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The effect of supplementary cementing materials on alkali-silica reaction: A review

Michael Thomas

Department of Civil Engineering, University of New Brunswick, Fredericton, New Brunswick, Canada

A R T I C L E I N F O

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A B S T R A C T

This paper reviews studies on the effect of supplementary cementing materials (SCM) on alkali-silica reaction (ASR). SCMs control expansion due to ASR by binding alkalis and limiting their availability for reaction with alkali-silica reactive aggregate. The efficacy of the SCM is dependent on the composition of the SCM. Increased amounts of SCM are required to control ASR as its calcium and alkali content increase, as its silica content decreases, as the alkali contributed by the Portland cement increases and as the reactivity of the aggregate increases. There is evidence that the alumina content of the SCM also affects its alkali-binding capacity, however, the precise role and contribution of the alumina is not clear.

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1. Introduction

The first published report on the phenomenon that later became known as alkali-silica reaction (ASR) appeared in the Engineering News Record in February 1940 [49]. In December of the same year the American Society of Civil Engineers (ASCE) published a second paper by Stanton [50] that most would consider to be the first definitive work on ASR. In this paper he not only demonstrated that damaging reaction would only occur if there was a sufficient quantity of alkalis in the Portland cement and reactive silica in the aggregate, but also that expansion was reduced when a pozzolanic cement was used. Ten years later, Stanton [51] further demonstrated that partially replacing Portland cement with a sufficient quantity of pozzolan (pumicite or calcined shale) eliminated deleterious expansion whereas replacement with similar quantities of ground quartz (Ottawa) sand did not, indicating that the beneficial action of the pozzolan extended beyond merely diluting the cement alkalis. In the early 1950s, various studies [2,7,12] showed that other supplementary cementing materials (SCM), namely fly ash and slag were also effective in reducing expansion.

Since these early studies there have been literally hundreds of studies and technical papers dealing with the effects of SCM on ASR and it is now generally recognized that the use of a sufficient quantity of a suitable SCM is one of the more efficient preventive measures for controlling expansion when a deleteriously reactive aggregate is used in concrete [60]. This paper reviews selected published works dealing with (i) the mechanisms by which SCM controls ASR, (ii) the effect of SCM composition on its efficacy in this role and (iii) test methods for determining the amount of SCM required to minimize the risk of damaging expansion to an acceptable level.

2. ASR mechanism and role of alkalis

The first stage of the alkali-silica reaction is the reaction between the hydroxyl ions (OH^-) in the pore solution and reactive silica in the aggregate; the silica is not directly attacked by the alkali metal cations (Na^+ and K^+). The alkalis contribute initially to the high

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E-mail address: mdat@unb.ca.

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concentration of hydroxyl ions in solution and later to the formation of an expansive alkali-silica gel. When poorly-crystalline hydrous silica is exposed to a strong alkaline solution, there is an acid-base reaction between the hydroxyl ions in solution and the acidic silanol (Si–OH) groups [13] as follows:

$$\equiv\text{Si–OH} + \text{OH}^- \rightarrow \equiv\text{Si–O}^- + \text{H}_2\text{O} \tag{1}$$

As further hydroxyl ions penetrate the structure, some of the siloxane linkages (Si–O–Si) are also attacked as follows [13]:

$$\equiv\text{Si–O–Si}\equiv + \text{OH}^- \rightarrow 2\equiv\text{Si–O}^- + \text{H}_2\text{O} \tag{2}$$

The negative charges on the terminal oxygen atoms are balanced by alkali cations (Na^+ and K^+) that simultaneously diffuse into the structure. The disruption of siloxane bridges weakens the structure and, provided sufficient reserves of alkali hydroxide are available, the process continues to produce an alkaline silicate solution.

The extent or rate of dissolution is controlled by the alkalinity of the solution and the structure of the silica. The solubility of poorly-crystalline or amorphous silica increases with pH; however, there have been few studies to determine the minimum hydroxide concentration of the pore solution required to initiate and sustain ASR in concrete. Diamond [16] reports that the threshold concentration is unlikely to be less than 0.25 M and Kollek et al. [33] suggest a threshold of 0.20 M.

The main source of alkalis in concrete is Portland cement; although other constituents (e.g., supplementary cementing materials, aggregates, and admixtures) may also contribute alkalis. External sources of alkalis, such as constituents of anti-icing and deicing chemical, may also be present in certain exposure conditions. Although the alkalis represent a small component of Portland cement (typical cement alkali levels in North America range from 0.20 to 1.30% Na_2Oe), they dominate the pore solution and after the first day of hydration at normal temperatures, the pore solution has become essentially a mixed solution of NaOH and KOH with low levels of other dissolved ionic species. The concentration of alkali metal hydroxides in solution depends on a number of factors, particularly the alkali content of the cement, the water/cement ratio (w/c) and the degree of hydration, and typically ranges from about 0.15 to 0.85 mol/l, corresponding to pH values ranging from approximately 13.2 to 13.9 [56].

Helmuth et al. [27] developed an empirical equation for predicting the hydroxyl ion concentration of the pore solution of mature Portland cement pastes as follows:

$$[\text{OH}^-] = 0.339(\text{PC}_{\text{alk}})/(\text{w/c}) + 0.022 \pm 0.06\text{mol/l} \tag{3}$$

where $[OH^-]$ is the molar concentration of hydroxyl ions in the pore solution, PC_{alk} is the alkali content of the cement (%Na_2Oe) and w/c is the water-to-cement ratio.

In the absence of calcium the alkali and silica would remain in solution [17]; however, abundant calcium is available as $Ca(OH)_2$ in Portland cement concrete, and an alkali-silica gel containing minor amounts of CaO forms as the initial reaction product. The gel that forms is hygroscopic and, as it imbibes water from the surrounding pore solution, it swells causing volumetric expansion of the concrete which may ultimately lead to cracking. With time, the calcium content of the gel increases and a portion of the alkalis are released back in to the pore solution [26,54].

The amount of expansion and resulting damage that occurs in concrete affected by alkali-silica reaction depends on a number of parameters including the availability of alkalis in the system, the nature and amount of reactive silica in the aggregate, exposure conditions (temperature and moisture availability) and the degree of internal and external restraint to movement (e.g. amount and distribution of reinforcing steel). The only one of these parameters that is affected by the incorporation of supplementary cementing materials in the concrete is the availability of alkalis.

2.1. Effect of SCM on the availability of alkalis

Although all SCMs contain some level of alkali and some may contain significantly more alkali than the Portland cement that they partially replace, the main mechanism by which SCMs reduce expansion due to ASR is by reducing the alkalis that are available to the concrete pore solution. Once the alkalis in the binder phase (Portland cement + SCM) of concrete are "released" by hydration they may be present in one of three ways: dissolved within the pore solution, bound by the hydration products or incorporated in alkali-silica gel. In the absence of reactive aggregate, alkalis will not be consumed by ASR and the partition of the alkalis between the pore solution and the hydrates is largely a function of the composition of the binder.

Numerous workers have shown that SCMs have a significant impact on the concentration of alkalis in the pore solution [1,5,6,9,10,14,15,16,18,34,19,20,22,25,30,31,33,36,39–41,43,44,46,62,63]). Studies on the effect of fly ash and slag on the pore solution of pastes have been reviewed by Thomas [52] and studies involving silica fume have been reviewed by Thomas and Bleszynski [55]. These studies show that the incorporation of most SCMs leads to a reduction in the concentration of alkali-hydroxides in the pore solution of pastes, mortar and concretes, the amount of reduction increasing with higher SCM replacement levels. Fig. 1 shows the evolution of the hydroxyl ion concentration of the pore solution extracted from sealed paste samples with w/cm = 0.50 and Fig. 2 shows the OH^- concentration at 2 years as a function of the level of SCM [5,40,44,46]. Silica fume is the most efficacious SCM in this role, at least initially, followed by metakaolin, low-calcium fly ash and slag. High-calcium or high-alkali fly ashes are less effective and have to be used at relatively high levels of replacement to produce a significant reduction in the pore solution alkalinity. It is interesting to note that in the case of the paste with 10% silica fume the OH^- concentration drops rapidly over the first 28 days but then starts to increase slowly with time beyond 3 months; similar behavior was observed in pastes containing 5% silica fume [46]. This behavior is not observed for pastes containing any of the other SCMs. As shown in Fig. 1, the long-term increase in the OH^- concentration seems to be prevented in pastes containing 5% silica fume by the addition of either slag (25%) or fly ash (15%). It is conjectured that the presence of alumina in the SCM possibly contributes in some way to prevent the long-term release of alkalis back in to the pore solution. Hong and Glasser [29] showed that introducing alumina into C–S–H, to form C–A–S–H, markedly increases its alkali-binding capacity and they suggest that this partially explains the beneficial effects of aluminous SCM with regards to reducing pore solution alkalinity and the potential for ASR.

Fig. 3 shows an empirical relationship between the OH^- concentration of the pore solution extracted from 2-year-old sealed pastes with w/cm = 0.50 [56,58] and a "chemical index" derived from

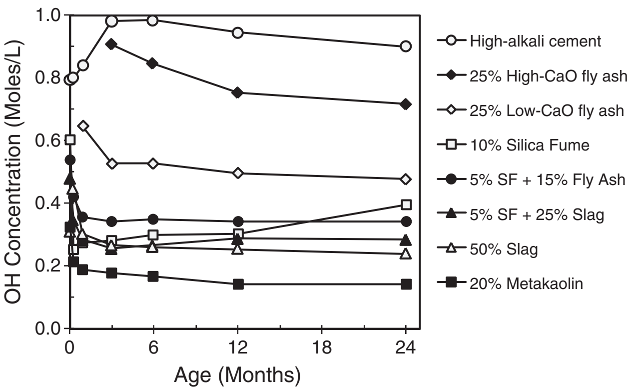

Fig. 1. Evolution of the pore solution in pastes containing SCM ([44]; Ramlochan et al. [4]; [5,46]).

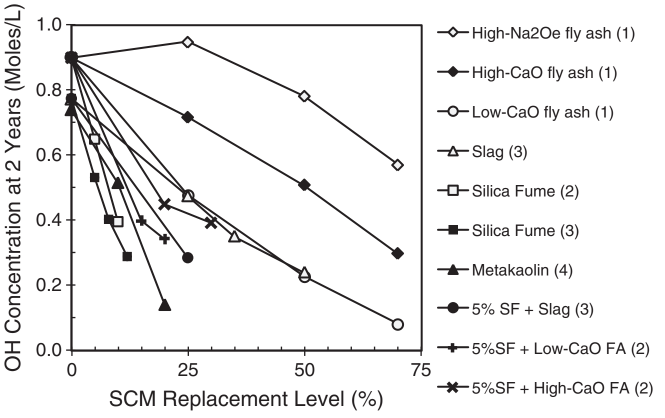

Fig. 2. Effect of SCM type and replacement level on the pore solution hydroxyl ion concentration at 2 years [5,40,44,46].

the chemical composition of the binder. A total of 79 different binders were tested including the following:

- 100% Portland cement at a range of different alkali contents (0.36 to 1.09% Na_2Oe)
- Binary mixes with 25 to 70% fly ash using 18 different fly ashes with a range of chemical compositions (1.1 to 30.0% CaO, 1.4 to 9.7% Na_2Oe)
- Binary mixes with 25 to 50% slag, 5 to 10% silica fume and 10 to 20% metakaolin; each SCM came from a single source
- Ternary mixes containing silica fume blended with either slag or fly ash; both low-calcium and high-calcium fly ash were used

The relationship was derived empirically to find the "chemical index" that was most reliably correlated to the OH^- concentration based on a least-square fit. The best-fit index was found to be the product of the equivalent alkalis and calcium divided by the square of the silica content of the binder $(Na_2Oe \times CaO)/(SiO_2)^2$. Although this is an empirical relationship it makes sense intuitively because the alkalinity of the pore solution can be expected to be a function of the alkalis in the binder and the ability of the hydrates to bind alkalis which has been shown to be a function of the calcium-to-silica ratio of the binder (see discussion below). The alumina content of the binder was not found to be statistically significant based on the empirical analysis conducted using this dataset, despite the apparent benefit of alumina discussed above.

Analyzing the composition of the pore solution extracted from a paste sample only provides one point on the equilibrium curve between bound and free alkalis. If the alkali content of the pore solution in concrete decreases, due perhaps to leaching or reaction with reactive silica in the aggregate, a portion of the bound alkalis may be released to regain equilibrium. It is important to establish what portion of the alkalis in a binder are "available" to a solution at a pH that is just able to sustain the alkali-silica reaction as it is these alkalis that are available to fuel the reaction. Shehata and Thomas [47] studied the alkali release characteristics of pastes produced with high-alkali cement and combinations of silica fume and various fly ashes. Paste samples, 1 to 3 years of age, were immersed in solutions of alkali hydroxide at initial molar concentrations of 0, 0.10, 0.25 and 0.40 and the change in concentration was observed to determine how much alkali was leached from the binder. Fig. 4 shows a selection of the data produced in this study. When mature paste samples were immersed in distilled water (pH = 7.0) almost all of alkalis present in the binder (80 to 90%) were released regardless of composition. As the alkali concentration of the leaching solution increased the amount of alkali released from the binder decreased and was strongly dependent on the composition of the binder. Pastes containing 100% Portland cement, 5% silica fume or 25% high-CaO fly ash still released a significant portion of the alkalis present in the binder (50 to 80%) even in the solution of the highest initial alkali concentration (0.40 M). Much less alkali (~20%) was released from pastes containing 25% low-CaO fly ash or ternary blends containing silica fume with either low-CaO or high-CaO fly ash. A correlation of the data [47] available for 24 different binders showed that the amount of alkali released to a solution with an initial alkali hydroxide concentration of 0.25 M (assumed to be the concentration necessary to sustain alkali-silica reaction) was related to the chemical composition of the binder as represented by the parameter $(Na_2Oe \times CaO)/(SiO_2)$.

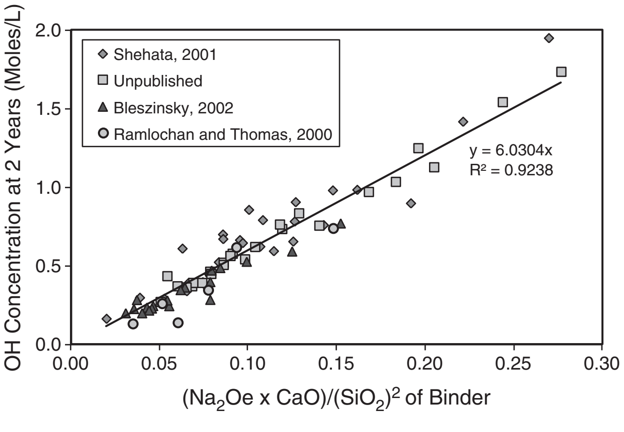

Fig. 3. Relationship between pore solution composition and the chemical composition of the binder.

The ability of SCMs to reduce the pore solution alkalinity is linked to their effect on the composition and alkali-binding capacity of the hydrates (especially C–S–H). Bhatty and Greening [3] found that C–S–H with a low Ca/Si ratio was able to retain more alkali (Na + K) compared to hydrates of higher lime to silica ratios. The addition of fly ash reduces the Ca/Si ratio of the C–S–H hydrates and there is a concomitant increase in the alkali content. Rayment [42] observed significant differences in the C–S–H composition of Portland cement and fly ash pastes after just 8 days curing at 20 °C. However, Uchikawa et al. [61] found little difference in pastes after 91 days at 20 °C but substantial changes due to the incorporation of fly ash after 60 days at 40 °C, indicating the role of the pozzolanic reaction in the CSH composition. Thomas et al. [53], reporting results for 7-year-old concretes containing reactive flint sand, showed that the alkali-binding capacity of C–S–H hydrates in concretes was increased significantly by the addition of fly ash. Uchikawa et al. [61] showed that slag has a similar effect to low-calcium fly ash on hydrate composition. Glasser and Marr [25] explain the differences in alkali absorption on the basis of the surface charge on the C–S–H which is dependent on the Ca/Si ratio. At high ratios, the charge is positive and the C–S–H tends to repel cations. As the Ca/Si ratio decreases the positive charge reduces becoming negative at low Ca/Si ratios, e.g. less than 1.3 [24]. Negatively charged C–S–H has an increased capacity to sorb cations, especially alkalis. Hong and Glasser [28] confirmed the importance of the Ca/Si ratio on the alkali-binding capacity of synthesized single-phase C–S–H but subsequently showed that the binding capacity could be greatly increased by introducing alumina into the C–S–H to form C–A–S–H [29].

Many of the studies on the alkali-binding of C–S–H have involved microanalysis (e.g. using scanning electron microscopy equipped with energy dispersive x-ray analysis) of the inner-product C–S–H forming around remnant alite and belite grains. However, outer-product C–S–H also forms by reaction between $Ca(OH)_2$ and pozzolans, but this phase is more difficult to identify and analyze separately than the inner-product C–S–H. The pozzolanic reaction is actually very similar to the alkali-silica reaction. The reactive silica in the pozzolan reacts first with the alkali-hydroxides in the pore solution and alkali-silica gel containing small amounts of calcium is formed. Over time, calcium exchanges for alkali in

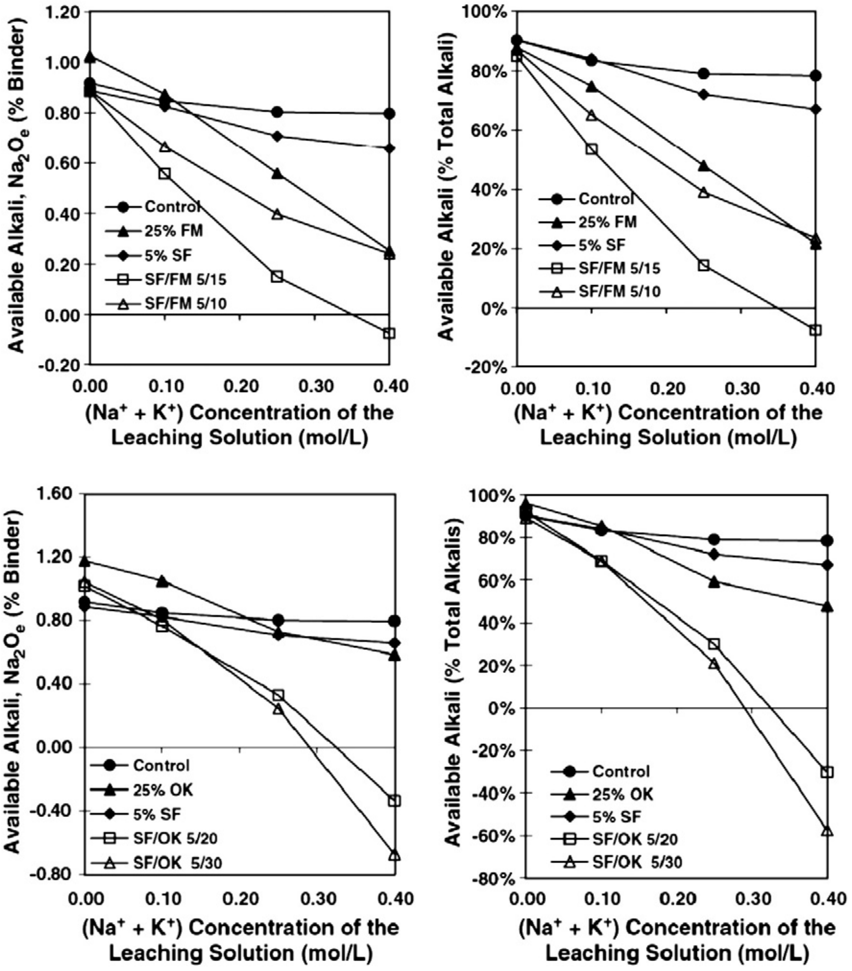

Fig. 4. Available alkalis in pastes with SCM stored in solutions of varying reactivity [47].

the gel and C–S–H forms with a relatively low Ca/Si ratio compared to that formed in Portland cement paste. The only substantial differences between this pozzolanic reaction and the alkali-silica reaction is the timescale over which the reactions occur and the absence of any detectable expansion due to the pozzolanic reaction. The lack of expansion can perhaps be explained by the fact that pozzolans are very-finely divided materials and the alkali-silica gel that forms and is subsequently converted to C–S–H is distributed throughout the cement paste, whereas the presence of reactive aggregate particles leads to the accumulation of larger deposits of alkali-silica gel in discrete locations that can become sites of expansion. The importance of the size and distribution of the reactive silica can be demonstrated in two ways. Firstly, it has been known since the formative work of Stanton [50] that if a reactive aggregate is ground to sufficient fineness (sub-180 μm in Stanton's studies) expansion is eliminated. Fig. 5 shows unpublished data from the author's laboratory relating to the effect of ground Vycor glass (sub-100 μm) on the expansion or mortar bars containing sand-sized Vycor glass as a reactive aggregate. The sand-sized Vycor glass behaves as a reactive aggregate causing expansion of the mortar with Portland cement as the only binder. However, the same material, when ground, behaves like a pozzolan when it is used to replace 20% of the Portland cement and prevents expansion. Secondly, if finely-divided pozzolans agglomerate and form sand-sized particles, these particles will behave like reactive aggregates and may result in expansion and cracking. This effect has been observed with agglomerated silica fume both in the field and in the laboratory. Fig. 6 (photo courtesy of Maria Juenger) shows a back-scattered electron image of a mortar bar containing agglomerated silica fume after storage in 1 M NaOH solution at 80 °C for 14 days [35]. The mortar, which contained non-reactive sand, expanded during test and the expansion was attributed to the reaction of the agglomerated silica fume.

3. Effect of SCM on the expansion of concrete

Stanton proposed a test method for evaluating the potential for cement-aggregate combinations to expand due to ASR in his first major paper on the subject [50]. This involved the manufacture of small mortar bars and storing them over water in sealed containers. Subsequent modifications included elevating the temperature to 38 °C (100 °F) and the test was eventually standardized to become

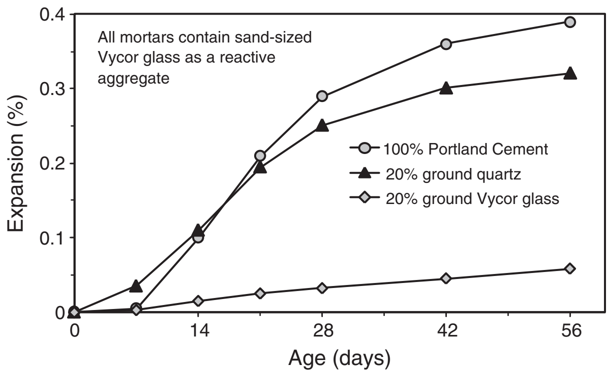

Fig. 5. Role of particle size on the behaviour of vycor glass.

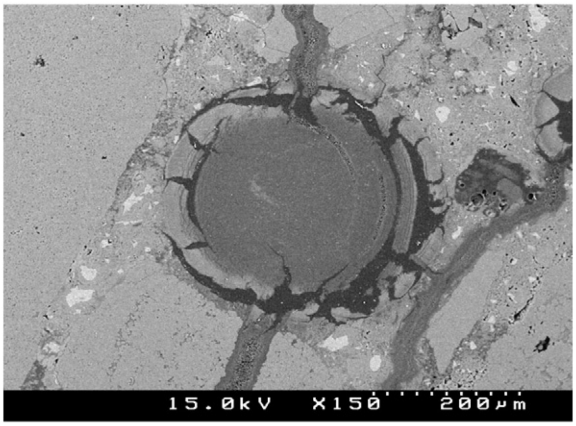

Fig. 6. Agglomerated silica fume particle behaving as a reactive aggregate and source of ASR expansion [35].

ASTM C 227. Pozzolans were often evaluated using a modified version of this test with either the job aggregate or a standard reactive aggregate, Pyrex glass; the test with Pyrex became standardized as ASTM C 441. ASTM C 227 is no longer widely used as it fails to detect many slowly-reacting aggregated because the small sample size and test conditions promote the leaching of alkalis from the bars; such a drawback is also a problem for evaluating SCMs [59]. ASTM C 441 is a much more rapid test (typically 14 to 56 days) because of the high reactivity of the Pyrex glass and leaching is less significant during the test. However, this test fails to account for the nature of the reactive aggregate which is known to impact the amount of SCM required, and tends to overestimate the amount of SCM required to control expansion with natural aggregates [59]. However, the use of Pyrex glass does allow a comparative evaluation of pozzolans and a number of investigators have used the test to observe the reduced efficacy of high-calcium ash compared with low-calcium ash [8,11,21,32,48]. Dunstan's [21] work was the most comprehensive with regards to fly ash composition. He reported results from Pyrex mortar bar tests for 17 ashes of varying chemistry and showed a reliable correlation between the calcium content of the ash and the expansion of mortar bars at 14 days.

The test methods most commonly used today to evaluate the efficacy of SCM in controlling ASR expansion are the concrete prism test (ASTM C 1293) and the accelerated mortar bar test (ASTM C 1567). The accelerated test is by far the most widely used test, however, it is only intended as a screening test and should not be relied upon for phenomenological studies. The test involves the immersion of small mortar bars in 1 M NaOH solution at 80 °C and this tends to mask the importance of the alkalis in the system under test. Since SCMs control ASR expansion mainly by reducing the availability of alkalis, providing an inexhaustible supply of alkalis is not desirable as eventually the beneficial effects of the SCM will be swamped by the ingress of alkalis from the storage solution. Furthermore, the very high temperature used in this test is not representative of the conditions that concrete encounters in the field. This review focuses on expansion tests involving concrete exposed either to field conditions or to accelerated conditions (up to 38 °C) in the laboratory (e.g. ASTM C 1293 concrete prism tests and similar tests).

3.1. Effect of SCM composition on expansion

Thomas and Folliard [56] stated that almost any SCM can be used to control expansion due to alkali-silica reaction provided it was used in sufficient quantity, the amount required varying significantly as shown in Fig. 7. The amount of SCM required is, of course, dependent on the composition of the SCM, but also on the reactivity of the aggregate, the quantity of alkalis supplied by the Portland cement (and other sources) and whether the concrete will be exposed to alkalis (e.g. seawater and deicing chemicals) during service. On one extreme, a highly efficient pozzolan with a high level of reactive silica and negligible alkali content, may be expected to eliminate damaging expansion with a moderately reactive aggregate when used with a moderate-alkali cement at replacement levels of about 10%; this scenario is represented by the left-hand curve in Fig. 7. On the other extreme, represented by the right-hand curve in Fig. 7, an SCM with a higher alkali and lower silica content might need to be used at a replacement level of 50 to 60% or more with a highly reactive aggregate and high-alkali cement.

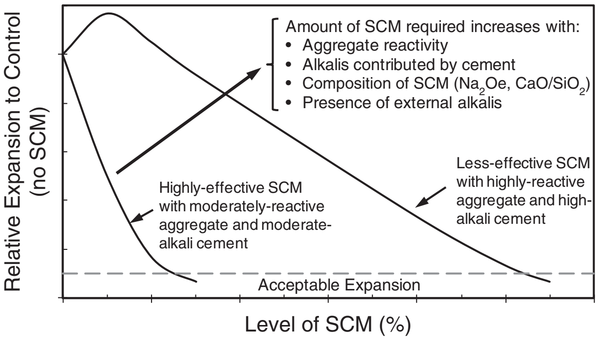

Fig. 7. Conceptual relationship between expansion of concrete and level of SCM.

Fig. 8 shows the expansion of concretes at 2 years as a function of the type and amount of SCM used; the tests were performed in a single laboratory using a reactive aggregate from a single source (siliceous limestone from the Spratt quarry in Ontario, Canada) and were, generally, performed in accordance with ASTM C 1293. Silica fume and metakaolin are the most efficient with regards to reducing the expansion at 2 years, followed by low-calcium fly ash. Slag, high-calcium fly ash and high-alkali fly ash were less efficient and had to be used at significantly higher replacement levels to control expansion to below 0.040% at 2 years. Generally, the effect of the different SCMs on the expansion of concrete prisms was consistent with their effect on pore solution alkalinity.

Fig. 9 (modified from [45]) shows the 2-year expansion of concrete containing 25% fly ash and a siliceous limestone (Spratt) aggregate; fly ashes from 29 different sources are shown in this figure. Fly ashes with low to moderate alkali (≤4% Na_2Oe) and calcium contents (≤20% CaO) are generally effective in controlling expansion below 0.040% at 2 years. As the calcium content increases above 20% CaO there is a marked increase in expansion with increasing calcium content. Fly ashes with high-alkali contents (>5% Na_2Oe) are not effective in controlling expansion when used at a replacement level of 25% regardless of the calcium content of the fly ash.

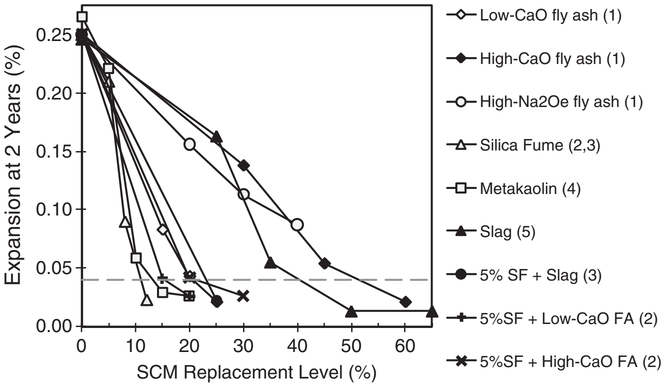

Fig. 8. Effect of SCMs on two-year expansion of concrete containing siliceous limestone (1—Shehata et al. [44], 2—Shehata and Thomas [46], 3—Bleszynski [5], 4—Ramlochan et al. [40]), 5—Thomas and Innis,1998).

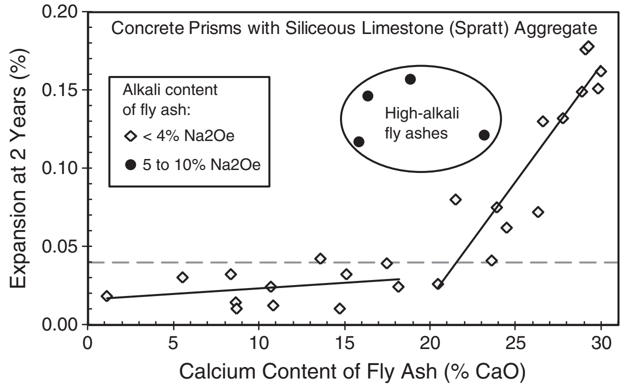

Fig. 9. Effect of the calcium content of fly ash on the two-year expansion of concrete containing siliceous limestone [46].

Fig. 10 shows an empirical relationship between the expansion of concrete at 2 years and a "chemical index" derived from the chemical composition of the cementing materials to produce 132 different concrete mixes which were tested in accordance with ASTM C 1293 [58]. The cementing materials used to produce these concretes were the same as those used for the pore solution study discussed above. The reactive coarse aggregate was siliceous limestone (Spratt). The best fit between expansion and chemical composition was found to be with the following index: $[(Na_2Oe)^{0.33} \times CaO]/(SiO_2)^2$. This relationship is not intended as a method for predicting expansion based on the chemical composition of the binder phase, but merely to examine what constituents of the binder tend to most influence ASR expansion. The relationship is likely quite different if a different reactive aggregate or, even, a different test method is used. However, the relationship does indicate that expansion is likely to increase as the alkali and calcium content of the binder increase or as the silica content decreases, and this is somewhat intuitive. It is interesting that the alkali content of the binder appears to play a less important role in determining expansion compared with the pore solution composition, but this is likely an artifact of the test conditions as significant leaching of alkalis occurs during the concrete prism test and this may reduce the apparent importance of the initial alkali content. This effect can be observed when looking at the expansion data for the concrete mixes produced with low-alkali cement. The expansion is lower than that expected based on the chemical composition. However, it is known that the concrete prism test will likely underestimate the expansion with low-alkali cement because of leaching [59]. As with the relationship with pore solution, the alumina content of the binder does not appear to significantly affect the expansion of concrete. The role of alumina, however, is not yet well understood and further study is needed to determine its impact.

3.2. Effect of cement alkalis

One of the drawbacks of the concrete prism test is that significant alkali leaching occurs during the test which means it cannot generally be used to determine the threshold alkali content required to initiate expansion with a specific aggregate or to determine how the minimum amount of SCM required varies as the alkali content of the cement changes [59]. Larger samples exposed under natural conditions should be relatively immune from the effects of alkali leaching, however, much longer testing periods are required.

Fig. 11 shows the expansion of 300-mm concrete cubes containing a reactive hornfels aggregate and stored outdoors at the National Building Research Institute (NBRI) in South Africa [37,38]. Two series of mixes were cast with cementitious contents of approximately 350 and 450 kg/m^3. Within each series 5% or 10% of the Portland cement by mass was replaced with an equal volume of silica fume, resulting in silica fume levels of 3.5% and 7.0% by mass. The "active" alkali content was maintained at a constant level within a given series by addition of alkali hydroxide (using the same Na_2O to K_2O ratio as the cement). The "active alkalis" included the available cement alkalis (using ASTM C 311) plus the alkali hydroxide, but excluded alkalis in the silica fume. The use of 3.5% or 7% silica fume delayed the onset of expansion and time to cracking in all cases. However, only the mixture at the lower cement content with 7% silica fume failed to expand after just over 7 years field exposure. These data clearly show the effect of alkali content on the efficacy of silica fume in controlling expansion. A replacement level of 7% silica fume appears to have been sufficient to provide long-term prevention of expansion when the "active alkalis" of the mix were just less than 4 kg/m^3 Na_2Oe but not at the higher alkali content of 5 kg/m^3 Na_2Oe.

Fig. 12 shows data from Fournier and co-workers (2004) for concrete blocks stored outdoors in Ottawa, Canada. The blocks contain a reactive greywacke coarse aggregate (Springhill Quarry in New Brunswick) and 420 kg/m^3 of cementing material. High-alkali Portland cement with 0.90% Na_2Oe was used to manufacture the blocks and in some cases the alkali content of the Portland cement component of the concrete was boosted to 1.25% Na_2Oe by the addition of NaOH to the mix water as per ASTM C 1293. The data in Fig. 12 show that although the differences in expansion between boosted and unboosted blocks is not large, increased amounts of SCM are clearly needed to control expansion to acceptable levels when the alkali content of the mixture is increased.

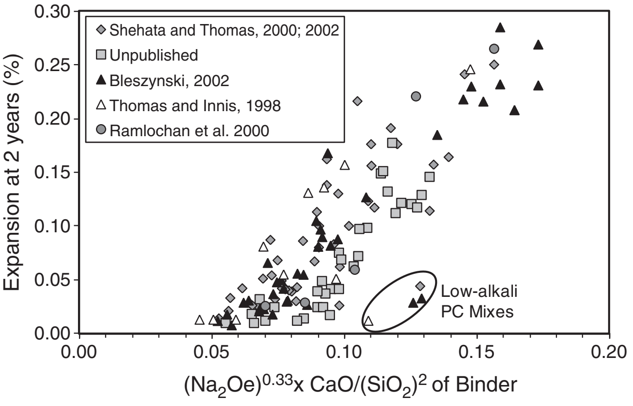

Fig. 10. Effect of binder composition on the expansion of concrete containing siliceous limestone.

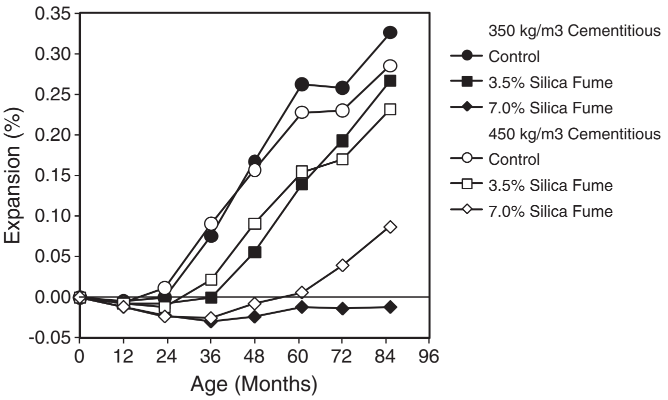

Fig. 11. Effect of cement alkalis and expansion of concrete containing silica fume [38].

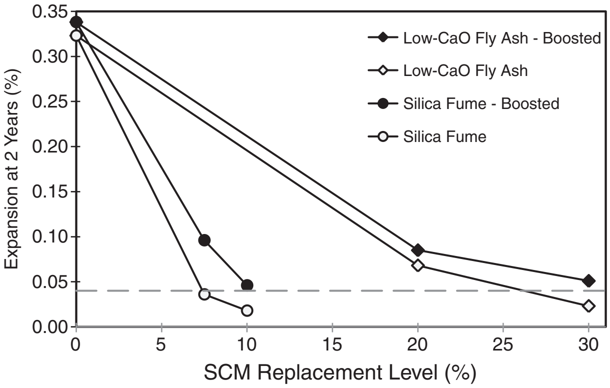

Fig. 12. Effect of cement alkalis on expansion of concrete containing fly ash or silica fume [23].

3.3. Effect of aggregate reactivity

Fig. 13 shows 2-year expansion data for concrete prism tests containing various reactive aggregates and different amounts of slag [57] or metakaolin [40]. It can be seen that the amount of slag required to limit expansion below 0.040% at 2 years varies between 35% and 50% depending on the aggregate type. Fig. 14 shows similar data for blocks exposed on an outdoor exposure site in Ottawa [23]; the blocks contain high-alkali cement (boosted to 1.25% Na_2Oe), either low-CaO Class F fly ash or silica fume, and aggregates of varying reactivity. For three of the reactive aggregates, which produced expansion levels between 0.097% and 0.219% when tested with 100% Portland cement, a fly ash replacement level of 20% or a silica fume replacement level of 7.5% was sufficient to reduce expansion below 0.040%. For the aggregates that produced an expansion of 0.338% when tested with 100% Portland cement, neither 30% fly ash nor 10% silica fume was quite sufficient to reduce the expansion below 0.040%, although expansions were much reduced (0.051% and 0.046% with 30% fly ash and 10% silica fume, respectively). For the aggregate that produced the largest expansion when tested with Portland cement (0.386%), significant expansion (0.148%) still occurred with 30% fly ash. In this figure, it would appear that the amount of fly ash required increases as the reactivity (as determine by the expansion when tested with Portland cement alone) of the aggregate increases.

4. Summary

Supplementary cementing materials are an effective means for controlling expansion due to alkali-silica reaction and most, if not all, SCMs can be used in this role provided they are used at a high enough level of replacement. The level of SCM required generally increases with the following parameters:

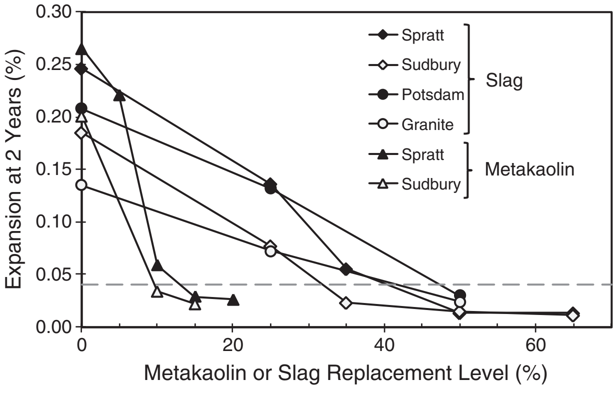

Fig. 13. Effect of aggregate type on the amount of metakaolin or slag required to control ASR expansion [40,52].

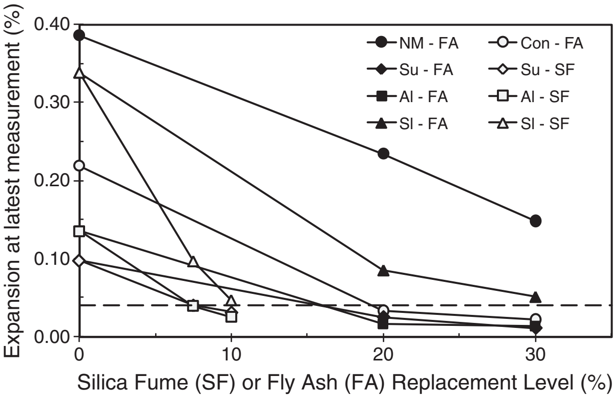

Fig. 14. Effect of aggregate type on the amount of silica fume (SF) or fly ash (FA) required to control ASR expansion [23]. NM, Con, Su, Al and Sl are different aggregates. FA and SF are fly ash and silica fume, respectively.

- The alkali available from the Portland cement increases (if significant alkalis are available from the aggregates—e.g. feldspars and greywackes—or from external sources, this will likely also increase the level of SCM required)
- The alkali from the SCM increases
- The CaO/SiO_2 of the SCM increases
- The reactivity of the aggregate increases

SCMs control ASR mainly by reducing the amount of alkalis available for reaction with the aggregate and the ability of SCMs to bind alkalis appears to be strongly related to the CaO/SiO_2 ratio of the SCM. SCMs that are low in alkali and calcium, and high in silica tend to be the most effective in reducing pore solution alkalinity and these materials can be used at relatively low replacement rates to eliminate damaging expansion. SCMs with increased amounts of alkali and calcium have to be used at higher replacement levels. There is evidence that the alumina may play an important role in determining the alkali-binding capacity of SCMs, the precise role of alumina is not obvious from the data available.

The relationships discussed here have been used in the development of recent guidelines for controlling expansion due to ASR [60] which vary the recommended minimum SCM level based on its composition, aggregate reactivity, Portland cement alkalis, the exposure condition and the criticality of the structure.

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