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Alkali–aggregate expansion inhibiting admixtures

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Abstract

Many concrete structures have exhibited deterioration due to the alkali–aggregate expansion reactions. A review has been prepared to describe the nature of the alkali–aggregate reactions, test methods that are adopted to evaluate the aggregates for their potential to cause expansion and the methods suggested to counter this reaction. Some methods seem to be effective but further work has to be carried out before establishing the efficacy of others. Results obtained using additives such as silica fume and other siliceous materials such as fly ash, slag, and rice husk ash have been discussed. Some chemicals based on lithium compounds have shown promise as, also, have other non-lithium bearing compounds. © 1998 Published by Elsevier Science Ltd. All rights reserved.

Keywords: alkali, aggregate, expansion, silica fume, fly ash, admixtures, lithium compounds, minerals, slag, siliceous additives.

INTRODUCTION

In the 1920s and 30s several structures built in California, U.S.A., developed severe cracking within a few years of their construction. In 1940 Stanton demonstrated that the alkali–aggregate expansion reaction was the main cause for such deterioration[1]. It was subsequently shown, that in these concrete structures a combination of high alkali cement and opaline aggregate was used. The cracking of concrete due to alkali–silica reaction was also recognized in many other countries. In 1957, another deleterious expansive reaction known as alkali–carbonate reaction was reported by Swenson[2]. Since then several international conferences have been held to discuss concrete failures resulting from alkali–aggregate expansion in many parts of the world.

The alkali–aggregate expansion (AA) involves chemical interaction between alkali hydroxides usually derived from cement and reactive components in the aggregate particles. In addition to alkali–silica and alkali–carbonate expansion reaction, a third type referred to as alkali–silicate reaction in concrete containing argillite and greywacke has been proposed, this reaction is generally slow and the mechanism is not completely understood.

Several publications have appeared describing in detail the possible mechanisms of the alkali–aggregate reactions. In the cement paste the presence of alkalis increases the pH to 13.5–13.9. It has been reported that the hydroxyl concentration of solution of concrete made with a high alkali cement may be 10 times as high as that made with a low alkali cement and 15 times that of a saturated $Ca(OH)_2$. In general terms the reaction in the first stage proceeds through the hydrolysis of the reactive silica by OH to form alkali–silica gel and a secondary overlapping stage involving the absorption of water by the gel, which will increase in volume as a result. The principal source of alkali is cement but other sources should not be ignored. The mixing water, sea water, and possibly some mineral constituents in the aggregate such as illitic clays, micas or feldspars, ground waters, deicing salts and admixtures are other sources. Some of the natural materials that have been identified as alkali-reactive in concrete include opaline silica, chalcedony, volcanic glass and siliceous cement/cryptocrystalline quartz. Some admixtures such as $CaCl_2$-based formulations and superplasticizers may aggravate alkali–silica reaction.

The alkali–silicate expansion reaction is the result of aggregates containing greywackes (sand stone containing feldspar or clays) and those that exfoliate such as vermiculites. Also phyllosilicates and other minerals are shown to react with alkaline solutions[3]. At high pH, reactions involving silicates, (zeolite and clay mineral) have been reported but the significance of these reactions to alkali–aggregate expansion still remains unknown[4].

The alkali–carbonate reaction differs from the other varieties in that the affected concrete does not contain significant amounts of silica gel and known alkali-expansive silica minerals have not been found in the aggregate. Details of the mechanism are still being debated. In one proposal, expansion is attributed to the growth and re-arrangement of brucite crystals in the restricted space in which de-dolomitization takes place.

Another suggestion is that the expansion is due to cryptocrystalline quartz (alkali-reactive silica is not uncommon in limestones)[5]. In the earliest explanation, Gillott[6] attributed the expansion to swelling pressure generated by pick-up of moisture by fine constituents, particularly dry clay exposed to de-dolomitization reaction.

Regardless of the type of rock or mineral, increases in expansion are influenced by alkali content, water and temperature and time of exposure. There are reactive and marginally reactive aggregates which promote good mechanical properties in concrete that may be available in close proximity to the construction activity and may have to be used. Use of low alkali cement and blending with additives may be needed with such aggregates. It is generally acknowledged that below a specific amount of alkali per cubic metre of concrete made with a reactive aggregate, very little expansion takes place. Technically low alkali cement is that containing alkali in amounts below 0.6% Na_2O equivalent (Na_2O equivalent = $Na_2O + 0.658\ K_2O$). Figure 1 shows the expansion of mortar containing cement with different amounts of Na_2O equivalent[7]. Expansion is generally lower as the ratio decreases. Replacement of Portland cement partly by fly ash, or blast furnace slag, silica fume or rice husk ash also reduces the expansion. The effect of lowering w/c ratio in concrete and its consequence on alkali–aggregate expansion has yet to be resolved. Lower w/c ratio enables better strengths, lower porosity, lower permeability, and lower mobility of alkali ions. However, pore alkali concentration will increase. Air entrainment may be able to reduce expansion by accommodating the reaction products. Avoidance of admixtures that contain large amounts of alkalis, use of low cement content, sealing concrete after providing adequate time lapse for drying, and coating of aggregate particles with an impermeable material are some of the measures that reduce the alkali–aggregate expansion reactions. Some admixtures, especially lithium salts, are known to reduce alkali–aggregate reactions.

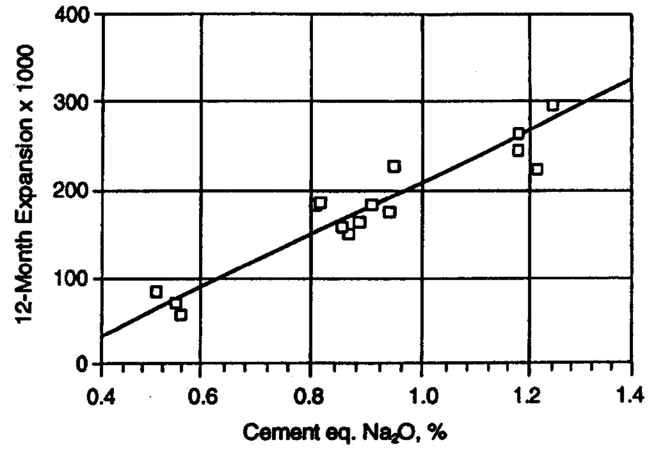

Fig. 1. Expansion of mortar containing different amounts of Na_2O.

TEST METHODS

In addition to ASTM standards, several accelerated tests[8–15] have been proposed to evaluate the aggregates for their potential to cause the deleterious alkali–aggregate reaction. The C 295-90 deals with the petrographic examination. This method determines the physical and chemical characteristics of materials, classifies and estimates the amount of the constituents. Additional measurements using XRD, DTA, IRA and others may be needed to substantiate petrographic examination. In the C 227-90 standard test method for potential alkali reactivity of cement–aggregate combinations, mortar bar is used. It is generally considered that the expansion is excessive if the length change exceeds 0.05% at 3 months or 0.1% at 6 months (ASTM C-33). This test should be supplemented by other methods such as the petrographic examination. The ASTM C 289-87 method tests the reactivity of aggregate with alkali in Portland cement concrete as indicated by the amount of reaction during 24 h at 80°C between 1 N NaOH solution and aggregate that has been crushed and sieved to pass 300 μm and retained on a 150 μm sieve. This test has to be used in conjunction with others. Although results are obtained quickly they may not be entirely reliable. The ASTM C 342-90 for the determination of volume change in cement aggregate combination is primarily intended for research purposes. Mortar is used in the test and the initial temperature and curing additives are similar to those proposed in C 227-90. There are two ASTM methods to determine the potential alkali reactivity in carbonate aggregates. In ASTM C 586-92 expansion of carbonate rocks while immersed in a solution of NaOH at room temperature is determined. The ASTM C 1105-89 entitled *Length Change of Concrete due to Alkali–Carbonate Rock*, assesses the potential for expansion of concrete caused by alkali–carbonate rock reaction. The ASTM standard C 441-89 refers to the effectiveness of mineral admixtures or granulated blast furnace slag in preventing excessive expansion of concrete due to the alkali–silica reaction. The Canadian Standards Association (CSA) A 23.2-14A, is entitled *Potential Expansivity of Cement–Aggregate Combinations (Concrete Prism Expansion Method)*. There are two versions of the test, one for alkali–carbonate reactive aggregate and another for slow/late-expanding alkali–silicate/silica reactive aggregates.

EFFECT OF SILICA FUME

The admixtures that are added to cement for reducing the alkali–aggregate expansion include chemical admixtures, and other admixtures such as silica fume, fly ash, slag and other siliceous based materials.

One of the effective methods of controlling expansive alkali–aggregate reaction is to blend silica fume admixture with the high alkali cement[16]. However, contradictory results have been reported on the effectiveness of silica fume to counteract alkali–aggregate expansion reaction[17–23]. Although small amounts of silica fume are found to be effective[22,23] at earlier times, they are somewhat ineffective at longer times[18–21]. There has also been concern that at larger dosages of silica fume, the fume itself may become a source that would react with the alkalis in cement[24,25]. The effectiveness of silica fume depends on a number of parameters, such as composition (SiO_2 and alkali contents), the percentage used, the type of alkali aggregate expansion reaction (alkali–silica or alkali–carbonate) and the type, fineness and alkali contents of cement.

Oberholster and Westra[18], using the Pyrex glass mortar prism test (ASTM C441-69), found that with silica fume as a blend, a ‘shrinkage’ of 0.008% occurred. The expansion results of mixtures containing mineral admixtures (silica fume and fly ash) are shown in Fig. 2[18]. The top curve shows the effect of dilution with low alkali cement. There is a continual decrease in expansion as equivalent Na_2O decreases from 0.97 to 0.68 at 30% replacement. All admixtures promote a decrease in expansion considerably lower than these values and their effect is not just the result of dilution. Assuming 0.1% expansion as the criterion for allowable expansion, a 10% by volume replacement of silica fume would be required, and silica fume was found to be the most effective of the mineral additions tested.

Olafson[26], applying a version of ASTM C 227 (modified version of Brotschi and Mehta) used crushed Pyrex as the aggregate and showed that when the pozzolan was of a high surface area

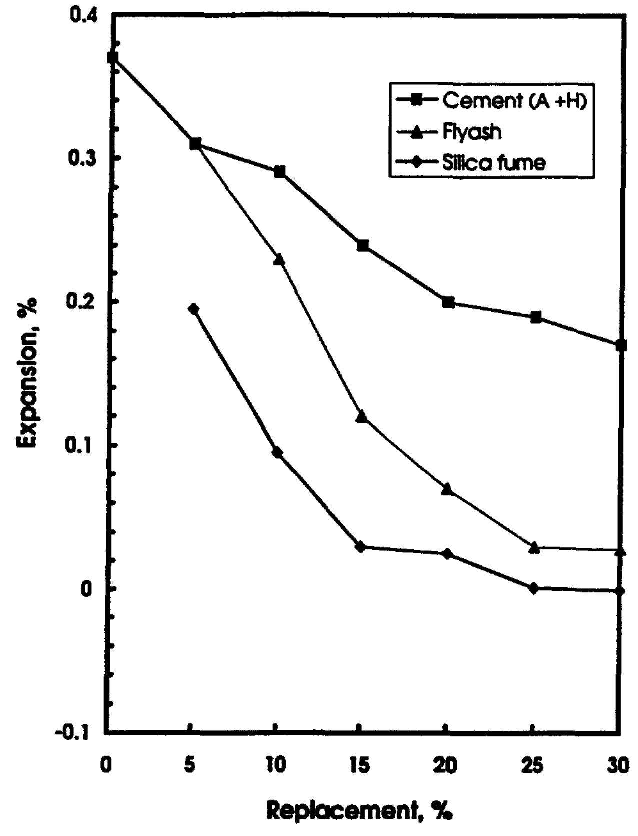

Fig. 2. Effect of cement H (0.97% NaOH) with increasing amounts of cement A (0.16% NaOH) on the linear expansion of mortar prisms.

type such as silica fume, lower quantities of addition were needed to contain the reaction. The results of longer term expansion measurement using an Icelandic sand and a cement with 1.39% equiv. Na_2O alkali is shown in Fig. 3[26]. At both 7.5 and 10% silica fume, the expansion after 3 yr is about 0.06%.

Perry and Gillott[21] have also shown the effectiveness of silica fume to control alkali silica reactions by using Pyrex as the reactive aggregate suggested in ASTM methods C227 and C441. In addition, they tested a very reactive opal from Nevada according to ASTM C227 except that temperatures of 25 and 50°C were used in addition to the standard 38°C. The amounts of cement replaced by the silica fume ranged from 0 to 40% by weight.

Results of experiments performed at 50°C show that replacement of cement by silica fume significantly reduced expansion, but it appears that 20% replacement might be required so that the reaction of the opal could be controlled (Fig. 4)[16]. Evidence presented in this work indicated, however, that superplasticizer addition at 15% replacement level of silica fume may influence expansion in a negative manner.

In the work of Durand *et al.*[27] the effectiveness of fly ash, slag and silica fume to counter the alkali–aggregate expansion was compared. Addition of silica fume at dosages of 5, 10 and 15% decreased the expansion by 4, 68 and 83% with respect to the reference mortar containing argillite. In concrete containing dolomitic limestone the corresponding values were 40, 48 and 54%. Soles *et al.*[28] found that in mortars using meta argillite (containing slowly reacting species) the effectiveness of silica fume occurred above the 10% level. Silica fume had practically no effect in concrete containing dolstone aggregate, even at 15% cement replacement.

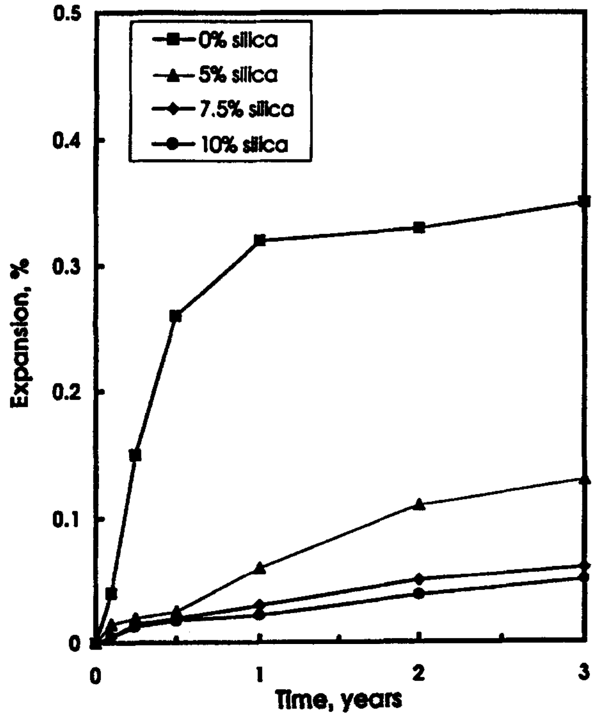

Fig. 3. Effect of silica fume replacement o linear expansion of mortar bars containing Iceland sand and cement containing 1.39% NaOH.

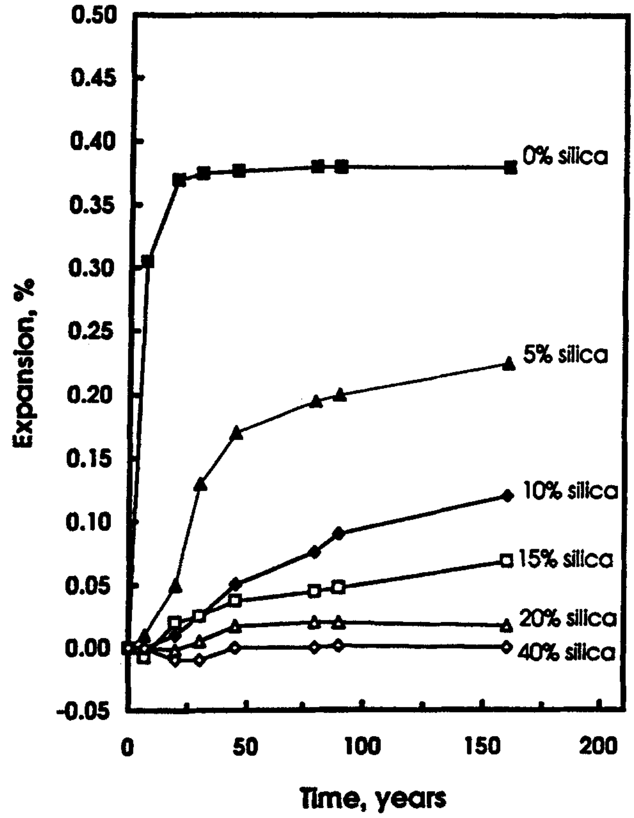

Fig. 4. Effect of silica fume replacement on the linear expansion of mortar bars containing 4% reactive opal.

In order to simulate realistic conditions Swamy[29] tested silica fume concrete under a hot–wet and hot–dry exposure regime. The concrete contained cement with 1% Na_2O equivalent, 15% fused silica as a replacement for sand and 10% microsilica. The addition of microsilica decreased the expansion of the reference concrete from 0.732 to 0.273% at 40 days. Crack patterns appearing in the specimens were also studied. They were identified with microsilica as very fine cracks at 0.159% (27 days) expansion and more visible cracks at an expansion of 0.260%. They were largely surface cracks. In the control specimens, at an expansion of 0.046% (7 days), visible cracks appeared. It was concluded that to evaluate the effectiveness of mineral admixtures to control alkali silica expansion, criteria that should be considered are control of expansive strain, control of cracking, preservation of concrete strength and modulus and control of structural deformation.

Air entrainment in concrete reduces the expansion due to alkali–aggregate reaction. Jensen[30] found that with 4% air voids, the expansion could be reduced by 40% and this was attributed to the accommodation of alkali–silica gel in the air void system. The effectiveness of a combination of silica fume and air-entrainment was studied by Wang and Gillott[31]. Both silica fume and air entrainment individually reduced the expansion but the combination reduced the expansion by the maximum amount. Table 1 compares the expansion values in mortar bars containing silica fume and an air entraining agent[31].

The possibility of increased alkali–silica reactivity in the presence of superplasticizers has been studied[32]. Mortar bars made with opal, 0, 6 and 12% silica fume and superplasticizer showed greater early reactivity and ultimate magnitude of expansion than the corresponding bars containing no superplasticizer [Fig. 5(A) and (B)][32]. At 12% silica fume addition the expansion was delayed for about 2 months. At 24% silica fume replacement no expansion occurred. In contact with the superplasticizer increased disorder coefficient and corroded appearance on the surface on opal became evident.

Table 1. Comparison of expansion of mortars containing silica fume and an air entraining agent

Silica fume (%)	*Expansion*	
	No air entrainment	*With air entrainment*
0	1.05	0.48
6	0.85	0.45
12	0.62	0.28

Hypotheses concerning the mechanism by which pozzolans provide resistance to alkali–aggregate reactions are generally centered on the type of C–S–H formed during the hydration of cement. When the CaO/SiO_2 ratio of the C–S–H formed is approx. 1.2 or lower, this product is suggested to have an increased capacity for accommodating Na_2O and K_2O in its structure, thereby reducing the hydroxyl ion concentration[33]. During normal hydration without the mineral admixture this ratio is about 1.5.

Direct measurements of pore solutions using a high-pressure press technique has demonstrated how as low as 5% silica fume reduced the hydroxyl ion concentration to levels below 0.3 mol l^{-1}[34]. The pH and (OH) concentrations have been determined in cement pastes containing 10 and 20% silica fume[35]. The pH and (OH) concentrations decreased in the presence of silica fume. There is a broad correlation between the hydroxyl ion concentration and the alkali–aggregate expansion. There are factors to be considered including the formation of refined pore structure and higher density of the matrix formed in the presence of silica fume that control the expansion reactions.

Based on morphological studies of cement pastes containing silica fume[36] it has been concluded that silica fume forms microcrystalline

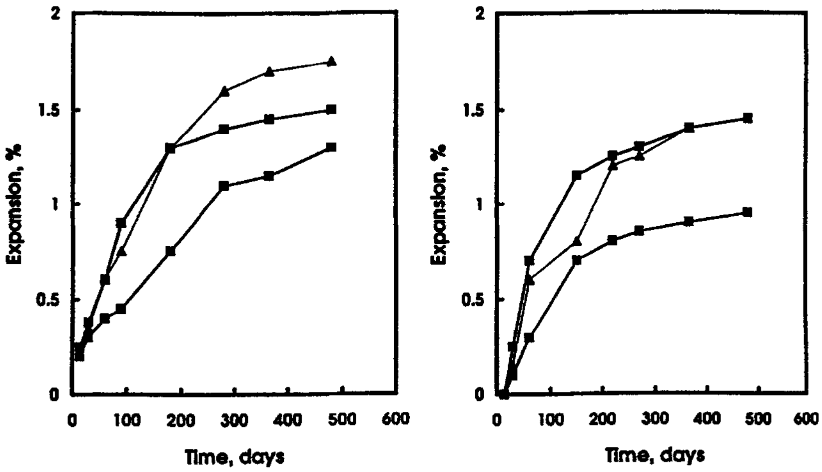

Fig. 5. Effect of silica fume and superplasticizer on expansion.

hydrosilicates containing alkalis similar to alkali–silica gels. The expansion property of this product is related to its potassium content. This product does not produce expansion because it occupies the available space in the paste and forms when cement is still plastic.

The long term effectiveness of silica fume has been questioned by a number of investigators[37–39]. The rate of expansion of silica fume concrete increased significantly in the longer run while that of the control leveled off. The proposed explanation for this observation includes, the recycling of alkalis which are entrapped initially in the low CaO/SiO_2 ratio and the existence of high alkali pozzolanic C–S–H.

Although there is clear evidence that the addition of silica fume effectively decreases the alkali–silica expansion in concrete, there is need for long term field data to determine all the parameters that influence the effectiveness of silica fume.

CHEMICAL ADMIXTURES

Lithium-based compounds

Chemical admixtures in small amounts are capable of influencing workability, air-entrainment, hydration rate, corrosion, bleeding and strength development. There are other applications of chemical admixtures. There has been increased activity in recent years to develop chemical and other admixtures to counteract the alkali–aggregate expansivity in concretes. It is also imperative that such admixtures should not affect other physical and chemical properties of concrete. Although substantial work has been carried out on the effect of the chemicals on the expansion reactions, relatively less attention has been directed to their effect on other properties of concrete and long term effects.

McCoy and Caldwell[40] were the first to investigate the effect of various chemicals on the expansion in mortars containing a high alkali cement and a highly reactive Pyrex glass. In Table 2 data on the effect of some salts on expansion due to alkali–aggregate reaction are given. The Li salts were generally the most effective.

The effect of some organic compounds on the alkali–aggregate expansion was also carried out and the results are given in Table 3. The most effective expansion reducing compounds are methyl cellulose and hydrolyzed protein. Addition of lactic acid, on the contrary, results in an expansion.

Table 2. Effect of salts on the reduction in expansion of mortars

Material	*Percent addition*	*Percent reduction in expansion (8 wks)*
Aluminium powder	0.25	75
Ba carbonate	1.00	3
Ca carbonate	10.0	–6
Cr phosphate	1.00	9
Cu chloride	1.00	29
Cu sulphate	1.00	46
Li chloride	0.50	34
Li chloride	1.00	88
Li carbonate	0.50	62
Li carbonate	1.00	91
Li fluoride	0.50	82
Li nitrate	1.00	20
Li sulphate	1.00	48
Na chloride	1.00	15
Na carbonate	1.00	44
NH_4 carbonate	1.00	38
Zn carbonate	0.50	34

It has been concluded from the above tables and from extensive earlier work that lithium salts, copper sulphate, aluminium powder, some proteins and air-entraining agents were capable of reducing the expansion significantly. Several other investigators have recently confirmed the effect of lithium compounds and some other chemicals on the alkali–silica reaction.

Lithium hydroxide is an effective additive that reduces the expansion caused by the alkali–silica reaction. Ramachandran[41] prepared seven mixes (Table 4) containing LiOH, opal and different amounts of alkali and studied their expansion characteristics after exposure to 25, 38 or 130°C (in an autoclave). The samples exposed to 25 or 38°C showed the following

Table 3. Effect of some organic compounds on the reduction in alkali–aggregate expansion

Organic compound	*Addition (%)*	*Percent reduction in expansion*
Lactic acid	1.0	–59.0
Linolic acid	1.0	37.0
Soybean oil	1.0	26.0
Acetone	1.0	16.0
Ethyl acetate	1.0	31.0
Glyceryl monostearate	1.0	20.0
Methy cellulose	1.0	52.0
Methyl cellulose	2.0	60.0
Saccharin	0.5	19.0
Hydrolyzed protein	1.0	56.0–76.0

Table 4. The composition of mortar mixes (cement:sand = 1:2.25)

Sample no.	*Na_2O equivalent*	*LiOH*	*Opal*
1	0.44	0.00	0.00
2	1.20	0.00	0.00
3	1.20	0.50	0.00
4	1.20	1.00	0.00
5	1.20	0.00	5.00
6	1.20	0.50	5.00
7	1.20	1.00	5.00

Table 5. Expansion of mortars containing different amounts of LiF or Li_2CO_3

Sample dosage (%)		*% Expansion (months)*				
		6	12	18	24	36
Reference	0.00	0.54	0.62	0.62	0.63	0.63
Ref+LiF	0.25	0.43	0.59	0.64	0.68	0.71
	0.50	0.04	0.06	0.06	0.06	0.06
	1.00	0.02	0.02	0.02	0.02	0.02
Ref+Li_2CO_3	0.25	0.46	0.61	0.62	0.62	0.63
	0.50	0.30	0.50	0.54	0.55	0.58
	1.00	0.03	0.04	0.04	0.04	0.05

behavior. Mix 5 exhibited the maximum expansion as it contained 1.2% Na_20 equivalent and 5% opal. Mix 6 with 0.5% LiOH had reduced expansion (Fig. 6). However, after 30 days there was a tendency of the mortar to gradually expand. Mix 7 containing 1.0% LiOH showed decreased expansion up to 50 days. Long term measurements have to be carried out to determine if this dosage is adequate to inhibit expansion.

One of the methods of studying the role of admixtures to counter the alkali silica expansion is to expose the mortars to an autoclave treatment. The samples mentioned in Table 4 were subjected to a temperature of 130°C for 5 h. Although samples 1–4 showed almost no expansion, 5–7 exhibited substantial expansion values. The sample 7 exposed to 25 or 38°C had low expansion values, implying that 1% LiOH inhibits expansion. However, the autoclave treatment suggested that 1% LiOH is not sufficient to inhibit the expansion. It is possible the LiOH changes the microstructure and weakens the bond forming characteristics of the mortar under the autoclave treatment. Caution should therefore be exercised when applying the accelerated test methods for evaluating the alkali–aggregate expansion characteristics of mortars.

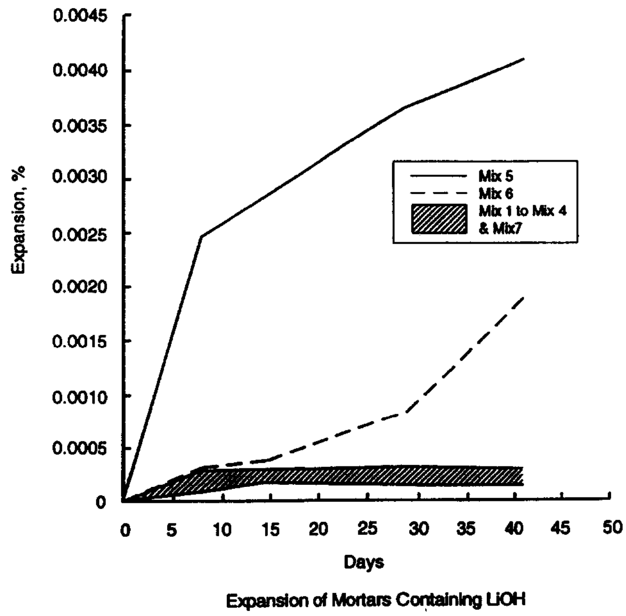

Fig. 6. Expansion of mortars containing LiOH.

A systematic investigation on the effect of lithium fluoride and lithium carbonate on the expansion of mortars (with 1% Na_2O equivalent) was carried out by Stark *et al.* and the results are shown in Table 5[42].

Although less soluble than LiOH, both LiF and Li_2CO_3 are capable of reducing the alkali–silica expansion. They seem to be converted to LiOH in pore solution. It is also obvious that in order to obtain good inhibition of expansion at least 0.5% LiF and 1.0% Li_2CO_3 would be required.

The mechanism of the inhibitive action of LiOH has been proposed by Stark *et al.*[42]. In the presence of KOH and NaOH the gel product incorporates Li ions. The amount of Li in this gel increases with its concentration. The threshold level of Na:Li is 1:0.67 to 1:1 molar ratio at which expansion due to alkali–silica reaction is reduced to safe levels. Diamond and Ong[43] found that when LiOH is added to mortar much more lithium is taken up by the cement hydration products than Na or K.

In another study involving LiOH, $LiNO_2$ and Li_2CO_3 it was found that all these compounds were able to decrease the expansion due to alkali aggregate reaction[44]. Of these compounds Li_2CO_3 was found to be more effective than the others. The relative inhibiting effect was considered to depend on the Li/Na ratio.

Ohama[45] also investigated the relative effects of carbonate, hydroxide and fluoride salts of Li. In dosages of 0.5, 0.7 and 1.0%, these compounds decreased the expansion. However, the effectiveness decreased when LiF and $LiOH.H_2O$ were added in amounts greater than 0.7%, although the compressive strengths of mortars were of same value at different dosages.

It appears from the work carried out so far, that not all lithium salts are effective in diminishing the alkali–aggregate expansion reaction[46]. The long term effects have to be evaluated and the optimum dosage requirements have to be evaluated. Much more work employing reliable predictive tests has to be carried out before the relative effects of various lithium compounds such as hydroxide, carbonate, nitrate, fluoride, perchlorate, chloride, etc, can be substantiated.

Non-lithium compounds

Attempts are continuously been made to find alternative materials to lithium compounds to counter the alkali–aggregate expansion. A few studies have been made on binary admixture systems. Hudec[47] tested several chemicals including phosphates, nitrates and borates of various cations and found that phosphates have good potential for countering the expansion, especially the alkali–silica type.

Several reports have suggested that the air-entraining admixture in concretes protects them against alkali–aggregate expansion. It is possible that the microbubbles that are entrained can accommodate the reaction products and thus lower the stress development in concrete[30,40,48]. An air-entrainment of 3.6% can cause a 60% reduction in expansion[49]. It can be expected that porous aggregate incorporation in concrete should also be able to diminish this expansion[50]. Some work carried out by Berube *et al*[51] would suggest that normal air entrainment in concrete may not have significant effect on alkali aggregate expansion. There is concern that the freeze thaw resistance of concrete may be affected if the gel products fill the pores.

The inclusion of retarders to an air entraining agent may result in larger decrease in expansion than when these admixtures are used individually. In Fig. 7 are given the expansion values produced by a combination of an air entraining agent with three types of retarders, viz., a commercial retarder (CR), citric acid (CI) and sucrose (SU). The data demonstrate that the expansion in the presence of both admixtures is substantially lower than when only the air entrainment is used[52]. The action of the retarder involves the change in the availability of lime and alkali, production of lower C/S ratio phase and delay in the formation of a rigid structure in the paste. Reduced expansion with air entraining agent–water reducer mixtures has also been substantiated[53,54].

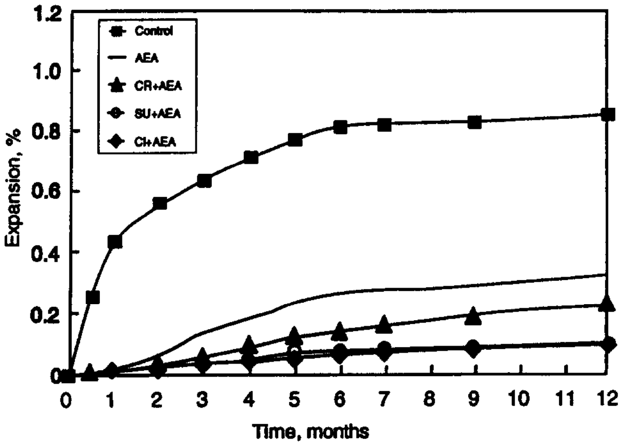

Fig. 7. Influence of dual admixtures on alkali–aggregate expansion.

The effect of various other chemical admixtures on the alkali–silica reaction has been studied and following conclusions have been drawn[55]. Calcium chloride increases expansion, rate of hydration and a rapid formation of the paste structure. Sucrose dramatically decreases the expansion. Other admixtures such as lactic acid, EDTA and oxalic acid have no effect. The addition of barium salts containing chloride, hydroxide, acetate, nitrate and chromate to concrete affect the expansion to different extents. The acetate and nitrate seem to be more effective than the others[56,57]. Similarly the sulphates, chlorides, and carbonates of Na and K are ineffective whereas the nitrates of Na and K have been found to be much more effective in reducing the expansion.

Ohama *et al.*[58] have found that alkyl alkoxy silanes are capable of reducing alkali aggregate expansion considerably. The effect of five types of silanes on alkali–aggregate expansion is evident from the results in Fig. 8. All the silanes decrease the expansion. AAS-2 to AAS-4 seem to be more effective than the others. AAS-1–5 are respectively methyl trimethoxy silane, hexyl trimethyl siloxane, octyl trimethyl silane, decyl trimethoxyl silane and hexadecyl trimethoxy silane. The mechanism of their action involves water repellency and air entrainment.

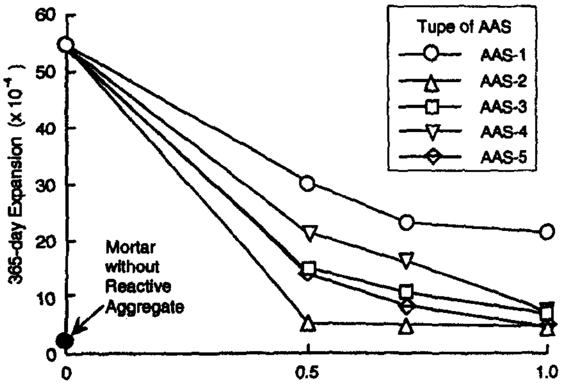

Fig. 8. The effect of silanes on alkali–aggregate expansion.

The possibility of using chelating agents to fix K ions was assessed by Hasni and Salomon[59]. Some reduction in expansion was obtained with crown ethers.

MINERAL AND RELATED ADMIXTURES

Introduction

The use of mineral admixtures in concrete results in several beneficial effects such as lower permeability, resistance to thermal cracking, decreased alkali–aggregate and sulfate expansion. Broadly mineral admixtures comprise natural mineral substances and by-products from industries. The Canadian Standard (A.23.5-1986) describes mineral admixtures. Class N is a raw or calcined natural pozzolan such as volcanic ash, diatomaceous earth, schist, and opaline hornfel. Fly ash consists of class F produced normally from burning anthracite or bituminous coal and class C, normally produced by burning lignite or sub-bituminous coal and generally shows hydraulic properties. Class G or H are granulated blastfurnace slags and class U is condensed silica fume produced from silicon or ferrosilicon industries and contains at least 85% SiO_2. Rice husk ash with pure silica in a non-crystalline form is also treated as a mineral admixture. Burnt clays and shales possessing pozzolanic properties, although not economical alternatives to slag or fly ash may also be considered as mineral admixtures.

Fly ash

The majority of fly ashes have a chemical composition in the range, 42–50% SiO_2, 16–30% Al_2O_3, 5–10% FeO and Fe_2O_3, 2–4% CaO and 5% alkalis[7]. The average particle size range of fly ash is 0.5–200 mm, specific gravity being 2–3, and a Blaine surface area of 250–325 $m^2\,g^{-1}$ for class F and 300–400 $m^2\,g^{-1}$ for class C. The pozzolanic activity of fly ash depends on its fineness and glassy content.

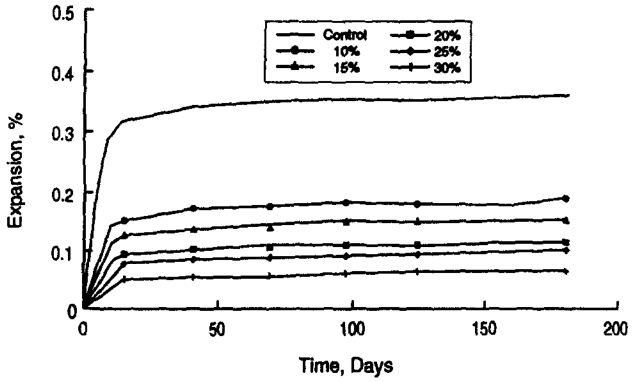

Fig. 9. The effect of different amounts of fly ash on expansion.

Fly ash in concrete is capable of reducing the alkali silica and alkali silicate/silica expansion. Figure 9 provides data on the effect of 0–30% fly ash on alkali–aggregate expansion in mortars[7]. It is obvious that the effectiveness of fly ash depends on its amount in the mortar. The degree to which expansion is controlled by fly ash depends on its physical and chemical nature. Pepper and Mather (Table 6) using four fly ashes, estimated the minimum replacement of cement by fly ash needed to reduce the expansion by 75%[60].

The effectiveness of fly ash depends amongst others on the alkali concentration in it[61,62]. Three fly ashes viz., A, B and C containing 2.34, 3.07 and 8.55% alkalis (as Na_2O) were mixed with concrete to evaluate the amount required to cause <0.04% expansion. Even 40% C was not sufficient to meet the performance criteria. The amorphous or glass content in fly ash is also a critical factor dictating its effect on alkali silica reaction.

Table 6. Minimum replacement levels of fly ash for reducing expansion

Material	*Minimum % replacement*		
	14 days	*6 months*	*Average*
Fly ash II	48	36	42
Fly ash III	52	36	44
Fly ash IV	45	34	40

The factors that are to be considered for assessing the role of fly ash as an inhibitor for the alkali–aggregate expansion are the following. The R_2O content in fly ash tends to accelerate the alkali–aggregate reaction, quartz and mullite in fly ash decrease the expansion, and the quantity of alkali in cement determines the effective amount of fly ash needed in the mix. An empirical formula has been suggested by Kobayashi and co-workers to assess the effectiveness of fly ash in alkali-attack prone concrete[63].

$$\Sigma CA + 0.83\Sigma FA - 0.046\Sigma F < \text{or} = 4.2 \text{ kg m}^{-3}$$

where ΣCA, ΣFA and ΣF represent total alkali content in cement, fly ash and the total amount of fly ash respectively. By applying the equation for 14 fly ashes. It can be seen that fly ash with an alkali content $> 5.5\%$ is not a desirable amount of addition. From the equation it can be deduced that if the cement has 1.2% alkali and fly ash with as high as 4% alkali, the expansion can be controlled with 20% fly ash. In practice however, a safety factor should always be included. The role of fly ash and slag to control the expansion due to alkali–carbonate reaction has been reported by Soles and Malhotra[64]. The two year study indicated that slags are more effective in reducing the alkali carbonate than alkali–silica reaction. In contrast, the condensed silica fume and natural pozzolans were much less effective in suppressing alkali–carbonate reaction than alkali–silica/silicate reaction. It has been reported that high volume fly ash concrete(cement:fly ash = 155:212 kg m^{-3}), irrespective of the methods used for evaluation, is highly effective in inhibiting expansion due to alkali–aggregate reaction[65].

Slag

Slag consists of silicates, aluminosilicates of calcium and other bases. The granulated slag is a glassy material that is obtained when molten slag is rapidly chilled. The chemical composition of slag depends on the type of pig iron produced and on the type of iron ore. The mean composition of slag is 30–40% SiO_2, 8–18% Al_2O_3, 40–50% CaO, 0–8% MgO, 0–1% FeO, 0–2% Mn_2O_3 and 0–2% S.

The ability of slag to control alkali–aggregate expansion was first reported by Cox in 1950[66]. Many subsequent studies have confirmed the effectiveness of slags. Important references to work on slags are to be found in international conferences organized by the American Concrete Institute and in other reference books[7,17]. There is some disagreement on the effect of slag on alkali–carbonate reaction. Several hypotheses have been put forward to explain the action of slag. They include dilution effect, pozzolanic action, entrapment of alkalis in the CSH phase, changes in the C/S ratio of the CSH phase, changed role of calcium hydroxide and decreased permeability of slag cement concrete.

Table 7. **PS9.5**The effect of different amounts of slag on alkali–silica expansion in mortars

Age (days)	*Average expansion (%) (slag content)*				
	0%	*30%*	*40%*	*60%*	*75%*
28	0.47	0.15	0.09	0.02	0.01
56	0.51	0.17	0.10	0.02	0.01
180	0.51	0.17	0.11	0.03	0.02
270	0.51	0.16	0.11	0.03	0.02

The relative effectiveness of different amounts of slags on the expansion of mortar with a high alkali (1.19% Na_2O) cement, has been tested adopting the ASTM C-441 (Table 7)[67]. The expansion is reduced in the presence of slag. There is a considerable expansion reduction at 60% addition. If the criterion that the expansion should be less than 0.1% at 1 yr is applied, it would be appear that at least 60% slag is required to control expansion.

The contribution of alkalis in slag to the alkali–silica reaction determines the total expansion. According to Hobbs slags contribute one half of their total alkali content to the reaction[68]. Alasali's more recent work would suggest that the alkali contribution could be between 0 and 100%[69]. Table 8 contains the expansion data for concrete containing four slag concrete mixes with various amounts of alkalis[69].

In Table 8, cement was replaced by 50% slag containing 0.65% Na_2O equivalent. Mix C-1

Table 8. The effect of alkali content on expansion in Portland cement/slag concrete

	Alkali (kg m^{-3})			
Mix no.	*Cement*	*Addition*	*Total*	*% Expansion in 1 yr*
C-1	1.5	0	1.5	0.126
C-2	1.5	1.5	3.0	0.382
C-3	1.5	2.5	4.0	0.553
C-4	1.5	4.5	6.0	0.657

contained 1.5 kg m^{-3} alkali. In mixes C-2, C-3 and C-4 the alkali content was increased to 3,4 and 6 kg m^{-3} respectively. The specimens were cured at 38°C. The results in Table 8 were compared with those obtained in concrete containing no slag. The expansion of these mixes in terms of alkali contents showed the following: expansion in C-1 to C-3 mixes containing slag was greater than that containing no slag, indicating that in concrete with cement replaced by 50% slag, deleterious expansion occurs at a lower level than would be expected if only portland cement and/or added alkali contributed to alkali reaction. The results suggest that slag was effectively contributing nearly 1 kg m^{-3} of alkali to mix C-1 (assuming alkali content is the only cause for expansion). In conclusion the data indicated that slag had contributed all of its alkalis to mix C-1, only 2/3 to mix C-2, 1/3 to mix C-3 and none to mix C-4.

Although slag is very efficient in decreasing expansion due to alkali–silica reaction, its influence on alkali–carbonate expansion reaction has yet to be resolved[27,70].

In summary it can be concluded that inclusion of large amounts of slag (both air-cooled and granulated types) are effective in reducing the alkali–silica reaction and in some instances alkali–carbonate reaction. The mechanism of this action is determined by the dilution effect, fundamental properties inherent to the slag and the amount of alkalis in the slag.

Other siliceous additives

In addition to silica fume, fly ash and slag there are other natural or processed siliceous materials that can be used to suppress the expansion caused by the alkali–silica reaction. By the addition of these materials the OH concentration in the pore solution is readily decreased. Diatomite has been used to control the alkali–aggregate expansion. Mehta tested the efficiency of a highly active pozzolan obtained by incinerating rice hulls. The surface area of these ashes was about 50–60 $\mathrm{m}^2\,\mathrm{g}^{-1}$[71]. Table 9 shows how, by adding 15% of this active material, the expansion can be reduced by about 95%[71].

Natural pozzolans have also been used to control expansions in alkali-prone concrete systems. Santorin Earth, a volcanic ash has been found to decrease expansions caused by alkali–silica reaction. In an accelerated test the expansion could be reduced from 0.7% for the reference, to about 0.15% with 30% Santorin Earth[72].

Table 9. Effect of rice husk ash on expansion of mortar

Rice husk ash (%)	*Reduction in expansion (% of control)*		
	14 days	*3 months*	*6 months*
5	52.2	50.2	49.3
10	90.4	87.8	86.6
15	97.4	95.0	94.0
20	98.6	96.9	95.8

Zeolitic materials have also been investigated for countering the expansions. In one study the incorporation of this admixture in an amount of 24% was found to be unacceptable. It could however, be used in concretes exhibiting marginal expansions[73].

Calcined clays have pozzolanic properties and some work has indicated that they are capable of reducing the alkali–silica expansion substantially. In a study by Andriolo and Sgaraboza[74] it was found that at addition levels of 15% calcined clay the expansion was reduced from about 0.18 to 0.02%. Metakaolin, obtained by calcination of china clay has been tested for its ability to decrease the alkali–silica expansion[75]. Metakaolin was added in amounts of 0, 5, 10,15, 20 and 25% (cement replacement). Expansion was monitored over a period of 18 months. The concrete without metakaolin expanded by 0.45% in 6–9 months. Expansion is reduced to less than 0.01% with 10–15% by weight of metakaolin. Metakaolin in concrete did not result in a decrease in the compressive strength.

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