

The Influence of Pulverised Fuel Ash on A.S.R., Behavioural Differences Between Mortars Containing Pyrex Glass and Beltane Opal

E.C. Robert*

*Harry Stanger Limited
Consulting Materials Engineers
Elstree, England*

ABSTRACT

The influence of pulverised fuel ash (pfa) on the expansion of mortar bars containing either Pyrex glass or Beltane opal has been studied. The experiments were conducted using a storage temperature of 38°C and generally followed the procedures described in ASTM C227 and C441. In addition to the expansion tests, the mortar bars and the liquid from the bottom of the storage containers were analysed to determine the level of alkalis present.

The results show significant behavioural differences between Pyrex glass and Beltane opal, both with respect to pfa and also independent of this material. When used with Pyrex glass, the pfa was found to reduce the expansions of the mortar bars for all mixes found to be expansive in the absence of pfa. For mortar bars containing Beltane opal, however, the pfa increased the expansion observed in all cases except at the pessimum.

Certain time dependent features of the ability, or otherwise, of pfa to reduce expansions were also noted. Again the effects produced with Pyrex glass and Beltane opal were found to differ.

The results are explained in terms of the relative affinities for reaction with the hydroxyl ion shown by the three siliceous materials. The practical implications of the time dependent trends are also discussed.

1. INTRODUCTION

This paper describes some of the results from a research programme (Robert, 1986) examining a number of aspects of the alkali-silica reaction (ASR). The full programme investigated the effects of using UK cements of differing alkali content, with and without pfa, the amount and type of reactive aggregate present, and the free water content of the mix. Physical tests were carried out to measure expansions and chemical analyses were performed on both the constituent materials and the experimental specimens.

The discussion concentrates on the performance of cementitious blends containing a high alkali cement (1.17% Na₂O_{eq}) with 45% pfa replacement by mass, used with either Beltane opal or Pyrex glass as reactive aggregate. Two free water contents are considered which correspond to free water : cement ratios (w/c) of 0.55 and 0.40 (Pyrex glass only) for mixes not containing pfa.

* Formerly of The City University, London where the research was financed by the Science and Engineering Research Council.

Full details of the materials used, the experimental procedures adopted, including the mix proportions and their referencing system, have been described elsewhere (Robert et alia, 1983), (Robert, 1986). In brief the cementitious materials were from UK commercial sources complying with BS 12 : 1978 (Portland cements), BS 3892 : Part 1 : 1982 (pfa) and BBA Certificate 81/841 (pfa). All aggregate materials were crushed and graded to the requirements of ASTM C441 which specifies equal proportions in five size fractions between 4.75mm and 150 μ m. All mortar bar specimens were stored at 38°C in sealed containers.

2. PRESENTATION OF RESULTS

2.1 Expansion of bars containing Pyrex glass

The numerical results (Robert et alia, 1983) show that expansion was reduced progressively by using pfa in combination with Portland cement in the range 0% to 45% by mass. At the 45% level the pfa reduced the expansion of the most reactive mix by about 90% at 6 months, as shown below in Figure 1.

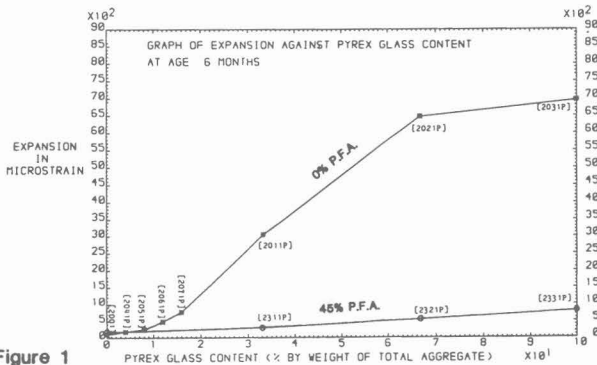


Figure 1

In general the expansion versus time graphs show rapid early expansion rates, producing most of the total observed expansion during the first two months after casting. However, some mixes showed significant expansion after two months and these tended to be those containing pfa and the higher free water content. In addition, most of these mixes showed a high degree of expansion, in excess of the ASTM 'harmful' limit of 1000 μ E at 6 months, despite the use of pfa.

The link between the use of pfa and the free water content of the mix is demonstrated in Figure 2 where pfa is shown to be more effective in reducing the expansion of mixes containing the higher free water content. This effect is so prominent that at high replacement levels the normal trend for greater expansions to be associated with the higher free water content is reversed. However, comparison of Figures 2 and 3 shows that the differential in effectiveness of pfa with respect to the two levels of free water content reduces with time, as shown by the movement of the intersection point on the two graphs towards greater pfa contents.

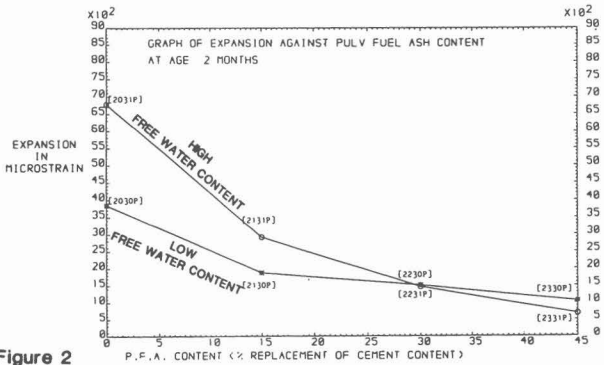


Figure 2

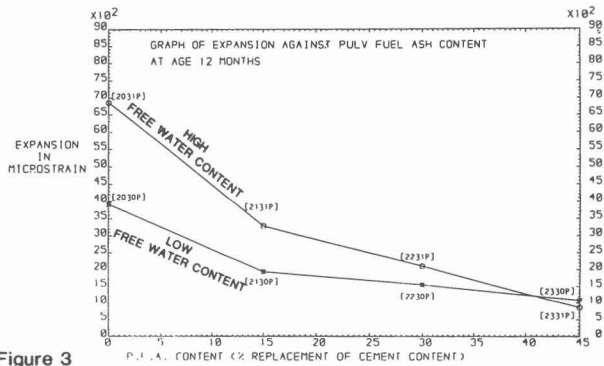


Figure 3

Further evidence of this time based trend was found by comparing the rates of expansion of similar mixes with and without the inclusion of pfa. In some cases, at later ages the rate of expansion of mixes containing pfa was found to exceed the rate of expansion of the corresponding non-pfa mix. Again this feature was found to be associated with the higher free water content.

Thus, the results show that the effect of pfa can be time dependent, the effectiveness in inhibiting expansion with Pyrex glass as reactive aggregate reducing as the age of the specimen increases.

2.2 Expansion of bars containing Beltane opal

The results obtained at 6 months from the specimens containing Beltane opal are shown in Figure 4. The mixes which did not contain pfa produced a strong pessimum effect at 4% Beltane opal content in contrast to the equivalent curve for mixes containing Pyrex glass (cf Figures 1 and 4).

The effect of pfa on the mixes containing Beltane opal was also different to the corresponding effect noted with Pyrex glass. For all mixes above the pessimum concentration the pfa caused an increase in expansion (Figure 4). However, at the pessimum concentration a 45% pfa content reduced expansion by approximately 50%.

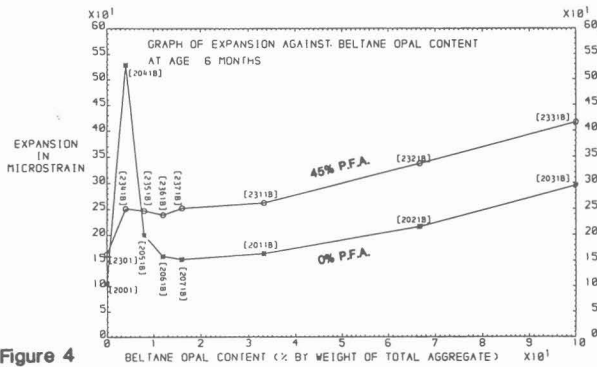


Figure 4

In general the expansion versus time graphs again show rapid early expansion rates producing most of the total observed expansion during the first two months after casting. In every case, however, the Beltane opal mixes gave some increase in expansion after 2 months. The increase was more significant for some mixes and continued up to the final measurement taken at 12 months. This effect was found to be associated with non-pfa mixes where the corresponding pfa mix produced a greater expansion, and the pfa mix at the pessimum where pfa produced a reduction in expansion.

3. DISCUSSION

It has been shown that there is a tendency for certain mixes to continue expanding for a longer period than others. Thus, there are differences in the way the rate of expansion changes with time. Expansion at later ages has been linked to mixes which contain pfa where the pfa has the ability to reduce expansion with Pyrex glass and Beltane opal, and certain non-pfa mixes containing Beltane opal where the corresponding use of pfa produces an increase in expansion. Before expanding this theory further let us first consider the nature of the three materials involved.

Beltane opal has been shown (Gutteridge and Hobbs, 1980) to contain typically over 90% silica, of which in excess of 80% is considered to be potentially reactive. Likewise a typical Pyrex glass has been shown (Figg, 1981) to contain approximately 80% siliceous material, again not all of which may be in a reactive form. Since pfa is also highly siliceous all three materials show considerable similarity. It therefore seems reasonable to presume that if the three materials are placed in the presence of any substance which reacts with silica they they will 'compete' with each other for supply of the reactant. The siliceous material with the greatest affinity for the reactant will therefore maintain a preferential reaction, at least in the first instance, and in the sense of ASR the three siliceous materials are in competition with one another for the hydroxyl ions in the pore solutions. Damaging expansion can occur if any of the products of such a reaction can absorb water and swell.

Since expansion due to ASR in the presence of Pyrex glass has been shown to be consistently reduced by pfa, the pfa must have a greater affinity for hydroxyl ions. With Beltane opal, however, the position is not so clear. Two possibilities therefore exist with respect to affinity for hydroxyl ions:-

Beltane opal > pfa > Pyrex glass	CASE A
pfa > Beltane opal > Pyrex glass	CASE B

The increase in expansion caused by the use of pfa with mixes containing

in excess of the pessimum Beltane opal content effectively rules out CASE B, at least for such Beltane opal concentrations. CASE A may therefore provide the true description. For the pessimum Beltane opal content, however, it appears that the pfa is able to maintain a preferential reaction. This is not necessarily in contravention of the description given in CASE A, due to the pessimum occurring at such a low Beltane opal concentration. A study of the mass ratio of Beltane opal to pfa at the pessimum reveals that for the 45% cement replacement level there is more than four times the quantity of pfa than Beltane opal. This may be sufficient to offset the greater affinity for hydroxyl ions shown by the Beltane opal and allow the pfa to react sufficiently and thereby cause a reduction in expansion.

Now, returning to the trends in relation to time, which were noted in the expansion results, the theory of preferential reactions due to differing affinities for hydroxyl ions can be developed further. Considering first the mixes containing Pyrex glass, we have evidence that pfa causes mortar bars to expand more slowly at early ages. This was particularly the case for the higher free water content mixes. Thus the pfa, having a greater affinity for hydroxyl ions, is able to maintain a preferential reaction with the negative ion and effectively starve the Pyrex glass of the hydroxyl ions it requires for expansive ASR to occur. We therefore have:-

$$\frac{\text{Rate of expansion of Pyrex/pfa mixes}}{\text{Rate of expansion of Pyrex/non-pfa mixes}} < 1 \quad (1)$$

However, the expansive activity of some of the mixes containing pfa was found to continue beyond the time when expansion had apparently ceased in the corresponding non-pfa mixes. Thus the situation would be changed to:-

$$\frac{\text{Rate of expansion of Pyrex/pfa mixes}}{\text{Rate of expansion of Pyrex/non-pfa mixes}} > 1 \quad (2)$$

As time progresses there are three factors which could contribute towards increasing the value of the quotient given in (1) above. Firstly, there is the tendency for pfa to release alkali metal ions as the pozzolanic reaction proceeds (Buttler et alia, 1981), (Robert et alia, 1983) which may result in an enhancement of the hydroxyl ion concentration. Secondly, pfa has been shown to reduce the amount of alkali metal ions leached out of mortar bars (Robert et alia, 1983). This again may enhance the hydroxyl ion concentration. Finally, the power of pozzolanic reaction itself is bound to diminish with time and thereby reduce the ability of the pfa to starve the Pyrex glass of hydroxyl ions. If these transitions are of sufficient power then the situation described in (2) above can be achieved.

Now let us study the comparable time related trends for pfa used in conjunction with Beltane opal. At the pessimum Beltane opal concentration the arguments presented in respect of expansion with Pyrex glass and pfa would seem to hold true. This is because the pfa is present in sufficient quantity, relative to the amount of Beltane opal, for it to react preferentially with the hydroxyl ions.

At all Beltane opal concentrations above the pessimum all the effects were reversed, pfa causing an increase in expansion and the non-pfa mixes tending to expand for a longer period. It has been deduced earlier that Beltane opal has a higher affinity for hydroxyl ions than pfa. The Beltane opal therefore has a preferential reaction with the hydroxyl ions and may be seen to effectively starve the pfa of the material it requires for the pozzolanic reaction to proceed at its normal rate. The ability of the pfa to inhibit expansion at early ages is therefore destroyed and we have:-

$$\frac{\text{Rate of expansion of Beltane opal/pfa mixes}}{\text{Rate of expansion of Beltane opal/non-pfa mixes}} > 1 \quad (3)$$

The increase in expansion caused by pfa is not fully explained by the preferential reaction with hydroxyl ions effect, other factors must therefore

be acting. If the pozzolanic reaction is being restricted by more highly reactive Beltane opal drawing most of the hydroxyl ions, at least at early ages, then the C-S-H gel contributed by the pfa will be delayed. We therefore have a reduced cement content mix with little contribution from the pfa which would produce a weaker, more permeable mix, both of which could result in greater expansion. In addition, the use of pfa has been linked with increased alkali contents in mortar bars (Robert, 1983) which may enhance the hydroxyl ion concentration in the pore fluids.

As time progresses the ability of the Beltane opal to act as a sink for hydroxyl ions will reduce as the most highly reactive sites are consumed. Thus, more hydroxyl ions will be available for the pozzolanic reaction which will help to curtail the ASR. In the non-pfa mixes, however, provided that the hydroxyl ion concentration remains above any threshold level, the less accessible and less reactive sites within the Beltane opal will continue to react. This will provide continuing, but slower, expansion. Eventually the stage is reached where:-

$$\frac{\text{Rate of expansion of Beltane opal/pfa mixes}}{\text{Rate of expansion of Beltane opal/non-pfa mixes}} < 1 \quad (4)$$

Thus the pairs of equations (1) & (2) and (3) & (4) occur in reverse order with respect to the inequality sign, that is Pyrex glass and Beltane opal show opposite trends with time.

4. IMPLICATIONS FOR THE USE OF PFA IN CONCRETE

The experimental evidence that expansion may continue longer in mixes containing pfa is indicative that pfa should be regarded as a 'delayer' rather than a permanent inhibitor. There was no indication, however, that the expansion at later ages would cancel out the large expansion reductions achieved by using pfa in most of the highly reactive mixes.

Under normal circumstances, therefore, the use of pfa in concrete represents an extra safeguard which can be provided against the often disastrous effects of ASR, provided that care is taken to examine aggregates for Beltane opal type behaviour. In practice the pfa would be used with aggregates which are only mildly reactive in comparison to Pyrex glass or Beltane opal, but which could cause serious problems if used with a high alkali cement. The inference is, therefore, that when the stage is reached where the pozzolanic reaction begins to diminish then the secondary factors which act will be capable of restricting the ASR to acceptably low levels.

Finally, it should be emphasised that for pfa to delay the onset of ASR successfully a sufficiently high cement replacement level should be used. On the basis of this experimental work 30%-45% pfa is recommended.

REFERENCES

- BUTTLER, F.G., Morgan, S.R. and WALKER, E.J. 1981. In Proc. of the 5th Int. Conf. on AAR in Concrete, Cape Town. Paper S252/38.
- FIGG, J.W. 1981. In Proc. of the 5th Int. Conf. on AAR in Concrete, Cape Town. Paper S252/77.
- GUTTERIDGE, W.A. and HOBBS, D.W. 1980. Cement and Concrete Research. Vol. 10, No. 2, pp 183-193.
- ROBERT, E.C. 1986. A Factorial Approach to the Study of Alkali - Silica Reaction in Concrete. PhD thesis, The City University, London.
- ROBERT, E.C., Boswell, L.F., BUTTLER, F.G. and MORGAN, S.R. 1983. In Proc. of the 6th Int. Conf. on Alkalies in Concrete, Copenhagen. pp 231-238.