RESEARCH ARTICLE

Alkali-silica reaction: understanding the phenomenon

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Abstract

The alkali-silica reaction in cementitious composites occurs through the chemical association of the solution contained in the matrix pores, which is strongly basic and rich in alkalis, and the reactive phases of some aggregates. For the process to begin, high relative humidity and a high concentration of total alkalis are required. The degradations resulting from this reaction involve expansion, cracking, exudation and decreased mechanical performance of the structure, which can cause it to break depending on the magnitude of the phenomenon. Understanding the reaction development process is necessary to propose measures that can effectively extinguish or mitigate the occurrence. One of the measures widely studied is the incorporation of supplementary cementitious materials in concrete. In Brazil, technical regulations already exist that recommend the use of these cementitious materials. The Northeast region of the country is a major producer of fly ash and granulated blast furnace slag, but not all of this material is destined for other industries. The article in question is a compendium of technical information from relevant research developed about alkali-silica reaction. His contribution is in the didactic approach that allows the understanding of students in the engineering area and professionals who do not have the expertise in the subject in order to stimulate future research on the use of supplementary cementitious materials in Northeast Brazil, mainly.

Keywords Alkali-silica reaction · Occurrence mechanism · Diagnosis · Mitigation measures · Supplementary cementitious materials · Review

1 Introduction

As is already known by many researchers, the alkali-silica reaction (ASR) is a type of endogenous pathological manifestation of high severity that can occur in cementitious composites subjected to certain chemical, temperature and humidity conditions. It develops between the reactive constituents of siliceous aggregates (amorphous, poorly crystallized or microcrystalline silica) and alkaline hydroxides present in the interstitial solution of the cement paste. The reaction product is a generally expansive gel that starts to occupy the pores of the cementitious composite [1, 2].

Three conditions are necessary for the occurrence of RAS: (1) high content of alkalis (notably sodium and potassium) that can be supplied by cement (main), chemical additives, mixing water, supplementary cementitious materials or by external sources (industrial and marine waters); (2) potentially reactive aggregate, characterized as one that has mineralogical phases sensitive to the alkaline environment; (3) and high humidity to allow the migration of ions and reactive species, in addition to acting on the formed reaction product causing expansion [1, 3].

As for the occurrence of ASR, about 20 years ago the Brazilian technical environment understood that the most susceptible buildings would be those with a large volume of concrete and that had more access to high humidity, such as dams, bridge pillars, hydroelectric plants and generators of wind power plants. Currently, there is a history of serious

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cases of ASR occurring in smaller structures, such as floors and foundations of commercial and residential buildings [4].

The number of identified cases of ASR in concrete structures in Brazil has increased due to the greater understanding of the pathological manifestation by the scientific community and/or the greater concern of the expert/diagnostic sector with the consequences. In addition, unfortunately, when cases are identified in the structures in service, in general, they are already in advanced development of the reaction, which makes treatment difficult.

As for the treatment of ASR, some mitigating measures are being studied, such as the use of lithium-based chemicals [5–7] and the use of supplementary cementitious materials as binders in addition or partially replacing cement [1, 8–10]. Some of these mitigating materials have shown to be effective in the proposal to avoid ASR and not just to reduce the development of the reaction [11].

Among the supplementary cementitious materials studied are active silica, fly ash, metakaolin and granulated blast furnace slag. The Northeast region of Brazil has an industrial complex that produces a large amount of ash from thermoelectric plants and granulated blast furnace slag from steel industries.

The fact is that the production of ash and slag in the region exceeds the flow given to them. So large amounts are deposited for long periods in storage tanks. For example, it is estimated a production of 474,500 ton/year of total ash, with 69,350 ton/year of heavy ash, 328,500 ton/year of fly ash and 76,650 ton/year of desulfurization residue. That is, 69% of the total by-product generated is characterized as fly ash. In addition, of the total ash produced, only about 34% is reused in other industries [12].

Given the seriousness of the consequences of ASR on concrete structures, detailed knowledge of this pathological manifestation becomes essential for the adoption of more appropriate prophylactic measures. On the other hand, the complexity of the phenomenon requires extensive knowledge about endogenous reaction in cementitious composites. Aiming at a didactic approach, this article deals with a compilation of technical information about the alkali-silica reaction from research already developed. It is intended that students and professionals not yet familiarized with the topic can understand and stimulate future research aimed at the use of supplementary cementitious materials from Northeast Brazil, mainly.

2 Reaction occurrence mechanism

Understanding the ASR mechanism is not so simple because it consists of several stages. However, Pan and colleagues [13] report that Glasser and Kataoka [14, 15] proposed a simplified two-step description. First, the reaction occurs between the hydroxyl ions (OH$^-$) present in the pores solution of the concrete and the reactive silica of the aggregate. It is important to highlight that, in a first moment, the alkalis (Na$^+$ and K$^+$) contribute to the increase in the hydroxyl ions concentration in solution and, then, contribute to the expansive gel formation. The presence of alkalis influences the aggregate reactivity and the reaction extent: when more alkalis is available, the concentration of OH$^-$ in the pore solution is higher and more silica is dissolved [16].

When the hydroxyl ions react with the reactive phases of the aggregate, they promote the rupture of the siloxane networks (Si–O–Si) to produce alkaline silicate and silicic acid, as in Eq. 1 [13].

$$\equiv Si - O - Si \equiv + R^+ + OH^- \rightarrow \equiv Si - O - R + H - O - Si \equiv \tag{1}$$
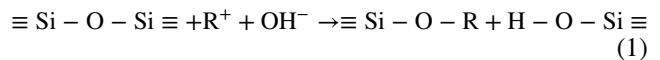
R$^+$ means an alkaline ion such as sodium and potassium ions (Na$^+$ and K$^+$). The weak silicic acid produced immediately reacts with more hydroxyl ions, as outlined in Eq. 2.

$$\equiv Si - O - H + R^+ + OH^- \rightarrow \equiv Si - O - R + H_2O \tag{2}$$
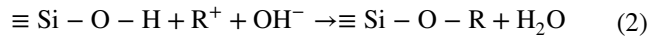
The alkaline silicate gel resulting from (1) and (2) is amorphous and hygroscopic. The second step, then, is the expansion of this gel by absorbing free water, as in Eq. 3, where n is the hydration number.

$$\equiv Si - O - R + nH_2O \rightarrow \equiv Si - O^- - (H_2O)n + R^+ \tag{3}$$
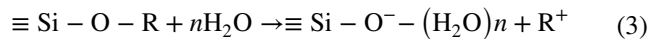
Virmani and Faridazar [17] carried out a series of experiments using the cristobalite silica mineral to represent the siliceous component of the aggregate favorable to ASR because it is reactive. The authors exposed the mineral to an aqueous mixture of calcium hydroxide [Ca(OH)$_2$] and three different types of alkaline hydroxide solutions [0.7 M of potassium hydroxide (KOH), 0.7 M of sodium hydroxide (NaOH) and 0.35 M KOH + 0.35 M NaOH] representing approximately the pore solution of a reactive concrete. Each test was carried out at three different temperatures (38 °C, 55 °C and 80 °C).

This study identified a distinct sequence of steps associated with the ASR mechanism. These steps are marked as I–IV in Fig. 1: (I) formation of hydrated calcium silicate (C–S–H); (II) formation of hydrated calcium silicate of high alkalinity and low calcium [C-(Na/K)-S–H]; (III) increased concentration of silica ions in the solution; and (IV) formation of ASR gels [(Na/K)–S–H].

Based on this sequence, the general mechanism of ASR begins with the silica dissolution, which, once in solution, reacts quickly with the available Ca^{2+} ions to produce C–S–H. During this period (step I), the concentrations of alkaline ions and the pH values remain more or less constant, but the amounts of remaining reactive silica and Ca(OH)$_2$ decrease significantly. Once the Ca(OH)$_2$ in the reagent

Fig. 1 Sequence of steps of the ASR mechanism obtained from the reagent system (mixture of α-cristobalite, Ca(OH)$_2$ and KOH solution at 55 °C) from the study by Virmani and Faridazar [17]
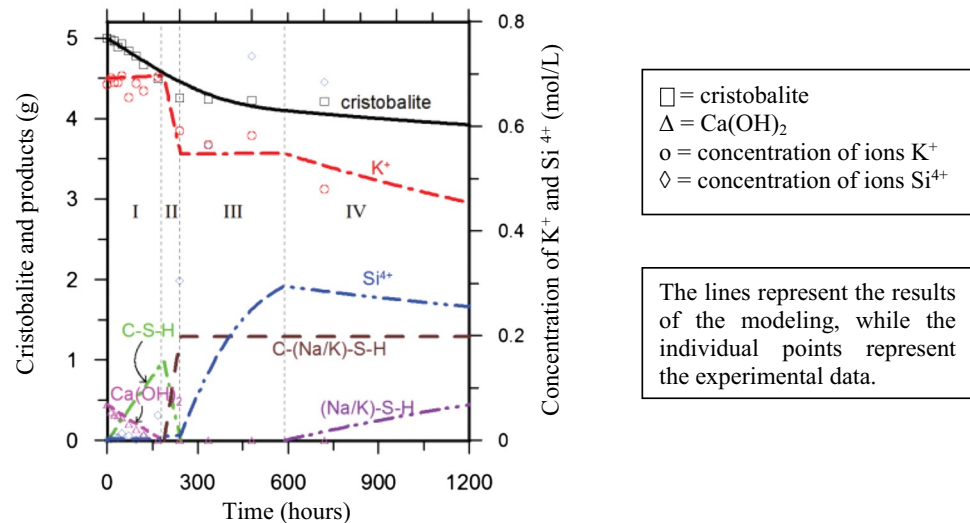
system is exhausted, the process of removing dissolved silica from the solution also ceases (or significantly decreases), causing an increase in the concentration of Si^{4+} ions. These dissolved Si^{4+} ions can react even more with the previously formed C–S–H generating polymerized C-(Na/K)-S–H (amorphous) with a reduced Ca/Si molar ratio (compared to the typical C–S–H gel) (step II). After the formation of this amorphous and polymerized C-(Na/K)-S–H gel, the rate of change in the alkali concentration decreases, but the concentration of Si^{4+} ions continues to increase up to a certain point (maximum) (step III). After this action, a decrease in the concentrations of Si^{4+} and alkaline ions occurs. The point at which the concentrations of Si^{4+} ions and alkaline ions begin to decrease coincides with the start of ASR (step IV) [17].

As a final product of ASR there is a gel concentrated in the concrete pores or on the aggregate particles surface called hydrated alkaline silicate gel and designated by (Na/K)-S–H in Fig. 1 (or A–S–H by some authors). Its chemical composition is uncertain and variable because it depends of the reagents concentration, the pore solution composition and the reactive phase present in the aggregate [17].

Helmuth and Stark [18] studied the gel compositions of the ASR in detail and concluded that they can be considered as mixtures of two components containing varying proportions of alkaline calcium silicate and alkaline silicate with almost fixed compositions. These authors stated that the final element of alkaline silicate has a composition by weight of 17% (Na$_2$O + K$_2$O) and 83% SiO$_2$, and the final element of alkaline calcium silicate has a composition of approximately 6.6% (Na$_2$O + K$_2$O), 52.6% CaO and 40.8% SiO$_2$.

In contrast, in a study on ASR in mortars composed of cement with high concentration of alkalis and natural sand containing opal, Diamond [19] concluded that the ASR gel has neither a low nor a high concentration of calcium,

but that it varies from one grain to another. He reported that the grain compositions individually cover almost the entire range of known gel compositions (already studied) and concluded that the ASR gel has a complex and highly variable chemical composition and that the compositional model proposed by Helmuth and Stark [18] can be useful, but not universal.

Hou, Struble and Kirkpatrick [20] conducted experimental investigations of the reactions between silica, alkaline hydroxide solution and calcium hydroxide. They identified that the hydrated alkaline silicate gel (A–S–H) formed from this reaction is comparable to that formed by ASR in concrete and that it does not form when portlandite [Ca(OH)$_2$] or C–S–H rich in calcium and poor in silica from normal Portland cement paste is available to react with silica. Under these conditions, they observed the formation of additional C–S–H by the reaction of Ca(OH)$_2$ with dissolved silica or the progressive polymerization of C–S–H. The authors also concluded that Ca^{2+} ion is essential for the significant formation of expansion related to the A–S–H gel.

2.1 The contribution of the reactive aggregate

The reactive potential of the aggregates is measured by the amount of reactive phases present, generally siliceous. Thomas [21] explains that silica is a material that dissolves in extremely basic or alkaline conditions. Under ambient conditions, amorphous fine silica grains dissolve more easily in high pH solvents than crystalline quartz.

To evaluate the reactivity of the aggregate, it is possible to carry out the following tests: rock petrographic analysis, determination of ASR expansion in mortar bars by the accelerated method (30 days), and determination of ASR expansion in concrete prisms by the long-term method (365 days). Additionally, it is also possible to evaluate the reactivity

by ASR expansion in concrete prisms using the accelerated method (140 days).

Brazil has the technical standard ABNT NBR 15577 [2] divided into seven parts that establishes the requirements for the use of concrete aggregates in order to avoid the ASR occurrence. It indicates the sampling procedures and test methods mentioned above. This Brazilian standard was mainly based on the ASTM C1260 [22] and ASTM C1778 [23] standards.

The Brazilian standard ABNT NBR 15577-3 [24] presents a list of rocks and minerals susceptible to the development of the reaction with alkalis and establishes the maximum acceptable values of one or more reactive phases to classify an aggregate as potentially harmless: 5% microgranular or deformed quartz, 3% chalcedony, 1% tridimite or cristobalite, 3% volcanic glass and 0.5% opal.

After the petrographic analysis, ABNT NBR 15577-1 [2] recommends to carry out the accelerated test on mortar bars. If the expansion obtained is greater than or equal to 0.19% at 30 days of age, the aggregate is potentially reactive. This result is confirmed by the long-term test of concrete prisms. For this last test, if the result obtained indicates expansion greater than or equal to 0.04% at 365 days of age, the aggregate is potentially reactive.

If the accelerated test in concrete prisms is chosen, the aggregate will be considered potentially reactive for expansion greater than or equal to 0.03% at 140 days of age. This accelerated test can be used when the aggregate is slowly reactive [2].

Mehta and Monteiro [25] report that the majority of reported cases of concrete expansion and cracking in which it is attributed to ASR are associated with reactive aggregate particles in the sand granulometry, especially in the range of 1–5 mm. For the authors, there are no satisfactory explanations for these observations due to the simultaneous interaction of many external factors; however, a lower tendency for water adsorption of silica-alkaline gels with a higher silica/alkali ratio and the relief of hydraulic pressure on the reactive particle surface when its size is very small may partially explain these observations.

2.2 The contribution of alkalis

The main source of alkali comes from Portland cement, since sodium and potassium are present in the clinker composition in significant amounts, with potassium being more common than sodium [25]. There may also be other internal sources such as chemical additives, mineral additions, mixing water and the aggregate itself. An example of an external source of alkalis would be humidity or alkaline water from an industrial or marine source into the concrete [3].

Berra, Mangialardi and Paolini [26] corroborate this statement when they explain that the majority of alkalis is available in concrete since the construction phase of the structures and comes, mainly, from cement, with possible minimal contributions from the mixture water and chemical mixtures. However, the increase in the alkaline concentration in the concrete can appear during the life of the structures when added with alkaline minerals (volcanic glass, feldspars, micas, clay minerals, nepheline and zeolites) release their alkalis in the concrete pore solution for a long time.

Cement alkali is divided into two categories: soluble and insoluble alkalis. The first category is found in sulfates and the second in solid clinker phases (silicates and aluminates). During the cement hydration, the supply of alkalis to the solution occurs more quickly coming from sulfates. The others, incorporated in the clinker grains, are only available as hydration is processed, more slowly. Regardless of the alkalis source, since a reaction between reactive aggregate and alkalis occurs slowly, all existing alkalis may participate in the reaction [3].

The alkalis content in cement is expressed as equivalent acid-soluble sodium oxide, the equivalent Na_2O ($Na_2Oeq.$), and calculated as in Eq. 4 [2].

$$Na_2O_{eq} = Na_2O + 0,658 K_2O \qquad (4)$$

The alkaline equivalent can be expressed in kg of $Na_2Oeq./m^3$ of concrete or as percentage (%) of the cement mass.

As Portland cement is the major responsible for the supply of alkalis in concrete, for a long time several researchers have used only the alkaline equivalent of cement as a guide for the ability to develop the reaction [1].

Currently, the active alkalis content that can be supplied by all concrete components (internal source) and the environment (external source) is calculated. Not all alkalis participate in the reaction because part of it can remain trapped in the crystalline network. Active alkalis are those that can be solved. For each concrete constituent, the active alkalis content A is calculated, $A = m \times a$, where a represents the total alkalis and m is a coefficient between 0 and 1. The values to be adopted for m are: $m = 0.5$ for slag; $m = 0.5$ for fine limestone; $m = 0.17$ for fly ash; $m = 1$ for clinker and $m = 1$ for gypsum. For aggregates, the value of m must be determined experimentally [1].

Mehta and Monteiro [25] report that investigations in Germany and England have shown that, if the total alkali content of concrete from all sources is below 3 kg/m^3, no harmful expansion will occur. Rivard and his colleagues [27] explain that this limit is accepted when using very reactive aggregates, but that some authors [28, 29] suggested that a limit of about 5 kg of Na_2O eq/m^3 of concrete would be acceptable when using aggregate with low reactivity, although this value is quite high and rarely found in structures in service. However, Ollivier and Vichot [1] warn that

even the 3 kg/m^3 content has been shown to be very high in some cases, with a performance approach based on ASR expansion tests being more used today. Thus, Shehata and Thomas [30] produced five concretes with different total alkali contents (5.25; 4.20; 3.70; 3.15 and 2.89 kg/m^3) composed of a silicon-reactive limestone as coarse aggregate and a non-reactive natural sand in all mixtures and carried out expansion tests in prisms after 2 years. The authors identified that the expansion of all five concrete mixtures exceeded 0.04% after 2 years (Fig. 2), although the expansion rate and the magnitude of the final expansion are clearly dependent on the alkali content of the concrete.

The Brazilian standard ABNT NBR 15577-1 [2] establishes some expansion mitigation measures due to ASR that include limiting alkali in concrete and/or using appropriate inhibiting materials, depending on the severity class of the reaction in structures. Among the measures, the standard limits the alkali content of concrete to values less than 2.40 kg of Na_2O eq/m^3.

2.3 The contribution of humidity

The third condition for the ASR occurrence is the high humidity rate in the cementitious composite achieved by the mixing water or by the relative humidity of the environment. It performs two functions in ASR: (1) it facilitates ionization and guarantees the transport of hydroxyl ions and alkaline cations; (2) it is absorbed by the alkaline silicate gel (final product of the reaction) and promotes expansions [1, 3, 8, 14–17, 25].

It is assumed that the critical internal relative humidity limit of the concrete capable of triggering and maintaining the reaction is above 80–85%. The expansion varies directly with the relative humidity of the concrete: for values below 70%, the expansion will be relatively low; and for values above 80%, it will increase exponentially. Thus, even with the presence of the gel (therefore with the reaction already triggered), if there is not enough moisture available, the expansion may be low and the cracks may not occur [1, 3, 16, 25].

3 ASR in concrete structures

In the diagnostic phase, evidence of ASR in concrete structures can be one or more of these characteristics [1, 3, 31, 32]:

– Cracking in the map form in concrete without reinforcement;
– Oriented cracking in reinforced concrete;
– Gel exudation on the concrete surface;
– Superficial stains;
– Macrocracks with visible discoloration along its edges;
– Displacements between paste and aggregate causing loss of adhesion in the area;
– Visible concrete expansion.

The affected coarse aggregates generally exhibit internal fracture, with cracks extending to the surrounding concrete matrix. If only the fine aggregate is reacting, cracks can form in the matrix without affecting the coarse aggregate particles. The gel can be present in cracks and voids and it can be present in the area around the edges of the aggregate particles. A network of internal cracks connecting particles of

Fig. 2 Effect of the alkali content of concrete on ASR expansion from the study by Shehata and Thomas [30]
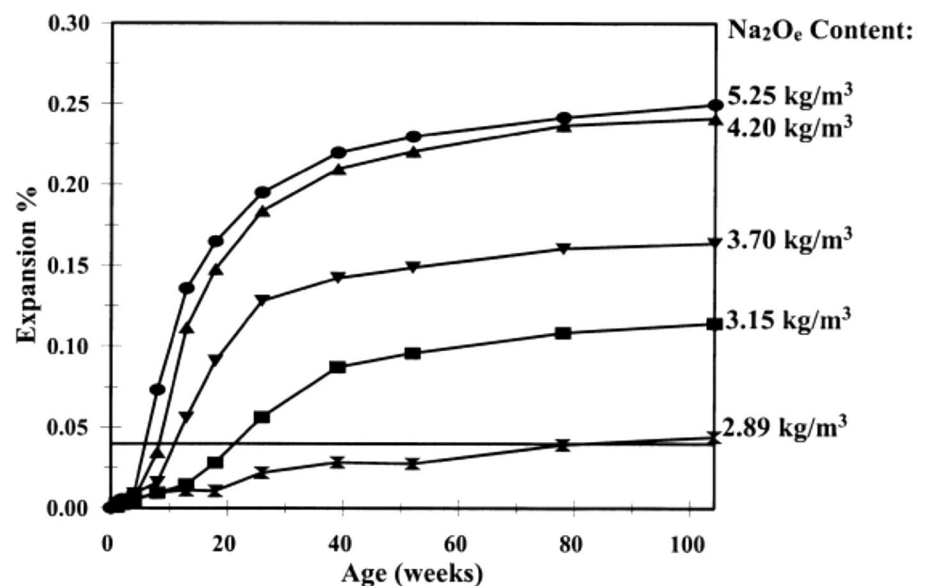
reacted aggregates is a strong indication that ASR is responsible for the breakdown (Fig. 3) [32].

ASR also generates negative effects on concrete properties. The modulus of elasticity is one of those affected and can be reduced over time due to the intense cracking produced by the expansions. In addition, the tensile and compressive strengths can be affected. However, depending on the reaction stage and the concrete characteristics, the compressive strength may have gains due to the formation of products in the concrete pores, creating a false result [33]. Cracking due to the concrete expansion can also cause displacements and movement of structures. Thus, the performance and durability of structures can be seriously affected depending on the ASR stage.

Farny and Kerkhoff [32] warn that harmful expansion does not occur without the reaction product (gel); but the reaction product can occur without the harmful expansion of ASR. As the gel has already been observed in undamaged concrete, of good quality, and its presence does not necessarily indicate that destructive ASR is occurring, a cause and effect relationship must link the presence of reaction products to the harmful expansion.

Although the reaction is hardly reported as a primary cause of structures collapse, it is known that the cracking resulting from it can favor other deterioration processes in reinforced concrete, such as carbonation and corrosion of reinforcement.

Studies by Swamy and Al-Asali [34] on concrete specimens with free expansion containing highly reactive aggregates showed losses of 40–60% in compressive strength, 65–80% in tensile strength, and 60–80% in the modulus of elasticity.

Gautam and his colleagues [35] investigated the effect of the multiaxial stress state on the expansion and mechanical properties degradation of the concrete affected by ASR. The authors produced concrete cubes with reactive aggregates and subjected them to uniaxial and biaxial stresses. The cubes were cured in an acceleration chamber maintained at 50 °C and 100% relative humidity and were tested for mechanical properties degradation. Breaking strength was seen as the most sensitive property to ASR with a loss of 50%; and the static elastic modulus reduced by 20%. The authors also noticed that in the direction where the tension was applied there was a significant expansion reduction with the transfer of this expansion to the directions with low tension.

The American Concrete Institute report on alkali-aggregate reactivity already stated that in a non-reinforced and unconfined concrete element, such as a concrete slab or beam, the highest degree of concrete deformation resulting from the ASR expansion will occur in the direction of less restriction [36].

On the other hand, in confined concrete structures the decrease in performance caused by ASR is less. Multon and Toutlemonde [37] identified this reducing effect of confinement in the ASR expansion through triaxial tests performed on reactive concrete samples that showed a decrease in the reaction evolution and in the gel formation. These authors stated that there is a transfer of expansion along the less compressed directions. Ferreira, Farage and Barbosa [38] carried out a similar study that corroborates the above and indicates that the cracks evolve more quickly on the structure surfaces where the reaction evolves freely.

4 ASR prevention and control measures

The prevention or control of ASR expansion involves the adoption of four isolated or joint measures [21, 39–41]:

1. Avoid the use of reactive aggregate. It is not always possible due to the availability of material in the region.
2. Use low alkaline cement. Sometimes it may not be available through the cement company due to the production flow; or, when using aggregates that release alkalis, even with the use of low alkaline cement, it is not possible to prevent expansion in the long term.
3. Use a chemical (chemical inhibitor). By strategic decision, this may not be a profitable option.

Fig. 3 Pattern of cracks inside the concrete and gel around the coarse aggregate due to ASR from the studies by Pan et al. [13], Farny and Kerkhoff [32]
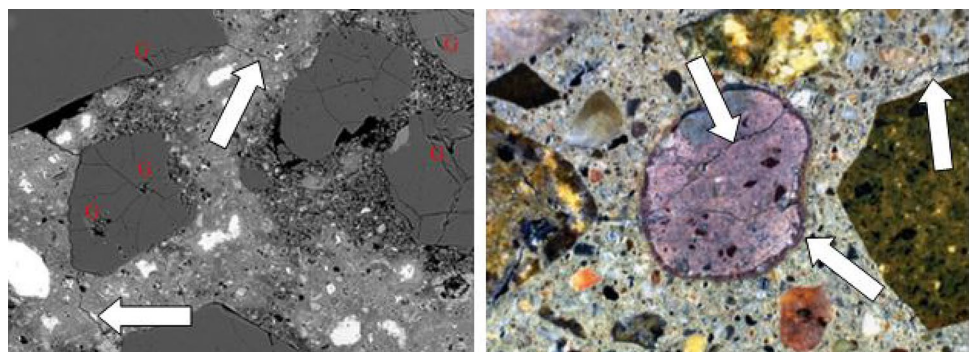
4. Partially replace high alkaline cement (if it is the only one available) with a cementitious material. Precise knowledge of the substitution content is necessary to guarantee an acceptable total active alkali content.

Therefore, it appears that all measures are plausible, but have their limitations, whether strategic, economic or in effectiveness.

How the research aims to evaluate ASR prevention measures from the use of inhibiting materials, this article will limit the approach of measures (3) and (4).

4.1 Use of chemical inhibitor

Stokes, Wang and Diamond [5] studied several lithium salts and argued that lithium nitrate ($LiNO_3$) had greater advantages. For them, $LiNO_3$ is not able to increase the expansion in case of underdosing, as occurs with LiOH and $LiCO_3$, nor does it present a danger of manipulation, as occurs with LiOH, due to its almost neutral pH.

Tremblay and his colleagues [6] wanted to identify which mechanisms could better explain the effectiveness of $LiNO_3$ against ASR. They did a series of experiments on cement pastes, concretes made with a variety of reactive aggregates, samples of composites made from cement paste and reactive aggregates particles, and a variety of natural aggregates with reactive mineral phases immersed in various solutions containing lithium.

The authors considered several mechanisms in the study: possible reduction in the pH of the pore solution; previous formation of a Si–Li reaction product (Si–Li gel) on the reactive silica grains or reactive aggregates particles that acted as a physical barrier against the main reaction; increased solubility of silica that would remain in solution without forming an expansive gel (ASR gel) [6].

The most coherent mechanism for the authors was the increase in the chemical stability of the reactive silica contained in the pore solution. This mechanism was strongly supported by the facts that: (1) an amorphous gel containing Na, K and Si, and probably also Li (undetectable by Scanning Electron Microscope), was the only type of reaction product observed in concrete samples that incorporated $LiNO_3$ and a variety of natural reactive aggregates; (2) this gel was exactly like the classic ASR gel and its abundance was proportional to the expansion obtained for the concrete; for example, for all concretes made with $LiNO_3$ and which showed no expansion or it was limited, none or only traces of the reaction gel were observed; and (3) the most reactive materials tested, including eight tested natural reactive aggregates, dissolved much less in $NaOH + LiNO_3$ (and LiOH) solutions than in a NaOH control solution [6].

For Hasparyk [33] and Schneider and colleagues [42], lithium is able to modify the physical–chemical, crystallographic and structural characteristics at the atomic level of the ASR products producing compounds with the incorporation of lithium with less capacity to expand, according to studies by diffraction of X-rays, infrared spectroscopy and nuclear magnetic resonance.

Kim and Olek [7] mention that researchers Lawrence and Vivian [43] believed that the dissolution of reactive silica depended heavily on the type of alkaline hydroxides (NaOH, KOH or LiOH) present in the system. These authors stated that the dissolution rate of silica was the lowest for LiOH and the highest for KOH. Wijnen and colleagues [44] also found similar patterns for the dissolution of reactive silica and suggested that the dissolution rate decreases with the increase in the ionic radius of alkaline species.

Kim and Olek [7] investigated which chemical steps in the ASR process are affected by the presence of Li^+ ions in the pore solution. They identified that, during the initial stages of exposure, the OH^- ions present in the pore solution continue to attack the siloxane bond of the silica mineral and to produce silanol groups. However, the presence of $LiNO_3$ prevents further dissolution of these groups (silanol). In contrast, in the absence of $LiNO_3$ in the system, these silanol groups are not preserved, being further deteriorated by the continuous attack of OH^- ions present in the solution and causing an increase in the Si concentration. The authors also observed that the addition of Li^+ ions prevents the complete reduction of $Ca(OH)_2$, unlike what occurred in the reactive system without $LiNO_3$.

4.2 Use of supplementary cementitious material

Ollivier and Vichot [1] claim that the different mechanisms proposed to explain the preventive role of these supplementary cementitious materials (SCM) are almost all due to an observation made a long time ago: the preventive activity is simultaneous with a pozzolanic activity.

Examples of SCM already studied are silica fume, fly ash, metakaolin, blast furnace slag, ground brick, natural pozzolan of volcanic origin and even fines obtained by grinding the reactive aggregate itself. The effectiveness of each type of SCM will depend on particular characteristics, such as fineness, chemical and mineralogical composition and alkali content. These characteristics and the knowledge of the reactive potential of the aggregate will define the optimum replacement content of Portland cement [25].

Based on this, as an example, Ollivier and Vichot [1] suggest that fly ash, especially with silico-aluminum composition, should have an alkali content of less than 2% or 3% in Na_2Oeq and content used in the dosage of at least 30% to help prevent ASR. Fournier and Bérubé [8], in laboratory investigations, found optimum levels of 20–30% for natural pozzolans, 30–35% for fly ash with low to moderate calcium content (< 20% CaO) and low alkali content (< 4.5%

Na$_2$Oeq), 50% for granulated blast slag and 10–12% for silica smoke.

Chen, Soles and Malhotra [45] investigated 15 types of SCM, including fly ash, blast furnace slag, condensed silica smoke and natural pozzolan, available in Canada and identified that not all were useful in suppressing the harmful expansion caused by ASR. However, the authors noted that the desirable characteristics of SCM to reduce expansion, revealed by multiple linear regression analysis, were: (1) high total concentration of $SiO_2 + Al_2O_3 + Fe_2O_3$; (2) particle size less than 45 µm; and (3) low alkaline content.

Some published studies indicate that the presence of alumina (Al_2O_3) in SCM contributes in some way to prevent the release of alkalis to the pore solution. Hong and Glasser [46, 47] believe that alumina contributes to fixing alkalis in C–S–H and reducing the alkalinity of the pore solution. However, authors like Chappex and Scrivener [48, 49] believe that this effect is extremely small and that the contribution of alumina is due to its performance directly in the aggregates reactive phases, in which the aluminum present in the pore solution will be able inhibiting the dissolution of amorphous silica from reactive aggregates. Shafaatian [9] evaluated the impact of aluminum on ASR using aluminum hydroxide [Al(OH)$_3$] as a mixture in the mortar and carried out microstructural studies. The author identified that the addition of Al(OH)$_3$ created an aluminosilicate layer with a thickness between 6 and 7 µm around the aggregate surface (Fig. 4) that protected it from dissolving by hydroxyl ions, resulting in reduced expansion.

Despite recent progress in understanding the mechanisms that allow SCM containing aluminum (such as metakaolin)

Fig. 4 Scanning electron microscopy of the reaction product on the aggregate surface in the presence of Al(OH)$_3$ from the study by Shafaatian [9]

and the LiNO$_3$ addition to limit the ASR extent in mortars and concrete, Leeman and colleagues [11] believe that some gaps still remain. For them, the effect of the SCM containing aluminum on the formed ASR products and the influence of the aggregates characteristics on the effectiveness of LiNO$_3$ are not yet clear. In their studies, the authors identified that the amount of aluminum present in the pore solution is only able to delay the dissolution of SiO_2, but not to change the morphology, structure and composition of the reaction products. On the other hand, LiNO$_3$ can suppress ASR by forming dense products that protect reactive minerals from subsequent reaction, but its effectiveness decreases with the increase in the specific area of reactive minerals in the aggregates.

Among the four ASR mitigation measures mentioned at the beginning of this topic, Chen, Soles and Malhotra [45] defend the use of SCM with pozzolanic characteristics due to the great availability of these materials and the need for the producing industries to give a legal disposal, in terms of laws, rules and decrees.

As previously mentioned, the Brazilian standard ABNT NBR 15577-1 [2] mentions the limitation of alkali in concrete and the use of inhibitory cementitious materials as expansion mitigation measures due to ASR. Among the inhibitory cementitious materials are Brazilian Portland cements CP II-E and CP III, consisting of different levels of granulated blast furnace slag; CP II-Z and CP IV, consisting of different levels of pozzolanic materials; active silica; metakaolin; or other pozzolanic materials in combination with any type of Portland cement. It is important to note that the standard does not suggest the use of a lithium-based product as an ASR inhibiting material.

The Brazilian standard informs that the efficiency of cementitious materials must be proven by the accelerated method in mortar bars, whose test result must be less than 0.19% at 30 days; or by the method of concrete prisms, whose test result must be less than 0.04% in 2 years. Depending on the degree of the aggregates reactivity, Portland cement inhibitors alone may not be sufficient to reach these levels of expansion mitigation. In this case, the standard suggests making a combination with other inhibitory materials, analyzing the combination contents in order to prove its efficiency in terms of the ability to inhibit harmful expansions.

5 Conclusions

The mechanisms that involve the alkali-silica reaction have gradually been better understood by the technical-scientific environment, which has enabled advances in the study of protective and mitigation measures of the anomaly, although there is still no consensus on their effectiveness.
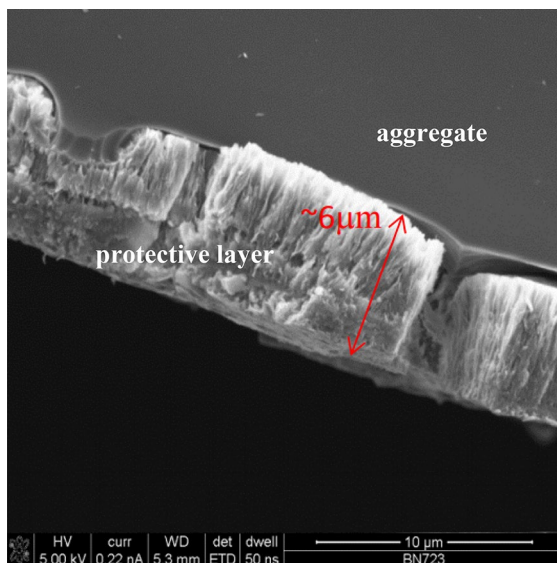
The great variability of the factors that provoke the reaction results in the lack of unanimity among researchers about the most appropriate prophylaxis. Throughout the article, some variables of the ASR were explained, such as the total alkalis concentration harmful to the cementitious composite, the potential for aggregates deleterious reactivity, the complexity of the structure damage, the effectiveness of reaction mitigating materials such as lithium and supplementary cementitious materials.

The fact is that there is still a lot to research on the topic. Severe cases of early deterioration of concrete structures resulting from the joint action of ASR with another pathological manifestation have been detected and the technical solution is not always the most economically viable.

On the other hand, the volume of by-products of industries installed in the Northeast of Brazil that are likely to be used as SCM is currently high. The industrial complex is continually growing and the flow given for these by-products does not grow at the same rate. It is understood that it is essential that construction professionals are aware of the technical advantages of these regional materials for the purpose of ASR mitigation. This article set out to explain in a clear and didactic way in order to boost this application.

Compliance with ethical standards

References

1. Olliver JP, Vichot A (ed traduction), Cascudo O, Carasek H (2014) Durabilidade do concreto: bases científicas para a formulação de concretos duráveis de acordo com o ambiente. IBRACON, São Paulo
2. Associação brasileira de normas técnicas (2018) ABNT NBR 15577-1 Agregados–reatividade álcali-agregado Parte 1: guia para avaliação dareatividade potencial e medidas preventivas para uso de agregados em concreto. Rio de Janeiro
3. Hasparyk NP (2011) Reação álcali-agregado no concreto. In: Isaia GC (ed) Concreto: ciência e tecnologia, vol 2. IBRACON, São Paulo, pp 933–1001
4. Figueirôa JP, Andrade T (2007) O ataque da reação álcali-agregado sobre as estruturas de concreto: a descoberta pioneira da ocorrência do problema em fundações de ponte e edifícios na Região Metropolitana do Recife. Ed. Universitária da UFPE, Recife
5. Stokes DB, Wang HH, Diamond S (1997) A lithium-based admixture for ASR control that does not increase the pore solution pH. In: Proceedings... Fifth CANMET/ACI International Conference, ACI SP173, pp 855–868
6. Tremblay C et al (2010) Experimental investigation of the mechanisms by which $LiNO_3$ is effective against ASR. Cem Concr Res 40:583–597
7. Kim T, Olek J (2016) The effects of lithium ions on chemical sequence of alkali-silica reaction. Cem Concr Res 79:159–168
8. Fournier B, Bérubé MA (2000) Alkali-aggregate reaction in concrete: a review of basic concepts and engineering implications. Can J Civ Eng 27:167–191
9. Shafaatian S (2012) Innovative methods to mitigate alkali-silica reaction in concrete materials containing recycled glass aggregates. Dissertation, Pennsylvania State University
10. Mahyar M, Erdoğan ST, Tokyay M (2018) Extension of the chemical index model for estimating alkali-silica reaction mitigation efficiency to slags and natural pozzolans. Constr Build Mater 179:587–597
11. Leeman A et al (2015) ASR prevention: effect of aluminum and lithium ions on the reaction products. Cem Concr Res 76:192–201
12. Silva DAA (2017) Avaliação das propriedades mecânicas e da durabilidade do concreto com cinzas da termoelétrica do Pecém/CE. Universidade Federal do Ceará, Dissertação
13. Pan JW et al (2012) Modeling of alkali-silica reaction in concrete: a review. Front Struct Civ Eng 6:1–18
14. Glasser D, Kataoka N (1981) The chemistry of alkali-aggregate reaction. Cem Concr Res 11:1–9
15. Glasser D, Kataoka N (1982) On the role of calcium in the alkali-aggregate reaction. Cem Concr Res 12:321–331
16. Ribeiro DV (coord) (2018) Corrosão e degradação em estruturas de concreto: teoria, controle e técnicas de análise e intervenção, 2rd. Elsevier, Rio de Janeiro
17. Virmani P, Faridazar F (2014) Alkali-silica reaction mechanisms and detection: an advanced understanding. Technical Report, School of Civil Engineering, Purdue University
18. Helmuth R, Stark D (1992) Alkali-silica reactivity mechanisms. In: Skalny JP (ed) Materials science of concrete III. American Ceramic Society, Westerville, pp 131–208
19. Diamond S (2000) Chemistry and other characteristics of ASR gels. In: Proceedings... 11th International Conference on Alkali-Aggregate Reaction, pp 31–40
20. Hou X, Struble LJ, Kirkpatrick RJ (2004) Formation of ASR gel and the roles of C–S–H and portlandite. Cem Concr Res 34:1683–1696
21. Thomas M (2011) The effect of supplementary cementing materials on alkali-silica reaction: a review. Cem Concr Res 41:1224–1231
22. American society for testing and materials (2014) ASTM C1260-14 Standard test method for potential alkali reactivity of aggregates (mortar-bar method). West Conshohocken, PA
23. American society for testing and materials (2016) ASTM C 1778 Standard guide for reducing the risk of deleterious alkali-aggregate reaction in Concrete. West Conshohocken, PA
24. Associação brasileira de normas técnicas (2018) NBR 15577-3 Agregados – reatividade álcali-agregado, Parte 3: análise petrográfica para verificação da potencialidade reativa de agregados em presença de álcalis do concreto, 2ed. Rio de Janeiro
25. Mehta PK, Monteiro PJM (ed traduction), Hasparyk NP (2014) Concreto: microestrutura, propriedades e materiais, 2nd edn. IBRACON, São Paulo
26. Berra M, Mangialardi T, Paolini AE (2018) Alkali release from aggregates in long-service concrete structures: laboratory test evaluation and ASR prediction. Materials 11:1–18
27. Rivard P et al (2007) Decrease of pore solution alkalinity in concrete tested for alkali-silica reaction. Mater Struct 40:909–921
28. Hobbs, DW (2000) Alkali levels required to induce cracking due to ASR in UK concretes. In: Proceedings... 11th International Conference on Alkali-Aggregate Reaction, pp 189–198

29. Nixon P, Blackwell B (2000) New UK guidance and specifications to minimise risk of damage to concrete from ASR. In: Proceedings… 11th International Conference on Alkali-Aggregate Reaction, pp 723–732

30. Shehata MH, Thomas MDA (2000) The effect of fly ash composition on the expansion of concrete due to alkali-silica reaction. Cem Concr Res 30:1063–1072

31. Sanchez LFM et al (2017) Tools for assessing damage in concrete affected by AAR coming from fine and coarse aggregates. IBRACON Struct Mater J 10:84–91

32. Farny JA, Kerkhoff B (2007) Concrete technology: diagnosis and control of alkali-aggregate reactions in concrete. Technical Report. Portland Cement Association, Washington

33. Hasparyk NP (2005) Investigação de concretos afetados pela reação álcali-agregado e caracterização avançada do gel exsudado. Universidade Federal do Rio Grande do Sul, Tese

34. Swamy RN, Al-Asali MM (1989) Effect of alkali-silica reaction on the structural behavior of reinforced concrete beams. Struct J 86:451–459

35. Gautam BP et al (2015) Alkali-aggregate reaction in nuclear concrete structures. Part 2: concrete materials aspects. In: Proceedings… 23th Conference on Structural Mechanics in Reactor Technology Manchester, Manchester

36. American concrete institute (1998) ACI 221.1R State-of-the-art report on alkali-aggregate reactivity, Farmington Hills, MI

37. Multon S, Toutlemonde F (2006) Effect of applied stresses on alkali-silica reaction-induced expansions. Cem Concr Res 36:912–920

38. Ferreira APG, Farage MCR, Barbosa FS (2013) Modelling of the mechanical behavior of concrete affected by alkali-aggregate reaction. Revista Escola de Minas 66:35–40

39. Krivenko P et al (2014) Mechanism of preventing the alkali–aggregate reaction in alkali-activated cement concretes. Cement Concr Compos 45:157–165

40. Saha AK et al (2018) The ASR mechanism of reactive aggregates in concrete and its mitigation by fly ash: a critical review. Constr Build Mater 171:743–758

41. Scott A, Alexander MG (2016) Effect of supplementary cementitious materials (binder type) on the pore solution chemistry and the corrosion of steel in alkaline environments. Cem Concr Res 89:45–55

42. Schneider JF et al (2008) Effect of lithium nitrate on the alkali-silica reaction gel. J Am Ceram Soc 91:3370–3374

43. Lawrence M, Vivian HF (1961) The reactions of various alkalies with silica. Aust J Appl Sci 12:96–103

44. Wijnen PWJG et al (1989) Silica gel dissolution in aqueous alkali metal hydroxides studied by 29Si-NMR. J Non-Cryst Solids 109:85–94

45. Chen H, Soles JA, Malhotra VM (1993) Investigations of supplementary cementing materials for reducing alkali-aggregate reactions. Cement Concr Compos 15:75–84

46. Hong SY, Glasser FP (1999) Alkali binding in cement pastes. Part I—the C–S–H phase. Cem Concr Res 29:1893–1903

47. Hong SY, Glasser FP (2002) Alkali sorption by C–S–H and C–A–S–H gels. Part II—role of alumina. Cem Concr Res 32:1101–1111

48. Chappex T, Scrivener K (2012a) Alkali fixation of C–S–H in blended cement pastes and its relation to alkali silica reaction. Cem Concr Res 42:1049–1054

49. Chappex T, Scrivener K (2012b) The influence of aluminium on the dissolution of amorphous silica and its relation to alkali silica reaction. Cem Concr Res 42:1645–1649