

**EXPANSION DUE TO ALKALI-SILICA REACTION AND  
THE INFLUENCE OF PULVERISED FUEL ASH**

by Dr D W Hobbs\*

**SYNOPSIS**

In accelerated laboratory testing the addition of pulverised fuel ash to a concrete containing a constant proportion of reactive material can prevent the destructive effects of the alkali-silica reaction from occurring. However there is field evidence that additions of pulverised fuel ash to a concrete containing a reactive constituent may not always be beneficial.

An extensive series of tests has been undertaken in which six good quality pfa's have been used, with known reactive opaline material as the aggregate.

Results obtained from a range of OPC 'concretes' showed that cracking was only induced by the alkali-silica reaction when the water soluble alkali content, expressed as equivalent  $\text{Na}_2\text{O}$ , was greater than  $2,5 \text{ kg/m}^3$ .

**SAMEVATTING**

Gedurende versnelde laboratoriumtoetse kan die byvoeging van poeierkoolas by 'n beton, wat 'n konstante hoeveelheid reaktiewe materiaal bevat, voorkom dat die vernietigende uitwerking van die alkali-silikareaksie plaasvind. Daar bestaan egter veldbewyse dat byvoegings van poeierkoolas by beton, wat 'n reaktiewe bestanddeel bevat, nie altyd voordelig mag wees nie.

'n Uitgebreide reeks toetse is uitgevoer waarin van ses soorte hoëgraad-poeierkoolas gebruik gemaak is met bekende reaktiewe opaal materiaal as aggremaat.

Resultate wat van 'n reeks gewone portlandsementbeton verkry is, het getoon dat krake slegs deur die alkali-silikareaksie opgewek is in gevalle waar die wateroplosbare alkali-inhoud, uitgedruk as  $\text{Na}_2\text{O}$  ekwivalent, groter as  $2,6 \text{ kg/m}^3$  was.

S252/30

Conference on alkali-aggregate reaction in concrete  
Cape Town - South Africa  
March 30 - April 3, 1981

Konferensie oor alkali-aggremaat-reaksie in beton  
Kaapstad - Suid-Afrika  
30 Maart - 3 April, 1981

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## 1. SUMMARY

The results of experimental studies to determine the effectiveness of six pulverised fuel ashes (pfa) in reducing expansion due to the alkali-silica reaction in mortar bars are described. In many of the tests the ratio of the water soluble alkali to reactive silica content of the mortar bars was chosen so as to ensure that the expansion produced by the reaction would be close to the maximum attainable with the particular cement, pfa and aggregate combination employed. It is shown that the relationship between the expansion observed at 200 days and the water soluble alkali content is independent of the content of pfa in the mortar bars.

## 2. INTRODUCTION

The amount of damage or cracking produced by the alkali-silica reaction (ASR) is related to the quantity of reactive aggregate and the total available 'alkali' in solution, the available 'alkali' being dependent upon both the mix proportions of the concrete, the water soluble alkali content of the cement, the water soluble alkali content of the aggregate and sometimes the diffusion of alkali from sources external to the concrete. This dependence upon available 'alkali' is illustrated in Figure 1 where the time to cracking is shown plotted against water soluble alkali content\* expressed as equivalent  $\text{Na}_2\text{O}$  for mortar bars having water soluble alkali-reactive silica ratios close to their most critical value and in Figure 2 where the expansion at 200 days is shown plotted against water soluble

alkali content for specimens having three alkali-silica ratios. Crushed Beltane opal having a particle size of 150 to  $300\mu\text{m}^2$ ,<sup>3</sup> was used as the reactive constituent within the aggregate and the mortar bars were stored under a small quantity of water in a room maintained at  $20^\circ\text{C}$ .

It is apparent from the data presented in Figures 1 and 2 that mortar in which the alkali to silica ratio is at the critical value will probably crack only if the water soluble alkali content is greater than  $2,5\text{ kg/m}^3$ . Since the lowest ratio of acid soluble to water soluble alkali content for the cements tested was 1,3 this means that cracking will probably only occur if the acid soluble alkali content of the mortar is greater than  $3,25\text{ kg/m}^3$ . A higher alkali content will be required to induce cracking and deleterious expansion in mortar which has either an alkali-silica ratio well away from its most critical ratio or alternatively, according to Gaskin, Jones and Vivian<sup>4</sup>, a siliceous constituent of lower reactivity than opal.

As the water soluble alkali content of pfa is relatively low compared to a cement it follows that the available alkali content of most concrete can be reduced by replacing part of the cement by pfa. Such a replacement will also reduce the alkali concentration in the pore water of the concrete in part due to the higher water to cement ratio and, according to some workers<sup>5,6</sup>, in part due to preferential reaction between the hydroxyl ions and pfa. Thus it would appear that replacing part of the cement by pfa should lessen the chance of a deleterious expansion occurring when the aggregate contains an alkali sensitive constituent. However field studies have shown that the addition of pozzolans, including pfa, to concretes containing a reactive siliceous constituent may not always be beneficial. For example Hadley<sup>7</sup> makes the following comments:

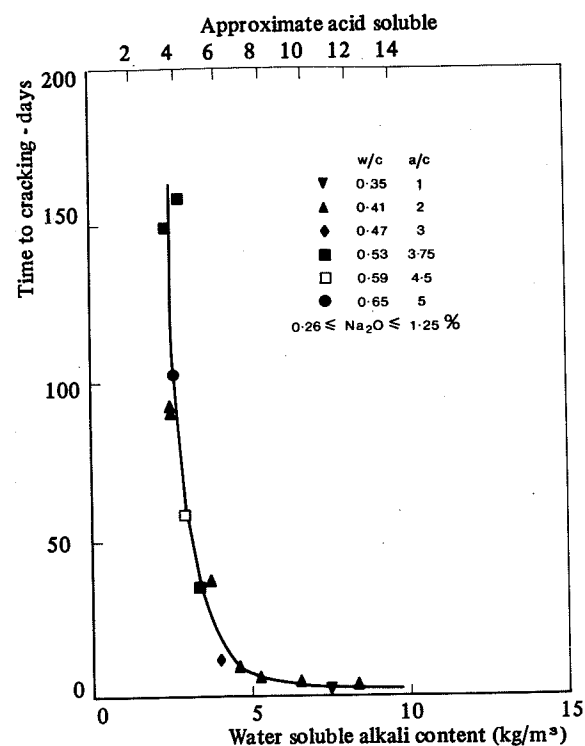


FIGURE 1: Variation of time to cracking with water soluble alkali content. 'Most critical' alkali-Beltane opal ratio.

\* The water soluble alkali content of 1 g of cement in 250 ml of distilled water at  $20^\circ\text{C}$  was measured at 24 hours as per the proposed amended method to BS 4550, part II.

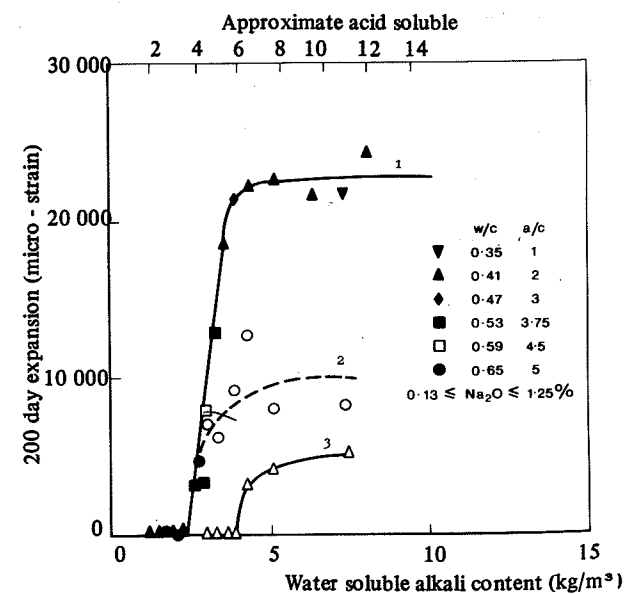


FIGURE 2: Variation of expansion at 200 days with water soluble alkali content. (1) 'Most critical' alkali-Beltane opal ratio. (2) Alkali-Beltane opal ratio = 0,12. (3) Alkali-Beltane opal ratio = 0,03.

cracking and excessive expansion have been caused by the ASR and it is this material which should be used in any test designed to determine the effectiveness of pfa, or other mineral admixtures, in reducing expansion of concrete due to ASR. Such tests have been carried out by Brinks and Halstead<sup>14</sup> and Lenzner and Ludwig<sup>15</sup>. Brinks and Halstead tested the effectiveness of 17 flyashes in preventing or reducing ASR using control specimens consisting of a 1:2 mix by mass with Ottawa sand containing 2 per cent reactive opal. The cement had an acid soluble alkali content expressed as equivalent Na<sub>2</sub>O of 0,9 per cent. In all other respects the ASTM C441 method was followed. At an age of 1 year it was found that the replacement of 35 or 50 per cent of the cement by pfa on a solid volume basis limited the expansion to a value comparable to that shown by mortar specimens containing non-reactive aggregate. At an age of one year it was also found that specimens prepared with 7 of the 17 flyashes in the 10 per cent replacement group showed more expansion than the control specimens.

The control specimens used by Lenzner and Ludwig<sup>15</sup> had an a/c ratio of 3,2, a w/c ratio of 0,5 and 4 per cent opaline sandstone by total mass of aggregate. The cement had an acid soluble alkali content of 0,9 per cent and the specimens were stored at 25 or 40 °C. Lenzner and Ludwig found that the replacement of 20 per cent by mass of the cement by flyash or the replacement of part of the aggregate by the same mass of flyash increased the expansion at early ages but reduced the expansion at later ages. Even so the expansion at 1 year for specimens stored at 25 °C was as high as 0,8 per cent.

TABLE 2 : Mix proportions

$\frac{w}{(c + pfa)}$	$\frac{a}{(c + pfa)}$	$\frac{pfa}{(c + pfa)}$ (%by mass)	alkali Beltane opal	pfa tested
0,41	2,75	0, 20, 40	0,067	All six
0,41	2,75	10, 30, 50	0,067	Ironbridge
0,53	3,5	0*, 30	0,067	All six
0,53	3,5	10, 20	0,067	Ironbridge
0,44	3,26	30*	0,067	Fiddlers Ferry, Eggborough, Ironbridge
0,41	2,75	20, 40	0,100	Ironbridge
0,41	2,75	20, 40	0,040	Ironbridge

\* These mixes had similar workabilities and produced mortars of similar 28 day compressive strength<sup>16</sup>

In the work reported by Brinks and Halstead<sup>14</sup> and Lenzner and Ludwig<sup>15</sup> a constant mass proportion of reactive aggregate was used. Thus their results relate only to arbitrary and variable alkali to silica ratios and cannot therefore be used to specify the cement replacement levels by pfa which are necessary to eliminate deleterious expansion due to ASR in concretes made using different cements and various mix proportions.

In the present paper results are reported on the effectiveness of six ashes in reducing expansion due to ASR using mortars in which the proportion of the reactive constituent was adjusted to ensure that the water soluble alkali-reactive silica ratio lay close to its critical value.

### 3. EXPERIMENTAL DETAILS

Expansion was measured at 20 °C on mortar specimens, 25 x 25 x 250 mm in size made from Thames Valley sand, plus a crushed opaline rock with particles in the size range 150 to 300 μm and cement blended with pfa. The opaline rock, known as Beltane opal, was obtained from the Beltane Quarry in Napa Valley, California, USA and was used in previous work<sup>17, 18</sup> where it was shown that the critical value for the ratio by mass of water soluble alkali to Beltane opal rock was about 0,06. Details regarding the six fuel ashes and the mix proportions used are given in Table 1 and 2 respectively and show that most of the mortar bars were made with an alkali to silica ratio close to the critical value. The cement used was an ordinary Portland cement of Bogue composition C<sub>3</sub>S 56 per cent, C<sub>2</sub>S 16 per cent, C<sub>3</sub>A 9,4 per cent and C<sub>4</sub>AF of 6,4 per cent with a water

'Although both Scholer<sup>9</sup> and Conrow<sup>9</sup> found that 'pozzolans' were effective in controlling expansion in accelerated laboratory tests, 'pozzolans' do not consistently prevent the field deterioration of the sand-gravel concretes . . . . . although Sutton<sup>10</sup> reports good results with pozzolans, Lerch<sup>11</sup> states in Bulletin 122 that, on the McPherson Test road 'pozzolans' were not effective in inhibiting map cracking and were found to increase both the number and width of the transverse cracks. Haboe<sup>12</sup> reports that studies by the Bureau of Reclamation have shown that additions of 'pozzolans' to sand-gravel concretes are sometimes actually harmful to concrete performance, and recommends that

'pozzolans' be used only after testing each specific aggregate-cement-pozzolan combination.'

The ASTM C441 test<sup>13</sup> is the test most commonly used to establish the effectiveness of a pfa in reducing expansion due to ASR. In this test the expansion of mortar bars, with fixed proportions of cement, admixture and Pyrex glass, is measured at 38 °C. The results are therefore only applicable to mortars and concretes with the specified mix proportions stored at 38 °C and containing Pyrex glass. However an opaline material is frequently found to be a constituent of the aggregate in those structures where

TABLE 1 : Analyses of pulverised fuel ashes\*

	Fiddlers Ferry	Eggborough	Ironbridge	Ratcliffe	Bold	Drax
SiO <sub>2</sub>	50,02	51,48	46,58	51,00	44,78	51,32
Fe <sub>2</sub> O <sub>3</sub>	9,02	8,70	14,24	10,14	13,75	10,29
Al <sub>2</sub> O <sub>3</sub>	26,83	28,08	25,22	26,22	26,91	25,81
MgO	0,93	0,93	0,95	1,08	1,00	0,90
SO <sub>3</sub>	0,79	1,15	1,29	0,90	0,91	0,58
L.O.I.	3,43	1,74	1,84	2,63	4,55	3,27
Moisture	0,18	0,18	0,20	0,27	0,20	0,18
Na <sub>2</sub> O (total)	0,88	1,13	0,80	1,30	0,70	0,98
Na <sub>2</sub> O (acid)	0,24	0,25	0,18	0,26	0,21	0,17
Na <sub>2</sub> O (water)	0,07	0,10	0,08	0,10	0,06	0,06
K <sub>2</sub> O (total)	3,90	3,85	2,35	3,35	3,80	3,80
K <sub>2</sub> O (acid)	0,72	0,56	0,33	0,39	0,62	0,29
K <sub>2</sub> O (water)	0,07	0,11	0,04	0,05	0,07	0,05
Chloride	0,003	-	0,002	0,001	0,007	-
Density (kg/m <sup>3</sup> )	2390	2290	2420	2200	2150	2130
Surface (m <sup>2</sup> /kg)	370	330	375	345	420	235
Mass percent greater than 45 μm	6,7	7,4	4,7	21,7	19,5	40,2

\* Sulphide was not detectable in any of the ashes.

taining pfa and this resulted in a reduced long term expansion. Mortars containing Ironbridge pfa expanded the least in the long term.

Additional test results obtained using Ironbridge pfa are shown plotted in Figures 6 to 9. In the latter two Figures the results were obtained on specimens having water soluble alkali-Beltane opal ratios of 0,100 and 0,040 respectively.

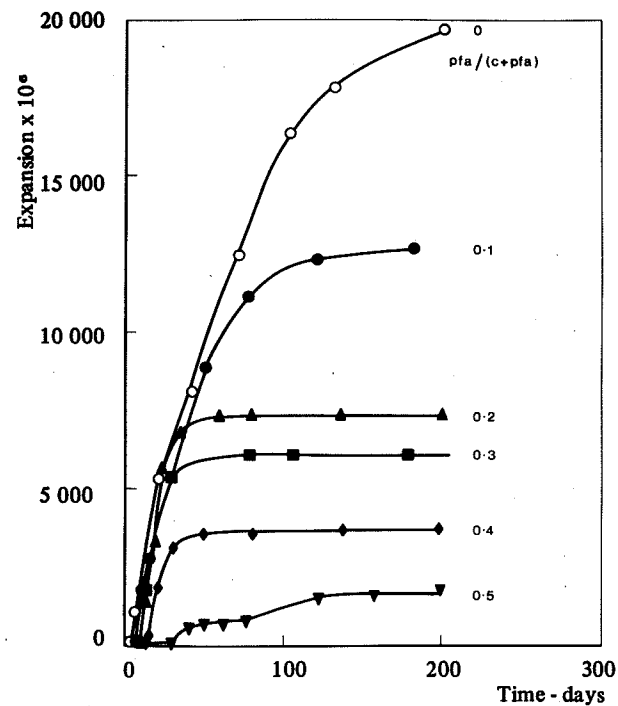


FIGURE 6: Variation of expansion with age and pfa content. Ironbridge.  $w/(c+pfa) = 0,41$ ,  $a/(c+pfa) = 2,75$ .

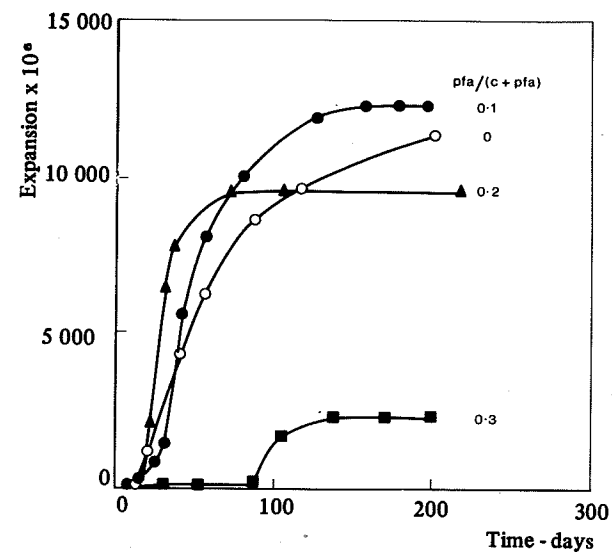


FIGURE 7: Variation of expansion with age and pfa content. Ironbridge.  $w/(c+pfa) = 0,53$ ,  $a/(c+pfa) = 3,5$ .

From Figures 6 to 9 it can be seen firstly that the replacement of part of a cement by pfa can in some instances increase the long term expansion and secondly that the expansion of blended cement mortars may be less sensitive to the opal content than the OPC mortars (compare Figures 3, 4, 8 and 9).

#### 5. DISCUSSION

**Time to cracking.** In Figure 10, (page 6) the time to cracking is shown plotted against the water soluble alkali content per unit volume of the mortar for specimens having an alkali to Beltane opal ratio close to the most critical value. The water soluble alkali content includes the contribution from both the cement and the pfa. The solid curve in Figure 10 is the same as that plotted in Figure 1.

An examination of Figure 10 shows that specimens containing pfa and having a water soluble alkali content in

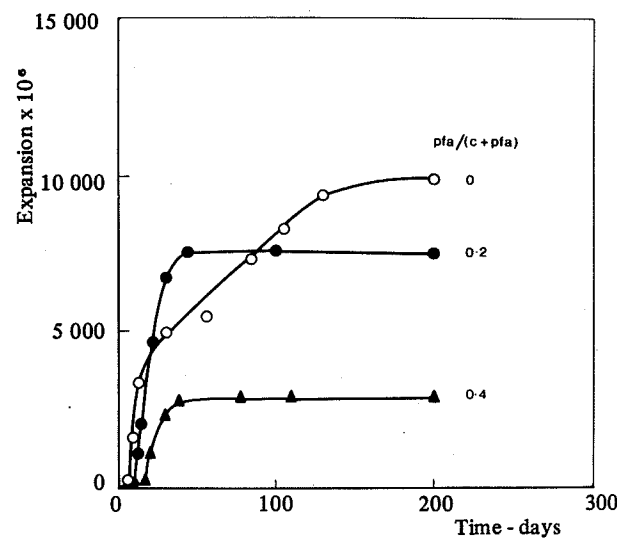


FIGURE 8: Variation of expansion with age at alkali-Beltane opal ratio of 0,10. Ironbridge.  $w/(c+pfa) = 0,41$ ,  $a/(c+pfa) = 2,75$ .

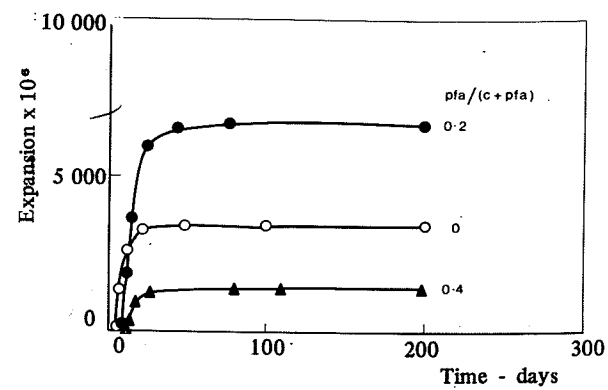


FIGURE 9: Variation of expansion with age at alkali-Beltane opal ratio of 0,04. Ironbridge.  $w/(c+pfa) = 0,41$ ,  $a/(c+pfa) = 2,75$ .

soluble alkali content' (expressed as equivalent  $Na_2O$ ) of 0,8 per cent by mass; an acid soluble alkali content of 1,04 per cent; a density of  $3130 \text{ kg/m}^3$  and a specific surface area of  $375 \text{ m}^2/\text{kg}$ .

The mortar bars were demoulded at 24 hours and two specimens from each batch were placed in polythene sleeves and immersed in approximately 10 g of water.

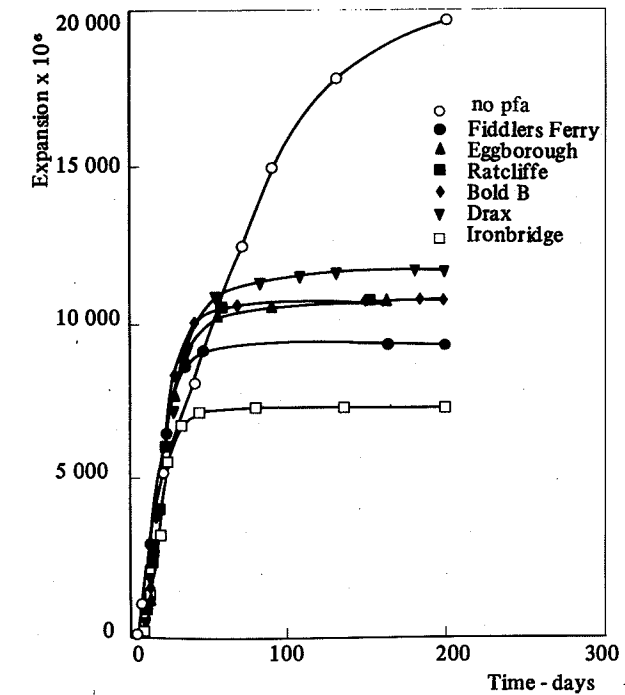


FIGURE 3: Variation of expansion with age.  $w/(c+pfa) = 0,41$ ,  $a/(c+pfa) = 2,75$ ,  $pfa/(c+pfa) = 0,2$ .

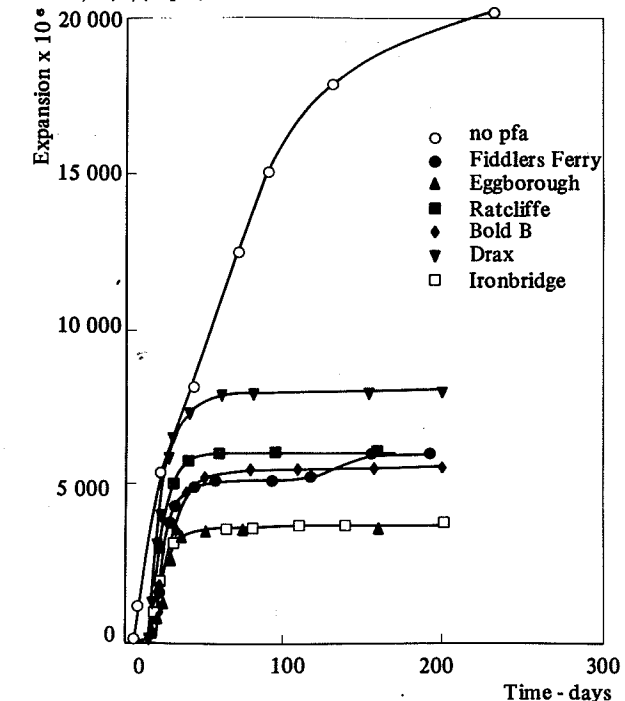


FIGURE 4: Variation of expansion with age.  $w/(c+pfa) = 0,41$ ,  $a/(c+pfa) = 2,75$ ,  $pfa/(c+pfa) = 0,4$ .

These specimens were set up in measuring rigs and expansion logged daily using inductive displacement transducers with a linear range of either  $4 \times 10^3$  or  $2 \times 10^4$  micro-strain together with recording equipment of a sensitivity equivalent to 1 micro-strain.

#### 4. RESULTS

Figures 3 and 4 show the relationship between expansion and age obtained using mortar bars having a water to blended cement ratio of 0,41, aggregate to blended cement ratio of 2,75 and cement replacements by pfa of 20 and 40 per cent by mass. A similar plot is given in Figure 5 for those specimens having a water to blended cement ratio of 0,53, an aggregate - blended cement ratio of 3,5 and cement replacements by pfa of 0 and 30 per cent by mass.

The specimens had an alkali-Beltane opal ratio of 0,067. An examination of these Figures shows that the specimens expand slowly at first and then at ages between 5 and 90 days there follows a fairly abrupt increase in the rate of expansion after which the rate of expansion decreases continuously. This sudden increase in the rate of expansion occurs when the mortar can no longer support the internal stress generated by the formation of the hydrous alkali-silica reaction product. From Figures 3 and 5 it can be seen that at cement replacement levels of 20 and 30 per cent the time to cracking was little influenced by the presence of pfa but Figure 4 shows that a cement replacement level of 40 per cent increased the time to cracking.

At early ages and after the specimens had cracked the rate of expansion was frequently greater for those specimens containing pfa than those without pfa. Thus replacement of part of a cement by pfa can increase the expansion observed at early ages. However at later ages the expansion rate was lower for specimens con-

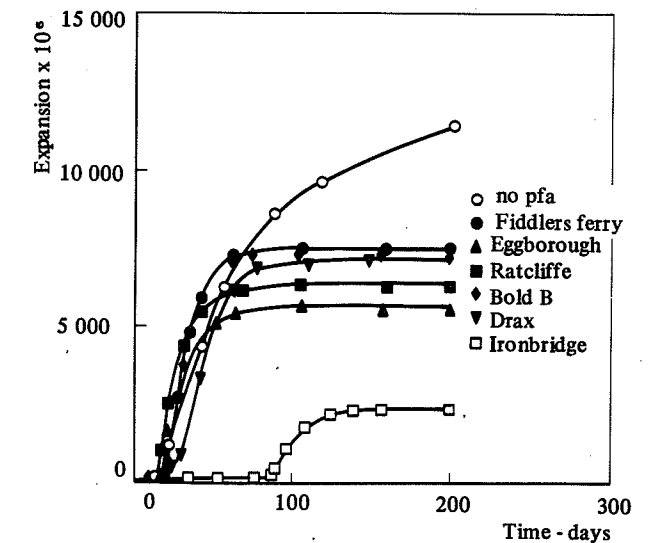


FIGURE 5: Variation of expansion with age.  $w/(c+pfa) = 0,53$ ,  $a/(c+pfa) = 3,5$ ,  $pfa/(c+pfa) = 0,3$ .

(b) The relationships between the expansion at 200 days and the water soluble alkali content for specimens tested at their most critical alkali-Beltane ratio is approximately independent of the content of pulverised fuel ash.

(c) Replacement of a part of a cement by pfa can sometimes increase the expansion due to the alkali-silica reaction. This situation arises when the resultant water soluble alkali content is in excess of 2,5 kg/m<sup>3</sup>.

#### ACKNOWLEDGEMENTS

The author is grateful to Mr F B Presley for preparing the specimens, Mr N Swinton for his assistance with the experiments, Mr M G Taylor for analysing the pulverised fuel ashes and Mr W A Gutteridge and Dr C D Pomeroy for helpful encouragement.

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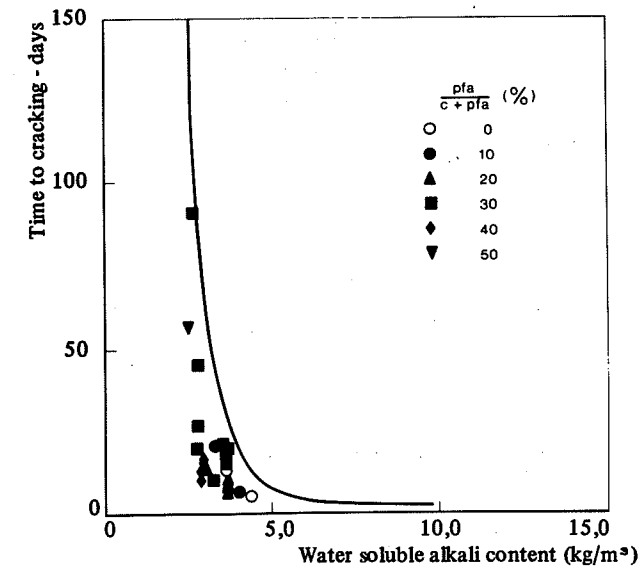


FIGURE 10: Variation of time to cracking with water soluble alkali content

excess of 2,5 kg/m<sup>3</sup> crack earlier than OPC mortars of similar water soluble alkali content. This, it is suggested is due to the slower strength development of blended cement mortars, particularly at early ages, in comparison with normal mortars. Thus mortars made using blended cements are less able to support the internal stresses generated by the formation of the hydrous alkali-silica reaction product than specimens without pfa.

#### 6. EXPANSION

In Figure 11 the observed expansion at 200 days is shown plotted against water soluble alkali content for blended cement mortars having an alkali-Beltane opal ratio close to the most critical value together with the relationship obtained for OPC mortars (see Figure 2). From Figure 11 it may be noted that although the expansion at early ages is greater for blended cement mortars than the OPC mortars the expansion at 200 days is nevertheless essentially the same for specimens of similar water soluble alkali content. Thus there is no evidence here to suggest that the hydroxyl ions are being depleted by the pfa.

From Figure 11 it follows that an alkali content in excess of 2,5 kg/m<sup>3</sup> is necessary to produce a deleterious expansion in mortars when the aggregate contains a reactive constituent. It may therefore be concluded that excessive expansions due to the alkali-silica reaction are unlikely to occur if the alkali content is less than 2,5 kg/m<sup>3</sup>. A more conservative limit of 2,25 kg/m<sup>3</sup> has been chosen as the

basis for Figure 12 where the 'safe' water soluble alkali content of a cement is shown plotted against the blended cement content in kg/m<sup>3</sup> of a concrete having cement replacement levels by pfa of 0 and 30 per cent by mass. The water soluble alkali content of the pfa was taken to be 0,1 per cent by mass. An indication of the probable magnitude of the acid soluble alkali content of the cement is given on the right hand side of the Figure.

#### 7. CONCLUSIONS

For the particular mixes and test conditions employed the following conclusions may be drawn.

(a) Cracking due to the alkali-silica reaction is only observed in specimens having water soluble alkali contents, expressed as equivalent Na<sub>2</sub>O, greater than 2,5 kg/m<sup>3</sup>. This figure includes the contribution from both the pulverised fuel ash and the cement.

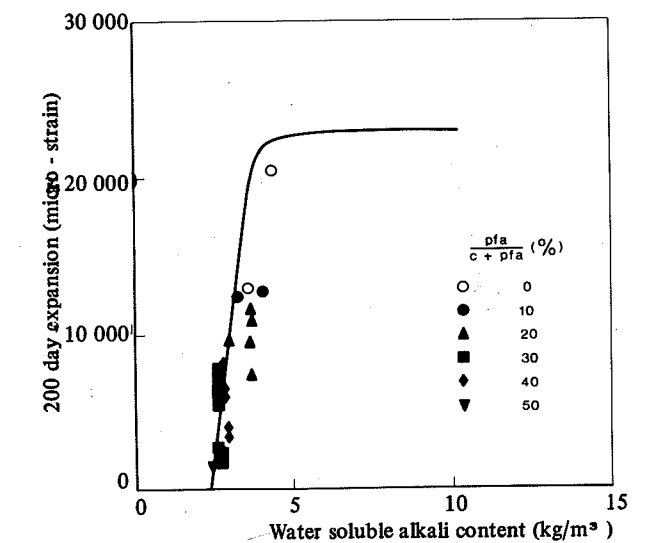


FIGURE 11: Variation of expansion at 200 days with water soluble alkali content

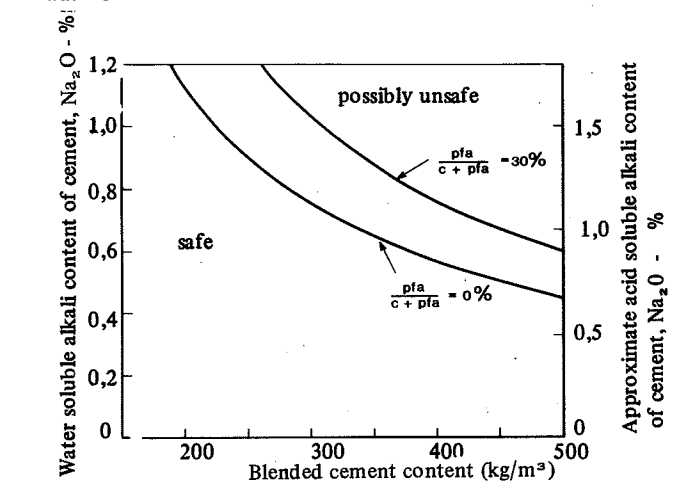


FIGURE 12: Variation of 'safe' water soluble alkali content of a cement with blended cement content

*Addendum:*

Table 1, page 2: add the following figures for CaO content, from left to right, which were not originally given. CaO 1,48, 1,27, 4,10, 2,05, 1,99, 1,24.

Also add the following figure which was not originally included:

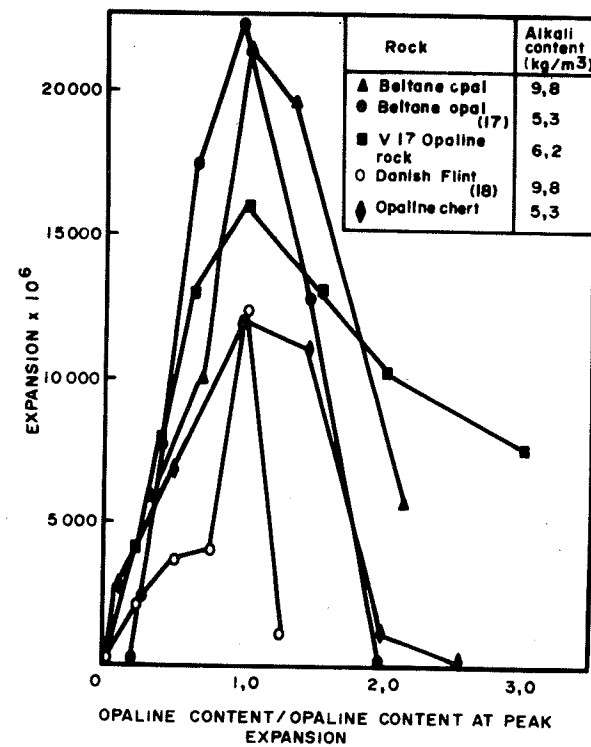


Figure 13: Comparison of expansion behaviour produced by four aggregates containing opaline material (The acid soluble alkali content is expressed as equivalent Na<sub>2</sub>O)

During the presentation of his paper, Dr Hobbs made the following addition to his printed material:

'This paper is concerned with the effect of replacing part of a cement by pfa, upon the expansion and cracking caused by the reaction between alkali and opaline material. Opaline material is often found to be a constituent of the aggregate in those concretes which have cracked as a result of the alkali-silica reaction.

'In our tests we use Beltane opal as reactive material which induces more extensive damage than most other reactive aggregates. In Figure 13 the expansion behaviour of specimens containing various amounts of Beltane opal is compared with that obtained when other reactive aggregates

are used. An opaline constituent in the aggregate has produced structural damage to concrete in Jersey, Denmark and Germany. Opaline material has been found in two UK aggregates.

'The level of expansion and damage which occurs in concrete as a result of the alkali-silica reaction is related to the quantity of reactive material present in the aggregate, as can be seen from Figure 13, and the total available alkalis in solution. The total available alkali in solution is dependent upon the available alkali content of the cement, the mix proportions of the concrete, the available alkali content of the aggregate and sometimes upon the diffusion of alkali from sources external to the concrete or even to alkali in the mix water.

From Figure 13 it can be seen that damage is greatest at a particular alkali-reactive silica ratio. This ratio is called the most critical ratio. The safe criterion that is used in the tests at the Cement and Concrete Association is simply that specimens tested at this most critical ratio must not crack as a result of alkali-silica reaction.

'From Figure 12 it can be seen that if the aggregate to be used contains a reactive constituent then the use of pfa as a partial replacement for OPC can allow one to use cements of higher alkali content without the danger of the concrete cracking. If a cement content of 400 kg/m<sup>3</sup> is taken as an example then at a cement replacement level of 30 per cent the safe cement alkali limit can be increased by 0,2 per cent.

'There is one major snag. This approach can not be used in practice because the water soluble alkali content of a cement is not normally measured or quoted. However, if a limit of 3 kg/m<sup>3</sup> is placed on the acid soluble alkali content of a Portland cement concrete then the limit for the acid soluble alkali content of a Portland cement in a blended cement concrete can readily be calculated simply by making allowance for the water soluble alkali content of the pfa.

*Additional references:*

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