

Alkali-Silica Reaction (ASR): Mechanisms and Mitigation

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Abstract

The alkali-silica reaction (ASR) in concrete is a significant issue in civil engineering, affecting concrete structures worldwide, resulting in expensive maintenance and reconstruction. The presence of ASR in several concrete facilities around the world highlights the necessity for research into early detection and subsequent mitigation strategies in structures. This article aims to provide an extensive literature review of the recent and relevant studies on the reaction mechanisms, conditioning factors (e.g., reactive aggregates content, alkalis and soluble calcium source, humidity), and mitigation measures of ASR. Despite the major technical progress in understanding and preventing ASR, the need for further research is emphasized.

Keywords:

Alkali-silica reaction, Concrete, Expansion, pH, Humidity

1 Introduction

Globally, concrete is undebatable, the most used construction material. As a result, research contributing to the extension of the service life of reinforced concrete structures are effective contributions to the sustainability of non-renewable natural resources, improving their environmental impact. The choice of concrete as a construction material is primarily justified by its durability, high fire resistance, low cost-benefit ratio, and low maintenance requirement. However, hostile conditions can cause concrete early deterioration and loss of structural integrity. The deterioration of concrete is a complex process influenced by several factors, such as the physical and chemical properties and the exposed condition of the concrete. The main processes that cause the deterioration of concrete include carbonation (Raupach and Schiessl 1997), alkali-silica reaction (ASR) (Diamond 1975), ingress of chloride ions (Rita B. Figueira et al. 2017), oxygen depletion (Böhni 2005), corrosion of steel (Bertolini 2008), spalling of concrete (Böhni 2005).

The ASR, first identified in 1940 (Stanton 2008), is an adverse reaction between the alkaline pore solution of concrete and several metastable forms of silica contained in many natural and manufactured aggregates (Poole 1991). Several research works have been carried out to better understand the physico-chemical mechanisms involved in ASR (Diamond 1975; 1976; Chatterji 1979; Urhan 1987; Hu et al. 2018; Kawabata and Yamada 2017; Saha et al. 2018; Rajabipour et al. 2015), including reviewing the state-of-the-art (Fournier and Bérubé 2000; Thomas 2011; Lindgård et al. 2012; C. Shi et al. 2015).

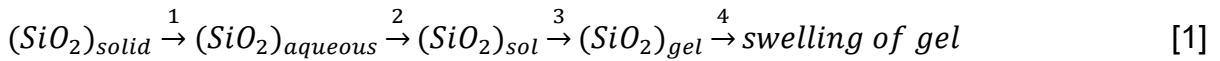
Mitigation measures have been widely studied, including controlling the alkali content in concrete, the use of supplementary cementitious materials (SCMs) such as fly ashes (FA), granulated blast-furnace slag (BFS), and silica fume (SF) (Saha et al. 2018; Kawabata and Yamada 2017; Joshaghani 2017; Z. Shi et al. 2018; Turk, Kina, and Bagdiken 2017), and lithium compounds (Feng et al. 2010; Lourdes M. S. Souza, Polder, and Çopuroğlu 2017). Despite the mitigation advancements, the continued existence of ASR in several concrete structures, including bridges, dams, spillways, and buildings globally (Saha et al. 2018; Carse and Dux 1990), highlights the need for research in early identification and mitigation in structures.

2 Objectives

This paper aims to review the current and significant achievements as well as existing knowledge concerning ASR reaction mechanisms, factors influencing ASR, and measures to mitigate ASR.

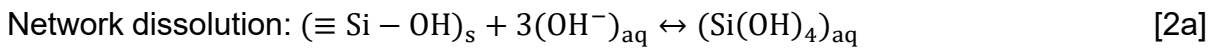
3 Reaction mechanisms

ASR damage is caused by a series of 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 (Rajabipour et al. 2015):

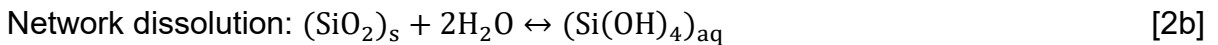


3.1 Dissolution of metastable silica

Silicates are mainly composed of a three-dimensional (3D) network of tetrahedral silica (SiO_2) units, with one Si atom in the center and four oxygen atoms around it (Varshneya 2013). Also, pure silica (SiO_2) frequently contains hydrogen or metallic elements such as sodium (Na), potassium (K), and calcium (Ca) that are linked to oxygen atoms. Silica structures exist as crystalline (Fig. 1a) or amorphous (Fig. 1b). Several articles have been published on silica dissolution in water for over a century (Iler 1979; Bunker 1994; Clark and Yen-Bower 1980). Most of the available research, on the other hand, focuses on pure silica and moderate alkalinity levels ($pH < 11$). It is generally known that in an alkaline environment, hydroxyl (OH) ions gradually attack the (Si-O-) bonds, leading to silica network dissolution:

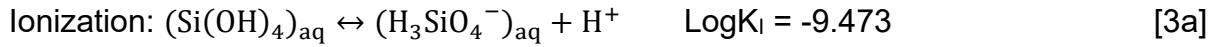


where (Si-OH) denotes the silanol groups found at the silica-water interface (Powers and Steinour 1955).. Eq. (2a) can also be expressed as Eq. (2b), which is more easily described thermodynamically but does not reflect the actual dissolution mechanism at high pH:

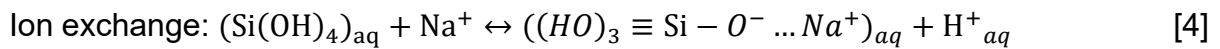


Walther and Helgeson (1977) reported the solubility product of reaction (2b) for different polymorphs of (SiO_2) solid and at different temperatures. For example, at 25°C, $\log K_{sp} = 3.999$ and 2.714 have been observed for α -quartz (crystalline and stable) and amorphous silica, respectively. As shown in Table 1, this information can

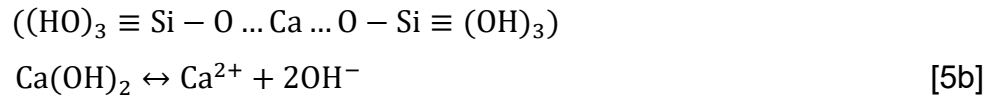
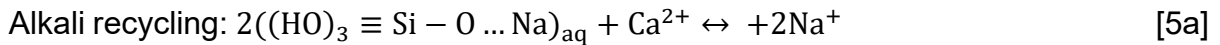
be utilized to compute the equilibrium solubility limit of SiO₂ in neutral water. The solubility increases with increasing temperature and decreasing silica crystallinity (Molchanov and Prikhidko 1957). At high pH, ionization of Si(OH)₄ occurs, leading to the formation of highly soluble ions (Sjöberg 1996):



The equilibrium solubility of silica species in an aqueous solution can be determined as a function of pH using the solubility products of processes (3a) and (3b), as illustrated in Fig. 2. It is observed that at high pH, the apparent solubility of silica increases by several orders of magnitude. It is also worth noting that at high pH, processes (2a), (3a), and (3b) continue in the direction of pH reduction. Furthermore, ion exchange reactions could occur to further lower the pH, for example:



where O...Na⁺ denotes that the bond is most likely a strong Van der Waals type. These reactions indicate that as ASR proceeds, the concrete pore solution's pH generally decreases. However, alkalis are recycled back into concrete pore solution (Eq.(5a)) as some alkalis included in the silica gel (gel mechanism discussed below) may be replaced by calcium ions. The resulting calcium deficit pore solution accelerates the dissolution of solid portlandite (Eq. (5b)) and increases the pH:

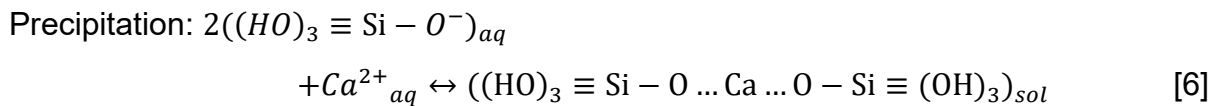


The above discussion is on the thermodynamics of silica dissolution. The dissolution rate of silica in pore solution is also critical to the overall rate of ASR. Although, limited literature on this subject, batch reactors (e.g., ASTM C1285 (ASTM Committee 2002)) have been employed in the few studies that have been done to quantify the dissolution rate of silica (e.g., quartz or fused silica glass) in water (Douglas and El-Shamy 1967; Dove and Crerar 1990).

3.2 Formation and gelation of colloidal silica

The dissolved species remain in the solution as long as the pH and temperature are maintained to avoid supersaturation with respect to aqueous silica, and there are

no Ca ions present (Gaboriaud et al. 1999). At high pH, aqueous silica species are negatively charged (Eqs. (3a) and (3b) and Fig. 2), and the resulting electrostatic repulsion precludes gelation. The aggregate dissolution diminishes and halts when aqueous silica reaches its solubility limit (Dent Glasser and Kataoka 1981). However, in portland cement (PC) concrete, this practically never occurs due to the presence of calcium ions in the pore solution leading to the formation of poly-metasilicates (Iler 1979).



Once a critical-size nucleus has been created, subsequent condensation converts it to nano-colloidal silica sol (Brantley, Kubicki, and White 2008). Larger metal silicate structures are formed when colloidal particles clump together in 2 or 3 dimensions, forming either a continuous and space-filling silicate (ASR) gel or more compact macro-scale precipitates (Scherer 1999; Hou et al. 2005).

3.3 Swelling of the gel

Many factors can explain the considerable absorptivity and swelling of ASR. The silica gel is porous and has a large surface area, and it contains many hydrophilic groups (e.g., -OH, -O...Na, and -O) (Fig. 1c) (Hench and Clark 1978). This leads to Osmosis, water adsorption, and gel swelling (Powers and Steinour 1955). According to Chatterji et al. (1986), the swelling is caused by differential kinetics of fast inward diffusion of detrimental ions such as Na^+ , Ca^{2+} , and OH^- into reactive sites and the slow outward diffusion of silica ions from these sites. Swelling has also been linked to the electrical double-layer repulsive forces that form on the gel's solid particles charged surface (Prezzi, Monteiro, and Sposito 1997; Rodrigues, Monteiro, and Sposito 1999). Swelling has also been related to an increase in the aggregate pore volume during the transition (Garcia-Diaz et al. 2006) and gel stiffness (Gholizadeh Vayghan, Rajabipour, and Rosenberger 2016).

4 Factors influencing ASR

ASR occurs only in specific conditions. The main requirements that must be met at the same time for the development of ASR in concrete are: (i) the presence of

reactive aggregates at a critical concentration range (ii) a high concentration of alkalis (iii) soluble calcium source (e.g., portlandite) (iv) high humidity conditions (Rajabipour et al. 2015; Hobbs 1988; Bérubé, Duchesne, et al. 2002).

4.1 Reactive aggregate content

The existence of reactive aggregates to alkalis is a prerequisite for ASR to occur. In theory, any aggregate containing silica can engage in ASR (Kurtis and Monteiro 2003). Reactive aggregates contain both reactive forms of silica that react quickly with sodium and potassium hydroxides (e.g., opal, tridymite, cristobalite, acid volcanic glass) and those which react slowly (e.g., chalcedony, cryptocrystalline quartz, and strained quartz) (Zapała-Sławeta and Owsiak 2016; Taylor 1997; Kurdowski 2014). The most popular methods for detecting aggregate reactivity to alkalis are based mainly on petrographic tests combined with mortar prism expansion tests (LNEC, 2007).

4.2 Alkalis and soluble calcium source

When Portland cement (PC) is hydrated, an interstitial concrete pore solution is formed, which is mostly constituted of calcium hydroxide ($\text{Ca}(\text{OH})_2$), potassium hydroxide (KOH), and sodium hydroxide (NaOH). Although the majority of alkalis in concrete are from cement, alkalis from other sources such as de-icing salts, additives (e.g., pozzolanic materials (Ichikawa 2009), Silica Fume (M. C. G Juenger and Ostertag 2004), Fly Ash (Saha et al. 2018), and mixing water can also contribute to the alkalinity of the concrete interstitial solution. The influence of Alkali in ASR is already discussed in section 3 above. Also, several published articles (H. Wang and Gillott 1991; Kim, Olek, and Jeong 2015; Kandasamy and Shehata 2014; Leemann et al. 2011; Myadraboina, Setunge, and Patnaikuni 2017; Maraghechi et al. 2016), has shown that $\text{Ca}(\text{OH})_2$ has a key role in ASR as a source of calcium ions (Ca^{2+}) that react with dissolved silica to generate the deleterious calcium-rich ASR gel rim around aggregate particles (Fig. 3).

4.3 Humidity

The impact of water on ASR expansions have received much attention in the literature (Multon and Toutlemonde 2010; Deschenes et al. 2018; Gholizadeh-Vayghan and Rajabipour 2017; Poyet et al. 2006; Larive, Laplaud, and Coussy 2000).

According to Larive et al. (2000), water appears to have a dual effect on ASR: as a reactive agent, influencing the rate of expansion at the creation of the reaction product, and as a transport agent for various reactive species. Reducing water exposure can slow or stop the process. The expansion, however, will resume at a quick pace after the concrete has held the required RH (relative humidity). According to Fournier and Bérubé (1993), for ASR development, concrete must be exposed to high humidity, greater than 80–85 % RH.

5 ASR mitigation

The mitigation measures of ASR aim to eliminate at least one of the four requirements (e.g., source of reactive silica, high alkalis concentration, a source of soluble calcium, and high humidity). The significant accomplishments in terms of controlling each requirement are discussed below:

5.1 Reduction of the alkalinity of the interstitial solution of the concrete

Cement is the primary source of alkalis in concrete. As a result, the alkali content of the concrete is calculated by multiplying the cement's alkali content (expressed as $\text{Na}_2\text{O}_{\text{eq}}$ by the cement dose and adding a factor that converts the amount from other constituents (R. B. Figueira et al. 2019). Alkali content control assumes that the cement manufacturers or suppliers certify the average alkali content and its variability. The alkali content of the interstitial concrete pore solution can be reduced by (i) limiting the alkali content in concrete by controlling the content of concrete soluble alkalis or using suitable binders; (ii) using a low alkali cement (e.g., total alkali content < 0.6% $\text{Na}_2\text{O}_{\text{eq}}$); and (iii) addition of mineral to the concrete (Lindgård et al. 2012). According to ASTM C150 (C01 Committee 2019), 0.6% $\text{Na}_2\text{O}_{\text{eq}}$ is accepted as the limit for cement to be used with reactive agents and is an optional limit when concrete contains deleteriously reactive aggregate. However, Leemann and Lothenbach (2008) showed that concrete mixtures prepared with cements with same $\text{Na}_2\text{O}_{\text{eq}}$ but differing K/Na ratios can expand differentially. Therefore, $\text{Na}_2\text{O}_{\text{eq}}$ parameter should be carefully considered when used to evaluate the possible reactivity of concrete mixtures (R. B. Figueira et al. 2019).

5.2 Use of non-reactive aggregates

Not all aggregates are prone to ASR, and this process can be reduced by using non-reactive aggregates. Aggregates are divided into three reactivity classes: class I – aggregates are not alkali reactive; class II – aggregates are potentially reactive to alkalis; and class III – aggregates are very likely to be alkali reactive. Aggregates that are primarily siliceous, or carbonates with possibly reactive silica content, are classified as class II-S or class III-S. Class II-C or III-C aggregates are mainly carbonate or combinations of potentially reactive carbonate types (Nixon and Sims 2016). The reactivity of an aggregate or mixture of aggregates is often determined by results from different tests such as petrographic characterization (C09 Committee 2019), measurement of silica dissolved, and expansion tests (Wallau et al. 2018).

5.3 Concrete moisture control

As previously stated, RH (above 80%) is required to induce ASR in concrete (Bérubé and Fournier 1993). Several research studies have investigated the impacts of moisture conditions (Multon and Toutlemonde 2010; Deschenes et al. 2018; W. Zhang, Min, and Gu 2016). Multon and Toutlemonde (2010) showed that if water is added, regardless of the age of an ASR damaged structure, it swells if the ASR gel is already formed. It was also speculated that the ASR reaction could have been halted by a lack of water in particular portions of the structure (Multon and Toutlemonde 2010). Therefore, any methodology that restricts water availability to concrete using reactive materials reduces the probability of ASR development. Several papers (Bérubé, Chouinard, et al. 2002; Richard A. Deschenes Jr, Murray, and Hale 2017; R. A. Deschenes Jr et al. 2018) have demonstrated the usefulness of silanes in delaying the development of ASR and thereby increasing the service life of concrete structures.

5.4 Modification of expandable properties of ASR gel

McCoy and Caldwell published the first report on lithium salts to prevent ASR in 1951, and was reported to be the most effective compound (McCoy and Caldwell 1951). Subsequent studies concerning the effectiveness of lithium compounds to mitigate ASR were conducted (Fournier and Bérubé 2000; Collins et al. 2004). The capacity of lithium to substitute calcium in ASR gel rather than K^+ and Na^+ was reported to explain the lithium ASR mitigation mechanism (Leemann et al. 2014;

Tremblay et al. 2010). **Table 2** summarizes the most representative research on the use of lithium compounds to minimize ASR that has been published in recent years.

5.5 Mineral additives

Mineral additives have played a significant role in the construction industry, contributing to the technological advancement of concrete and mortars. Mineral additives with pozzolanic properties, such as ground blast furnace slag (Angulo-Ramírez, Mejía de Gutiérrez, and Medeiros 2018; D. Wang et al. 2018), fly ash (Gholizadeh Vayghan, Wright, and Rajabipour 2016; Schafer et al. 2019), silica fume (Ramezani pour and Moeini 2018; Rostami and Behfarnia 2017), and Metakaolin (MK) (Shen et al. 2017; Z. Shi et al. 2018), as well as other minerals (Maria C. G. Juenger and Siddique 2015), have been proposed as useful in preventing ASR. **Table 3, 4, 5, and 6** shows the most relevant manuscripts published in recent years concerning the use of BFS, FA, SF, and MK to mitigate ASR, respectively.

6 Conclusion and prospects

The alkali-silica reaction (ASR) is one of the crucial concrete durability concerns in recent decades. Multiple factors influence the complexity of ASR chemical reactions. An overview of recent and relevant studies on the reaction mechanisms, conditioning factors, and mitigation strategies of ASR is presented in this paper. Three primary reaction mechanisms, including dissolution of metastable silica, formation and gelation of colloidal silica, and gel swelling, were discussed. Three conditioning factors were also debated: the reactive aggregates content, alkalis and soluble calcium source, and humidity conditions. The information gathered shows that several efforts had been devoted to understanding the fundamentals of ASR, which is reflected by the considerable amount of data published in the last few decades.

Five preventive measures were proposed, including silanes to control concrete moisture. Lithium compounds and mineral additives have also been employed to prevent ASR. Despite the major technological advancement in understanding and mitigating ASR, the capacity to fully understand and describe the development of ASR remains incomplete. Therefore, the need for systems to provide more information on ASR initiation process and further progression is of utmost importance.

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Tables:**Table 1**

Thermodynamic solubility limit (mM) of various SiO₂ polymorphs in neutral water. Calculated using data from (Walther and Helgeson 1977). Source: (Rajabipour et al. 2015)

| 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 |

Table 2

The most relevant manuscripts published since 2011 concerning the use of lithium compounds to mitigate ASR. Source: (R. B. Figueira et al. 2019)

| Year | Source | Li compounds | Main results and conclusions |
|------|---------------------------|--|---|
| 2013 | (Demir and Arslan 2013) | Li ₂ SO ₄ , LiNO ₃ , Li ₂ CO ₃ , LiBr | Li compounds applied at the ratio 0.5–3.0% proved to be effective in reducing length changes. The lowest changes were obtained with 3% of Li ₂ CO ₃ . |
| 2014 | (Leemann et al. 2014) | LiNO ₃ | Li decreased the ASR expansion and bound preferentially leading to a faster depletion in the pore solution. |
| | (W. C. Wang 2014) | LiOH and LiNO ₃ | Changes of water-soluble alkali and Li content were studied to understand the effect on ASR by adding FA and lithium compounds simultaneously. LiNO ₃ addition exhibited improved performance in increasing water-soluble Li/(Na + K) ratio compared to LiOH addition. |
| 2015 | (Leemann et al. 2015) | LiNO ₃ , Aluminium | The effect of aluminium (from metakaolin (MK) and calcium aluminate clinker) and LiNO ₃ on the mitigation of ASR was investigated. MK lead to a slower SiO ₂ dissolution and formation of reaction products. LiNO ₃ suppressed ASR. |
| 2016 | (Kim and Olek 2016) | LiNO ₃ | Li prevented the dissolution of reactive silica. The ASR control was explained by the formation of physical barrier in certain areas of the reactive aggregate exposed surface. ASR was dependent on the dosage of LiNO ₃ . |
| | (Islam and Ghafoori 2016) | LiNO ₃ | LiNO ₃ was more and less effective in the presence of highly and less reactive aggregates, respectively. A good agreement was found between the required optimum experimental and analytical Li dosages to inhibit the excessive mortar expansion. |

| | | | |
|------|---|---|--|
| | (Zapała-Sławeta and Owsiak 2016) | LiNO ₄ | The addition of a molar ratio of Li/(Na + K) = 0.74 decreased the expansion of mortars made with reactive gravel aggregate until reach the safe and non-destructive level. |
| 2017 | (Lourdes M. S. Souza, Polder, and Çopuroğlu 2017) | LiOH | Studies on the influence of Li ⁺ migration on different levels of ASR development. Na ⁺ and K ⁺ removal, Li ⁺ migration (combined with Na ⁺ and K ⁺ removal) and Li ⁺ diffusion on ASR expansion were assessed. Li ⁺ migration led to the lowest post- treatment expansion levels. |
| 2018 | (L. M. S. Souza, Polder, and Çopuroğlu 2018) | Li ₂ CO ₃ , LiOH and LiNO ₃ | Type and concentration of Li compounds in the analyte to be used on electrochemical migration repair technique were studied. The concentration of the solution, rather than the type of Li salt, affected migration. |
| | (Demir, Sevim, and Kalkan 2018) | Li ₂ SO ₄ , LiNO ₃ , Li ₂ CO ₃ , LiBr, LiF | The optimum amount of Li additives changed according to the compound (e.g. 3% Li ₂ SO ₄ , 1.5–3% LiNO ₃ , 0.5–3% Li ₂ CO ₃ , 0.5–3% LiF). ASR was affected by the type and additive ratio. |

Table 3

The most relevant manuscripts published since 2011 concerning the use of BFS to mitigate ASR. Source: (R. B. Figueira et al. 2019)

| Year | Source | Main results and conclusions | BFS/Cement (wt %) |
|------|---|---|-----------------------|
| 2011 | (Karakurt and Topçu 2011) | The influence of blended cements and sulphate resistance of concrete on ASR were studied. FA and BFS reduced ASR and sulphate damages compared to PC. BFS showed improved results. | 10, 20, 30, 40 and 45 |
| 2014 | (Beglarigale and Yazici 2014) | Study on the combination of brass-coated steel microfiber and BFS on ASR mitigation. ASR expansion was reduced and BFS was effective at preventing the mechanical property loss. | 20 and 40 |
| 2017 | (Z. Shi et al. 2017) | Study of alkali dosages impact on ASR in activated slag mortars. Alkali activated slag mortars showed improved performance compared to PC under accelerating condition. | NR |
| 2018 | (Angulo-Ramírez, Mejía de Gutiérrez, and Medeiros 2018) | Alkali-activated Portland hybrid blended cement and a Portland blended cement were compared to 100% ordinary PC. The material based on PC had highest susceptibility to ASR, followed by the alkali-activated hybrid material and the blended cement with 80% ground BFS. | 80 |

Table 4

The most relevant manuscripts published since 2011 concerning the use of FA for mitigation of ASR. Source: (R. B. Figueira et al. 2019)

| Year | Source | Main results and conclusions | FA/Cement (wt %) |
|------|--|---|------------------------|
| 2011 | (Thomas et al. 2011) | Concrete blocks with reactive aggregates, different levels of high-alkali cement and two sources of FA were assessed outdoor. All blocks without FA showed excessive expansion and cracking within 5–10 years of production. FA replacement levels of 25% or 40% were effective in reducing ASR expansion. | 25, 40 |
| | (Esteves et al. 2012) | Study on the influence of blended cements with different types of pozzolans on ASR. NZ, FA, and ground BFS were used. NZ, FA, and ground BFS reduced the ASR expansion. | 10, 20, 30, 40, 45 |
| 2012 | (Shafaatian et al. 2013) | Study on the effect of FA from biomass combustion in ASR mitigation. The biomass FA incorporation mitigates the ASR. Expansion decreased with the increasing content of FA. | 20, 30 |
| 2013 | (Kizhakkumodom Venkatanarayana n and Rangaraju 2013) | FA fineness influenced the ASR within the range of the average particle size (APS) of FA (~10–30 μm). ASR had an exponential relation with SiO_2 , CaO , $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$, $\text{CaO} + \text{MgO} + \text{SO}_3$, SiO_2 equi and CaO equi for FA with $\text{APS} < \sim 10 \mu\text{m}$. Expansion was a linear function of CaO , $\text{CaO} + \text{MgO} + \text{SO}_3$, and CaO equi and a logarithmic function of SiO_2 , $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ and SiO_2 equi for FA with $\text{APS} < 5 \mu\text{m}$ | 25 |
| | | Study on the contribution of different mechanisms for ASR mitigation by FA using ASTM C1567 test. Experimental and computer simulation were combined. | 15, 20, 25, 30, 35 |
| 2014 | (Wright, Shafaatian, and Rajabipour 2014) | FA ability to control ASR generated by recycled glass sand. Capacity of CIM [312] to predict the FA dosage for ASR was assessed. It was concluded that the model parameters must be revised. | 10, 15, 20, 25, 30, 35 |
| | (Kandasamy and Shehata 2014) | Ternary blends of high-calcium FA and slag for ASR mitigation were studied. Ternary blends did not offered advantage over binary blends and of individual material for the same SCM. Capacity to retain alkalis increased with the blend ability to consume $\text{Ca}(\text{OH})_2$. The alkali leaching test was proposed as a tool to compare the efficiency of different blends. | 20, 30, 40, 50 |
| | (Yıldırım and Sümer 2014) | FA's effect was studied by ASTM C 227, ASTM C 1260 and autoclave methods. The 12-month results agree with the AMBT. Samples whose mixing water was pure were in a good correlation on the basis of 12-month results. | 10, 20, 30, 40, 50 |
| 2015 | (Schumacher and Ideker 2015) | The ability of high CaO and/or high-alkali (Na_2Oeq) FA to mitigate ASR in mortar was assessed. Low and | 25, 35, 45 |

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|------|---|--|----------------|
| | | moderate CaO content FA were more effective compared to higher CaO and Na ₂ O _{eq} FA. The methodology worked for low CaO and alkali FA. It was concluded that to predict replacement levels of moderate to high-alkali FA adjustments were necessary. | |
| | (S. Wang 2015) | Expansion, pore solution, compressive strength and alkali leaching of biomass and coal FA were investigated. Class F mixes showed improved behaviour. Class C reduced expansion with restricted efficiency. Biomass FA showed equivalent expansion reduction to that of Class C. | 15, 25, 35 |
| 2016 | (Gholizadeh Vayghan, Wright, and Rajabipour 2016) | Extended CIM was developed to predict the FA dosage for ASR mitigation. Extended CIM offered acceptable prediction accuracies for both Class C and F FA. | N.A. |
| | (Williamson and Juenger 2016) | Alkali-activated FA concrete showed promising performance compared to ordinary PC concrete in ASR mitigation. | 45 |
| 2017 | (Kawabata and Yamada 2017) | Study on the role of FA in ASR mitigation and at pessimum proportion. ASR was reduced at pessimum proportion. FA increased the latency time. | 10, 20, 30 |
| | (Joshaghani 2017) | Study on the effect of trass and FA under short- and long-term experiments. FA was more effective than trass in strength development. 20% FA was the optimum content. | 10, 20, 30 |
| | (Turk, Kina, and Bagdiken 2017) | Study of binary and ternary systems (FA and LSP) on ASR. ASR decreased with FA increase. Ternary blend of 20% FA/LSP was the most effective. | 10, 15, 20, 30 |
| 2018 | (Z. Shi et al. 2018) | Study on effect of FA and MK on ASR in water-glass-activated slag mortars. Both FA and MK mitigated the ASR of the waterglass-activated slag mortars. | 30 |

Table 5

The most relevant manuscripts published since 2005 concerning the use of SF for mitigation of ASR. Source: (R. B. Figueira et al. 2019)

| Year | Source | Main results and conclusions | FA/Cement (wt %) |
|------|--------------------------------------|---|------------------|
| 2005 | (Bektas, Turanli, and Monteiro 2005) | Expansion of mortar bars containing various amounts of SF, expanded perlite, and natural perlite were studied. Both expanded and natural perlite showed potential to suppress the ASR. Expansion decreased with increased SF content. 8% and 12% SF had a similar expansion rate. Samples with 16% SF met ASTM C1260 limit. | 4, 8, 12 and 16 |
| 2007 | (Maas, Ideker, and Juenger 2007) | Three types of SF using reactive and non-reactive aggregates were tested. Large SF agglomerates were not linked to ASR cracking. When SF was alkali silica reactive, there was a pessimum effect with expansion related to the percentage of SF used. Lower amounts resulted in higher expansions. | 2, 4, 6 and 10 |

| | | | |
|------|--------------------------|--|------------------|
| 2008 | (C. Zhang and Wang 2008) | Influence of SF, BFS and FA on ASR at 70 °C was studied. SF, BFS and FA inhibited the ASR only under appropriate content. SF contents < 10% did not influenced the ASR, between 15% 20% delayed the expansion. | 5, 10, 15 and 20 |
|------|--------------------------|--|------------------|

Table 6

The most relevant manuscripts published since 2011 concerning the use of MK for mitigation of ASR. Source: (R. B. Figueira et al. 2019)

| Year | Source | Main results and conclusions | FA/Cement (wt %) |
|------|-------------------------------|--|------------------|
| 2012 | (Estevess et al. 2012) | The use of MK was effective in limiting the AMBT expansion when used with biomass FA (20% FA + 10% MK). The effectiveness of MK was justified by the finer particle size and the chemical composition. | 10 |
| 2014 | (Yazıcı, Arel, and Anuk 2014) | Studies on the effects of cement replacement by MK on mechanical properties, ASR, resistance to sulphate, absorption capacity and permeability. 10–20% of MK increased the ASR resistance. Enhanced results were obtained for mortars containing 15–20%. | 5, 10, 15, 20 |
| 2015 | (Pouhet and Cyr 2015) | ASR of geopolymers mortars containing only MK in the presence of six different sands were studied. Sands in MK based geopolymers mortars activated by sodium silicate did not lead to ASR characteristic of PC mortars. | NR |
| 2018 | (Z. Shi et al. 2018) | Mitigation effects of FA and MK on ASR in water-glass-activated slag mortars were investigated. Both mitigated the ASR. Optimum dosage of FA was 30%. Expansion decreased with MK increase and was suppressed when the slag was replaced by 70% of MK. | 10, 30, 50, 70 |

Figures

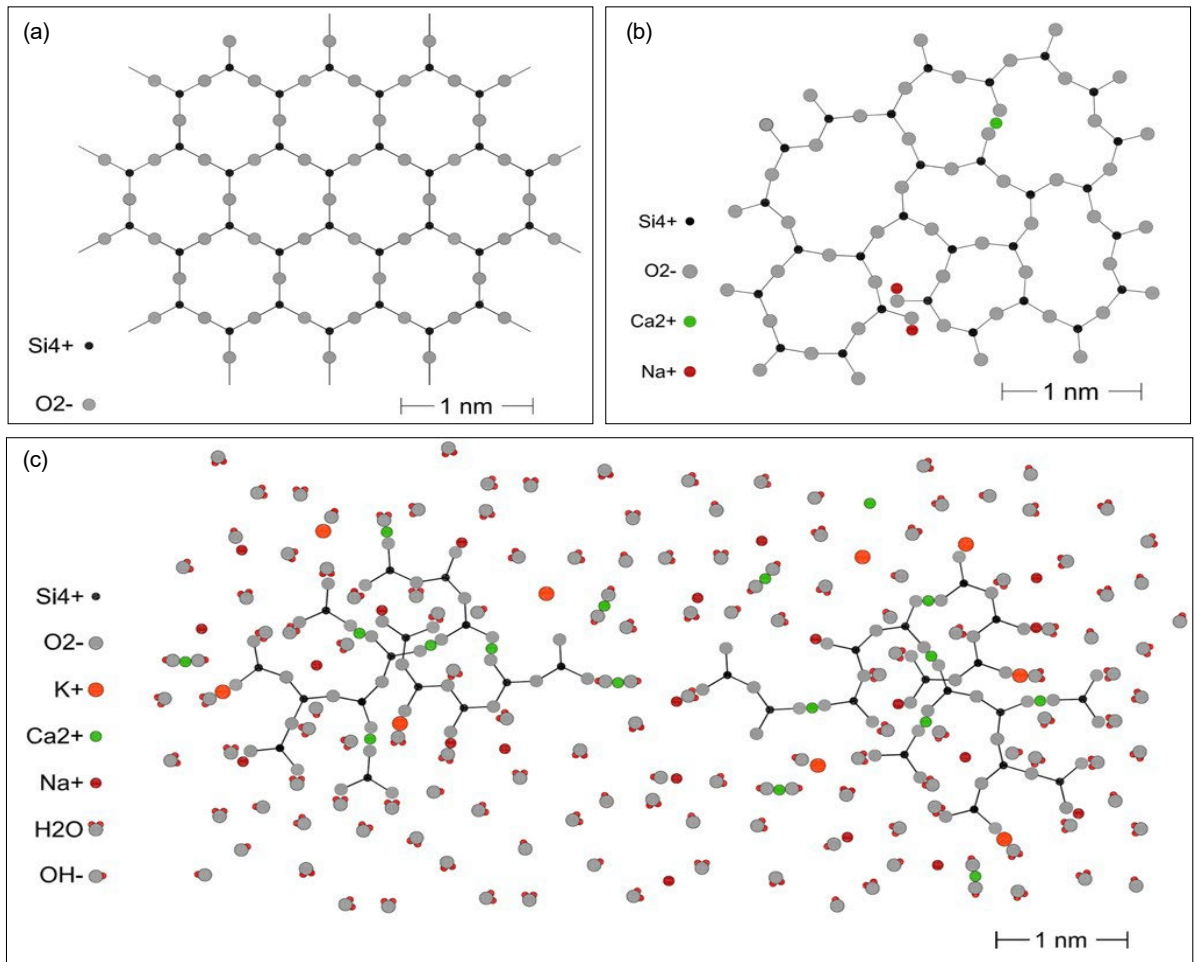


Fig. 1. (a) 2D ball and stick representation of quartz (a common form of crystalline solid SiO₂) (b) amorphous solid SiO₂ (c) alkali-silica (ASR) gel composed of clustering of colloidal silica particles surrounded by the gel's pore solution. Source: (Rajabipour et al. 2015)

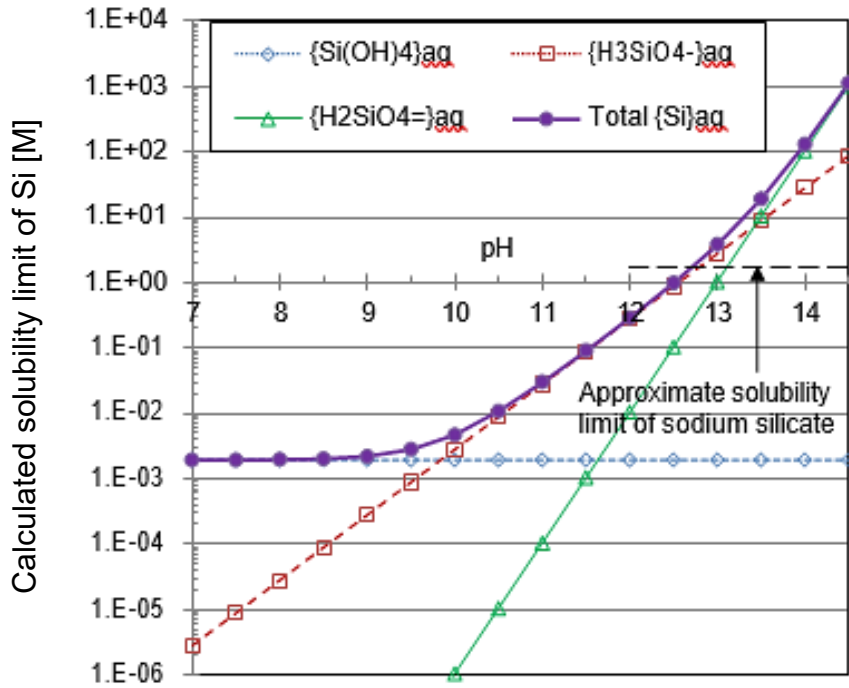


Fig. 2. The calculated solubility limit of amorphous SiO_2 in water as a function of pH ($T = 25^\circ\text{C}$). Source: (Maraghechi 2014)

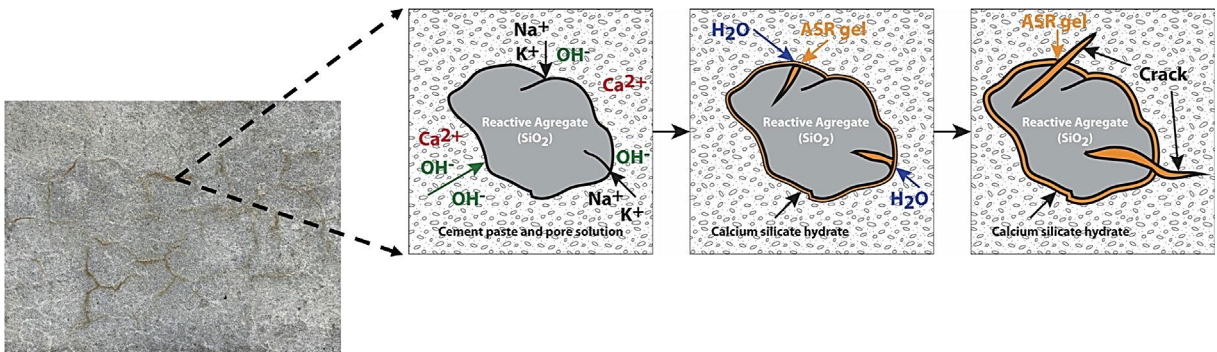


Fig. 3. Schematic representation of the mechanism of the ASR in concrete. Source: (R. B. Figueira et al. 2019)