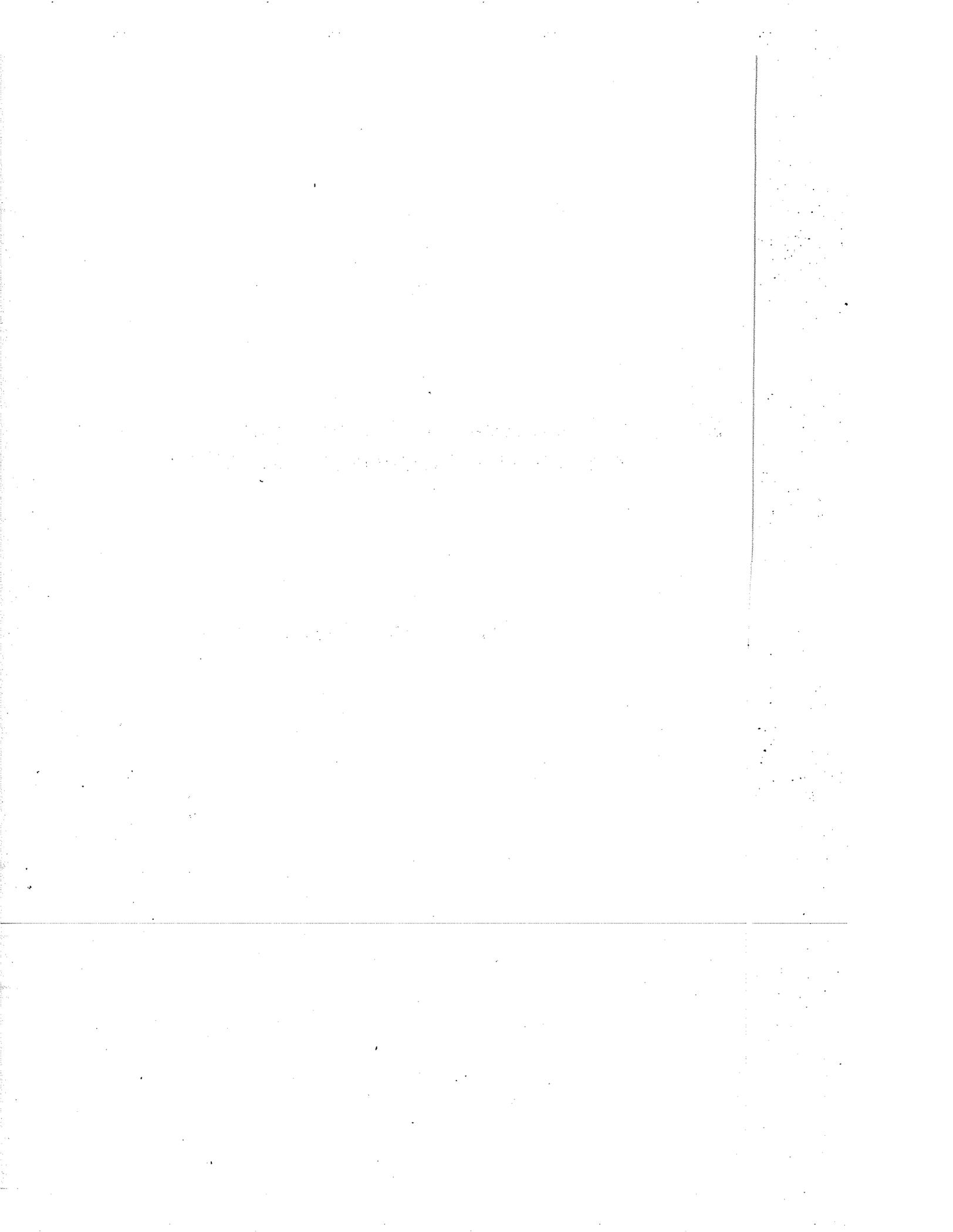


**SESSION 2**

**Effect of Mineral and Chemical Admixtures  
on Alkali-Aggregate Reaction**

**Keynote Lecture  
Dr. D. W. Hobbs**



**EFFECT OF MINERAL AND CHEMICAL ADMIXTURES  
ON ALKALI-AGGREGATE REACTION**

D W Hobbs

British Cement Association, Wexham Springs, Slough  
Berkshire SL3 6PL, United Kingdom

ABSTRACT

The use of mineral and chemical admixtures to prevent expansion due to the alkali-silica reaction (ASR) was first reported 40 to 50 years ago. Today there is still not universal agreement on the manner and extent to which these admixtures influence ASR expansion. This paper briefly reviews the literature dealing with the effectiveness of fly ash, slag, pozzolans, microsilica and chemical admixtures in reducing the risk of abnormal expansion due to ASR.

1. INTRODUCTION

A method of reducing or preventing the expansion of concrete due to the alkali-silica reaction (ASR) is to replace a proportion of a high alkali Portland cement by a mineral admixture (latent hydraulic binder). This approach has been used successfully in a number of structures. There is, however, not universal agreement that mineral admixtures are always effective. The following statement appears in a report prepared by a US committee[1].

'Use of silica fume in adequate dosage appears to reliably prevent damage. Use of fly ash, natural pozzolan and slag may prevent damage, but testing of the specific material is usually necessary to ensure favourable results in practice since some materials of this type are relatively ineffective or indeed hazardous'.

The effectiveness of a mineral admixture in reducing expansion due to ASR is often assessed using the ASTM C-441 test. In this test the expansion of mortar bars with fixed proportions of cement, mineral admixture and Pyrex is measured at 38°C. The results of this test can only be taken to be applicable to mortars and concretes with the specified mix proportions containing Pyrex and stored at 38°C. The C-441 test is unsatisfactory because Pyrex, unlike natural aggregate, is non-porous and contains a large quantity of alkalis which may be released into solution. The test also uses a binder content of about 600 kg/m<sup>3</sup> and at this level the reactivity of the mineral admixture may be substantially different to that at a more normal cement content. The test also recommends that the mineral admixture may be considered effective if it reduces expansion by 75%. This implies that the mineral admixture may be used in a concrete even if abnormal expansion, commonly assumed to be an expansion greater than 0.05%, is observed to occur.

In the field, pfa and natural pozzolans have not always proved effective in preventing cracking and expansion due to ASR. Examples are:-

(i) A test road constructed at McPherson, Kansas [2]. In this road 25% of the cement was replaced by one or other of three mineral admixtures - two natural pozzolans and a fly ash. It was found that the three pozzolans increased the number and width of the transverse cracks. Increased expansion from the use of fly ash has more recently been reported in Nebraska, Missouri, Iowa and Indiana [3].

(ii) The Hanshin Expressway in Japan. A proportion of the piers supporting this expressway, which cracked as a consequence of ASR, contain about 20% fly ash by mass of cement[4].

In this paper the literature dealing with the effectiveness of fly ash, slag, pozzolans, microsilica and also chemical admixtures in reducing the risk of deleterious expansion due to ASR is briefly reviewed.

## 2. FLY ASH (LOW LIME)

### 2.1 Alkalis in Fly Ash

Fly ash is a high glass content by product of the electricity industry. Fly ash in concrete reacts with water and the calcium hydroxide released by a Portland cement to form calcium silicate and calcium aluminate hydrates. This reaction, at normal temperatures, occurs at a much slower rate than the hydration reactions of Portland cement. The alkalis in a fly ash are bound in the glassy phases and at normal temperatures are released at a much slower rate than those present in a Portland cement. The total alkali content of fly ashes expressed as equivalent sodium oxide range from about 0.7 to 7.8% by mass. This compares with a range of about 0.3 to 1.6% by mass for a Portland cement.

The partial replacement of a cement by fly ash influences the total available hydroxyl ion content, setting time, entrapped air content and strength development. All of these factors may have an influence upon the effectiveness of fly ash in reducing the risk of cracking due to ASR but its most important influence is perhaps its effect upon total hydroxyl ion content. Strength data have shown that the contribution to strength of a fly ash, and consequently its reactivity, is dependent both upon the percentage of cement replaced and the binder content [5], it is therefore likely that the effectiveness of a fly ash in reducing the risk of cracking due to ASR will be dependent upon both of these parameters.

In 1987 Nixon and Page [6] reviewed the published results of hydroxyl ion and alkali ion determinations on samples of pore fluid expelled from pastes and mortars in which part of the cement had been replaced by fly ash whilst maintaining a constant water-binder ratio. In 1988 further test data were published by Kawamura and Takemoto[7]. In this work, the expelled fluid is assumed to be representative of the uncombined water within the specimens and to determine the total hydroxyl ion content it is necessary to know the uncombined water content. From the published data the following conclusions may be drawn, firstly, that at low replacement levels, 5 to 10%, the effective hydroxyl ion contribution from a fly ash may be substantially higher than the contribution from an equivalent mass of a high alkali cement [7], secondly, that at higher replacement levels the contribution may be substantially less [6] and, thirdly, that the partial replacement of a low alkali cement by fly ash may be ineffective in reducing the total hydroxyl ion content[6]. Nixon and Page suggest that at late ages, fly ash may reduce the alkalis in the pore solution below that produced by simple dilution of the cement alkalis.

The alkalis released from a fly ash have also been measured using the ASTM C-311 test method and using a modified test procedure in which the alkali released by fly ash is determined when blended in various proportions with a Portland cement [8]. Using the former approach Barlow and Jackson [8] observed that the alkali released by the three UK fly ashes tested ranged from 33 to 39% of their total alkali content and using the latter approach it was deduced that the alkali released from the one UK fly ash tested decreased with increasing percentage of fly ash, ranging from 48% at a fly ash content of 50% to 24% at a fly ash content of 70%.

The pore solution studies described above are not necessarily applicable to concretes containing reactive silica because the presence of such silica would deplete hydroxyl ions and alkali ions from the pore solution and this would change the mass balance. This could well lead to release of alkalis from the components of the paste. This is supported by the results of leaching tests on Portland concrete cubes and cubes in which 50% by mass of a high alkali cement was replaced by fly ash with an equivalent sodium oxide content of 3.32% by mass [9]. Here the distilled water in which the cubes were immersed can be regarded as analogous to reactive silica as this water also depletes ions from the pore solution within the concrete.

## 2.2 Expansion Tests

In 1986 Hobbs reviewed [9] much of the published data on the effectiveness of fly ash in reducing expansion in mortars and concretes containing natural reactive aggregates. More recent papers include those by Kawamura and Takemoto [7], Carrasquillo and Snow [10] and Perry et al [11]. Many investigators have carried out expansion tests on Portland cement/fly ash mortars containing natural reactive aggregates but relatively few tests have been carried out on concrete and rarely have tests been carried out at the critical alkali-silica ratio or at low reactive silica contents. The reactive aggregates used in the tests have been mainly aggregates containing opaline silica or volcanic glass.

The effective alkali contribution from a fly ash (or slag) can be estimated using the approach illustrated in Figure 1 where the expansion is shown plotted against the alkali contributed by the Portland cement. If this approach is used, then it is necessary to carry out tests on mortars and concretes made with a range of Portland cement alkali levels. The specimens should be tested at their critical alkali-silica ratio or alternatively using the aggregate grading which is to be used on site. Tests should also be included at the binder contents which may be used in practice and if tests are carried out at a high temperature then it is necessary to correlate the results with observations made at temperatures which the concrete is subjected to in the field.

In the tests on mortars and concretes the replacement of 30% of a high alkali cement by fly ash has generally been found to reduce expansion due to ASR but an analysis of the results of expansion data reported by a number of investigators leads to the conclusions that the effectiveness of a fly ash is dependent upon its total alkali content [7,9-12] and that in the presence of fly ash deleterious expansion can occur at lower alkali contents than would be expected if only the Portland cement alkali contribution was important [9,12]. This is illustrated in Figures 2 and 3 where expansion results obtained on mortars [9,13] and on concrete respectively are shown plotted against Portland cement alkali contribution. Some expansion test data have

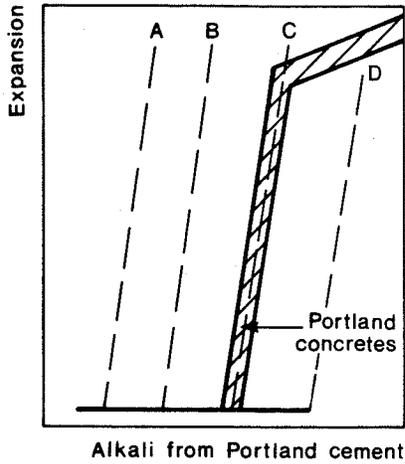


Figure 1. Procedure for determining effectiveness of fly ash (or slag). If 30% cement replaced the effective alkali contribution is: A-higher than cement, B-the same, C-zero, D-negative.

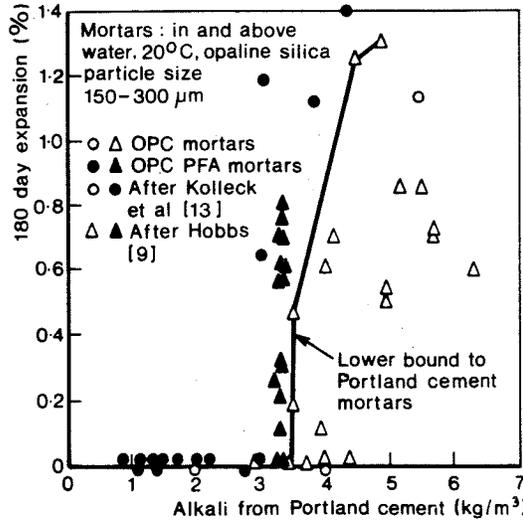


Figure 2. Variation of expansion at 180 days with acid soluble alkali content contributed by Portland cement.

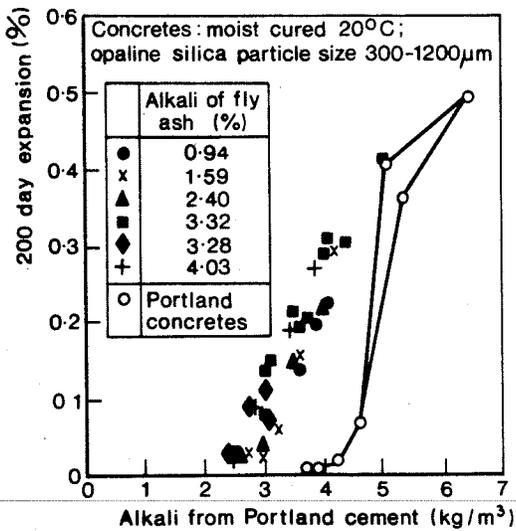


Figure 3. Variation of expansion at 200 days with alkali content contributed by Portland cement.  $50 \geq 100f/(c+f) \geq 20$ ,  $w/(c+f) 0.41$ ,  $a/(c+f) 3$ , Thames Valley coarse. 2 replications.

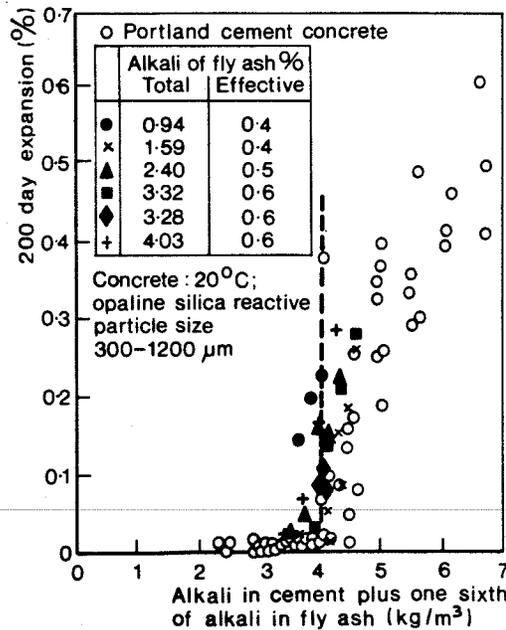


Figure 4. Variation of expansion at 200 days with alkali in cement plus one sixth of alkali in fly ash.

been reported which do not support the conclusion that fly ash makes a positive alkali contribution to the reaction [14-16]. Nixon et al [16] have postulated that UK reactive aggregates react more slowly than those tested in the laboratory and hold the view that with such aggregates the assumption that fly ash makes no alkali contribution to the reaction may be a conservative one in relation to cements with moderate to high alkali content. However evidence does exist that certain UK aggregates can contain a small proportion of a highly reactive form of silica[17].

From the data shown in Figures 2 and 3 it may be concluded that the effective alkali contribution from the fly ashes, at cement replacement levels in excess of 20%, was very approximately one sixth of their total alkali content[12]. This is illustrated in Figure 4 where expansions obtained on concrete are shown plotted against Portland cement alkali plus one sixth of the fly ash alkali. In these tests the proportion of opal was varied to ensure that the concretes were tested close to their critical alkali-silica ratio based on the assumption that fly ash contributes no alkalis to the reaction. Note that the effective alkali contribution of the lowest alkali fly ash was substantially higher than one sixth of its total alkali content indicating that parameters other than fly ash alkali contribution may be influencing expansion. Several investigators have reached a similar conclusion [6,7,11].

In the case of mortars in which only 5-20% by mass of a high alkali cement was replaced by fly ash it has sometimes been observed that expansion is increased [7,10,18]. This means that at low replacement levels the effective alkali contribution from a fly ash may be higher than that of a high alkali Portland cement.

### 3. SLAG

#### 3.1 Alkalis in slag

Ground granulated blastfurnace slag (slag) is a high glass content by product produced in the manufacture of iron. Slag reacts in the presence of calcium hydroxide and water to form calcium silicate and calcium aluminate hydrates. At normal temperatures the reaction occurs at a slower rate than those of Portland cement, however with today's slags the compressive strength gain after 28 days for concretes moist cured at 20°C is not markedly different to that of a plain Portland concrete. In slag the alkalis are bound in the glassy phases and are released at a slower rate than those in a Portland cement, but at a faster rate than those in a fly ash. The acid soluble alkali content of slags expressed as equivalent sodium oxide range from about 0.3 to 2.6% by mass.

The partial replacement of a cement by slag influences the same parameters as does fly ash but its influence is also likely to be dependent upon its fineness. In the context of ASR, a slag's most important influence is probably its effect upon total hydroxyl ion content. Strength data indicate that the reactivity of slag is dependent both upon the percentage of cement replaced and the binder content, both of these parameters are therefore likely to influence the effectiveness of slag in reducing the risk of cracking due to ASR.

Nixon and Page [6] have reviewed the results of analyses on the pore fluid extracted from samples containing slag. In 1988 further test data were published by Kawamura and Takemoto [7]. According to the published data slag makes a positive contribution to the total hydroxyl ion and alkali

content but the contribution is less than that of a high alkali cement but more than that of a low alkali cement[6]. Kollek et al [13] found that the contribution declined with increasing slag content and Kawamura and Takemoto [7] found that at a slag content of 5% the contribution could be higher than that from an equivalent mass of a high alkali cement.

Barlow and Jackson[8] have measured the alkali released by three slags using the ASTM C-311 test method and the alkali released by one slag using a modified test procedure in which the slag was blended with various proportions of a Portland cement. Using the former approach it was observed that the alkali released by the slags ranged from 39 to 63% of their total alkali content and using the latter approach it was deduced that the alkali released by the slag was higher than that observed using the normal ASTM C-311 test procedure and that the proportion of alkali released decreased with increasing percentage of slag.

### 3.2 Expansion tests

Much of the published data on the effectiveness of slag in reducing expansion in mortars and concretes containing natural reactive aggregates was reviewed in a paper published in 1986 [9,12]. More recent papers include those by Kawamura and Takemoto[7], Kollek et al[13] and Yamamoto et al[19]. Nearly all the reported expansion tests have been carried out on mortars and rarely have tests been carried out at the most critical alkali-silica ratio or at low reactive silica contents. The reactive aggregates tested have been mainly aggregates containing opaline silica or to a lesser extent volcanic glass. The effective alkali contribution from a slag can be estimated using the approach illustrated in Figure 1.

In the tests on mortars and concretes containing natural reactive aggregates, the partial replacement of a high alkali cement by more than 20% slag has been found to reduce expansion due to ASR, but the partial replacement of 5% of a high alkali cement by slag has been found to increase expansion. It has been suggested that the reduction in expansion is due to a slower diffusion of hydroxyl ions in a concrete containing slag. Whilst this may be so if the hydroxyl ions were diffusing into the concrete from an external source, it is unlikely to be so when the hydroxyl ions are already present and distributed throughout the paste matrix.

Expansion test data published by Oberholster and Westra[15] indicate that slag may make a negative effective alkali contribution to the reaction[9]. However, an analysis of the results of expansion test data obtained by a number of other investigators [9] leads to the conclusion that, in the presence of slag, deleterious expansion can occur at lower alkali contents than would be expected if only the Portland cement alkali content was important. This is illustrated in Figure 5 where expansion data obtained by Kollek et al [13] on mortars using three slags is shown plotted against the Portland cement alkali contribution. The highest alkali slag was found to be least effective in reducing expansion. Kawamura and Takemoto [7] in tests on eight slags with alkali levels ranging from 0.43 to 0.57% by mass found an excellent correlation between expansion and alkali level of the slag, however, published expansion data obtained by Lenzner and Ludwig [20] using slags of three alkali levels, show no dependence of expansion upon the alkali level of the slag.

Figure 6 shows the results of recent expansion tests carried out at BCA on concretes in which between 30 to 55% of a high alkali cement was replaced by

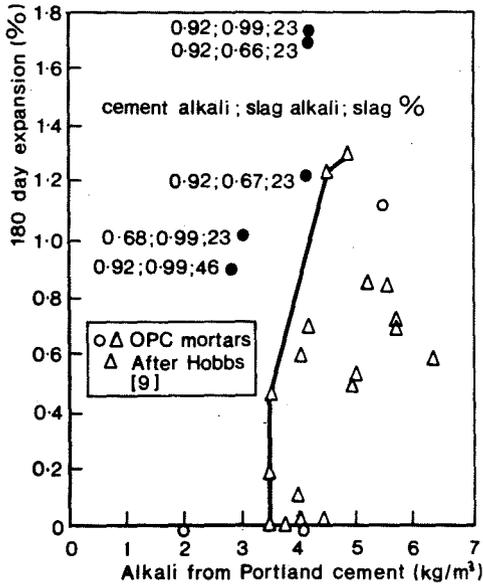


Figure 5. Variation of expansion at 180 days with acid soluble alkali content contributed by Portland cement (Mortars coarse, 2 replications in or above water, 20°C, opaline silica particle size 150-300 μm).

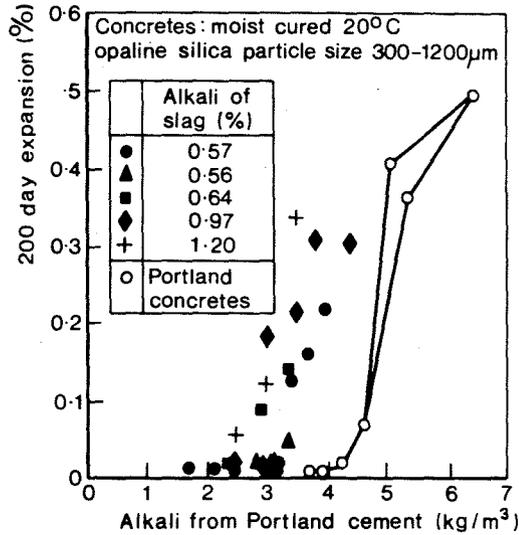


Figure 6. Variation of expansion at 200 days with alkali content contributed by Portland cement. 55 ≥ 100 s/(c+s) > 30, w/(c+s) 0.41, a/(c+s) 3, Thames Valley Mortars coarse, 2 replications.

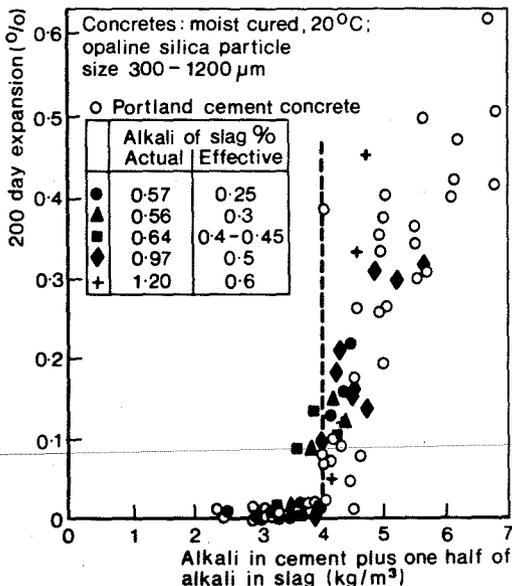


Figure 7. Variation of expansion at 200 days with alkali in cement plus one half of alkali in slag.

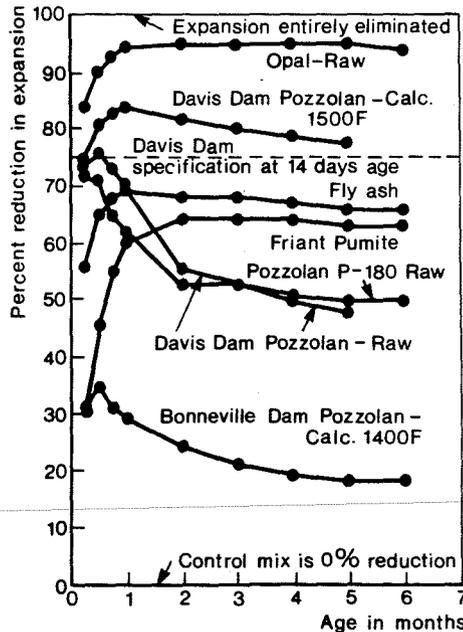


Figure 8. Reduction in expansion due to ASR by replacement of 20% of cement with various pozzolans (1:2.25 mortar, cement alkali 1.23%, crushed Pyrex, 38°C).

one or other of five slags. In these tests the proportion of the opaline constituent used was adjusted to maintain the ratio of alkali to reactive silica close to its critical value, the assumption being made that slag contributes no alkalis to the reaction. The effective alkali content of the slags was approximately one half or more of their acid soluble alkali content. This is illustrated in Figure 7 where expansion is shown plotted against Portland cement alkali plus one half of the slag alkali.

#### 4. NATURAL AND ARTIFICIAL POZZOLANS

##### 4.1 Effect upon expansion

A natural or artificial pozzolan is a fine material containing silica which in the presence of water combines with lime at normal temperatures to produce compounds having hydraulic properties. Volcanic glass is the most widely used natural pozzolan. Calcination at temperatures below 1100°C can convert essentially inert substances into pozzolans and can improve or reduce the quality of some pozzolans [21]. In a number of the early investigations carried out in the 1940's it was found that the partial replacement of a high alkali cement by certain pozzolans could prevent expansion due to ASR occurring. For example, Blanks in 1949 [22] found that effective pozzolans included calcined siliceous (opaline) shale, certain pumicites and tuffs, opal, Pyrex glass and diatomaceous earth. However, Blanks also found that Bonnerville Dam pozzolan 'was entirely ineffectual as an inhibitor of expansion'. Some results obtained by Blanks are shown plotted in Figure 8. Finely ground aggregates containing high proportions of reactive silica, if used in sufficient quantities can also inhibit abnormal expansion from occurring (< 20 μm).

Mielenz et al [21] classified pozzolans in terms of their essential reactive ingredient as following:

Activity Type: 1	Essential Reactive Ingredient: Volcanic glass
2	Opal
3a	Kaolinite-type clay
3b	Montmorillonite type clay
3c	Illite type clay
3d	Mixed clay with vermiculite
4	Zeolites
5	Hydrated oxides of aluminium

Pozzolans of activity types 1, 2, 3a and 3b are according to Mielenz et al the most promising for control of alkali-silica reactivity with type 2 being superior to all others.

In tests on a 1:2.25 mortar mix, Stanton [23] found that 10 to 15% replacement of a cement with an alkali content above 1.0% by mass, by Monterey opaline cherts, cherty shales and porcelaneous shales was sufficient to prevent deleterious expansion from occurring. A similar conclusion was reached for a Californian high opal content chert. These pozzolans had silica contents and alkali levels probably above 80% and below 1.3% by mass respectively. Stanton found that lower silica pozzolans namely Purgatory Hill Clay (SiO<sub>2</sub> 63%, Na<sub>2</sub>O 3.9%) and Fresno pumicite (SiO<sub>2</sub> 72%, Na<sub>2</sub>O 6.0%) were less effective in preventing expansion. Lerch [3] found that neither calcined Mowry shale

(SiO<sub>2</sub> 66%, Na<sub>2</sub> 1.4%) nor calcined Monterey shale (SiO<sub>2</sub> 63%, Na<sub>2</sub>O 2.4%) were effective in reducing expansion. Stanton also concluded that 'the activity of the pozzolan appears to be related to the percentage of silica readily soluble in sodium hydroxide'. Pepper and Mather [24] reached a similar conclusion.

#### 4.2 A possible explanation for the action of pozzolan

Fly ash and slag when used as partial replacements for high alkali Portland cement act primarily as alkali diluters. However, in the case pozzolans, it can be argued that their use as a partial replacement for cement promotes the formation of a calcium-alkali-silicate hydrate whilst the concrete is in a fresh state. This rapid reaction can be attributed to the presence of fine particles containing opaline or amorphous silica. With certain pozzolans used in sufficient quantities, the sodium and potassium alkalis released by the Portland cement (and pozzolan) may be largely depleted, or alternatively reduced to a threshold level, before the concrete develops strength. The reactive silica present in the aggregate will then either not react or alternatively will react at an insufficient intensity to induce abnormal expansion. If it is assumed that the alkali-silica ratio in the hydration product is similar to that of the ASR gel, then the partial replacement levels of Portland cement by 'amorphous' silica, necessary to ensure that the reaction is essentially complete prior to the concrete developing strength, can be estimated from the expansion curves for mortars and concretes containing opaline silica [12]. Table 1 gives the minimum percentages of 'amorphous' silica by mass of cement which may be sufficient to prevent abnormal expansion assuming the 'amorphous' silica content of the aggregate is 0.5, 2 and 4% by mass of total aggregate. The percentage required is dependent both upon the mix proportions and the proportion of reactive silica in the aggregate. The percentage required is also dependent upon the alkali content of the cement. Table 1 is applicable to a pozzolan consisting solely of 'amorphous' silica and consequently the replacement levels are lower bounds. The replacement levels necessary to prevent abnormal expansion will increase as the 'amorphous' silica content of the pozzolan reduces and as the alkali present in this silica increases. For a pozzolan containing 70% 'amorphous' silica, with an equivalent sodium oxide content of 3.0% by mass all of which is present in its 'amorphous' silica fraction, the higher percentages given in Table 1 should be roughly doubled.

#### 5. MICROSILICA

Microsilica (silica-fume) is a by product of the manufacture of silicon metal or ferro-silicon alloys. Microsilica contains between 84 and 98% by mass of amorphous silica with an average particle diameter of less than 0.1µm. When present in a concrete it hydrates at a much faster rate than Portland cement. The equivalent sodium oxide content of a micro-silica is less than 2.4% by mass.

The use of microsilica as a partial replacement for a Portland cement promotes the formation of a calcium-alkali-silicate hydrate while the concrete is in a fresh state. This rapid reaction is due to the ultra-fine amorphous silica particles. A number of investigators have shown that the partial replacement of a high alkali cement by a sufficient quantity of microsilica can prevent abnormal expansion from being induced by ASR. The minimum replacement levels obtained by a number of investigators are given in Table 2. According to Hobbs [12], the minimum cement replacement level by microsilica necessary to prevent expansion depends upon the alkali content of the cement,

Table 1 - Minimum percentage of 'amorphous' silica required to prevent cracking due to ASR. Cement equivalent  $\text{Na}_2\text{O}$  1.05%.

Water/cement	Aggregate/cement	'Amorphous' silica content *		
		Opaline silica content †		
		0.5	2	4
0.35	1	11.5	10	8
0.41	2	12	8	4
0.47	3	9.5	5	0
0.53	3.75	7	1.5	0
0.59	4.5	7	0	0

\* % by mass of cement. † % by mass of aggregate.

the mix proportions, the reactive silica content of the aggregate and the proportion of amorphous silica and equivalent sodium oxide in the microsilica.

Table 1 gives the minimum cement replacement levels estimated by Hobbs for a microsilica consisting of a 100% amorphous silica. The replacement levels are applicable to a cement with an alkali content of 1.05% by mass and should only be taken as a guide as the use of microsilica may induce changes in the properties of the concrete which influence the replacement levels. For a microsilica containing 80% amorphous material with an equivalent sodium oxide content of 2% by mass, the higher percentages in Table 1 should be increased by about 60%. The minimum replacement levels predicted by Hobbs are compared with those determined experimentally in Table 2 [12]. With one exception, there is broad agreement between the observed and predicted minimum replacement levels. Up to 20% replacement of a high alkali cement (1.05%) by microsilica may be necessary to prevent abnormal expansion due to ASR in a high cement content concrete.

## 6. CHEMICAL ADMIXTURES

### 6.1 Influence upon expansion

The use of chemical admixtures to prevent expansion due to ASR was first reported in 1950 [29]. Nearly 40 years later the use of chemical admixtures for this purpose are still in an experimental stage. According to Mailvaganan [30] the requirements of a suitable admixture are as follows: (1) It should form a relatively soluble hydroxide, (2) It should react to produce an insoluble silicate (3) The ions must not interfere with or modify the cement hydration reactions and (4) The ions should not take part in the alkali-aggregate reaction to form other expansive materials. They should of course also be of reasonable cost and harmless.

The addition of small quantities (less than 1% by mass of cement) of alkali sulphates, chlorides, nitrates and carbonates at the mixer stage have been observed to increase the expansion of mortars [12,31,32]. Mehta [31] and Nakono et al [32] found that expansion was influenced greatly by the alkali compound used, but the effects observed by these investigators were not the same apart from sodium chloride which induced the highest [32] or second highest expansion [33]. Hobbs [9] observed a smaller dependence of expansion upon the alkali compound added but found that sodium chloride had the most adverse effect upon expansion.

Table 2 Microsilica. Minimum replacement levels necessary to prevent expansion

Reference	Microsilica		Mix proportions		Reactive Silica (%)	Equivalent Na <sub>2</sub> O cement (%)	Minimum microsilica content (%)	
	SiO <sub>2</sub> (%)	Equivalent Na <sub>2</sub> O (%)	w/c	a/c			Observed	Predicted
15	94	0.48	-	1.5	Low	0.97	15	13
25	95	-	0.45	2.25	4.0	High	4	4
26	94	0.53		2.25	2.0	1.00*	20	11
27	91	2.38	0.40	0.75	5.0	0.76	20	16
28	88	2.15	0.40	0.75	5.0	0.76	15	15
28	89	1.97	0.40	0.75	5.0	0.76	15	15
28	87	1.44	0.40	0.75	5.0	0.76	15	14
12	96	0.34	0.41	3.0	0.5	0.93	5-10	9-10
12	96	0.34	0.41	3.0	1.0	0.93	5-10	7-9

\* Aggregate replaced by microsilica. + Sodium hydroxide added.

McCoy and Caldwell [29] found that small additions of a number of substances (generally < 1% by mass of cement) increased the expansion of mortar bars containing Pyrex glass, including barium carbonate, calcium and ferric chlorides, nickel nitrate and lactic acid. The substances which were most effective in reducing expansion, at the addition(s) employed, were copper sulphate, the lithium salts and air-entraining agents, the greatest reductions being achieved with lithium salts. The effectiveness of copper sulphate, lithium carbonate and two air-entraining agents were further checked using mortars containing opal. The two air-entraining agents and 1% lithium carbonate were found to significantly reduce ASR expansion but copper sulphate did not. Hobbs [9] also found in tests, on concretes containing a pessimum quantity of opal, that expansion was reduced by air-entrainment but even at an air content in the hardened concrete of 3.6% observed deleterious expansion. The alkali content in these concretes was 5.0 kg/m<sup>3</sup>.

## 6.2 Air Entrainment

In field concretes containing a reactive aggregate which have not shown cracking due to ASR, gel can often be found filling or partially infilling air voids. The gel is therefore able to migrate through undamaged concrete. It is also known that, in concretes containing a reactive sand, the alkali content necessary to induce abnormal expansion increases as the porosity of the coarse aggregate goes up. It is therefore likely, as McCoy and Caldwell's [29] results show, that air-entrainment will reduce the risk of expansion and cracking due to ASR and also that the effect will be most marked when copious quantities of gel are not formed in the concrete e.g. the reactive silica content is well below the pessimum. The author finds it surprising that such little research, particularly on externally stored concrete, has been carried out in this important area.

## 7. ACKNOWLEDGEMENTS

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