4 \rightarrow \text{Q}_3$ de-polymerization of silica by hydroxyl attack, where they found a five-fold increase in the aggregate pore volume during this transition. The swelling magnitude is also related to the gel stiffness, which is a function of the degree of crosslinking between the colloidal particles (e.g., higher Ca gels are generally stiffer and more viscous [51,53]).

3. Effect of aggregate properties

Understanding the behavior of the aggregate, as the main reactive phase, is fundamental to improving our scientific understanding of ASR and the way ASR is mitigated. Currently, a common practice is to rely on the results of standardized tests (e.g., the accelerated mortar bar test, AMBT (ASTM C1260 [60]) or the concrete prism test, CPT (ASTM C1293 [61])), to classify aggregates as: non-reactive, moderately reactive, highly reactive or very highly reactive [62,63]. These reactivity levels are then often used to determine appropriate levels of mitigation using supplementary cementitious materials (SCMs) and/or chemical admixtures. While this approach may be practical, it does little to capture the influence of aggregate composition and physical properties on the magnitude and rate of ASR. Specifically, the effect of non-siliceous components of aggregates (e.g., Na, K, Ca, Al, and Fe-bearing phases) on ASR is poorly understood. In addition, it is unclear why the same aggregate may exhibit very different ASR expansion depending on its particle size (e.g., larger particles may show larger ASR expansion) or why some aggregates react at their surface while others only react within internal micro cracks and defects [64,65].

3.1. Aggregate composition and mineralogy

Poole [1] has suggested that it is incorrect to consider rock type (e.g., basalt) as a criterion for an aggregate's ASR potential; and instead,

attention should be focused on the mineral constituents of the rock. The thermodynamic stability of silica minerals decreases as the degree of microstructural disorder increases. Amorphous SiO_2 (e.g., opal, natural or synthetic glass) is known to be the most reactive, followed by meta-stable crystals (e.g., cristobalite and tridymite), micro-crystalline silica, and other crystalline forms containing many lattice defects, residual strains, or internal microcracks. Amorphous and crypto-crystalline silica forms could be due to rapid cooling from a molten state; residual stresses and microcracks could be due to rock deformation under geological forces [66] and also during aggregate processing and crushing [65]. Some natural materials that have been identified as ASR reactive are listed in Table 2. It should be noted that aggregates often contain more than one mineral and the volume of the reactive mineral needed to produce deleterious ASR can be as small as 1% [1,14]. The rock matrix porosity (e.g., in chert) or presence of cracks in aggregates allow access of concrete pore solution to the reactive silica that could be embedded in the interior of aggregates. Silica micro-porosity resulting in a large surface area also promotes ASR.

3.2. Aggregate size

The link between aggregate size/gradation and expansion has been and still is the subject of study. In general, ASR expansions are expected to increase with reduced particle size, because of the increased surface area of reactive aggregates [14,69]. However, experimental observations and field reports have showed that the greatest observed expansion varies non-monotonically as a function of aggregate size, and the most deleterious effects may occur for aggregates of some intermediate/pessimum size. For example, Stanton [14] found that a siliceous magnesian limestone shows the highest reactivity for particles in the range 0.18 to 0.6 mm, while smaller particles showed no expansion. Poyet and colleagues found that for flint, the smallest size fraction had an ASR mitigating effect [70]. Using an Alpine chloritic schist, Dunant and Scrivener found that the size fraction yielding the most expansion was 2 to 4 mm [71]. Multon and colleagues [72], in a study which also investigated the effect of alkalinity, found similarly for a siliceous limestone that the fraction that yielded the most expansion was 1.25 to 3.25 mm. In both of these studies, the different size fractions of aggregates had the same mineralogy. Recycled soda-lime glass aggregates show the highest expansions in the size range 1.18 to 2.36 mm (again while maintaining the same composition and mineralogy) [64,73]. This pessimum size effect has also been observed in the field and has led to recommendations like that of French [74] who noted the most deleterious aggregates to have a size from 4 to 10 mm. Interestingly, silica fume, when well dispersed, is an effective ASR mitigator; however, poorly dispersed silica fume agglomerates have been reported to result in severe ASR [75,76].

Different hypotheses have been put forward to explain the pessimum aggregate size effect. Very fine reactive aggregates may reduce or even suppress the expansion, probably due to a pozzolanic

Table 2
Some natural silicates susceptible to ASR [1,19,17,67,68].

Name	Description	Example rock types
Opal	Amorphous silica; a form of highly condensed silica gel (contains 4–9% water); always highly reactive	Occurs as primary or secondary mineral in rocks such as chert, flint, shale, limonite, sandstone, rhyolite, marl and basalt
Volcanic glass (e.g., Obsidian)	Reactive in some cases	Common minor constituent of fine-grain volcanic rocks such as basalt, rhyolite, andesite
Cristobalite and tridymite	High-temperature polymorphs of SiO_2 ; Are stable only at high temperature, but can crystallize and persist meta-stably at lower temperatures	Can occur in volcanic rocks
Cryptocrystalline (fine grain) quartz and other fibrous silica (e.g., chalcedony)	Moderately reactive	Constituents in rocks such as cherts and flints and as cementing material in greywacke
Mylonite	Highly crystalline silica, embedded in other minerals	Common Norwegian reactive material
Strained quartz	Only mildly reactive but degree of reactivity increases with strain	Quartzite

reaction [77,78], but this does not explain the observation with larger aggregates. In natural sands, it is likely that certain reactive minerals dominate certain sieve sizes. As such, reactivity does not necessarily increase for smaller particles. A related hypothesis is that the amount of reactive material in contact with pore solution differs as a function of the aggregate size. In this view, the observed differences in reactivity of different size particles is due to the time needed to diffuse OH^- to the reactive sites, which may be in the interior of aggregates [72]. A related model proposed by Bažant and Steffens [79] suggests that the swelling pressure of the ASR gel strongly depends on the size of reactive aggregates and is maximum at some intermediate particle size. Another theory is that the effects observed can be explained by fracture mechanics. The stress magnitude that causes splitting of an aggregate, depends on the aggregate size; as such the overall macroscopic ASR expansion and its rate are aggregate size dependent. Detailed microstructural modeling showed results that are consistent with this theory, although instead of a single crack, the model considered development of a crack network in each aggregate [71]. Maraghechi et al. [65] observed that the reactivity of recycled glass aggregates depends significantly on the size/width of residual cracks that exist in the interior of aggregates, which are formed during aggregate crushing. They found that larger aggregates (>1.2 mm) contain wider cracks and show higher ASR reactivity. They also showed that annealing glass aggregates to heal the residual cracks before mixing in concrete can significantly reduce the magnitude of ASR expansions.

Overall, the following conclusions can be drawn. (a) Aggregate reactivity depends on its size, and the trend of this dependence may not be predictable (e.g., smaller aggregates are not necessarily more reactive). (b) The size dependence of reactivity could be due to different reasons for different aggregates. (c) Because of such size dependence, aggregates need to be tested at the same size that they will be ultimately used in field concrete. For example, crushing potentially reactive coarse aggregates to allow testing their reactivity in a mortar bar test (e.g., ASTM C227 or ASTM C1260) could be erroneous [23].

3.3. Reactive aggregate content

Certain aggregates (e.g., flint and chert) containing highly-reactive forms of silica have been documented to exhibit a pessimum aggregate content. As summarized by Hobbs [2], for these aggregates, ASR expansion increases with the proportion of reactive aggregate until a maximum is reached (i.e., the pessimum content or proportion). For higher contents of reactive aggregate, expansions decrease, and in some instances, reach a point where no expansion is observed at a sufficiently high proportion of reactive aggregates. The pessimum content varies depending on the alkali loading of concrete, with higher alkalis resulting in a larger pessimum content. Above the pessimum aggregate content,

there is believed to be a surplus of reactive silica, which may consume or neutralize the available alkalis before the concrete has even hardened [80,81]. Several authors have suggested that the pessimum proportion will occur when the ratio of reactive silica/available alkalis is equal to 6 [2,45,77].

The pessimum aggregate content effect holds some interesting implications:

- Mitigation may not be necessary for certain aggregates displaying pessimum behavior, provided they are not used in combination with non-reactive aggregates. Engineers can essentially use the reaction against itself to prevent expansion with pessimum aggregates, and this is an accepted practice in several European countries [82]. However, not all aggregates displaying pessimum behavior will contain sufficient reactive silica to self-mitigate [83].
- Pessimum behavior may lead to false negatives in accelerated laboratory tests such as the AMBT [84]. Such aggregates may only be correctly identified as reactive by the CPT where they are paired with a non-reactive aggregate or by replacing a fraction of the aggregate in the AMBT with non-reactive aggregates.

While the mechanism of the pessimum behavior with respect to the proportion of reactive silica appears to be well-explained, testing methods need to be updated to deal with pessimum aggregates. The approaches given by Brouard [82] and Drimalas and co-workers [84] show promise. It is also possible that the so-called pessimum size may be interrelated with the pessimum proportion, and more work is needed to fully describe this relationship, because tests such as the AMBT and CPT use specific aggregate gradations [82,85].

3.4. Surface vs. intra-particle reaction and its impact on ASR rate

At the crux of the issue of aggregate reactivity is the accessibility of the alkaline pore solution to reactive silica. If the aggregate particle is composed entirely of reactive silica (as is the case with many volcanic and synthetic glasses, which have uniform composition throughout their volume), the aggregate surface may react quickly with the alkaline pore solution to form ASR gel at the surface (Fig. 3a). However, if the reactive silica is absent at the surface and is contained as fine reactive particles distributed within a non-reactive matrix of the aggregate (as is the case with many greywackes and siliceous limestones), it takes time for the pore solution to come into contact with the reactive silica and as a result, the reaction proceeds more slowly and the gel forms within the aggregate. In addition, the presence of pre-existing micro-cracks in the aggregate's interior will play an important role in the alkali-silica reaction. As more surface area is exposed, the reaction rate should increase.

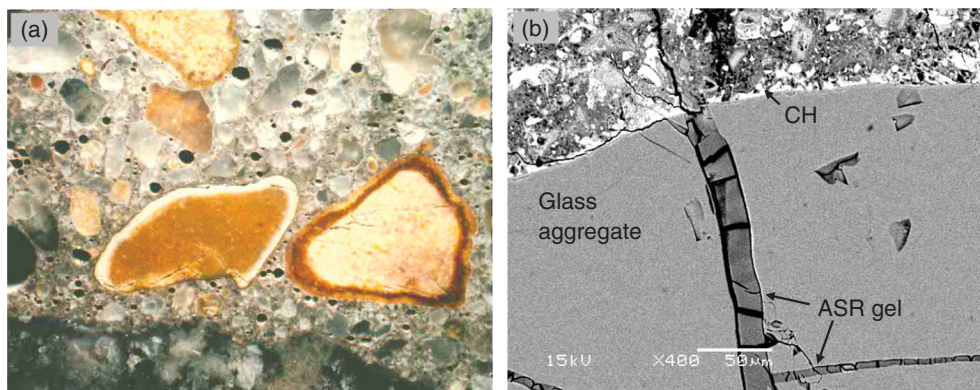


Fig. 3. (a) ASR occurring at aggregate surface for granite gneiss (right) and chert particles [88], (b) despite homogenous composition of soda-lime glass particle, ASR occurs in the interior of aggregate (through pre-existing microcracks) while the interface with cement paste is protected, possibly due to presence of solid portlandite [86].

However, the local chemistry at the aggregate surface (in contact with cement paste) could be different than the chemistry at the surface of intra-aggregate cracks. Rajabipour and coworkers [64,65,86] observed that for soda-lime glass aggregates (Fig. 3b), the presence of solid portlandite at the aggregate surface favors formation of innocuous pozzolanic C–S–H [87], which forms a physical barrier against further dissolution of glass and progression of ASR [41]. However, due to absence of portlandite in the interior of the aggregate, ASR can proceed freely through the intra-aggregate microcracks, resulting in further cracking and deterioration of the aggregate.

4. Alkalies

Sufficient alkalis are required to raise the pore solution hydroxyl concentration to a level (e.g., 0.2 to 0.25 M [89,90]) at which the aggregates are attacked at a significant rate, and to sustain the attack over time. While the majority of alkali contribution is linked to the cement (e.g., alkali sulfates), aggregates and SCMs can also supply alkalis to further exacerbate the reaction. In addition, external sources, such as seawater or deicing salts, could also increase the alkalinity of the concrete. This section discusses studies to evaluate alkali contributions from aggregates, SCMs, and external sources, as well as differences in the mechanisms of ASR as it relates to the type of alkali cation (i.e., Na^+ , K^+ , and Li^+).

4.1. Alkali contribution by aggregates

Alkalies can be found in both reactive and non-reactive aggregates. Reactive aggregates are those that contain a metastable silica structure that is attacked and dissolve by OH^- ions, leading to formation and swelling of ASR gel and ultimately cracking of concrete. When alkalis are present within this reactive silica structure (e.g., see Fig. 1b), they can be gradually released into the pore solution as the silica dissolves. For example, Shafaatian [91] showed that when soda-lime glass aggregates or soda-lime glass powder/SCM is used in concrete, Na is released into pore solution as a result of glass dissolution, and this maintains a high pH level in the pore solution of the concrete over a long period of time.

Furthermore, even some alkali-containing aggregates that are classified as non-reactive, have been shown to contribute to the alkalinity of concrete pore solution. Even though these aggregates are not considered alkali-silica reactive (e.g., because of their low expansion when tested according to the accelerated mortar bar test, ASTM C1260 [60]), they may contain releasable alkalis in certain mineral phases. Minerals known to release alkalis include alkali feldspars, micas, zeolites, and clay minerals [92–97]. The exact mechanism of alkali release by non-reactive minerals is not completely understood but it could be through some ion exchange reactions (e.g., replacement of Na from siliceous aggregate with Ca from pore solution; Eqs. (5a) and (5b) above).

It has been suggested [98] that alkali release from non-reactive aggregates can be large enough to influence the concrete prism test (CPT, ASTM C1293 [61]) results. Field studies [94,99] of dams have found cases where the total concrete alkalis measured by hot-water extraction exceeded the estimated alkali contribution by portland cement, in many cases by more than 1.0 kg/m^3 of concrete (or approximately 0.25 to 0.30% $\text{Na}_2\text{O}_{\text{eq}}$ by mass of cement, assuming concrete with a typical cement content). In at least one case [99], deleteriously expansive ASR was attributed to alkalis released by the aggregates.

Hobbs [2] summarized that certain aggregate types including artificial glasses, volcanic glass and Witwatersrand quartzite could contribute significant quantities of alkalis to concrete. He also pointed out that in the southwestern United States, the combination of low-alkali cements with certain rhyolites and andesites resulted in cracking of concrete pavements by ASR. He attributed this to alkali contribution from these aggregate types. In South Africa, the Witwatersrand quartzite was shown to contain between 0.1 and 0.7% $\text{Na}_2\text{O}_{\text{eq}}$, and ASR was implicated in concrete containing both the fine and coarse aggregate

from this source [100]. Goguel [92] showed that in selective leaching tests on rapidly-cooled basalts that contained poorly crystallized feldspars, the alkali release was approximately 1.0% $\text{Na}_2\text{O}_{\text{eq}}$ of cement mass, whereas a well-crystallized basalt only produced about 0.1% $\text{Na}_2\text{O}_{\text{eq}}$ of cement mass after leaching. Thermodynamic analysis by Wang and co-workers [101] showed that in alkaline solutions with a $\text{pH} > 13$, the greatest release of alkalis from alkaline minerals in aggregates followed the order of: dawsonite > leucite > nepheline > dehydration analcime > paragonite > muscovite > jadeite > Na-feldspar > K-feldspar. They also showed that a maximum contribution of alkalis was mostly affected by the pore solution/aggregate ratio rather than the level of the pH of the pore solution.

Batic and co-workers [102] conducted accelerated mortar bar tests on basalts containing montmorillonite and volcanic glass from Argentina that were suspected of causing ASR in structures. Examination of thin sections showed that both volcanic glass and montmorillonite participated in ASR by supplying soluble silica. In addition, the alkalis in montmorillonite could interchange with Ca^{2+} from the concrete pore solution, liberating Na^+ or K^+ . A zeolite (sodic, potassic) was found to be the principal component observed in the ASR reaction products.

In contrast to previous research which relied on indirect measurements of alkali leaching potential from aggregates, Constantiner and Diamond [103], measured the pore solution of concretes containing aggregates with varying alkali-bearing feldspar minerals. They confirmed that these minerals did contribute alkalis to the pore solution of concrete. They further demonstrated that some of these alkalis were tied up in the alkali-silica reaction products. Work by Ideker and co-workers [98] also showed that alkali release from the so-called “non-reactive” natural granitic fine aggregate fraction of a concrete mixture in the concrete prism test (CPT) could contribute alkalis to the pore solution in the 38 °C (standard) version of the test and in a non-standard accelerated version run at 60 °C. This granitic sand and seven other fine aggregates in the study, were classified as non-reactive based on a 14-day expansion of less than 0.10% in ASTM C1260 (AMBT) [60] testing. In addition to alkali release, the non-reactive fine aggregates, when combined with the benchmark reactive coarse aggregate Spratt (a Canadian siliceous limestone), were shown to produce a high variance in the CPT results (both at 38 °C and 60 °C).

More recent work by Giannini [104] suggests that a highly-reactive fine aggregate from El Paso, Texas, commonly known as Jobe, may release significant quantities of alkalis. This aggregate has been the subject of numerous ASR studies [105–107], particularly when rapid and severe expansion from ASR is desired. Pulverized samples of the aggregate subjected to hot-water extraction with a soak time of 24 h released an average $\text{Na}_2\text{O}_{\text{eq}}$ of 0.24 kg/m^3 (by mass of concrete), assuming the aggregate would constitute 30% by mass of concrete. Fig. 4 shows

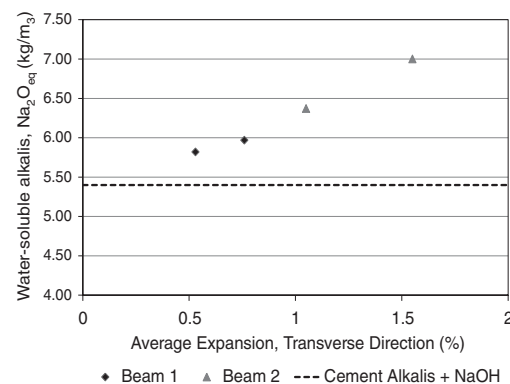


Fig. 4. Water-soluble alkali content (kg/m^3 of concrete) for two full-scale beams after two years of outdoor exposure, plotted against expansion. Dashed line represents total alkalis from cement and NaOH admixture at mixing. Adapted from Ref. [104].

water-soluble alkali data for cores taken from full-scale beams fabricated in the laboratory using this aggregate and left in outdoor exposure site for two years. Water-soluble alkali contents measured via hot water extraction ranged from 0.42 to 1.60 kg/m³ greater than the known contribution from portland cement and NaOH addition. This may help explain the extraordinary capacity of this aggregate to contribute to expansive ASR, even at very low alkali loadings from non-aggregate sources. However, based on these data, researchers would be wise to exercise caution with this aggregate, and avoid using it as the sole reactive aggregate in phenomenological studies.

4.2. Testing for alkalis in aggregates

Considerable research efforts have been placed on evaluating the alkali contribution of aggregates by performing solution-based leaching tests. Typically aggregates (or concrete) are processed to a certain fineness and exposed to water (distilled or deionized), alkaline solution (e.g., 1 N NaOH) and/or an alkaline solution plus Ca(OH)₂. The aggregates are allowed to react (or leach alkalis) at different temperatures, typically 38–80 °C and for varying time periods. The solution is analyzed and the alkali release is quantified. Pore solution expressed from cement pastes, mortars and concrete has also provided useful information on the contribution of alkalis from various sources. Since it is difficult to obtain pore solution from field concrete, destructive techniques involving the aforementioned leaching tests are generally used. In testing of 17 Canadian aggregates, Bérubé et al. [94] determined that an alkaline soak solution of 0.7 N NaOH or KOH was the most representative of conditions inside concrete. Alkalis released in these tests ranged from 0.1 to 12.7 kg/m³ (by volume of a typical concrete mixture) after 578 days – several times greater than that obtained by soaking in lime-saturated or pure water. A task group from RILEM committee TC 219-ACS is currently working to develop and standardize a reliable method for measuring alkalis released by aggregates to be designated as RILEM AAR-8 method. This is expected to be completed in the near future, but additional work will be needed to determine criteria for interpreting test results [108].

4.3. Alkali contribution by SCMs

Certain SCMs (primarily some moderate- to high-Ca fly ashes) include significant contents of alkalis (e.g., Na₂O_{eq} > 6% by mass [109, 110]). Monitoring of outdoor exposure concrete blocks [111] show that some mixtures with high-alkali SCMs show acceptable ASR performance only up to 10 years, but after this time cracking began to appear. This was potentially due to slow release of alkalis from SCMs. All such mixtures had expansions less than 0.04% after 2 years in the concrete prism test (CPT), and therefore would not have been expected to exhibit expansive behavior in outdoor exposure. This further points out a limitation in the CPT that the users should be aware of.

Currently, no standard test method is available to quantify the total alkalis contributed by SCMs to concrete pore solution over the service life of a structure, or the rate at which alkalis are released. This significantly impacts the ability to predict the service life of structures, especially based on accelerated ASR tests. ASTM C114 [112] provides test methods for determining the total and water-soluble alkalis in SCMs, and a test method for determining “available alkalis” in pozzolans is provided in ASTM C311 [113]. The ASTM C311 procedure involves leaching alkalis from a paste sample immersed in a saturated limewater solution for 28 days, and has been the subject of criticism for both under- and over-estimating available alkalis [114,115]. Recommendations to improve this method include extending the test to allow more alkalis to leach out [114], or using a more alkaline soak solution with an [OH⁻] in the region of 0.25 mol/L [115].

There remains little agreement internationally regarding the percentage of total alkalis in SCMs (particularly in fly ashes) that can be considered available for ASR. Low-Ca fly ashes are much more

effective at increasing the alkali-binding capacity of C–S–H than high-Ca ashes. This greatly increases the availability of alkalis for ASR where “high-alkali + high-Ca” fly ashes are used [115,116]. Efforts to develop a reliable standardized test method or methods should attempt to take this into account, and given the widespread use of fly ashes in mitigating ASR in new concrete, such a test method is of critical importance.

4.4. External alkalis

External sources of alkalis include seawater, deicers, and anti-icers. Seawater comprises approximately 3.5% of salts, with NaCl being the primary constituent. Sources of alkalis in deicing and anti-icing chemicals include NaCl, alkali acetates, and alkali formates. The latter two classes of chemicals do not contain chlorides, and are typically used in corrosion-sensitive airfield and bridge deck applications.

Potassium acetate (CH₃COOK), in particular, has attracted significant attention in the last decade for potentially accelerating cases of ASR in airfield pavements containing reactive aggregates [117–121]. Laboratory studies by Giebson et al. [122] showed that potassium acetate can react with portlandite in the cement paste to form calcium acetate and increase the hydroxyl concentration of the pore solution. Other laboratory studies suggest that this mechanism can lead to ASR in concrete containing reactive aggregates, even if normally effective mitigating measures such as low alkali loadings, fly ash, or slag are used [123, 124]. Outdoor exposure testing and observations from suspected field cases seem to indicate that the potential for potassium acetate to lead to distress in the field may be significantly overestimated by laboratory tests, which are commonly conducted using elevated temperatures, small specimens, and immersion in highly concentrated solutions (e.g., 50% potassium acetate). Field applications of deicers and anti-icers occur during or prior to cold-weather precipitation events. As a result, they are diluted by melting snow and ice, while the lower temperatures will impede any diffusion into and reaction with the concrete [124].

Cores from a pavement exposed to ten years of potassium acetate applications showed an increased potassium content to a depth of only 5 mm, while distress from ASR was detected uniformly through the depth of the pavement [124,125]. Hayman et al. [124] reported that slabs containing reactive aggregates placed in outdoor exposure and periodically treated with potassium acetate in Texas, USA (mean annual temperature = 20.8 °C) experienced an increase in expansion over untreated control slabs. Companion specimens in New Brunswick, Canada (mean annual temperature = 5.6 °C) treated with 100 applications each winter for three years exhibited no increase in distress compared to controls. At the time of this writing, there are no reports in the literature that describe the performance of concrete exposed to potassium acetate over a period of time equivalent to the expected service life of a bridge or airfield pavement. Therefore, it is not possible to state that potassium acetate will never lead to worsening ASR in field structures.

The ingress of NaCl into concrete, either from marine exposure or its use as a deicing salt, has also been thought to exacerbate certain cases and laboratory studies of ASR [126–129], while having no effect on expansion in others [130,131]. Although the overall effect on the pore solution pH caused by the addition of NaCl should be neutral [131], Cl⁻ ions can react with aluminate phases to form Friedel's salt (calcium chloroaluminate) and can be replaced in the pore solution with OH⁻ ions released to maintain charge neutrality [132]. However, Suryavanshi et al. [133] noted that Friedel's salt forms primarily by two mechanisms: one that binds Cl⁻ ions and releases OH⁻ ions from portlandite or AFm phases to the pore solutions, and another that involves adsorption of chlorides to AFm phases and binding of Na⁺ ions to the C–S–H. Both mechanisms may occur simultaneously, and binding is primarily limited by the C₃A and C₄AF contents of the cement. The adsorption mechanism does not increase the pore solution alkalinity because no OH⁻ ions are released; therefore, the formation of Friedel's salt does not guarantee an increase in pore solution pH. Yuan

et al. [134] state that it may be possible to predict chloride binding capacity of concrete from the cement composition if only portland cement is present. However, for binder systems involving one or more SCMs, more work is needed before chloride binding capacity can be adequately modeled. This has significant implications not only for ASR in concrete exposed to chloride-based deicers and marine environments, but also for service-life prediction related to corrosion of steel reinforcement.

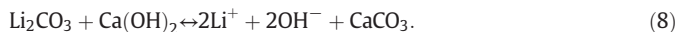
4.5. Lithium

The use of lithium compounds to control ASR was first reported in 1951 by McCoy and Caldwell [135]. In this study, over 100 different chemical compounds for controlling ASR were investigated using the ASTM C227 [15] test method. A wide range of lithium compounds that nearly eliminated expansion at 8 weeks of exposure at 38 °C were deemed the most promising. After this, research on lithium compounds was nearly stagnant until the late 1980s. Much of the focus of research since that time has been on understanding the mechanisms by which lithium compounds control or reduce ASR [136–145]. A thorough summary can be found in several review documents [146–148]. Three main lithium compounds emerged as candidates for controlling ASR: LiOH, LiCO₃ and LiNO₃. From the research completed in the late 1980s through early 2000, several mechanisms were postulated by which lithium compounds may control ASR:

- Lithium may reduce the dissolution rate of silica,
- Lithium may impede formation of alkali–silica gel,
- Lithium may reduce repulsive forces between the colloidal gel particles of ASR, thus reducing swelling, and
- Lithium may incorporate into the alkali–silica gel, altering its properties and expansion.

Kawamura and Fawa [149] and Mo [150] both noted changes in the chemical composition of the alkali–silica gel in mortars as dosages of LiOH and Li₂CO₃ increased, leading to gels with a lower CaO/SiO₂ ratio. Silica appeared to react with lithium preferentially over other alkali species. Mo and co-workers [151] hypothesized that the smaller ionic radius and higher charge density of lithium (compared to Na or K) was responsible for the latter phenomenon, but none of these studies could explain why the reaction product with lithium was less expansive. Later work by Leeman and co-workers [163] and Bulteel and co-workers [152] supports the hypotheses that lithium may reduce the solubility and dissolution rate of silica.

From laboratory studies and field experience, LiNO₃ emerged as the preferred lithium compound for controlling ASR, as many other lithium salts increase the pH of pore solution by reacting with Ca(OH)₂; for example:



LiNO₃ does not significantly raise the pore solution pH due to the relatively high solubility of the calcium analog Ca(NO₃)₂ [141].

Initially, it was proposed that the dosage rate of lithium to control ASR be based on the molar concentration of sodium and potassium supplied by the portland cement. A molar ratio [Li]/[Na + K] of 0.74 or greater emerged from work by McCoy and Caldwell [135] as the dosage rate needed to control ASR, and this dosage rate was used until the mid to late 2000s. At this time, research by Tremblay and co-workers [144] showed that one dosage rate of lithium was not equally effective across all classes of aggregates. They investigated 12 aggregates of different mineralogies and showed that 50% of the reactive aggregates responded well to the standard dosage (0.74 molar ratio). For three of the aggregates tested, a higher dosage of LiNO₃ ranging from 0.75 to 1.04 was required to control ASR. For the remaining three aggregates, a 1.11 molar ratio was not sufficient to limit ASR below the 0.04% expansion

limit of the concrete prism test (CPT). They also showed that the response of lithium to aggregate reactivity level and mineralogy could not be easily correlated. Therefore, they recommended performance testing to determine the safe level of lithium based on the specific type of potentially reactive aggregate being investigated [153]. This was confirmed by Drimalas and co-workers [154] where long-term exposure of concrete blocks incorporating different aggregate types and various dosages of lithium-based salts exposed for up to 16 years showed a varying response to lithium based on aggregate type. In their study, Drimalas, et al. demonstrated that either 30% class C fly ash (27.7% CaO) or a LiNO₃ dosage providing molar ratio [Li]/[Na + K] = 0.56 (equivalent to 75% of the standard dosage of 0.74 molar ratio) were both effective in reducing the expansion of highly reactive fine aggregate from Texas, with the 75% LiNO₃ showing no expansion observed after 3500 days in outdoor exposure. However, a mixture with 30% class C fly ash and 75% LiNO₃ dosage only showed a 50% reduction in expansion compared to 30% class C fly ash alone, reaching an expansion of 0.20% at 3500 days. This demonstrates that there may not be synergistic effects in terms of expansion reduction when lithium is combined with fly ash of certain composition. Specifically interactions between Ca and Li are unknown and could be significant.

Work by Feng and co-workers [145] focused on Vycor glass disks and glass disks sandwiching a cement paste and exposed to solutions of NaOH, NaOH plus calcium, and NaOH plus calcium and lithium. Their findings showed that in the presence of lithium and calcium, a layer of Li–Si crystals was formed on the surface of the glass disk that helped to protect the silica from further dissolution. Furthermore, the presence of calcium formed a dense rigid alkali–silica gel composed of Li with low-Ca concentrations. These authors postulated that this gel would have a low capacity to absorb moisture and thus a low swelling capacity.

Later work by Tremblay and co-workers [155] did not support many previously held theories about the mechanisms by which LiNO₃ may reduce ASR. Mechanistic work relying on pore and immersion solution analysis, XRD, SIMS and petrographic examination provided results suggesting the following classes of mechanisms may be unlikely as the cause of ASR reduction by Li: pH reduction, increased solubility limit of silica to prevent gelation, formation of a protective coating, non-expansive crystalline product, and non- to less-expansive amorphous gel. From their study, the mechanism most supported was that the presence of lithium provided increased chemical stability and reduced dissolution of reactive silica due to reasons other than pH reduction or formation of a protective coating [155]. Clearly, this debate has not been settled and more research into the impact of lithium salts on different aggregate mineralogies is needed to definitively make conclusions on the mechanisms by which lithium controls alkali–silica reaction in concrete. Furthermore, the long-term efficacy of lithium nitrate needs to be verified through correlation of laboratory studies and the growing body of information available from field exposure. This is specifically important in light of shrinking resources and availability for low-calcium low-alkali fly ash to control ASR.

4.6. Research needs for alkalis

Future research should address the apparent disconnect between accelerated laboratory tests, often conducted at temperatures of 38 to 80 °C and near-100% relative humidity, and variable real-world conditions experienced by a concrete structure over its service life. This may involve working with the growing database of field exposure sites to identify how fluctuating environmental conditions can impact the availability of alkalis in field concrete.

The current understanding of the threat posed by alkali release by aggregates is primarily based on accelerated solution-leaching studies in the laboratory, as well as several anecdotal cases involving structures in the field. Systematic research is needed to establish the expected alkali release from aggregates of a range of mineralogies in concrete

with a range of alkali loadings. This is particularly important for long-life hydraulic structures where the combination of alkali release, alkali migration, and a near-constant supply of moisture in the structure could result in an alkali concentration sufficient to trigger and then maintain expansive ASR. This research would be facilitated by the many outdoor exposure sites that have been constructed over the past couple of decades; specimens on these sites are well-documented with respect to their materials, initial alkali loadings, and expansive behavior. Researchers should couple testing of exposure site specimens with laboratory tests such as the forthcoming RILEM AAR-8 method.

The widespread use of SCMs in mitigating ASR demands an improved understanding of alkali release and binding by these materials. Fly ashes, with their widely variable chemistry (sometimes with very high alkali contents), are perhaps in greatest need of attention. In North America, the future of reliable sources of fly ash are uncertain as utilities shift to fuels other than coal, and other SCMs are being looked to for ASR mitigation. It is likely that the same questions regarding alkali availability will abound in new mitigation materials. Research on alkali release from SCMs should be conducted in parallel with research on alkali release from aggregates.

Another significant research need is to examine the differences between Na and K with respect to ASR because most accelerated tests use NaOH, rather than KOH, to boost alkali loadings. However, most cements contain a higher proportion of K_2SO_4 versus Na_2SO_4 . Investigations should focus on whether the composition of alkali boosting solutions in ASR studies should be matched to the chemistry of the cement. Studies of expressed pore solution are particularly valuable, but are not without flaws. Some researchers suggest that it may be more difficult to express Na than K, and have observed a change in the ratio of these species as increasing pressures are applied [156–158]. Even the most advanced apparatus can only express about 40% of the available pore solution at a pressure of 1000 MPa [159]. The composition of the remaining 60% remains uncertain. Rather than pursuing higher pressure pore solution expression devices, the authors encourage researchers to agree upon a standardized pressure and overall procedure, enabling them to better compare results obtained in different laboratories.

In each of the above areas, it will be critical to identify where alkalis in concrete reside. This is likely to require a combination of bulk analysis techniques (e.g., water- and acid-soluble alkali testing, and pore solution analysis) and micro-analytical techniques (e.g., SEM-EDS, EMPA, and micro-XRF).

5. Calcium

Two major roles played by calcium in the alkali–silica reaction are:

- Exchange with alkalis in the reaction products (gel) – “alkali recycling”, and
- Its impact on the composition and properties of the reaction products (gel), and its expansion.

5.1. Alkali recycling

Hansen [160] first proposed that calcium may replace alkalis (Na and K) in the reaction products (i.e., ASR gel), thereby regenerating alkalis for further reaction. Note that the pore solution pH can therefore increase by dissolution of portlandite to compensate for Ca uptake, according to Eqs. (5a) and (5b). Hansen's hypothesis was based on the observation of depleted portlandite in the cement paste immediately in contact with ASR gel in cracks. He observed a darkening of the paste adjacent to gel-filled cracks or around the periphery of reacting aggregates and attributed this to the reduction in the quantity of portlandite, which he confirmed by petrographic examination. Knudsen

and Thaulow [161] showed, using electron probe microanalysis of concrete, that gel formed within or close to aggregates was low in calcium and high in alkali. But as the distance from the aggregate increased, the calcium content of the gel increased, presumably due to close association with the calcium-rich cement paste. Thomas [162] compared the composition of ASR gels found in 7-year-old laboratory concrete and a 55-year-old concrete dam with the composition of calcium-silicate hydrate (C–S–H) in the concrete from the dam. The data expressed as alkali/silica and calcium/silica atomic ratios are presented in Fig. 5. The composition covers a wide range, but it appears that there is a reasonable relationship between the alkali and calcium contents (i.e., as the calcium content increases, the alkali content decreases). This supports the concept of a cation exchange with the calcium replacing the alkali in the initially alkali-rich reaction products. This exchange occurs as a portion of the gel migrates away from the aggregate particle and comes into contact with the calcium-rich cement paste. The data in the figure indicate that the process continues slowly as the concrete ages and that the composition of the reaction product may ultimately approach something similar to C–S–H. This “final product” appears to retain very little alkali, indicating that almost all of the alkali that originally participated in the reaction process may be eventually recycled to participate in further reaction.

Thomas [162] suggested that alkali recycling might partially explain why in many large concrete dams, the expansion continues for decades and does not appear to reach a maximum value. This is not the case for laboratory tests (e.g., ASTM C1293 [61] where specimens are stored over water), in which the expansion–time relationship is typically represented by an S-shaped curve, reaching a maximum after a few years or less. In large structures, alkali recycling may continue to fuel ASR (until all the reactive silica or portlandite are consumed), whereas in laboratory specimens, leaching of the alkalis from the specimens eventually reduces the alkali concentration to a level below that necessary to sustain ASR.

5.2. Effect of calcium on the properties of ASR gel and its expansion

A number of experimental studies have concluded that significant expansion only occurs when an adequate supply of calcium is available in the form of portlandite. In systems with abundant alkali hydroxides and reactive silica, but no portlandite, silica dissolves and remains in solution [44,163]. Although the precise role that calcium plays in gel expansion remains unclear, a series of mechanisms have been proposed, as listed below [164]:

- High calcium concentrations in the pore solution prevent the diffusion of silica away from reacting aggregate particles [18,165].
- If calcium is not available, reactive silica dissolves in alkali hydroxide solution without causing damage [50,164].
- The formation of calcium-rich gels is necessary to cause expansion,

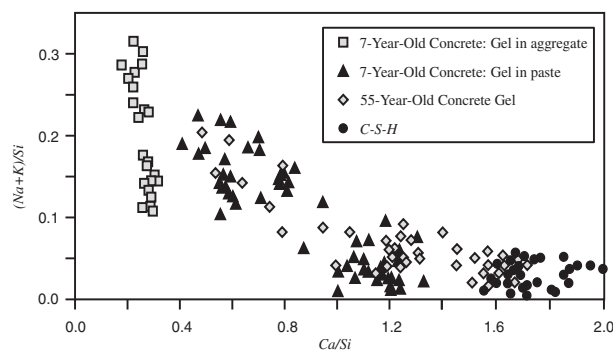


Fig. 5. Composition of alkali–silica gels in concrete. From Ref. [162].

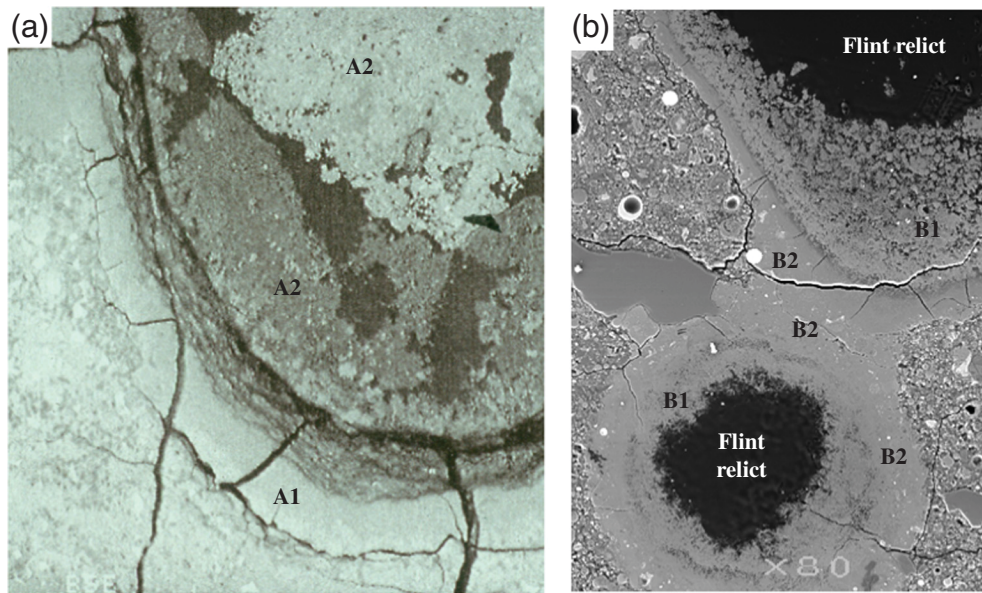


Fig. 6. BSE images of polished samples from (a) portland cement concrete showing high-alkali gel (A2) within flint grain and high-calcium gel (A1) around periphery of grain, and (b) fly ash (40%) concrete showing high-alkali, low-calcium gel (B1) within dissolved (relict) flint grain and gel (B2) penetrating and “saturating” cement paste surrounding flint relicts without causing damage. Width of view approximately 2 mm for both images. From Ref. [51].

either directly or indirectly through the formation of a semi-permeable membrane around reactive aggregate particles [51,164,166]. Fig. 6 shows the formation of a high-calcium, alkali–silica reaction product in concrete containing reactive flint aggregate.

- Calcium increases the viscosity and yield strength of gel, resulting in larger stress magnitudes generated by the gel expansion [51,53].

The important role of available calcium (in the form of portlandite) is supported by the following reported observations:

- Expansion of mortars or concretes containing reactive aggregate can be prevented by removal of the $\text{Ca}(\text{OH})_2$ prior to immersion of the sample in alkaline solutions. Chatterji [18] removed the $\text{Ca}(\text{OH})_2$ from concrete by leaching, and Thomas [164] carbonated the $\text{Ca}(\text{OH})_2$ by exposing mortar bars to an enriched- CO_2 environment.
- Pozzolans are effective in controlling the expansion of concretes (and mortars) immersed in alkaline salt (including alkali hydroxide) solutions [51,137,167,168]; and this has been attributed to the consumption of $\text{Ca}(\text{OH})_2$ by the pozzolanic reaction, which reduces the availability of calcium for ASR. Bleszynski and Thomas [51] showed considerable evidence of reaction in concrete containing 40% fly ash and a reactive flint sand after 4 years immersion in 1 NaOH at 80 °C, but no expansion. ASR gel was observed to be migrating into and saturating the cement paste surrounding reactive flint particles, with no

signs of damage to concrete (Fig. 6b). They attributed this to the very low viscosity of the reaction product in the absence of calcium. By contrast, other workers [169,170] showed that the addition of CaO can induce expansion in concretes containing fly ash or silica fume.

- Urhan [171], summarizing observations from a number of studies, proposed that there is a progressive passage from low viscosity alkali–silica gel to C–S–H and that, this is accompanied by a change in the physical and mechanical properties of the gel. Fig. 7 illustrates the changes in composition, physical and mechanical properties, and structure of the reaction product. Gel with low calcium content may have a high swelling capacity, but the viscosity is very low. On the other hand, gel high in calcium is more rigid, and does not swell. Although not explicitly stated by Urhan [171], at some point the composition of the gel is such that the gel has sufficient swelling capacity and viscosity to cause damage to the surrounding cement paste. However, earlier work of Struble and Diamond [172] did not report a noticeable reduction in the free swelling and swelling-pressure characteristics of calcium bearing silica gels in comparison with sodium silica gels.

6. Role of aluminum

Research on the role of Al on ASR has been limited; but there is evidence that the presence of soluble Al may help in mitigating ASR. Al-rich SCMs (e.g., fly ash, metakaolin) were found to be more effective against ASR than SCMs that were only rich in silica (e.g., silica fume) [173–175]. Schumacher and co-workers [176,177] and later Warner [178] showed evidence that fly ash with $\text{Al}_2\text{O}_3 > 20 \text{ wt.}\%$ were better able to control ASR than comparative fly ashes with lower alumina but similar calcium oxide contents. Warner et al. [179] demonstrated that binary and ternary blends of SCMs rich in Al_2O_3 had several effects on pore solution chemistry compared to mixtures with lower Al_2O_3 : (1) the pore solution pH was lower; (2) aluminum was found in increased amounts in pore solution and this remained stable and/or increased up to 90 days of age; (3) potassium amounts were reduced in pore solution; and (4) ternary blends were most effective at depleting CH. They also demonstrated that fly ashes with $\text{Al}_2\text{O}_3 < 20\%$ could be augmented with

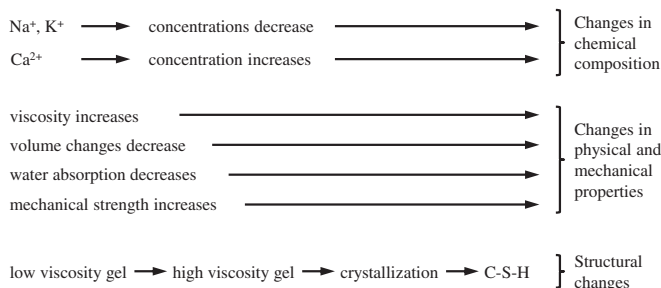


Fig. 7. Changes in the nature and properties of the alkali–silica reaction product [171].

alumina powder to improve ASR mitigation efficiency. Their work further showed that ternary blends of fly ash with either metakaolin or ultra-fine fly ash (both rich in Al_2O_3) showed improved ASR mitigation compared to just fly ash on its own. Work by Shafaatian [91] shows significant reduction of ASR expansion when $\text{Al}(\text{OH})_3$ was admixed in ASTM C1260 mortars.

Possible explanations for the beneficial effects of Al on ASR can be summarized as:

- Reducing silica dissolution rate from aggregates, by Al adsorption on the surface of reactive silica and/or formation of a diffuse zeolite barrier [180–182];
- Reducing the pore solution pH by formation of C–A–S–H, which improves alkali binding capacity over C–S–H [183];
- Reaction with and consumption of portlandite to form calcium aluminate phases;
- Reducing swelling of ASR gel;
- Densifying pore structure, and reducing permeability of concrete.

Among the above possible mechanisms, limited past research has been conducted on the first and second mechanisms. Chappex and Scrivener [182,184] demonstrated that presence of aluminum in pore solution can limit the dissolution of silica from aggregates. Two potential mechanisms have been suggested to explain how Al may impact the dissolution of silica in alkaline environments. (1) Al can react with the silica and form an aluminosilicate layer on the silica surface, which could protect the substrate silica against further attack of hydroxyl ions [185]. (2) Presence of Al in the solution, “passivates” or “poisons” the surface of silica glass through surface adsorption of the $\text{Al}(\text{OH})_4^-$ ions. The negatively charged aluminosilicate surface sites thus formed, repel OH^- ions and thus depress their attack on the silica structure [180,186].

Aluminum is known to interact with C–S–H to form the aluminum-modified calcium silicate hydrate C–A–S–H. Komarneni and co-workers [187–189] demonstrated through NMR studies on tobermorite that Al was mainly found in C–S–H in tetrahedral coordination $\text{Al}[\text{IV}]$ occurring in both Q2 and Q3 chain sites that linked across interlayers. They suggested that this linkage played an important role in cation exchange properties. Other researchers [190,191] also demonstrated that Al can be incorporated in C–S–H as $\text{Al}[\text{IV}]$ and $\text{Al}[\text{VI}]$. Lognot and co-workers [192] proposed that Na^+ played an important role in providing charge balance when Al substituted for Si in C–S–H. Recently, Sun et al. [193] prepared Al-substituted C–S–H by precipitation and showed significant increases in basal spacings when Al was incorporated into C–S–H. They concluded that alumina was present in the interlayer and that the substitution of Si by Al provides a (–) site that must be charge balanced by a net (+) charge (e.g., Na^+ , K^+), resulting in alkali binding.

The work of Hong and Glasser [183] showed that C–A–S–H may be better able to bind alkalis and reduce the pH of pore solution. They demonstrated that for synthetic C–A–S–H with low Ca/Si ratio (0.85), the alkali binding capacity was dramatically improved for both Na^+ and K^+ in comparison to a C–S–H not incorporating alumina. Chappex and Scrivener [194], however, suggested that incorporation of alumina may not increase the alkali binding capacity of C–S–H in real cementitious materials (compared to synthesized C–A–S–H previously studied). They suggested that reduction of silica dissolution as a result of adsorption of aluminum on the silica surface is more likely to explain the benefits of aluminum in reducing ASR.

A central theme from these studies emerged; a better understanding in real cement pastes and concretes is essential for further study and determination of the efficacy of alumina modified C–A–S–H. In fact, Hong and Glasser [183] highlighted this shortcoming, stating that “to understand the behavior of real concretes, it is important to consider

the response to changing alkali concentrations of the gel phase mainly in the undersaturated region and, if possible, determine the role of Al”. In a real concrete undergoing ASR, the concrete pore solution alkalinity is a dynamic system changing as the reaction progresses and potentially even fluctuating due to alkali recycling with calcium [162,164]. What remains unclear is how stable the system is. Binding alkalis in the short-term has been demonstrated in the laboratory. However, a reduction in binding capacity as concrete ages (e.g., pore solution pH decreases due to ongoing ASR or carbonation depleting $\text{Ca}(\text{OH})_2$) could be detrimental to such mitigation measures.

7. Effect of exposure conditions

Although ASR expansion is significantly dependent on the availability of moisture [2,195,196], research on interactions of water and ASR gel (and how gel properties are affected by moisture content, temperature, and pressure) has been very limited. Most available conclusions are based on expansion of concrete stored at particular relative humidity (RH) as opposed to direct testing of the gel. These results are difficult to interpret and reproduce since they are also greatly affected by the elastic and fracture properties of concrete. It is believed that an internal RH > 80% is required to support expansive ASR [197]; but specimens stored at drier environments may still undergo silica dissolution and gelation reactions, although swelling will only occur after the specimens are moved back to a humid environment [1,198]. Larive et al. [199] argued oppositely that water only increases concrete expansion when it is available during formation of the ASR gel; any subsequent water additions will not cause extra swelling [200]. Poyet et al. [201] showed that the RH threshold to support expansions depends on temperature, and concrete at 59% RH and 60 °C can undergo ASR. This is understandable as the moisture content of concrete, and thus the moisture available for swelling of ASR gel, is dependent not only on the internal RH but also on the temperature. This is further an indication that accelerated laboratory tests that do not mimic and significantly depart from the real life cyclic temperature and moisture conditions may be poor indicators of real concrete behavior and durability.

Using the analogy with C–S–H, it may be presumed that ASR gel has a certain moisture content and expansion capacity at 100% RH, and will undergo partly irreversible shrinkage and swelling with cycling RH [202,203]. The magnitudes of shrinkage and swelling are also likely dependent on gel composition and temperature. Such information on ASR gels is largely unavailable. By exposing dried synthetic gels to water, Struble and Diamond [172] measured the swelling capacity of a number of ASR gels and reported significantly different results (e.g., 0.5% to 81.6% free swelling) even for gels with fairly similar compositions. It is important, however, to note that pre-drying could disturb the structure and properties of gels. Also, in exposure to ambient CO_2 (e.g., while drying), ASR gel is gradually carbonated, which affects its properties [204]. No data are available on the rheological properties (e.g., yield strength, viscosity) of ASR gel as a function of its composition, moisture content, and temperature.

Research is needed to determine how much moisture is absorbed by ASR gel at a given temperature and relative humidity, and how much swelling this causes. Does the swelling stop under confining pressure; in other words, what level of stress is generated when the gel is restrained from expanding? Can this stress be relieved by hydraulic flow of the gel through cement paste's pore network (which depends significantly on the yield strength and viscosity of the gel, as well as permeability of the matrix)? And how are all these parameters affected by the gel composition, moisture content, and temperature? Answering these questions are important for correctly predicting the ASR performance of concrete in a given location/exposure environment and to better assess how certain species (e.g., Li, Ca, Al) affect the properties of ASR gel.

8. ASR mitigation

A classic conclusion that is drawn from the above discussions is that ASR requires four main prerequisites: (1) a source of reactive silica (commonly contained in aggregates), (2) alkalis or more correctly, OH^- ions in concrete pore solution to attack silica, (3) a source of soluble Ca (e.g., portlandite) to react with dissolved silica and form deleterious gel, and (4) access to moisture to allow gel expansion [1,2]. As a result, mitigation methods are often targeted at eliminating one or more of such prerequisites.

Mitigation methods can be divided into methods that are applicable for new concrete and those that can be used for existing structures. For new concrete, the following mitigation options could be available [25, 62]:

- Use of non-reactive aggregates (e.g., those producing less than 0.04% expansion in ASTM C1293 test [61] or less than 0.1% in ASTM C1260 test [60]): Due to limited availability of truly non-reactive aggregates in many locations, this option is not often practical.
- Limiting the alkali content of concrete: For example, a maximum alkali content of $\text{Na}_2\text{O}_e = 1.8 \text{ kg/m}^3$ of concrete (to be achieved using low alkali cement) is specified by AASHTO-PP65 [62] for structures with moderate ASR risk. A major challenge with this approach is that it only considers the alkali contribution of portland cement and does not account for alkalis in aggregates, SCMs, and other admixtures. As discussed in Section 4 above, these non-cement alkalis could be significant and lead to deleterious ASR. However, it is unclear what fraction of the total alkalis in these non-cement sources is leachable and available for ASR. For structures with high ASR risk (e.g., infrastructure components utilizing moderately to highly reactive aggregates), limiting concrete's alkali content should not be the sole mitigation strategy.
- Use of supplementary cementitious materials (SCM): These primarily reduce the alkalinity (pH) of pore solution by OH^- consumption and alkali binding, consume portlandite, and reduce permeability and mass transport of concrete, all due to the pozzolanic reaction [205, 206]. Using a sufficient quantity of SCM is the most common method of ASR mitigation for new structures. SCMs with low CaO and low alkali contents have been shown to be the most effective [205]. However, using SCMs is not without challenges: (a) high replacement levels of portland cement with SCM can negatively impact other concrete properties such as setting, strength development and freeze–thaw/scaling durability, especially in cold construction season; (b) the availability of high quality SCMs (e.g., low alkali class F fly ash) in some locations has become uncertain as power plants shift to fuels other than coal, and new environmental regulations have led to producing ashes that no longer meet concrete specifications (ASTM C618 [207]). This, in turn, puts more pressure on other SCM sources (e.g., blast furnace slag). There is a clear need for development and evaluation of non-conventional, yet economically viable SCM sources for ASR mitigation.
- Use of lithium admixtures: Laboratory and field studies, as summarized in Section 4.5 above, have documented the effectiveness of admixed lithium compounds (e.g., LiNO_3) in mitigating ASR in new concrete; although, the mechanism of mitigation is not clearly understood. The main challenges with these admixtures are their relatively high cost and limited availability of lithium. Li is a scarce and strategic element, making up less than 0.002% (20 ppm) of the earth's crust. New ASR inhibiting chemical admixtures that are cheaper and composed of more abundant ingredients should be sought.

In comparison with new structures, options for ASR mitigation in existing and already affected structures are much more limited. Lithium treatment (e.g., topical application, vacuum impregnation, electrochemical impregnation) has had limited success due to the low penetration depth of Li (10 to 20 mm) [208]. Electrochemical impregnation (where surface applied Li^+ is electrostatically attracted to negatively

charged rebar) shows higher penetration depth but comes at the cost of OH^- release at the cathode (negatively charged rebar) due to electrochemical reduction of water. Currently, the most viable mitigation method for existing structures is limiting concrete's access to external moisture by improved drainage, application of penetrating sealers, and use of cladding [8]. Application of restraint and confinement (e.g., FRP wrapping of columns, enclosing affected concrete with new prestressed concrete) has shown some success. Other methods for treating the symptoms (and not the cause) of ASR include crack filling (to reduce the risk of subsequent damage by freeze–thaw or corrosion), and slot cutting (e.g., in dams) to relieve ASR induced compressive stresses.

9. Modeling — state of the art and future prospects

Reliable modeling of ASR could be an extremely useful tool for prediction of the remaining life of affected structures, for optimum scheduling of repairs, and for design of these repairs. The available experimental methods are especially inaccurate with respect to predicting the future performance and progression of ASR in structures in service, and reliable models could have great utility in supplementing laboratory experiments and field monitoring.

ASR modeling can be characterized in terms of the method (numerical or analytical), the scope (structural or material-level), and the physical assumptions underlying the model. Analytical models are fast, but provide relatively crude estimations. Numerical and finite element models (e.g., Fig. 8) can be computationally expensive, but can provide a more detailed understanding of the processes being simulated. Mechanical or chemo-mechanical models can be formulated at the material or at the microstructure level, with only the former being practical for engineering applications and the latter being preferable for scientific investigation. Predictive approaches for kinetics require modeling of diffusion and chemistry. As these are not well understood, it is expected that future works will considerably improve these aspects. In the current state, physics-based models only exist at the microscale level for mechanical aspects, whereas all other models used in practice are largely empirical.

The analytical model from Bažant and Steffens [79] assume that the kinetics of ASR is driven by the diffusion of the alkalis to the aggregates, and that the reaction occurs at the aggregate surface. Homogenization techniques are then employed to derive the macroscopic swelling [79, 209]. This model does not however produce reasonable predictions of the free expansion of the laboratory samples in most cases. Building on the work of Larive [210] and the assumption that the reaction occurs

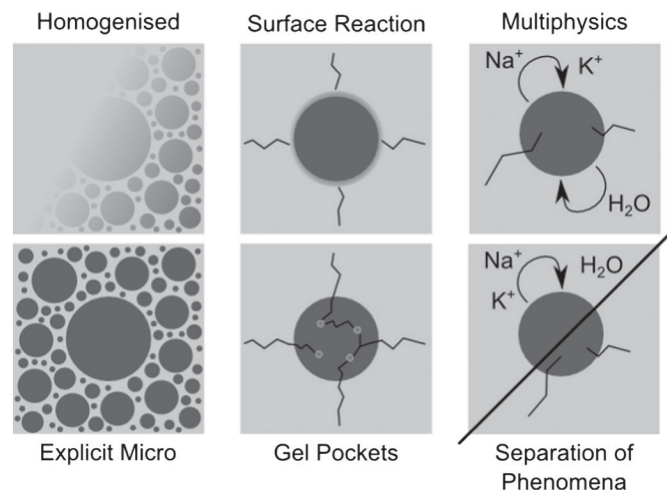


Fig. 8. ASR models can be formulated from different microscopic foundations, integrate diffusion, and treat the microstructure explicitly or through homogenization.

at the aggregate surface, Multon and colleagues [211] have proposed that the shape of the expansion curve versus time could be explained partly by the need to fill the interfacial transition zone pores before paste cracking can occur. The model they derived has been used to reproduce a number of experimental observations, notably linking the aggregate gradation and the effect of applied stress on the measured expansion [72,212]. This model has been applied to real structures by Grimal and co-workers [213,214]. However, more than 20 largely empirical parameters are used in this model, and the microscopic foundations do not match experimental observations (e.g., this model assumes surface reaction of aggregates, which is not always the case) [215,216]. Microscopic approaches to modeling have tried to minimize the number of free parameters by deriving the behavior of ASR from first principles.

If the progress of the reaction is tracked as a function of the amount of gel produced, the diffusion and chemical aspects become decoupled from their mechanical consequences. Ichikawa and Miura [217] have developed a chemical and thermodynamic model of the reaction, which allowed them to predict the expansive pressure of the gel and its density. Using fracture-mechanical approaches, Reinhart and Mielich [218] analytically, as well as Dunant and Scrivener [219] using finite elements, showed that the shape of the expansion curve could be explained from first principles. The expansion is explained by the formation of cracks in the aggregates and the paste. The cracks themselves are caused by the swelling pressure induced by ASR gel pockets. Dunant and Scrivener showed that gel pockets located through the aggregates were a necessary aspect of the models. The micro-mechanical approach was further validated by modeling concrete under load and identifying the contributions of individual aggregate classes [71,220]. This approach to modeling ASR provided insights on the degradation process, which could not have been obtained using purely experimental approaches. However, it involves complex micro-mechanical modeling using a purpose-developed framework [221,222]. Recent developments by Giorla and colleagues [223,224] indicate that although the ultimate free expansion is not affected by the rate of the reaction, laboratory tests may overestimate the damage compared to the field where the slower rate of reaction allows creep to relax most of the damage in the cement paste. Although microstructural simulations provide insights on the validity of the models used, they cannot currently be used to provide answers to engineering problems.

The future of ASR modeling will probably see a combination of micro and macro scales, where the macroscopic models are derived from the microscopic simulations. In particular, an open question in the study of ASR is the anisotropy of the expansion under various loading conditions, themselves frequently a product of the concrete expansion. Another axis of development is in predicting the ASR kinetics. Currently, models assume an Arrhenius law to extrapolate from laboratory experiments to the field. However, although this works well for the expansion, it is likely to be wrong for the evolution of mechanical properties, particularly strength. A model integrating the research in thermodynamics and chemistry with micro-mechanics is still forthcoming. This is of special practical importance as the interaction of creep and ASR in structures is critical in planning for repairs. Finally, there are currently no published models which account for the effects of SCMs or other ASR-inhibiting admixtures in concrete.

10. Conclusions

The following summarizes the most important conclusions of this paper:

- ASR is a result of a number of sequential reactions: dissolution of silica, formation of sol, formation of gel, and swelling of the gel. The underlying chemical reactions along with some thermodynamic information were presented in this paper. However, more research is needed to better quantify the thermodynamics and kinetics

data, especially in conditions more similar to concrete's interior; e.g., accounting for aggregate composition and heterogeneity, local pore solution composition at silica surface, and effects of temperature, pressure/restraint, and humidity on the reaction parameters. This knowledge could be very powerful in developing more efficient ASR inhibiting admixtures, and ability to predict and optimize service life through computer models and laboratory and field experiments.

- Aggregate reactivity depends not only on the type of silica mineral it contains, but also on the size/distribution of these minerals within aggregate structure. Reactive aggregate size and content have documented effects on ASR expansion, and often an intermediate particle size (i.e., the “pessimum” size) and intermediate content (i.e., the “pessimum” content) result in the highest expansion. Also, it is important to note that contrary to a common belief, ASR does not always occur at the aggregate–cement paste interface, but may only occur in the interior of some aggregates.
- Internal alkali release from non-portland cement sources in concrete can be a significant contributor to ASR in structures with long service lives and/or low cement alkali loadings. Standardized methods for measuring the potential releasable alkalis from aggregates and SCMs are needed. These methods must include criteria for interpreting results in a manner relevant to field performance.
- LiNO_3 has emerged as the preferred lithium compound for controlling ASR, as many other lithium salts increase the pH of pore solution. However, not a single prescribed Li dosage or $[\text{Li}]/[\text{Na} + \text{K}]$ molar ratio is effective against aggregates of different reactivity. Future research on the long-term efficacy of LiNO_3 , in better correlating laboratory and field data to determine an optimum Li dosage, and in better understanding of the mechanisms of ASR mitigation by Li is beneficial.
- Presence of calcium is required for formation of ASR gel; otherwise the dissolved silica could remain innocuously in the pore solution. In addition, Ca plays two specific roles with respect to ASR: (a) it can replace alkalis in ASR gel (i.e., recycle alkalis back into pore solution), and thus maintain a high pH in the pore solution, and (b) it impacts the properties (e.g., viscosity, yield strength, swelling capacity) of ASR gel.
- There is evidence that presence of soluble Al in pore solution helps in mitigating ASR. The exact mechanisms are unknown, but the effects could be due to reducing silica dissolution, improving alkali binding and reducing the pH, consuming portlandite, reducing swelling of the gel, or densifying the pore structure and reducing the permeability of concrete.
- Limited qualitative information is available on the composition versus rheological and swelling properties of ASR gels. Research is needed to quantify the effect of gel composition, temperature, humidity, and pressure/restraint on the gel's structure, moisture uptake, and swelling.
- There is a strong need for synthesis, development, and assessment of new ASR mitigation methods (e.g., new or unconventional SCMs, new chemical admixtures, and innovative treatment methods) applicable to new and, more importantly, to existing structures.
- Considerable progress has been made in understanding the micro-mechanics of ASR. This has led to predictive models valid for samples of laboratory size. Much is still needed to integrate the chemical aspects of the reaction in these models. There are also a number of well-established macroscopic models, used for the management of real structures. These are unfortunately largely empirical and need to be constantly amended to track the observed changes in the field. In future, reactive-transport and micromechanical models should serve as a base for formulating more robust macroscopic predictive models.

Acknowledgments

The authors would like to thank Mr. Asghar Gholizadeh for his assistance in reviewing the manuscript and providing insightful comments.

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