EFFECT OF SLAG CEMENTS AND AGGREGATE TYPE ON ALKALI-AGGREGATE REACTION AND ITS MECHANISMS

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ABSTRACT

The effects of cement and aggregate type upon alkali-aggregate reaction have been evaluated by: a chemical method (ASTM C 289), an accelerated mortar bar test of Brotschi and Mehta /1/, physical adsorption data; zeta potential, solution analyses, and microstructural observations. Type II/I portland cements of normal alkali content were used with partially glassy basalt, and Beltane opal. Minimal expansion but some dissolution was found in the former. The use of cement containing granulated blast furnace slag diminished significantly the amount of alkali-aggregate reaction. Aluminum content was important in minimizing expansive reaction.

Key Words: Alumina/silica ratio, innocuous reaction, solution analysis, alkali.

INTRODUCTION

The durability of concretes made with various types of aggregate depends very significantly upon the extent and type of interaction between the matrix and the rock.   The interactions of alkalis in concrete for particular combinations of cement with the rocks used as aggregate depend upon the chemical composition, fineness and porosity of those rocks as well as on the concentration of alkali ions in the pore fluid. Some reactions occurring are deleterious, while others are generally beneficial [e.g., pozzolanic reaction between $Ca(OH)_2$ and silica].

Van Aardt and Visser /2/ studied the reaction of $Ca(OH)_2$ with rocks containing minerals of the feldspar group to produce hydrated calcium silicate, hydrated calcium aluminate and a hydrated calcium aluminosilicate. If alkalis were present the products included calcium-alkali silicate hydrates (products with d-spacings 12-16 Å) which appeared to be responsible for the expansion of mortars and concretes. They /3/ suggested that formation of calcium aluminate hydrates will reduce the extent of alkali-aggregate reaction (AAR) by reduction of $Ca(OH)_2$ content in pore fluids. Tang Ming-Shu and Han Su-Fen /4/ found that the expansion due to aluminous and supersulphated cement is negligible compared to portland cement when opal is present as reactive aggregate. These results were attributed to the removal of $Ca(OH)_2$ from pore fluids.

Way and Cole /5/, on the other hand, studied the reaction between $Ca(OH)_2$ and rocks and found that the attack on plagioclase structures is accompanied by release of Ca^{+2} ions which can react with silicates to form limited-swelling lime-silica-alkali complexes, and with aluminate ions forming calcium aluminate hydrates.

The preventive effect of granulated blast furnace slag was extensively studied and was attributed to be due to either low permeability of cements containing slag (Bakker /6/) or due to combinations with alkali metal ions (Smolczyk /7/).

The purpose of this paper is to examine and interpret the innocuous reactions of some feldspathic, partially glassy rocks (basalt) and the mechanism of reaction of slag with alkalis.

EXPERIMENTAL

Specimen Preparation; Characterization

Type II/I portland cement (Blaine surface area = 3680 cm^2/g) having normal alkali level, and granulated blast furnace slag (5550 cm^2/g) were used. X-ray diffraction examination of the Beltane opal showed that it could be classified as Opal-CT /8/. Basalt containing a siliceous glassy component was used. The chemical compositions of the materials used are shown in Table I.

The opal and basalt were crushed and ground and the fractions 50-100, 100-200 and 200-325 were separated. The first fraction was used in the chemical test (ASTM C 289) and the other two were mixed together in 50% equal fractions to be used in mortar bar experiments.

Mortar bars were prepared according to the accelerated test method of Brotschi and Mehta /1/. Three sets of bars were made. Table II summarizes the compositions. In all cases, the aggregate/cement (A/C) ratio was 1.25 and the w/c ratio was 0.5, (which was found to produce a sufficiently workable paste with flow of 120 mm as recommended by ASTM C 109). The mortar bars were maintained at 100% RH; and a temperature of 43°C. They were allowed to cool to room temperature before measurement of length change according to ASTM C 490. Four mortar bars were prepared for each mixture for length change measurements and a fifth one for other tests.

An Accusorb 2100E was used to establish adsorption-desorption isotherms of N_2-gas at liquid N_2 temperature. An ISI DS-130 SEM equipped with an EDX unit was used to identify phases formed in mortar bars. For zeta potential studies, the electrophoresis technique, the method and apparatus described previously /9/, was used.

TABLE I

Chemical Composition of Materials Used.

Name	Opal	Basalt	II/I Cement	Slag
NRL designation	B09	C31	II-02	D64
SiO_2	86.6%	54.0%	20.9%	32.7%
Al_2O_3	5.58	13.4	3.96	10.0
TiO_2	0.33	2.05	0.31	0.48
Fe_2O_3	0.18	13.6	3.47	0.86
MgO	0.12	3.21	3.96	11.0
CaO	0.02	7.16	63.10	42.04
MnO	<0.01	0.203	0.032	0.476
Na_2O	0.13	3.02	0.41	0.25
K_2O	0.26	1.67	0.41	0.55
P_2O_5	0.04	0.42	2.22	<0.05
SO_3	1.01	n.d	1.40	—
L.O.I.	5.93	1.0	1.05	*
S	—	—	—	1.28
Totals	100.23%	99.73%	100.20%	99.74%

*The loss-on-ignition value for this sample was negative (i.e. sample gained weight on heating indicating the existence of sulfur as sulfide or sulfur rather than SO_3.

TABLE II

Summary of Compositions of Mixes Used.

Designation	Composition
CB	II/I cement + Beltane Opal
CBZ	II/I cement + (50% Opal + 50% Basalt)
CZ	II/I cement + Basalt
SB	35% II/I cement + 65% slag) + Beltane Opal

Dissolution Kinetics

One gram samples of aggregate (50-100# sieve size) were placed in plastic vials. In the first set of experiments (10 mL) of three different liquids: deionized water, saturated $Ca(OH)_2$ and 1N NaOH solutions were placed separately on the aggregates. The plastic vials were sealed and shaken vigorously for a few seconds, then placed immediately in an oven at 43°C, with their bottoms horizontal to ensure that layers of particles settling from suspension are of uniform thickness. In the second and third sets of experiments, sliced discs from both Type II/I cement and slag cement (35% II/I cement + 65% slag) were allowed to settle and rest over the aggregate pad prepared in a similar way as in the first set. The discs having weights of 0.75-0.76 grams were sliced from cylinders previously hydrated for 24 hours at room temperature (w/c ratio = 0.50). At designated times, 5 mL portions were withdrawn from each vial for analysis. Precautions were taken to avoid withdrawal of suspended solid material, using a small piece of filter paper to plug the pipette tip. The solutions were analyzed by atomic emission spectrometry.

RESULTS

The results of the chemical test (ASTM C 289) suggested that both opal and basalt should give deleterious reaction with cement. However, the mortar bar expansions (Fig. 1) show that only opal is deleterious, but that the basalt should be innocuous. The use of cement containing granulated blast furnace slag furthermore was found to diminish significantly the amount of alkali-aggregate reaction of the opal.

Adsorption-desorption isotherms of N_2-gas were determined for both types of aggregate before and after the chemical test (ASTM C 289). The isotherms were of type II with apparent hysteresis loops. Zeta potential was measured for the same aggregate samples. The BET surface areas, total pore volumes and ξ-potential values are summarized in Table III.

The results of solution analyses are presented in Figures 2, 3, 4, and 5 for Si^{+4}, Al^{+3}, Ca^{+2} and total alkali metals ($Na^+ + K^+$) respectively. Figure 2 shows that whenever $Ca(OH)_2$ is present in the solution, the amount of dissolved silica is appreciably diminished due to C-S-H insolubility. The Al^{+3} (Fig. 3) can only be detected in the solution with NaOH present. Its concentration is very small in the case of opal but it is present in appreciable quantity in the case of basalt (probably from feldspar or glass dissolution). The Al^{3+}/Si^{+4} mole ratio in solution remains almost constant in the case of opal but decreases with time in the case of basalt, indicating an increase in Al_2O_3/SiO_2 ratio in the solid phase. This could be related to the formation of calcium aluminate hydrates and to the innocuous behavior of this rock.

Figure 4 shows that the solution in contact with the slag always has a lower concentration of Ca^{++} ions than has that with cement. The lower value is attributed to the ability of slag to combine with Ca^{++} ions. In both cases Ca^{++} decreases continuously with time due to formation of C-S-H gel. Figure 5 shows that considerable amounts of alkali ions are dissolved into solution

TABLE III

BET Surface Areas, Total Pore Volumes and ξ-potentials of Aggregates Before and After the Chemical Test.

		BET (m^2/g)	Vp (mL/g)	ξ-potential (-mv)
Opal	Before Ch. Test	5.65	0.01117	14.50
	After Ch. Test	16.94	0.0470	57.60
Basalt	Before Ch. Test	6.76	0.0132	27.45
	After Ch. Test	4.08	0.0112	53.08

from basalt even though its expansive behavior proved to be innocuous. The solution in contact with slag has a lower alkali ion concentration than the one with cement. The curves for alkali ion contents in solutions with slag run almost parallel to those for the Ca^{++} ion concentration. This fact could be attributed to the affinity of slag for combining not only with Ca^{++} ions but also with alkali ions. This throws some light on the chemical aspects of the role of slag in preventing deleterious alkali-aggregate reaction.

Figures 6-9 show some SEM micrographs for different cement aggregate mixes.

DISCUSSION

The innocuous behavior of certain aggregates and of granulated blast furnace slag are probably the result of a combination of two major factors, physical and chemical. The first is related to the shape and size of particles and of the pores incorporated into them. The second depends on the chemical affinity of components towards ions that initiate deleterious type reactions, and on the nature of compounds or phases resulting from such reaction.

Keeping the shapes and sizes of particles constant in both aggregates used leaves the pore size as a controlling factor for the physical part of the above-mentioned reaction. The opal and basalt had similar particle size distributions and the same particle shape. The surface areas and pore volumes shown in Table III indicate that both opal and basalt when treated with alkali have closely similar average pore radii. Thus, the differences between those two rocks toward alkali-aggregate reaction depend primarily on the differences in their chemical constitution. The surface area and total pore volume increase almost four times in the case of opal but undergo only minor changes with basalt. This indicates that there is a drastic change in the pore structure of opal due to severe chemical attack by NaOH, while there is only minor change in the basalt, revealing much less chemical attack.

The zeta-potential values were found to increase in both aggregates, four times in the case of opal and twice in the basalt. This again reflects the relative severity of the attack on opal. However, the fact that the negative charge on the surfaces of both aggregates increases upon NaOH treatment could be ascribed to the hydrolysis of the silicate surface, and reaction of silanol groups on the surfaces, releasing protons to the solution and replacement with other cations (such as Na^+) carrying less positive charge/unit area.

The dissolution curves indicate that the alkali solution dissolves not only silica but also alumina. The latter will rapidly form C_4A hydrates, which later transform to C_3AH_6 or possibly C_3ASH_4-$C_3AS_2H_2$ under the effect of high pH and moderate temperature. This transformation is generally favored both by the low water demand for C_3AH_6 and by higher temperature. The C_4A hydrates and C_3AH_6
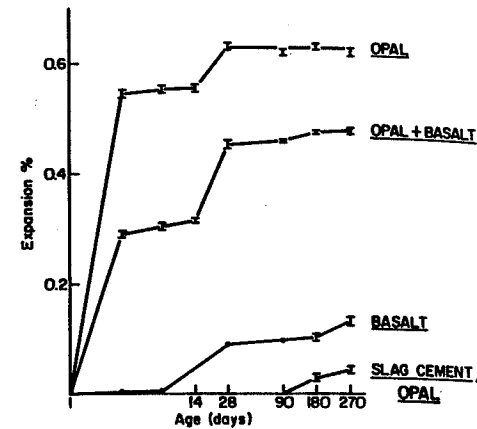
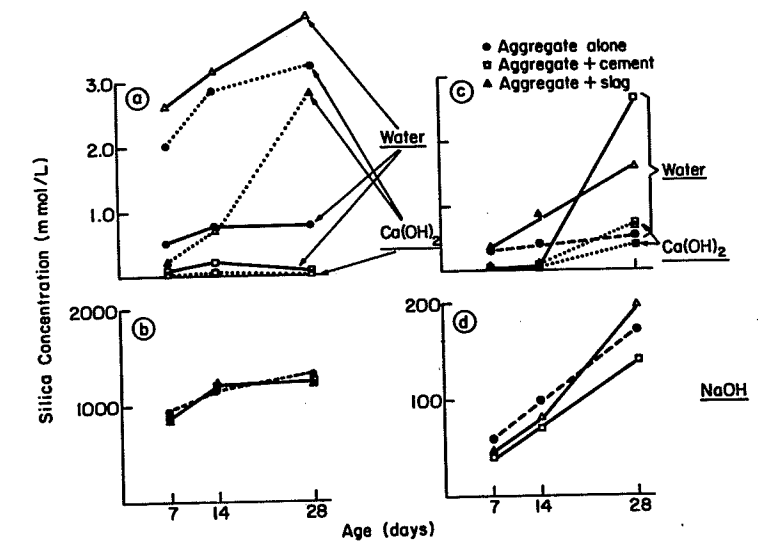Fig. 1. Mortar bar expansions. Each point is average of 4 bars. σ are included.

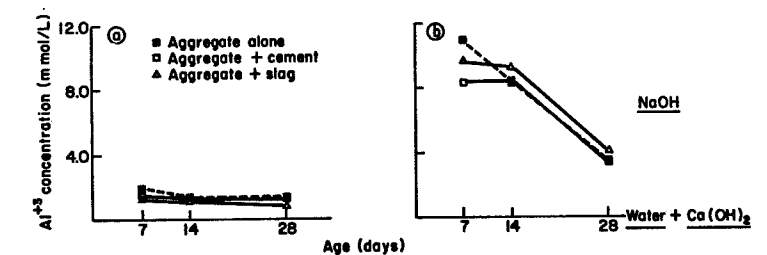Fig. 2. Silica dissolved from opal (a,b) and basalt (c,d).

Fig. 3. Al^{+3} dissolved from opal (a) and basalt (b) in 1N NaOH solution.

incorporate substantial amounts of Ca^{++} and OH^- groups which can reach 7 OH^- groups per one Al atom. It is expected that this will reduce the extent of attack of OH^- on the silicate tetrahedra and could limit the gel formed in vicinity of aggregate to having a high Ca^{++}/alkali ratio leading to an innocuous type of reaction.

The function of Al_2O_3 in maintaining the course of reaction in an innocuous form, once recognized can be evaluated further. The total Al_2O_3/SiO_2 molar ratio is plotted for the mixes used, including both the cement and aggregate, against % expansion produced at a particular time, in Fig. 10. The result is a straight line. These plots at any given age, gave straight lines parallel to that one presented. As the Al_2O_3/SiO_2 ratio increases the alkali-aggregate reaction shifts from deleterious to innocuous type. Thus, it is concluded that rocks containing high alumina content (feldspars) may give innocuous reactions. In other studies /10/ it was also shown that at elevated temperatures Al can substitute for Si in the tobermorite structure, accompanied by Na ions, which may also provide a mechanism involving Al for fixing the alkali ion.
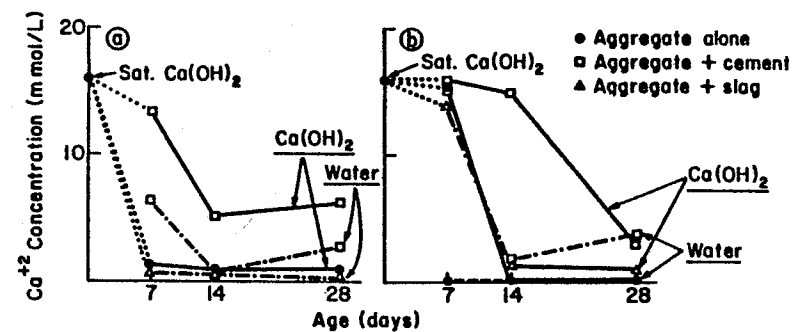
Fig. 4. Ca^{+2} concentration in $Ca(OH)_2$ and water [opal (a); basalt (b)].
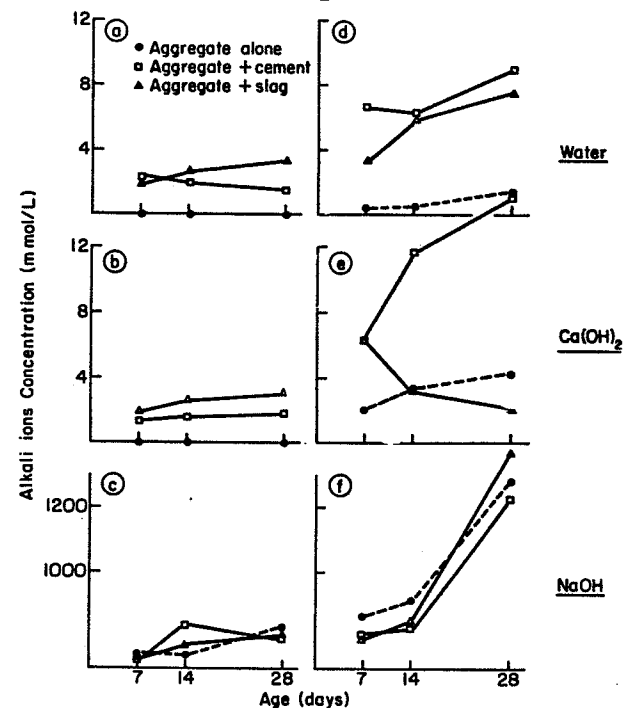

Fig. 5. Alkali ions concentration dissolved in different solutions;
(a), (b), and (c) for opal and (d), (e) and (f) for basalt.

It could be also concluded that using high alumina cement could prevent the alkali-aggregate reaction. Tang Ming-Shu and Han Su-Fen /4/ found that using aluminous cement gave the same expansion values as those without beltane opal, attributing their results to the removal of $Ca(OH)_2$ from the pore fluid.

The success of slag to suppress the alkali-aggregate reaction is not only due to the low permeability of slag pastes to alkali ions /6/ but also due to its ability to combine and fix the alkali metal ions from solution. This agrees with the results published by Smolczyk /7/ based on alkali metal ion diffusion experiments.
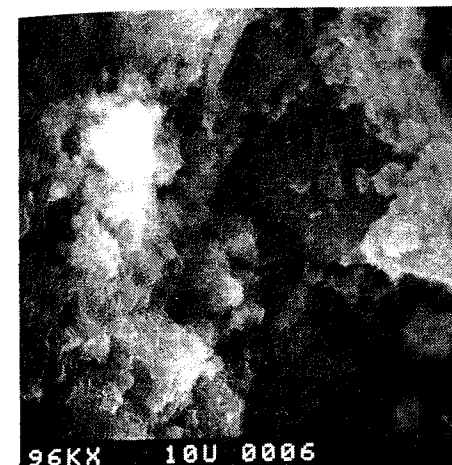

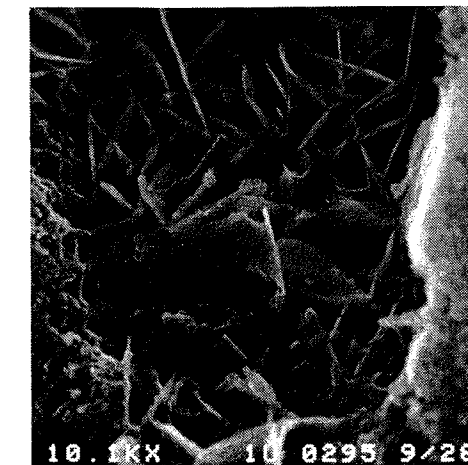Fig. 6. Cement + Opal (7 days). Intensive gel formation distributed all over the mortar.

Fig. 7. Cement + Basalt (7 days). Hexagonal plates of calcium aluminate hydrates.
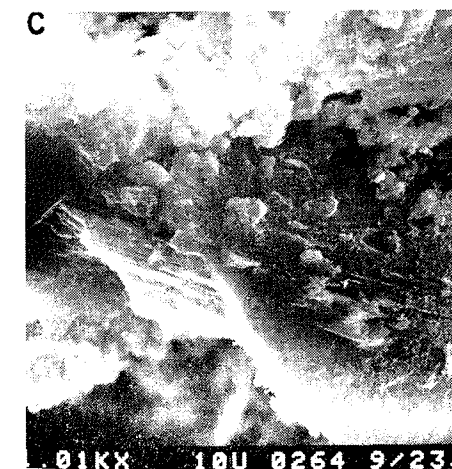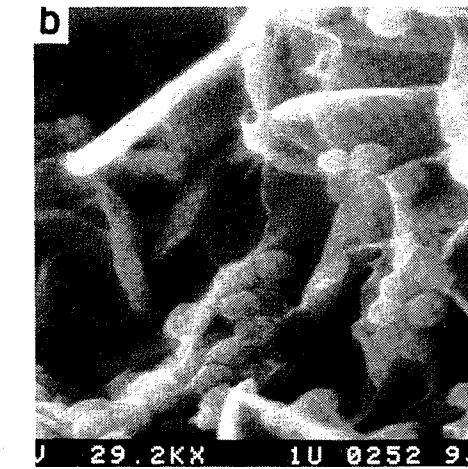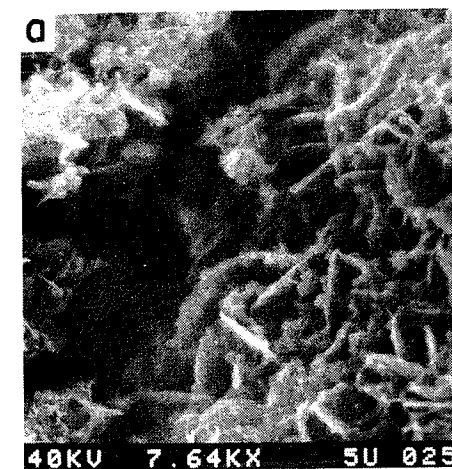

Fig. 8. Cement + Basalt + Opal (7 days). (a) Hexagonal plates of calcium aluminate hydrates with foiled edges. Some basalt grains are recognizable (upper left). (b), Higher magnification of (a) showing the formation of cubic hydrogarnet possibly as single crystals. (c) Opal grains with extensive gel formation around surfaces.
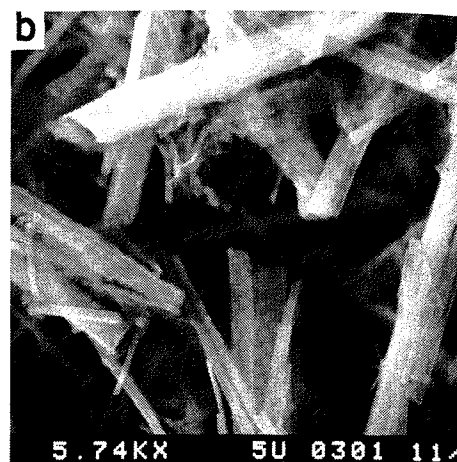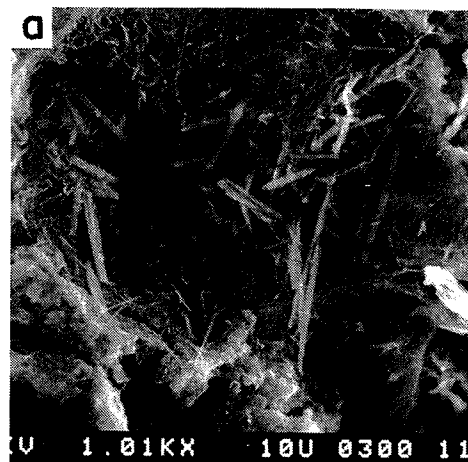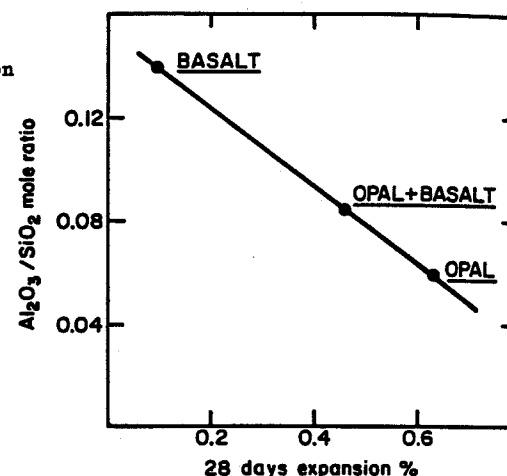
Fig. 9. Cement + Basalt (180 days).
(a) Fibrous structure of thaumasite/
woodfordite. (b) Higher magnification
of (a).

Fig. 10. (Right) Plot of 28 days
expansion vs. Al_2O_3/SiO_2 mole ratio.

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REFERENCES

/1/ Brotschi, J. and Mehta, P.K., Cem. Concr. Res. **8**, 191 (1978).
/2/ Van Aardt, J.H.P. and Visser, S., CSIR – Research Report No. BRR 574,
    Pretoria (1982).
/3/ Van Aardt, J.H.P. and Visser, S., CSIR – Research Report No. BRR 577,
    Pretoria (1982).
/4/ Tang Ming–Shu and Han Su–Fen, 7th Intl. Cong. Chem. Cement, Vol. II, p. 94,
    Paris (1980).
/5/ Way, S.J. and Cole. W.F., Cem. Concr. Res. **12**, 611 (1982).
/6/ Bakker, D.F.M., Conference on Alkali–Aggregate Reactions in Concrete,
    S252/29, South Africa (1981).
/7/ Smolczyk, H.G., Symposium on Alkali–Aggregate Reaction, p. 183, Reykjavik
    (1975).
/8/ Jones, J.B. and Segnit, E.R., J. Geol. Soc. Australia, **18**, 57 (1971).
/9/ Daimon, M. and Roy, D.M., Cem. Concr. Res. **8**, 191 (1978).
/10/ Komarneni, S. and Roy, D.M., Cem. Concr. Res. **12**, 773 (1982).

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ABSTRACT

The influence of pulverised fuel ash on the expansion due to the alkali
silica reaction has been studied at $38^{\circ}C$. The expansions of mortar bars
made with a high alkali Portland cement and containing a pulverised fuel
ash of BS 3892 Part 1 : 1982 quality were monitored and both pyrex glass
and Beltane opal were used as expansive aggregates. The expansions were
measured at regular intervals and the bars were analysed at the end of six
months in order to determine the amount of alkali removed from the bars.

The results show that the expansion caused by the alkali silica reaction
was reduced when pulverised fuel ash was used to replace some of the Port-
land cement despite the fact that such replacements led to a considerable
increase in the dilute acid soluble alkali content of the bars. It was
also found that the amount of alkali leached from the bars was reduced
when pulverised fuel ash was incorporated.

The results are explained in terms of changes in permeability with time due
to the pozzolanic or acid-base reaction of the pulverised fuel ash. (Key-
words : expansion, mortar bars, alkali content, pfa).

1.   INTRODUCTION

The results described in this paper have been obtained as part of a
detailed study of the alkali silica reaction (ASR) in which both physical
and chemical aspects of the reaction have been investigated. In the full
programme the influence of pulverised fuel ash (pfa) at different replace-
ment levels, the type and amount of reactive aggregate and the water content
have been studied with respect to Portland cements of low ($0.46\%Na_2O_{eq}$),
medium ($0.72\%Na_2O_{eq}$) and, high ($1.17\%Na_2O_{eq}$) alkali contents. There is only
room in this paper to describe the results obtained with the Portland cement
of highest alkali content but the results obtained with the other Portland
cements show similar trends.

Whenever possible, existing standard test methods were used. In particular,
all expansion measurements were conducted on 25 x 25 x 250mm mortar bars
produced and conditioned in accordance with ASTM C 227-71 and ASTM C 441-69.
The latter standard was suitably modified to allow for the use of pulverised
fuel ash at more than one replacement level. The chemical analyses for
sodium and potassium content were carried out according to the method
described in BS 4550.

2.   MATERIALS

2.1   Portland Cement

A high alkali cement from a particular works of a major UK producer was
used. The relevant chemical and physical properties of this cement were:
relative density = 3.03, $\%Na_2O$ = 0.40, $\%K_2O$ = 1.17, $\%Na_2O_{eq}$ = 1.17.

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