

Mitigating Alkali Silica Reactions in the Absence of SCMs: A Review of Empirical Studies

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Abstract

The mechanism and severity of alkali-silica reaction (ASR) is subjective to the conditions of the availability of moisture and sufficient alkali content, and the presence of reactive aggregates. Since the 1940s, key focus has been placed on the reduction of alkali content by way of addition of supplementary cementitious materials (SCMs). However, the cost of SCMs and the realization that the availability of these materials could become limited in the untold future has influenced some researchers to investigate the development of protocols for the use of aggregates minimizing the likelihood of potential severe ASR. This paper presents a summary and review of the various strategies that have been adopted in recent years for the mitigation of ASR without utilising the addition of SCMs.

Keywords: Aggregate properties; Alkalis; Alkali-silica reaction; Particle size distribution; Supplementary cementitious materials.

I Introduction

The discovery of the alkali-silica reaction by Stanton (Lane 1994; Stanton 1940) has served as a backdrop on which numerous investigations have been conducted to date. ASR occurs when there is sufficient alkali and reactive silica present in the pore solution of concrete (Stanton 2008). Controlling the reaction or reducing the risk of deleterious ASR may be achieved by reducing or eliminating one or more of these reactants in the concrete (Stanton 1950).

Stanton et al. further experimented with the efficacy of pozzolans in mitigating ASR. Replacing a part of the cement with pumicite reduced ASR and the incidence of expansion (Stanton 1950). Various other studies have been conducted with other supplementary cementitious materials (SCMs) including fly ash (Kandasamy & Shehata 2014; Moser et al. 2010; Shafaatian et al. 2013), slag (Fernández-Jiménez & Puertas 2002; Gifford & Gillott 1996; Malvar et al. 2002), silica fume (Boddy, Hooton & Thomas 2000; Hasparyk, Monteiro & Carasek 2000) and, accordingly, a combination of SCMs (Hussain 1991; Kandasamy & Shehata 2014). Whereas this mitigation method yet proves to be effective in alleviating deleterious ASR expansion, it is important to note that SCMs are generally obtained as by-products from manufacturing operations (Higgins et al. 2011; Lothenbach, Scrivener & Hooton 2011; Ramlochan, Thomas & Gruber 2000). Thus, these materials are not readily available for use in all parts of the world and, where SCMs are routinely employed in mitigation, there is a tendency for these by-products to deplete as sources are exhausted. Additionally, due to the differences in geological origins of the parent materials, differences in the compositions of the SCMs may exist which may limit the potential of using these SCMs to mitigate expansion due to ASR.

In light of this, alternative methods to reduce ASR in the absence of using SCMs need to be investigated. This paper therefore reviews (i) parameters that result in ASR and (ii) alternative strategies for ASR mitigation. Published work on studies that have been conducted on mitigating ASR without SCM addition are discussed. The authors also hope to make recommendations on methods that could be possibly applied in further studies on potential ways of controlling ASR induced deleterious expansions.

Part One: Influences for Alkali-Silica Reaction

Alkali-silica reaction is dependent on the simultaneous presence of three factors (Islam 2010; Nixon & Sims 2016a):

- alkali content of the concrete and alkalinity of the pore solution
- a source of reactive silica, and,
- the sufficient supply of water as the reaction medium.

ASR occurs when predisposed forms of silica in the reactive aggregate react with alkali in the pore solution to form an expansive silica gel. The gel then expands upon absorption of water thereby causing cracking at a micro scale. The initiation of micro cracks by ASR gel expansion has the potential to extend and result in severe structural damage on a macro scale of the concrete structure (Berra, Mangialardi & Paolini 2005; Diamond 1975; Esteves et al. 2012; Fournier & Bérubé 2000; Ghanem, Zollinger & Lytton 2010; Nixon & Sims 2016a). The absence of one of the factors required to initiate deleterious ASR arrests or inhibits the potential for expansion (Hobbs 1988; Understanding Cement). Therefore, strategies for mitigation of deleterious ASR are generally aimed at reducing the influence of one or more of these factors. However, the source of reactive silica and the availability of moisture in concretes may not be controllable. This is due to differences in composition of the available materials and the eventualities of environmental conditions. (Nixon & Sims 2016a). As such, the focus on mitigation strategies has generally been in the reduction of alkalis in the pore solution through the limiting of alkali content of the concrete.

1.1 Sources of alkali

Concrete pore solution containing large concentrations of alkali ions and small concentrations of calcium ions are considered highly alkaline. The presence of sufficient alkali is critical to the onset and persistence of ASR in concrete (Rajabipour et al. 2015). This accounts for the limits placed on the allowable alkali content for cement and concretes used in countries such as Canada, New Zealand and Australia (Bérubé et al. 2002; Civil Engineering ; Freitag 2012; Leming & Nguyen 2000). Additionally, the maximum alkali content that will not incite ASR is dependent on the reactivity of the aggregate used in the concrete (Thomas et al. 2006). Most of the alkalis available for reaction in concretes are known to be supplied by the Portland cement used in the mix. Other sources of alkali release include SCMs, aggregates, chemical admixtures, de-icing agents, unpotable mix water and external sources such as the service environment.

Alkalis in Cement

The alkalis in cement clinker are unavoidable. They are derived mainly from sulphate constituents used to manufacture the clinker e.g., shale. The alkali content of Portland cement has changed over time. It has increased due to changes in the manufacturing process of cement as well as differences in the composition of raw materials used to manufacture the clinker (Diamond 1975). Typically, the alkali content in cement ranges from 0.2 – 1.1% by weight of oxide. The alkalis are made available by the hydration of cement and are present in the pore solution of concrete as hydroxides of sodium (Na) and/or potassium (K) ions. ASR is dependent on the total alkali ion content as both sodium and

potassium ions have similar reactivities. Thus, the alkali content in the pore solution can be defined as an equivalent percent (Na_2O_e) of Na and K.

The concentration of hydroxide ions in the pore solution (pH) is dependent on the water-cement ratio (w/c), the alkali content and the extent of hydration of the cement (Thomas 2011) and can be empirically estimated from Equation 1 (Helmuth et al. 1993).

$$[\text{OH}^-] = 0.339 \text{ Na}_2\text{O}_e \% / (\text{w/c}) + 0.022 \pm 0.06 \text{ mol/L} \quad (1)$$

Equation 1 has been derived from studies assessing the effect of water-cement ratio on the pH of the pore solution. Different types of cements exhibit variability in their amount of water-soluble Na and K alkali ions (Diamond 1975) available, with the concentration of alkalis in pore solution typically being in the range of 0.15 to 0.85 mol/L (Thomas 2011).

Supplementary cementitious materials

SCMs may contain alkalis (Chappex & Scrivener 2012; Scholz, Hübert & Hüniger 2016) and in certain cases much higher amounts than that of Portland cement. These alkalis are known to be released slowly over time and may contribute to the formation of deleterious ASR in concrete at a later age (Rajabipour et al. 2015; Shafaatian et al. 2013). The effect of the alkali released from SCMs is dependent on the presence of alumina ions and the amount of free silica available to react. Studies on the use of fly ash for ASR mitigation showed that, fly ashes with high calcium content and high alkali content exhibit poor ASR mitigating capabilities (Chen, Soles & Malhotra 1993; Shafaatian et al. 2013). These low fly calcium fly ashes were reported to have low alumina ion content and thus, low alkali binding properties. Neither the rate nor the amount of alkali release in SCMs for ASR occurrence in the life time of a concrete structure in service is certain (Rajabipour et al. 2015).

Releasable alkalis in aggregates

One other source of alkali that is equally difficult to quantify is the possible release of alkalis from the aggregates used for concrete production. Consecutively, instances occur where ASR expansions are still observed when low alkali content cement is used in concrete (Association et al. 1992; Grattan-Bellew 1995; Olague, Wenglas & Castro 2003; Stark & Bhatti 1986). Both reactive and non-reactive aggregates may contain releasable alkalis (Rajabipour et al. 2015). Nevertheless, the amount of alkalis released that contribute to the pore solution alkalinity is tentative and typically varies with the type of aggregate used in concrete. Methods for assessing these variables are currently under investigation by the RILEM committee (Nixon & Sims 2016a). Alkalis in aggregates may be encapsulated within the metastable silica structure of the aggregate and only released slowly as the silica is dissolved by OH^- ions (Rajabipour et al. 2015). The release of alkalis from aggregates maintain a high pH in the pore solution of the concrete for the formation of ASR. Alkali release from these aggregates are slow and could be delayed up to 20 years. Under severe conditions, some aggregates could release alkalis up to 10% of the alkali present in the Portland cement (Islam 2010). In particular, the Witwatersrand quartzite of South Africa has been found to contain about 0.7% Na_2O_e alkalis (Blight et al. 1981). Examples of alkali releasable aggregates are those that contain minerals such as feldspar, zeolite and dawsonite (Bérubé & Fournier 2004). Additionally, aggregates, particularly those sourced from marine and coastal locations, may be contaminated with sea salt. Sea salt (NaCl) adsorbed by the aggregates in these environments can contribute to the available alkali in concrete.

Chemical admixtures and external sources

Chemical admixtures are typically added to concrete to enhance its fresh and hardened properties. However, chemical admixtures such as retarders, air-entrainers, accelerators, water reducers and high range water reducers may also contain sodium and potassium compounds that also add to the alkali content in concrete. The contribution of alkalis in admixtures is typically disregarded in the calculations of the total alkali content of concretes due to the low amounts that are generally added.

Similarly, external factors such as the service environment (usually marine) and the use of de-icing agents containing alkalis are difficult to quantify. Alkalis present in de-icing agents such as NaCl, alkali (Na^+ , K^+) acetates and alkali formates can contribute to alkali presence in pore solution. These factors are known to have an effect on the occurrence of ASR (RILEM 2008) and need to be considered for the performance of concrete in service.

1.2 Chemical mechanism of alkali-silica reaction

ASR occurs when hydroxyl ions in the pore solution of concrete progressively attack the siloxane bond ($\equiv\text{Si-O-Si}$) of silica resulting in the dissolution of SiO_2 network and the formation of silanol ($\equiv\text{Si-OH}$) bonds. This network dissolution reaction (Broekmans 2004; Walther & Helgeson 1977) is shown further in Equation 2:



At elevated pH, $\text{Si}(\text{OH})_4$ further dissolves, producing three Si-O⁻ species which are then balanced by Na^+ and K^+ ions in solution to form alkali silicates. The dissolution of silicate ions consumes OH^- ions and thus a decrease in alkalinity (pH) occurs. This initiates the polymerization reaction of the silicate ions to form SiO_2 gel. Meanwhile Ca^{2+} ions (from cement), present in the pore solution, react to substitute alkali ions in these gels and accelerate the precipitation of the dissolved silica to form the ASR gel; a calcium-alkali-silicate hydrate (Walther & Helgeson 1977). The process of releasing alkali ions allows the regeneration of high pH that will result in further dissolution of the silica. The gel formed is semi-permeable and thus possess the capacity to absorb moisture and in some cases cause deleterious expansion. Similarly, further alkalis precipitate and contribute to the expansive nature of the gel.

The presence of moisture plays a key role in the outcome of ASR acting as a medium to transport the reactants required to give ASR (Broekmans 2004). It is reported that without the presence of moisture, ASR gels formed cannot result in deleterious expansion (Saouma & Perotti 2006; White Paper). Moisture is imbibed by ASR gels from the (in service) environment and from mix water used during concrete production. It goes without saying then that the water-cement ratio and the moisture available for curing play a pivotal role in reducing the potential for ASR. Usually, ASR gel expansions thrive in environments with internal relative humidity above 85% (Fournier & Bérubé 2000). A study by Poole showed that by partially drying concrete specimens, a partially dehydrated ASR gel structure was achieved with the rate of ASR formation decelerated. However upon rehydration, re-expansion of these specimens occurred except for specimens that were dried and carbonated prior to moisture contact (Poole 1992).

A debate exists on the role of calcium in the deleterious expansion of moisture imbued ASR gel (Bleszynski & Thomas 1998). In his doctoral dissertation, Islam stated that C-(N,K)-S-H silicate gel was non-swelling whereas N(K)-S-H silicate gels were found to be expansive (Islam 2010). Conversely, some researchers disagree with this reporting that, in the absence of calcium, silicate gel will remain in solution (Diamond 1989). Portlandite ($\text{Ca}(\text{OH})_2$ or C-H) is partially soluble and thus dissolves to aid a high pH of the pore solution thereby increasing ASR (Bažant & Steffens 2000). Similarly, the exchange that occurs between Ca^{2+} and Na^+ (or K^+) ions encourages swelling of the gel (Wang & Gillott 1991). The expansive nature of ASR gel is dependent on the amount of calcium in the gel. High calcium content gels form cross-linked bonds between Ca^{2+} and $2(\text{Si-O}^-)$, which inhibits expansion. However, there is not enough Ca^{2+} in the pore solution (as compared to Na^+ and K^+) and the cement cannot produce Ca^{2+} fast enough to form non-expansive C-S-H phases. Consequently, a low Ca^{2+} concentrated silica gel is formed. These gels are unable to form cross-linked bonds and thus imbibe water and become expansive (Shon, Mukhopadhyay & Zollinger 2006).

Reactions leading to ASR often begin at the aggregate interface (Multon, Sellier & Cyr 2009; Rajabipour et al. 2015). It is therefore important to consider the physical and mechanical property influence of the reactive aggregate on ASR as well. Likewise, the properties of the overall concrete structure and the cement component could potentially contribute to ASR. A critical review of these

associated factors can be considered as the initial step in establishing an alternative method to reducing the potential for ASR occurrence.

1.3 Physical mechanism of alkali-silica reaction

Where the particle surface is theorized as the point of accessibility for hydroxyl ions to reach reactive silica within the aggregates, in practice some aggregates possess readily available reactive silica on their surfaces; as a result a much faster rate of ASR is observed (Ponce & Batic 2006; Rajabipour et al. 2015). This behaviour is common with cherts and granite gneiss (Lane 1994). Another aggregate feature that potentially contributes to the rapid deterioration by ASR is surface micro cracking. These micro cracks can naturally occur from the weathering and formation of the rock or artificially from the process of comminution into various size fractions (manufactured sand) (Ponce & Batic 2006). The presence of micro cracks allows for permeability such that the pore solution can further react with metastable silica causing the ASR reaction to proceed quicker. Micro cracks also expose more surface area thus an increase in the rate of reaction can also result.

Additionally, aggregate shape can contribute to the ingress of gel and physical expansion of ASR. Typically, aggregate used in concrete may vary from rounded (spherical) to sub-rounded (irregular) and angular in shape (Teychenné et al. 1975). Natural aggregates assume a more rounded shape while crushed aggregates are more likely to be platelike and angular in shape (Teychenné et al. 1975). The influence of particle shape is rarely mentioned in literature. However, where it has been reported, angular particles have been stated to cause a reduction in workability (Shao et al. 2000). The irregular shape of such aggregates provides difficulty in compactibility thus increasing the porosity of the concrete matrix. The evaluation of ASR potential for crushed reactive aggregates (manufactured sand) have been reported to show higher expansion in their intermediate size fraction, compared to natural uncrushed aggregates (Ramyar, Topal & Andiç 2005). This was attributed to the angularity and change in surface texture due to the crushing of aggregates to reduced particle size. These authors also reported the effect of aggregate reactive size on ASR expansion was more evident for crushed aggregate compared to natural sand. Although some exceptions to surface texture do exist (gritstone), uncrushed rounded aggregates tend to exhibit a smoother surface. The presence of a smoother surface generally reduces the level of cohesion between the aggregate-cement interfaces and consequently affects the strength of the concrete. Moreover, a weakened interface suggests that the aggregates easily pull away from the concrete matrix as result of very little expansion from the ASR gel. Thus, the actual expansion recorded may not entirely be due to the reactive nature of certain aggregates but rather due to the presence of more cracks that could potentially lead to permeation of the silica and essentially increase the rate at which ASR gel spreads throughout the concrete matrix.

Mix design protocols in current standards for laboratory testing to evaluate aggregate reactivity recommend an approximate amount of 420 kg/m³ of cement in a standard concrete mix (Thomas et al. 2006). One important role of cement in concrete is to bind aggregates together. In reinforced concrete, it performs other roles such as transferring structural load to steel (or other) reinforcement (Callister Jr & Rethwisch 2012). A correct assumption can be drawn here, that by reducing the amount of cement used in concrete (lean mix), the amount of alkali introduced into the mix is also reduced. However, the implication of this would be insufficient bonding between the aggregates and reinforcement. Thus, should ASR expansion occur, the aggregates could easily be pulled away from each other resulting in the formation of larger cracks and the detachment of the concrete matrix.

An uncommon auxiliary factor that may not be accounted for but can significantly affect the mechanism of ASR is unexpected constituents found in the cement binder. Due to the different sources of raw materials used for the manufacture of cement, their mineralogical composition may vary resulting in surplus supply of ASR reactive components. In a study conducted by Shafaatian et al., Portland cement used was found to contain 19% SiO₂. When assessed alone, this cement showed the highest amount of SiO₂ in pore solution suggesting the silica was metastable and potentially reactive. Relatedly, this could account for severe distress due to ASR observed in the SEM/EDX analysis of the hardened concrete (Shafaatian et al. 2013).

1.4 Laboratory test methods and standards for evaluating alkali-silica reaction potential of aggregates.

A selected number of strategies and methods exist for identifying the reactivity potential of aggregates and aggregate-cement combinations to ASR. These can be categorized as:

- Petrographic examination
- Chemical tests
- Field performance
- Expansion tests

In many cases, petrographic examination of the aggregates is conducted prior to further aggregate testing. The information obtained from petrographic examination guides the selection of the tests required to specify the reactivity potential of the aggregates (Nixon & Sims 2016b). Petrographic examination conducted following Australian Standard AS 1141.65 requirements provide results that are considered to be reliable indicators of potentially deleterious ASR (Nixon & Sims 2016c; Standards Australia 2008). Aggregates composed of metastable and amorphous quartz such as chalcedony and microcrystalline quartz as well as strained quartz are known to exhibit ASR (Monnin et al. 2006). These minerals are identifiable and quantifiable via petrographic methods. Other characterization methods such as X-Ray Diffraction (XRD), X-Ray Florescence (XRF) and Energy Dispersive X-ray Spectroscopy (EDX) may also be used (Verstraete, Khouchaf & Tuilier 2004) to identify the mineralogical composition of aggregates.

ASTM C 298 incorporates a chemical test method to evaluate the reactivity potential of aggregates to ASR (Ferraris et al. 2009; Torii et al. 2003), where the reactivity of the aggregate is assessed on the basis of the amount of silica dissolved in sodium hydroxide solution. Although this test method has been recently withdrawn, owed to its inability to detect carbonate rock constituents, it is utilized as a supplementary test to petrographic examination. The amount of silica dissolved may aid to determine the reactivity potential of aggregates based on a predetermined scale that separates different categories of aggregate reactivity.

The evaluation of field performance is the most reliable approach for ASR assessment of aggregates (Thomas et al. 2006). This method allows for effective and preventive measures to be implemented for reactive aggregates by developing a reliable relationship between the behaviour of these aggregates under field conditions and the efficacy of the preventive measures applied to these aggregates in service (environmental conditions) over time. However, owing to the limited number of structures evaluated, insufficient databases available and the inconsistencies in records reported, this method is difficult to implement. Nonetheless, a successful example of the use of field performance for evaluating aggregate reactivity potential and the efficacy of SCM (fly ash) as a preventive measure for ASR is seen with the Lower Notch Dam (LND) in Canada (Thomas et al. 2006). The addition of fly ash within the range of 20-30% to the concrete containing both reactive coarse aggregate and high alkali cement resulted in the retardation of the onset of ASR for 30 years. The results obtained from the LND project have helped establish an approximate amount of 25% fly ash as an effective measure in mitigating the occurrence of ASR. The field performance of concrete structures consisting of similar reactive aggregates was instrumental in the design of ASR related test methods for Canadian standards that have also progressed and adopted into the current ASTM expansion test methods (Thomas et al. 2006).

The physical expansion test is the most widely used method for determining the reactivity of aggregates and aggregate combinations. This method accelerates the ASR reaction (or lack thereof) and provides results within a relatively short period of time. This is achievable through the oversupply of alkali to mortar or concrete by either immersion in highly alkaline solution or the integration of highly alkaline solution into the test specimen creating an ASR conducive environment for rapid reaction. Due to the aggressive nature of the reaction environment, the test methods are conservative and may produce false indication of aggregate reactivity behaviour (Thomas et al. 2006). As such, these test methods should be used primarily to identify non-reactive aggregates and confirm the reactivity potential of aggregates (Nixon & Sims 2016b). Nonetheless, aggregates that pass these severe test environment conditions (particularly AS 1141.60.2) are indeed acknowledged

to not cause ASR damage in concrete. Commonly used expansion test methods are the mortar bar method (ASTM C227), accelerated mortar bar method (AS 1141.60.1), concrete prism test (AS 1141.60.2) and the accelerated concrete prism test (AS 1141.60.2) conducted at 60°C (STandards Australia 2014c). A detailed description of these test methods, their procedures and interpretation of results obtained is readily available in literature concerning ASR (Fournier & Bérubé 2000; Nixon & Sims 2016b). Different countries and organisations may refer to these standards by specific names. However, only a slight variation in the test methods are noted. These changes exist to accommodate the difference in mineralogical compositions of aggregates and the alkali limitations across different countries. For all the expansion tests, an expansion index is given to classify the reactivity potential of aggregates as non-reactive, slowly reactive or very reactive (Fournier et al. 2004; Lindgård et al. 2012).

Another classification index reliant on the measurements of expansion is ASTM C1778-16. This test method categorises aggregate reactivity into four (4) classes based on the level of expansion recorded for the aggregates after a 14-day test period following the AS 1141.60.1: accelerated mortar bar test method. The expansion index on all these test methods vary. However, they are expected to give a corroborative classification on the reactivity of an aggregate and this is not always the case. Certain aggregates that are found to be reactive using one expansion method may be classified as innocuous by another expansion method. This could be attributed to the different conditions under which these aggregates are tested (Thomas et al. 2006) and may also relate to the limitations of the existing standardized test methods.

Other expansion test methods for evaluating aggregate susceptibility to ASR include the autoclave mortar bar test (Duchesne & Bérubé 1992) and the Chinese accelerated mortar bar test (Lu, Fournier & Grattan-Bellew 2004).

Part Two: Alkali Silica Reaction Mitigating Strategies

2.1 The role of supplementary cementitious materials (SCMs) in mitigating ASR

The role of SCMs in mitigating ASR is well documented (Thomas 2011). These materials partially replace the Portland cement and form part of the cement binder in the concrete. Adding the correct amount of SCMs is effective in hindering reactions leading to the formation of deleterious ASR gels. SCMs reduce the amount of alkalis (and pH) that are available in the pore solution by undergoing a pozzolanic reaction over time (Diamond 1989).

SCMs with high SiO₂ and Al₂O₃ contents have high efficacy to mitigate ASR (Chappex & Scrivener 2012; Scholz, Hübert & Hüniger 2016). When the alkalis in the binder (cement and SCMs) are released, they coexist as ions in the pore solution that are bound by hydration products or fused into the ASR gel (Lothenbach, Scrivener & Hooton 2011; Thomas 2011). At high pH, the alumina ions from the SCMs are released into the pore solution which react with silica to form aluminosilicate precipitates. Al³⁺ ions replace Si⁴⁺ ions in the tetrahedral network of the silica causing a charge imbalance which consumes alkali ions (Na⁺, K⁺) in solution to form the tetrahedral structure. Consequently, the alkalinity of the pore solution is also reduced. Hydration of cement provides portlandite (Ca(OH)₂) that partially dissolves to supply Ca²⁺ aiding in the precipitation of C-S-H and C-A-S-H gels (Hong & Glasser 2002). A homogeneous distribution of SCMs in the concrete matrix ensures a wide dispersal of the precipitated gels thus reducing the risk of deleterious expansion.

Although SCM efficacy in mitigating ASR is widely acknowledged (Esteves et al. 2012; Higgins et al. 2011; Kandasamy & Shehata 2014; Moser et al. 2010; Shafaatian et al. 2013), the use of SCMs may not be cost effective. Additionally, many countries either do not have viable sources of SCMs or do not permit the use of SCMs as part of the binder systems in mitigating ASR. Consequently, a need for developing strategies to mitigate ASR in the absence of SCMs is required. This has led to the influx of series of studies on mitigating strategies that do not require the use of SCMs. These mitigating strategies are cost effective and allow versatility in implementation based on the intended application of the concrete in service.

2.2 Alternative alkali-silica reaction mitigating strategies

2.2.1 Cement adjustment

The use of low alkali content cements in concrete can be considered as an ideal method in many cases in reducing the occurrence of ASR. Low alkali cement are those whose alkali content would typically fall below the fixed allowable alkali content limit of 0.6% (Na_2O_e) (Standards New Zealand 2009; Thomas et al. 2006). However, such low cement alkali contents can be difficult to achieve in practice due to the limited availability of natural resources containing low alkali contents. The current environmental requirements on cement manufacture as well as new methods used in clinker manufacturing have resulted in the volatilization and condensation of high amounts of alkalis in the kiln thus causing an increase in the alkali content of the cement produced.

Ordinary Portland cement contains several elements including aluminium (C3A, C4AF) that is typically unreactive to form C-A-S-H phases. However, the alumina-silicate formed in the pozzolanic reaction in the presence of reactive Al has been reported to retard the dissolution rate of silica through the adsorption and formation of a protective layer on silica surfaces (Bickmore et al. 2006; Sang et al. 1994). Owing to this, aluminium bearing substrates are currently being used to pre-treat reactive silica aggregates for concrete production (Brykov, Anisimova & Rozenkova 2014). Likewise, a recent study (unpublished thesis) has demonstrated that the use of aggregates with high aluminium contents could potentially reduce ASR. Consequently, an inference can be made that by adding interground reactive alumina such as gibbsite in Portland cement the cement itself could assume ASR mitigating properties.

2.2.2 Aggregate contribution

Aggregates form the major part of concrete. Consequently, it is important to consider the ways in which the chemical and physical properties of aggregates can be harnessed to reduce deleterious expansion due to ASR.

Aggregate particle size

Recent studies have focused on ways of reducing ASR occurrence by identifying and eliminating the most reactive aggregate particles through the evaluation of particle size distribution; also known as the pessimum size effect. The use of particle size distribution as an effective method in mitigating ASR has been reported in literature (Multon et al. 2010; Multon et al. 2008). However, there is some disagreement on the relative reactivity of particle size ranges (Multon et al. 2010). Smaller particles tend to have an increased surface area implying that a larger amount of metastable silica is available to react with OH^- ions and therefore ASR is amplified (Lindgård et al. 2012; Wigum 2012). Contrary to this, studies conducted by some researchers have shown a lower expansion rate prevails for smaller particle size (Multon et al. 2008; Poyet et al. 2007). Interestingly, in one further study (Lu, Fournier & Grattan-Bellew 2006), it was realised that neither the largest nor smallest particle size was reactive, rather, an intermediate range of particle sizes exhibited the highest potential for ASR. In a study conducted on opal aggregates, it was observed that larger aggregate particles exhibited slow and prolonged ASR expansion while small aggregate particles exhibited rapid and shortened ASR expansion (Diamond & Thaulow 1974). These results were obtained by using aggregates comprised of dissimilar mineralogical compositions. Additionally, the test methods and conditions utilised in these studies varied and are imprecise to conclude on a generalized particle size range that causes the most deleterious expansion. What can be established though is, the aggregate size that causes the most ASR damage is dependent on the type of reactive aggregate present and its inherent composition. Again, in natural sands, the reactive mineral responsible for ASR may be found in a specific particle size. This does not necessarily mean the particle size of aggregate in itself reduces ASR (Rajabipour et al. 2015)

In work conducted by Multon et al. on the effect of particle size and alkali content on ASR, various aggregate particle size fractions of a reactive siliceous aggregate were tested with non-reactive aggregate to determine the particle size effect on ASR expansion. At the end of 500-day

expansion monitoring, an exponential decrease in expansion was observed in mortar specimens containing aggregates of particle size range 160 to 315 μm , 80 to 160 μm and 0 to 80 μm . Aggregate fractions with particle size below 160 μm exhibited ASR expansion below 0.01%. The particle size range 80-0 μm showed the least expansion of -0.003% whereas the particle size range 630-1250 μm showed the most expansion. As the amount of 0-80 μm particles increased in the mortar specimens, the ASR expansion was observed to reduce significantly. This behaviour was consistent at both alkali content levels tested. The authors attributed this behaviour to the occurrence of a porous crowning effect and binder (cement) restraint. Generally, pores exist around aggregates in the concrete matrix to which ASR gel can flow and expand freely. These pores are smaller for smaller particle sizes than for larger particle sizes; thus, aggregates with larger particle sizes encourage a larger spread of ASR gel and expansion throughout the concrete matrix. Smaller particles are also easily restrained by the cement binder during the swelling of ASR and result in less expansion (Multon et al. 2010). In a different study (Multon et al. 2008), the alkali level of the mortar specimens were raised to (Na_2O_e) 6.2 kg/m^3 and 13.4 kg/m^3 by adding NaOH to the mix water in order to determine the combined effect of alkali content and particle size on ASR expansion. The expansion tests revealed similar observations. Of the different particle sizes investigated, the largest aggregate particle size showed the most expansion at either alkali levels.

Furthermore, standardized procedures for concrete mix design are often adopted by industry. Evaluation requires a specific size grading aimed at improving workability, strength and durability of the concrete. As such, very fine sized aggregate particles (considered deleterious) are generally discarded. Nonetheless, some studies have shown that the use of very fine siliceous reactive aggregate typically below 125 μm in particle size aids in the reduction of ASR by assuming a pozzolanic role (Ferraris & Ferraris 1995; Nixon & Sims 2016d). Thus, the reintroduction of fractions of very fine siliceous reactive aggregate into concrete that would otherwise be discarded during aggregate processing operations could potentially be used to mitigate ASR. This method can be applied to aggregates exhibiting pessimum and self-mitigating behaviour (Rajabipour et al. 2015). Although this method is capable of reducing ASR expansion, a limitation lies in the difficulty in incorporating these various particle sizes into concrete for monitoring expansion as current expansion test methods require a specific gradation for the screening of aggregates for ASR potential (Drimalas et al. 2012; Standards Australia 2014a, 2014b).

The pessimum effect on ASR expansion as a function of aggregate particle size and mortar specimen size has also been studied (Gao et al. 2013). It was observed that for larger sized specimens, no pessimum effect was exhibited for all aggregate sizes investigated. However, a distinct reduction in ASR expansion was noted when the 0 to 315 μm sized aggregate was used in mortars. This behaviour is most likely due to the formation of ASR gels around aggregate particles that adjoin to interconnecting pores that do not cause expansion (Multon et al. 2010). For the same amount of reactive silica content, more ASR gel can move into these non-expansive regions for smaller aggregate size than for larger aggregate size. This explains why smaller aggregate size shows less expansion.

Aggregate blending

Except for a few monomineralitic rocks such as igneous anorthosites, the majority of aggregates used in concretes contain a significant amount of silica usually in the form of quartz. However, not all forms of silica in aggregates are reactive towards ASR formation. The reactivity of silica is dependent on its state of disorder, crystallinity, undulatory angle, solubility in alkaline solution and performance in physical expansion tests (Buck 1983; Folliard et al. 2004; Fournier & Bérubé 2000). Generally, examples of reactive forms of silica include cherts, opal, volcanic glass, chalcedony and quartz that is typically microcrystalline, cryptocrystalline and strained (Castro & Wigum 2012), all of which can be identified through the petrographic examination of the aggregates.

The proportion of silica that can lead to the most damaging reaction will depend upon the reactivity of the silica. When a reactive aggregate is mixed with a non-reactive aggregate at different proportions, the amount of reactive aggregate (essentially reactive silica) at which the most damaging

reaction will take effect is referred to as the pessimum amount (Nixon & Sims 2016b). In the broad sense, the amount of reactive component needed for ASR reaction for most siliceous rocks could be as low as 2 % (Forster et al. 1998). ASR mitigation by aggregate blending involves combining highly reactive siliceous aggregates with non-reactive aggregates (determined through expansion tests) such that the pessimum amount is not reached. This method, when properly implemented, can result in the effective mitigation of ASR (Nixon & Sims 2016a). It is reported that the pessimum amount occurs when the ratio of reactive silica to alkali is typically 6 (Glasser & Kataoka 1981; Rajabipour et al. 2015). Thus, irrespective of the size of the aggregate particle, expansion will increase if the pessimum amount is met (Rajabipour et al. 2015). As the reactivity (expansion) of a known reactive aggregate is unpredictable when used in combination with other aggregates, it is important that tests are conducted on the aggregate combination as intended for use in the concrete.

2.2.3 Concrete mix design

Two critical factors to consider during mix design are those of the water-cement (w/c) ratio and cement-aggregate (c/a) ratio. The effect of w/c on ASR is inconsistent and rather relies on the age and properties of the aggregate used in the concrete (Ferraris & Ferraris 1995). At high w/c ratio, the concentration of the hydroxyl ions available in pore solution are reduced and dissolution of the silica is slow. Literature suggests that the porous nature of the aggregate is responsible for a decrease in ASR expansion as w/c increases (Mladenović et al. 2004). In this sense, a direct relationship can be established between the amount of water required in a concrete mix and the surface texture of the aggregate. Porous aggregates adsorb more water to retain a saturated surface dry condition during the pre-mixing and mixing of the concrete. This water, generally held in the pores of the aggregate, tends to dilute the alkaline ions in the pore solution and essentially reduces the alkalinity required for ASR gel formation. Subsequently, this slows down the reaction and leads to a decrease in expansion. In a separate study (Collins & Bareham 1987), it was found that replacing dense aggregates with porous aggregates resulted in a decrease in expansion from 7% to 3%. Although the authors of this study suggested the decrease was possibly due to differences in aggregate compositions they go on to explain that higher water contents needed for concretes incorporating porous aggregates decrease the concentration of alkali ions thus reducing their effect on silica dissolution. Petrographic examination of the concrete revealed lower levels of silicate gel and little evidence of pore filling. Porous aggregates can therefore be considered as a potential solution to reducing ASR. Conversely, an increase in pH of pore solution will result when the w/c ratio of concrete is low. This favours the dissolution of silica and thus increases the extent of ASR induced expansion (Lindgård et al. 2012).

The alkali content of concrete can be reduced by using a lower c/a ratio. However, a change in c/a ratio also requires a change in w/c ratio of the concrete. This approach has the potential to decrease the concrete strength and resistance against ASR induced expansion by reducing the binding capacity of the cement holding the aggregates together. A study conducted in Canada (MTQ 1997) revealed that reducing the cement content in concrete to 365 kg/m³ was effective in mitigating ASR induced expansion that would otherwise expand when the cement content was increased to 420 kg/m³ (Bérubé et al. 2000). Admittedly, research is still on-going in this area for finding appropriate c/a combinations that aid to reduce the availability of alkalis in concrete and also meet the desired strength and durability requirements of the concrete in service.

On a separate note, the alkali content at which an aggregate exhibits its highest expansion during AMBT and CPT tests may also vary when compared to its behaviour under field conditions. A report by Thomas et al. revealed that aggregates used in fieldwork showed symptoms of ASR at much lower alkali content when cement with lower alkali content was used in concrete (Thomas et al. 2006). This cause was attributed to the higher amount of alkali required to initiate expansion in test specimens rather than in real structures. Accordingly, this infers that the alkali content and its effect on ASR is dependent on more than one factor and reinforces the importance of aggregate reactivity evaluation by field performance while presenting queries on the applicability of standard test methods available and commonly used to evaluate aggregate potential for ASR expansion (Thomas et al. 2006).

2.2.4 Concrete matrix properties

The mix design process methods and practices leading to the transportation, handling, placement, consolidation and finishing of fresh concrete have a tremendous effect on the resistance of hardened concrete to ASR induced expansion. Construction practices that result in the formation of air voids in concrete may lead to higher ASR expansion. The presence of voids (particularly inter-connected voids) in concrete encourages the flow of pore solution throughout the matrix providing a conduit for rapid attack of the metastable silica present in aggregates. Nevertheless, when voids are present, the ASR gel is able to move easily into these vacant spaces and cause less expansion (Hobbs, Bensted & Barnes 2002). This typically relieves the stress build-up that leads to cracking of the concrete. Visual imaging applied to identifying the presence of ASR gels in such concretes is difficult as the gel could eventually harden within the pores (Mladenovič et al. 2004). It is therefore critical that the lack of image identification of ASR reaction products is not misunderstood as the absence of the ASR reaction from the concrete. Gel migration could however be unpredictable and occur rapidly in voids. Thus, it is important to practice proper consolidation practices and minimize voids in concrete as an effective means of reducing the potential to ASR expansion.

II Conclusions

This study was carried out to provide further understanding into the various mechanisms involved in ASR induced expansion in the quest to obtain effective mitigating strategies. There are published studies available that discuss the influence of aggregate properties on the outcome of ASR. Although extensive research is available on mitigation strategies for ASR, a large number of questions still remain unanswered. In the end, a proven possibility exists for the mitigation of ASR without the addition of SCMs. It is thus concluded that:

- Studies into the use of reactive alumina such as gibbsite addition in cements is important and recommended as an alternative to the addition of SCMs which may not be readily available worldwide. Aluminium reacts with silica to form non-expansive C-A-S-H phases in concretes thereby inhibiting ASR.
- The effects of a reactive aggregate on the rate of ASR induced expansion is not only dependent on the mineralogical composition but also dependent on the physical properties of the aggregate such as particle size, particle shape and surface texture.
 - The use of angular shaped aggregates in concrete can potentially increase the extent of ASR expansion and using porous textured aggregates can potentially cause a reduction in the extent of expansion due to ASR.
 - Aggregate blending and particle size variation are effective methods for ASR mitigation. Although, the most reactive particle size and the pessimum amount of reactive silica is dependent on the mineralogical composition of the aggregate.
 - Very fine micron sized reactive aggregates ($< 75 \mu\text{m}$) that exhibit pessimum behaviour have the potential to initiate a self-mitigating process by assuming a pozzolanic reaction when they are introduced into concrete.
- A higher w/c ratio could potentially decrease alkalinity of the concrete pore solution thereby reducing the extent of silica dissolution and expansive ASR gel formed.
- A lower c/a ratio may potentially allow an increase in allowable alkali limits in concretes (and cements) and the use of aggregates that otherwise would be considered deleterious.
- Conforming to proper concrete handling, placement and finishing practices play a key role in aiding the extent of ASR. Well consolidated concretes have minimum voids that can limit the permeation of ASR gel and expansion in the concrete.
- It is important to assess the viability and validity of using alternative mitigating strategies on a wider range of aggregates globally in order to establish an accurate portfolio for the behaviour of the various classes of aggregates. A more consistent outcome encouraging the use of these mitigation strategies could provide a framework for the endorsement of future

codes of practices for alternative ASR mitigation strategies to be employed in regular practice.

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References

- Association, C.E., Pigeon, M., Inc, T. & Stoian, A. 1992, Expansion Test Methods for Mass Concrete Exposed to Alkali Aggregate Reaction, Canadian Electrical Association.
- Bažant, Z.P. & Steffens, A. 2000, 'Mathematical model for kinetics of alkali-silica reaction in concrete', *Cement and Concrete Research*, vol. 30, no. 3, pp. 419-28.
- Berra, M., Mangialardi, T. & Paolini, A. 2005, 'Alkali-silica reactivity criteria for concrete aggregates', *Materials and structures*, vol. 38, no. 3, pp. 373-80.
- Bérubé, M.-A., Duchesne, J., Dorion, J. & Rivest, M. 2002, 'Laboratory assessment of alkali contribution by aggregates to concrete and application to concrete structures affected by alkali-silica reactivity', *Cement and Concrete Research*, vol. 32, no. 8, pp. 1215-27.
- Bérubé, M.-A., Durand, B., Vézina, D. & Fournier, B. 2000, 'Alkali-aggregate reactivity in Quebec (Canada)', *Canadian Journal of Civil Engineering*, vol. 27, no. 2, pp. 226-45.
- Bérubé, M.-A. & Fournier, B. 2004, 'Alkalis releasable by aggregates in concrete: significance and test methods', *Proceedings of the 12th International Conference on Alkali-Aggregate Reaction in Concrete*, vol. 1, Beijing, China, pp. 130-1.
- Bickmore, B.R., Nagy, K.L., Gray, A.K. & Brinkerhoff, A.R. 2006, 'The effect of Al (OH) 4⁻ on the dissolution rate of quartz', *Geochimica et Cosmochimica Acta*, vol. 70, no. 2, pp. 290-305.
- Bleszynski, R.F. & Thomas, M.D. 1998, 'Microstructural studies of alkali-silica reaction in fly ash concrete immersed in alkaline solutions', *Advanced Cement Based Materials*, vol. 7, no. 2, pp. 66-78.
- Blight, G., McIver, J., Schutte, W. & Rimmer, R. 1981, 'The effects of alkali-aggregate reaction on reinforced concrete structures made with witwatersrand quartzite aggregate', *Proc. 5th Int. Conf. on AAR in concrete*, Cape Town (South Africa).
- Boddy, A., Hooton, R. & Thomas, M. 2000, 'The effect of product form of silica fume on its ability to control alkali-silica reaction', *Cement and concrete research*, vol. 30, no. 7, pp. 1139-50.
- Broekmans, M.A. 2004, 'Structural properties of quartz and their potential role for ASR', *Materials Characterization*, vol. 53, no. 2-4, pp. 129-40.
- Brykov, A., Anisimova, A. & Rozenkova, N. 2014, 'The Mitigation of Alkali-Silica Reactions by Aluminum-Bearing Substances', *Materials Sciences and Applications*, vol. 5, no. 06, p. 363.
- Buck, A.D. 1983, 'Alkali reactivity of strained quartz as a constituent of concrete aggregate', *Cement, concrete and aggregates*, vol. 5, no. 2, pp. 131-3.
- Callister Jr, W.D. & Rethwisch, D.G. 2012, *Fundamentals of materials science and engineering: an integrated approach*, John Wiley & Sons.
- Castro, N. & Wigum, B.J. 2012, 'Assessment of the potential alkali-reactivity of aggregates for concrete by image analysis petrography', *Cement and Concrete Research*, vol. 42, no. 12, pp. 1635-44.
- Chappex, T. & Scrivener, K.L. 2012, 'The influence of aluminium on the dissolution of amorphous silica and its relation to alkali silica reaction', *Cement and Concrete Research*, vol. 42, no. 12, pp. 1645-9.

- Chen, H., Soles, J. & Malhotra, V. 1993, 'Investigations of supplementary cementing materials for reducing alkali-aggregate reactions', *Cement and Concrete Composites*, vol. 15, no. 1-2, pp. 75-84.
- Civil Engineering, Limiting the alkali content of the concrete, viewed 25 March 2018, <<http://www.civilengineeringx.com/dccc/limiting-the-alkali-content-of-the-concrete/>>.
- Collins, R. & Bareham, P. 1987, 'Alkali-silica reaction: suppression of expansion using porous aggregate', *Cement and Concrete Research*, vol. 17, no. 1, pp. 89-96.
- Diamond, S. 1975, 'A review of alkali-silica reaction and expansion mechanisms 1. Alkalies in cements and in concrete pore solutions', *Cement and Concrete research*, vol. 5, no. 4, pp. 329-45.
- Diamond, S. 1989, 'ASR-another look at mechanisms', *Proceedings of the 8th International Conference on Alkali-Aggregate Reaction*, Kyoto, Japan, pp. 83-94.
- Diamond, S. & Thaulow, N. 1974, 'A study of expansion due to alkali—silica reaction as conditioned by the grain size of the reactive aggregate', *Cement and Concrete Research*, vol. 4, no. 4, pp. 591-607.
- Drimalas, T., Ideker, J., Arrieta, G., Folliard, K., Fournier, B. & Thomas, M. 2012, 'Evaluating combination of aggregates in the accelerated mortar bar test', *Proceedings, 14th International Conference on Alkali-Aggregate Reactivity in Concrete*.
- Duchesne, J. & Bérubé, M. 1992, 'An autoclave mortar bar test for assessing the effectiveness of mineral admixtures in suppressing expansion due to AAR', *Proc. 9 th Int. Conf. on Alkali-Aggregate Reaction in Concrete*, vol. 1, pp. 279-86.
- Esteves, T., Rajamma, R., Soares, D., Silva, A., Ferreira, V. & Labrincha, J. 2012, 'Use of biomass fly ash for mitigation of alkali-silica reaction of cement mortars', *Construction and Building Materials*, vol. 26, no. 1, pp. 687-93.
- Fernández-Jiménez, A. & Puertas, F. 2002, 'The alkali—silica reaction in alkali-activated granulated slag mortars with reactive aggregate', *Cement and concrete research*, vol. 32, no. 7, pp. 1019-24.
- Ferraris, C.F. & Ferraris, C.F. 1995, 'Alkali-silica reaction and high performance concrete'.
- Ferraris, M., Salvo, M., Ventrella, A., Buzzi, L. & Veglia, M. 2009, 'Use of vitrified MSWI bottom ashes for concrete production', *Waste management*, vol. 29, no. 3, pp. 1041-7.
- Folliard, K.J., Ideker, J., Thomas, M.D. & Fournier, B. 2004, 'ASSESSING AGGREGATE REACTIVITY USING THE ACCELERATED CONCRETE PRISM TESTS', *Aggregates: Asphalt Concrete, Portland Cement Concrete, Bases, and Fines. Twelfth Annual Symposium International Center for Aggregates Research (ICAR); University of Texas at Austin; Texas A&M University System; Aggregates Foundation for Technology, Research & Education (AFTRE); National Stone, Sand & Gravel Association (NSSGA); Florida Rock Industries*.
- Forster, S.W., Akers, D.J., Lee, M.K., Pergalsky, A., Arrand, C.D., Lewis, D.W., Pierce, J.S., Barger, G.S., MacDonald, D.R. & Pisaneschi, R.R. 1998, 'State-of-the-art report on alkali—aggregate reactivity', *Am. Concr. Inst. ACI*, vol. 221, pp. 1-23.
- Fournier, B. & Bérubé, M.-A. 2000, 'Alkali-aggregate reaction in concrete: a review of basic concepts and engineering implications', *Canadian Journal of Civil Engineering*, vol. 27, no. 2, pp. 167-91.
- Fournier, B., Chevrier, R., de Grosbois, M., Lisella, R., Folliard, K., Ideker, J., Shehata, M., Thomas, M. & Baxter, S. 2004, 'The accelerated concrete prism test (60 C): variability of the test method and proposed expansion limits', *Proc. of the 12th Int. Conf. on AAR in Concrete, Beijing (China)*, pp. 314-23.
- Freitag, S.A.G., R; Milestone, N.B 2012, 'Alkali Silica Reaction, Minimising the Risk of Damage to Concrete Guidance Notes and Reccomended Practise, Second Edition', *Cement and Concrete Association of New Zealand*, no. Technical Report 3.
- Gao, X.X., Multon, S., Cyr, M. & Sellier, A. 2013, 'Alkali—silica reaction (ASR) expansion: pessimum effect versus scale effect', *Cement and Concrete Research*, vol. 44, pp. 25-33.

- Ghanem, H., Zollinger, D. & Lytton, R. 2010, 'Predicting ASR aggregate reactivity in terms of its activation energy', *Construction and Building Materials*, vol. 24, no. 7, pp. 1101-8.
- Gifford, P. & Gillott, J. 1996, 'Alkali-silica reaction (ASR) and alkali-carbonate reaction (ACR) in activated blast furnace slag cement (ABFSC) concrete', *Cement and concrete research*, vol. 26, no. 1, pp. 21-6.
- Glasser, L.D. & Kataoka, N. 1981, 'The chemistry of 'alkali-aggregate' reaction', *Cement and Concrete Research*, vol. 11, no. 1, pp. 1-9.
- Grattan-Bellew, P. 1995, 'Laboratory evaluation of alkali-silica reaction in concrete from Saunders Generating Station', *Materials Journal*, vol. 92, no. 2, pp. 126-34.
- Hasparyk, N.P., Monteiro, P.J. & Carasek, H. 2000, 'Effect of silica fume and rice husk ash on alkali-silica reaction', *ACI Materials Journal*, vol. 97, no. 4, pp. 486-92.
- Helmuth, R., Stark, D., Diamond, S. & Moranville-Regourd, M. 1993, 'Alkali-silica reactivity: an overview of research', *Contract*, vol. 100, p. 202.
- Higgins, D., Sear, L., King, D., Price, B., Barnes, R. & Clear, C. 2011, 'Cementitious Materials: The Effect of GGBS, Fly Ash, Silica Fume and Limestone Fines on the Properties of Concrete', Surrey.
- Hobbs, D., Bensted, J. & Barnes, P. 2002, 'Alkali-silica reaction in concrete', *Structure and Performance of Cements*. Bensted J, Barnes P (eds) Spon Press, London, pp. 265-81.
- Hobbs, D.W. 1988, *Alkali-silica reaction in concrete*, Thomas Telford Publishing.
- Hong, S.-Y. & Glasser, F.P. 2002, 'Alkali sorption by CSH and CASH gels: Part II. Role of alumina', *Cement and Concrete Research*, vol. 32, no. 7, pp. 1101-11.
- Hussain, S.E. 1991, 'Effect of microsilica and blast furnace slag on pore solution composition and alkali-silica reaction', *Cement and Concrete Composites*, vol. 13, no. 3, pp. 219-25.
- Islam, M.S. 2010, *Performance of Nevada's aggregates in alkali-aggregate reactivity of Portland cement concrete*, University of Nevada, Las Vegas.
- Kandasamy, S. & Shehata, M.H. 2014, 'The capacity of ternary blends containing slag and high-calcium fly ash to mitigate alkali silica reaction', *Cement and Concrete Composites*, vol. 49, pp. 92-9.
- Lane, D.S. 1994, *Alkali-silica reactivity in Virginia*, Virginia Transportation Research Council.
- Leming, M.L. & Nguyen, B.Q. 2000, 'Limits on alkali content in cement—results from a field study', *Cement, Concrete and Aggregates*, vol. 22, no. 1, pp. 41-7.
- Lindgård, J., Andiç-Çakır, Ö., Fernandes, I., Rønning, T.F. & Thomas, M.D. 2012, 'Alkali-silica reactions (ASR): literature review on parameters influencing laboratory performance testing', *Cement and Concrete Research*, vol. 42, no. 2, pp. 223-43.
- Lothenbach, B., Scrivener, K. & Hooton, R. 2011, 'Supplementary cementitious materials', *Cement and Concrete Research*, vol. 41, no. 12, pp. 1244-56.
- Lu, D.-Y., Fournier, B. & Grattan-Bellew, P. 2004, 'A comparative study on accelerated test methods for determining alkali-silica reactivity of concrete aggregates', *Proc. 12th Int. Conf. Alkali-Aggregate Reaction in Concrete*, International Academic Publishers/World Publishing Corporation, Beijing, vol. 1, pp. 377-85.
- Lu, D., Fournier, B. & Grattan-Bellew, P. 2006, 'Evaluation of accelerated test methods for determining alkali-silica reactivity of concrete aggregates', *Cement and Concrete Composites*, vol. 28, no. 6, pp. 546-54.
- Malvar, L.J., Cline, G., Burke, D., Rollings, R., Sherman, T. & Greene, J. 2002, 'Alkali-silica reaction mitigation: state of the art and recommendations', *Materials Journal*, vol. 99, no. 5, pp. 480-9.
- Mladenović, A., Šuput, J., Ducman, V. & Škapin, A.S. 2004, 'Alkali-silica reactivity of some frequently used lightweight aggregates', *Cement and Concrete Research*, vol. 34, no. 10, pp. 1809-16.
- Monnin, Y., Dégrugilliers, P., Bulteel, D. & Garcia-Diaz, E. 2006, 'Petrography study of two siliceous limestones submitted to alkali-silica reaction', *Cement and concrete research*, vol. 36, no. 8, pp. 1460-6.

- Moser, R.D., Jayapalan, A.R., Garas, V.Y. & Kurtis, K.E. 2010, 'Assessment of binary and ternary blends of metakaolin and Class C fly ash for alkali-silica reaction mitigation in concrete', *Cement and Concrete Research*, vol. 40, no. 12, pp. 1664-72.
- Multon, S., Cyr, M., Sellier, A., Diederich, P. & Petit, L. 2010, 'Effects of aggregate size and alkali content on ASR expansion', *Cement and Concrete Research*, vol. 40, no. 4, pp. 508-16.
- Multon, S., Cyr, M., Sellier, A., Leklou, N. & Petit, L. 2008, 'Coupled effects of aggregate size and alkali content on ASR expansion', *Cement and Concrete Research*, vol. 38, no. 3, pp. 350-9.
- Multon, S., Sellier, A. & Cyr, M. 2009, 'Chemo-mechanical modeling for prediction of alkali silica reaction (ASR) expansion', *Cement and Concrete Research*, vol. 39, no. 6, pp. 490-500.
- Nixon, P.J. & Sims, I. 2016a, 'RILEM Recommended Specification: AAR-7.1—International Specification to Minimise Damage from Alkali Reactions in Concrete—Part 1: Alkali-Silica Reaction', *RILEM Recommendations for the Prevention of Damage by Alkali-Aggregate Reactions in New Concrete Structures*, Springer, pp. 131-45.
- Nixon, P.J. & Sims, I. 2016b, 'RILEM Recommended Test Method: AAR-0—Outline Guide to the Use of RILEM Methods in the Assessment of the Alkali-Reactivity Potential of Aggregates', *RILEM Recommendations for the Prevention of Damage by Alkali-Aggregate Reactions in New Concrete Structures*, Springer, pp. 5-34.
- Nixon, P.J. & Sims, I. 2016c, 'RILEM Recommended Test Method: AAR-1.1—Detection of Potential Alkali-Reactivity—Part 1: Petrographic Examination Method', *RILEM Recommendations for the Prevention of Damage by Alkali-Aggregate Reactions in New Concrete Structures*, Springer, pp. 35-60.
- Nixon, P.J. & Sims, I. 2016d, 'RILEM Recommended Test Method: AAR-2—Detection of Potential Alkali-Reactivity—Accelerated Mortar-Bar Test Method for Aggregates', *RILEM Recommendations for the Prevention of Damage by Alkali-Aggregate Reactions in New Concrete Structures*, Springer, pp. 61-77.
- Olague, C., Wenglas, G. & Castro, P. 2003, 'Influence of alkalis from different sources than cement in the evolution of alkali-silica reaction', *Materiales de Construcción*, vol. 53, no. 271-272, pp. 189-98.
- Ponce, J. & Batic, O.R. 2006, 'Different manifestations of the alkali-silica reaction in concrete according to the reaction kinetics of the reactive aggregate', *Cement and Concrete Research*, vol. 36, no. 6, pp. 1148-56.
- Poole, A.B. 1992, 'Introduction to alkali-aggregate reaction in concrete', Van Nostrand-Reinhold, New York, pp. 8-75.
- Poyet, S., Sellier, A., Capra, B., Foray, G., Torrenti, J.-M., Cognon, H. & Bourdarot, E. 2007, 'Chemical modelling of alkali silica reaction: influence of the reactive aggregate size distribution', *Materials and Structures*, vol. 40, no. 2, p. 229.
- Rajabipour, F., Giannini, E., Dunant, C., Ideker, J.H. & Thomas, M.D. 2015, 'Alkali-silica reaction: current understanding of the reaction mechanisms and the knowledge gaps', *Cement and Concrete Research*, vol. 76, pp. 130-46.
- Ramlochan, T., Thomas, M. & Gruber, K.A. 2000, 'The effect of metakaolin on alkali-silica reaction in concrete', *Cement and concrete research*, vol. 30, no. 3, pp. 339-44.
- Ramyar, K., Topal, A. & Andıç, Ö. 2005, 'Effects of aggregate size and angularity on alkali-silica reaction', *Cement and concrete research*, vol. 35, no. 11, pp. 2165-9.
- RILEM, T. 2008, '219-ACS 'Alkali-silica reactions in concrete structures': recommended specification: AAR-7.1 International Specification to minimise damage from alkali reactions in concrete Part 1', *Alkali-silica reaction*, (unpublished draft).
- Sang, J.C., Jakubik, R.F., Barkatt, A. & Saad, E.E. 1994, 'The interaction of solutes with silicate glass and its effect on dissolution rates', *Journal of non-crystalline solids*, vol. 167, no. 1-2, pp. 158-71.
- Saouma, V. & Perotti, L. 2006, 'Constitutive model for alkali-aggregate reactions', *Materials Journal*, vol. 103, no. 3, pp. 194-202.
- Scholz, Y., Hübert, C. & Hünger, K.-J. 2016, 'The influence of supplementary cementing materials on the dissolution of aggregates in alkaline solutions'.

- Shafaatian, S.M., Akhavan, A., Maraghechi, H. & Rajabipour, F. 2013, 'How does fly ash mitigate alkali-silica reaction (ASR) in accelerated mortar bar test (ASTM C1567)?', *Cement and Concrete Composites*, vol. 37, pp. 143-53.
- Shao, Y., Lefort, T., Moras, S. & Rodriguez, D. 2000, 'Studies on concrete containing ground waste glass', *Cement and Concrete Research*, vol. 30, no. 1, pp. 91-100.
- Shon, C.-S., Mukhopadhyay, A.K. & Zollinger, D.G. 2006, 'Evaluation of Alkali-Silica Reaction Potential of Aggregate Using Dilatometer Method', *Airfield and Highway Pavement: Meeting Today's Challenges with Emerging Technologies*, pp. 646-58.
- Standards Australia 2008, AS 1141.65- Methods for sampling and testing aggregates-Alkali-aggregate reactivity, SAI Global, Sydney, Australia.
- Standards Australia 2014a, AS1141.60.1 Methods for sampling and testing aggregates- Potential alkali-silica reactivity, SAI Global, Sydney, Australia.
- Standards Australia 2014b, AS 1141.60.2- Methods for sampling and testing aggregates-Potential alkali-silica reactivity, SAI Global Limited, Sydney, Australia.
- Standards Australia 2014c, Methods for sampling and testing aggregates- Potential alkali-silica reactivity, SAI Global, Sydney, Australia.
- Standards New Zealand 2009, NZS 3122, New Zealand.
- Stanton, T. 1950, 'Studies of use of pozzolans for counteracting excessive concrete expansion resulting from reaction between aggregates and the alkalis in cement', *Symposium on Use of Pozzolanic Materials in Mortars and Concretes*, ASTM International.
- Stanton, T.E. 1940, 'Influence of cement and aggregate on concrete expansion', *Engineering News-Record*.
- Stanton, T.E. 2008, *Expansion of concrete through reaction between cement and aggregate*.
- Stark, D. & Bhatti, M.S. 1986, 'Alkali-silica reactivity: effect of alkali in aggregate on expansion', *Alkalies in concrete*, ASTM International.
- Teychenné, D.C., Franklin, R.E., Erntrøy, H.C. & Marsh, B. 1975, *Design of normal concrete mixes*, HM Stationery Office.
- Thomas, M. 2011, 'The effect of supplementary cementing materials on alkali-silica reaction: A review', *Cement and Concrete Research*, vol. 41, no. 12, pp. 1224-31.
- Thomas, M., Fournier, B., Folliard, K., Ideker, J. & Shehata, M. 2006, 'Test methods for evaluating preventive measures for controlling expansion due to alkali-silica reaction in concrete', *Cement and Concrete Research*, vol. 36, no. 10, pp. 1842-56.
- Torii, K., Tomotake, H., Osafo, A.K. & Echigo, T. 2003, 'Compatibility between ecocement produced from incinerator ash and reactive aggregates in ASR expansion of mortars', *Cement and concrete research*, vol. 33, no. 4, pp. 571-7.
- Understanding Cement, Alkali-silica reaction in concrete, United Kingdom, viewed 21 March 2018, <<https://www.understanding-cement.com/alkali-silica.html>>.
- Verstraete, J., Khouchaf, L. & Tuilier, M. 2004, 'Contributions of the environmental scanning electron microscope and X-ray diffraction in investigating the structural evolution of a SiO₂ aggregate attacked by alkali-silica reaction', *Journal of materials science*, vol. 39, no. 20, pp. 6221-6.
- Walther, J.V. & Helgeson, H.C. 1977, 'Calculation of the thermodynamic properties of aqueous silica and the solubility of quartz and its polymorphs at high pressures and temperatures', *Am. J. Sci.*, vol. 277, no. 10, pp. 1315-51.
- Wang, H. & Gillott, J. 1991, 'Mechanism of alkali-silica reaction and the significance of calcium hydroxide', *Cement and Concrete Research*, vol. 21, no. 4, pp. 647-54.
- White Paper, Flatline Alkali-Silica Reaction with Pumice-Blended Cement for Pennies a Yard, viewed 19 December 2017, <www.hesspumice.com/pumice-pages/PDFs/Whitepaper-PumiceStompsASR.pdf>.
- Wigum, B.J. 2012, 'Assessment and development of performance tests for Alkali Aggregate Reaction in Iceland', *Proceedings of the 14th International Conference on Alkali-Aggregate Reactions in Concrete*.