

# THE 9TH INTERNATIONAL CONFERENCE ON ALKALI - AGGREGATE REACTION IN CONCRETE 1992

## THE ASR EXPANSION OF CONCRETE PRISMS MADE FROM CEMENTS PARTIALLY REPLACED BY GROUND GRANULATED BLASTFURNACE SLAG

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Expansions of laboratory concrete specimens made from slag cements and containing a synthetic reactive silica demonstrate that under the conditions of the test method, the alkalis contained in slags can be capable of supporting the asr in a similar manner to those contained in Portland cement. Some supplementary chemical tests provide assistance in interpreting the expansion results.

### INTRODUCTION

Several countries now have nationally recognised codes of practice for designing concrete mixes which minimise the risk of asr damage. One method which these documents often recommend is replacing 50% or more of the ordinary Portland cement (opc) by ground granulated blastfurnace slag (ggbs). There have been, however, a number of results from laboratory test programmes indicating that this process may not always be effective.

Kawamura et al (1) found in some laboratory tests that a slag of moderate alkali content used to replace 30% of a higher alkali Portland cement only marginally alleviated asr expansion in mortar bars containing natural opaline aggregates. In another test, a second slag of lower alkali content than the cement used actually increased expansion. Hobbs (2) has quoted other examples of slag alleviating asr to a lesser extent than expected.

In a previous paper (3), Moir and Lumley presented laboratory test results which showed that, although the onset of expansion was delayed, the asr behaviour of a slag could be very similar to that of an opc of the same equivalent soda content.

The present paper updates the earlier paper and adds results obtained with a high alkali slag. Some chemical tests are also included.

### EXPERIMENTAL DETAILS

#### Materials

Of the four cements used in the programme, the alkali contents of A and B were high, while those of C and D were moderate. The alkali levels of slags L and P were moderate. Slags N and T had low and high alkali contents respectively. Slag P had been produced by the pelletization process while the other three had been granulated by quenching. Chemical and physical data of these eight materials are given in Table 1. Various

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TABLE 1 - Chemical and Physical Characteristics of Cements and Ground Slags

	Cements				Ground Slags			
	A	B	C	D	L	P	N	T
SiO <sub>2</sub>	19.3	20.6	21.6	20.0	33.0	35.4	36.1	35.0
IR*	0.20	0.13	0.51	0.70	0.41	0.36	0.13	0.10
Al <sub>2</sub> O <sub>3</sub>	5.7	5.0	5.3	6.8	11.8	12.7	9.9	12.3
Fe <sub>2</sub> O <sub>3</sub>	2.0	2.1	1.7	2.2	1.6	0.3	0.79	0.6
Mn <sub>2</sub> O <sub>3</sub>	0.04	0.05	0.11	0.03	0.64	0.89	0.51	0.43
P <sub>2</sub> O <sub>5</sub>	0.28	0.04	0.04	0.15	0.01	0.01	0.01	0.01
TiO <sub>2</sub>	0.25	0.22	0.26	0.32	0.59	0.76	0.36	0.52
CaO	62.4	65.4	64.2	64.5	41.3	41.3	41.0	40.9
MgO	2.5	1.8	2.4	1.1	9.0	6.7	9.5	7.8
SO <sub>3</sub>	4.0	2.4	2.8	2.9	0.13	0.14	-	0.3
S <sub>2</sub> <sup>3</sup>	-	-	-	-	0.86	0.76	1.1	1.1
LOI <sup>†</sup>	1.4	1.0	0.7	0.9	0.8	0.6	0.6	0.2
K <sub>2</sub> O total	1.22	1.13	0.79	0.69	0.51	0.60	0.35	0.83
Na <sub>2</sub> O total	0.34	0.12	0.15	0.23	0.32	0.24	0.18	0.64
K <sub>2</sub> O w/s	1.18	0.98	0.68	0.56	0.01	0.01	0.01	0.01
Na <sub>2</sub> O w/s	0.23	0.07	0.10	0.10	0.02	0.03	0.03	0.01
eq Na <sub>2</sub> O tot	1.14	0.86	0.67	0.68	0.66	0.63	0.41	-
Free lime	0.4	1.4	0.8	0.9	-	-	-	-
% glass	-	-	-	-	81	90	96	100
CM 1	-	-	-	-	1.88	1.71	1.67	1.74
CM 2	-	-	-	-	1.52	1.36	1.40	1.39
Particle Densities kgm <sup>-3</sup>	3110	3150	3140	3110	2950	2920	2910	2890
SSA m <sup>2</sup> kg <sup>-1</sup>	401	362	400	391	498	451	561	437

\* Insoluble residue determined according to BS 4550.

† Loss on ignition. Corrected for S<sup>2-</sup> oxidation

$$CM\ 1 = \text{Chemical Modulus} = \frac{CaO + MgO + Al_2O_3}{SiO_2} \text{ to BS 6699 : 1986 (4)}$$

$$CM\ 2 = \text{Chemical Modulus} = \frac{CaO + MgO}{SiO_2} \text{ to BS 6699 : 1992}$$

blends containing 30%, 40%, 50%, and 60% slag were prepared in a dry powder blender.

The reactive silica employed throughout the tests was calcined flint cristobalite (cfc) of particle size 1 to 2 mm (5).

Preparation and Treatment of Test Specimens

75 x 75 x 270 mm prisms were individually cast from hand mixed concretes made with BS 4550 granodiorite coarse aggregate and silica sand. Specimens were made in sets of five for each mix tested, the prisms containing 0% cfc and four levels of cfc chosen to cover the expected pessimum content. The cfc replaced part of the coarser sand fractions on a volume basis.

Binder contents of 225, 275, 350, and 450 kg/m<sup>3</sup> were chosen according to the alkali content of the cement and slag combination with the objective of either finding the threshold alkali level above which expansion occurred, or to compare the performances of certain binders at a given alkali level.

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Prisms had stainless steel reference studs cast into the end faces to facilitate length change measurements, and were cured and permanently stored in an atmosphere maintained at 20°C and 100% RH.

### Chemical Tests

Polypropylene vials of 20 ml capacity were completely filled with cement paste, capped, and sealed with adhesive tape. Each paste was mixed by hand in a beaker for 4 minutes at a water/solids quotient of 0.4.

The vials were stored at  $20 \pm 1^\circ\text{C}$  until the time of test, then broken open and the hardened paste crushed to  $-5 \text{ mm}$  in a nitrogen filled glove box. This material was vacuum dried at  $35 \pm 2^\circ\text{C}$  for 24 hours and then ground, under nitrogen, to  $-90 \mu\text{m}$ . LOI was determined on this powder at  $900^\circ\text{C}$  for 15 minutes in nitrogen. A further portion was extracted with an EDTA solution by the method outlined by Ernroy (6). The resulting residue consisted essentially of unhydrated slag, but also contained hydration products such as meixnerite and hydrotalcite, and insoluble components from the calcium sulfate set retarder. The potassium content of each paste residue was determined and related to the unhydrated slag after allowing for the other components by using information taken from work by Harrison et al (7) and Taylor (8).

Some of the  $-90 \mu\text{m}$  powder was ground on to  $-53 \mu\text{m}$  for the QXRD evaluation of calcium hydroxide.

### RESULTS

#### Prism expansions

Concrete prism expansion results are detailed in Table 2. Concrete alkali contents are tabulated for 50% release of alkali from the slag, and for 100% release ( $k_s = \frac{1}{2}$  and 1 respectively). The expansions relate to the specimen showing the greatest expansion of the four cfc prisms in a set (closest to pessimum) minus the moisture movement of the control prism. Significant expansion has taken place in some concretes of less than  $3 \text{ kg/m}^3$  equivalent soda. It is noteworthy that several slag cement concretes which expanded in excess of 0.1% did not start until 9 months or more old, and that expansion was sometimes continuing at over three and a half years age.

Tests with slag L at the 60% replacement level were started at a later date than the main programme and there may be more reaction to be seen. Meantime, the expansions of 0.2% and 0.1% of the 450 and 350  $\text{kg/m}^3$  mixes respectively are larger than expected. In the case of the leaner mix it is even greater than the 0.09% of the 50% replacement level concrete.

The high alkali slag T which was blended with cement B, produced much larger expansions than the opc in the concretes at the three cement contents and three replacement levels tested, strongly suggesting that a substantial proportion of the slag's alkalies had been released.

Figure 1 depicts the performance of slags L, P, and T when blended with cement B. The slag P clearly has a beneficial effect in reducing asr expansion when it replaces more than 30% of the opc. Slag L is of little benefit at any level up to 50% replacement despite its having a lower alkali content than opc B.

Slag N was clearly very successful in reducing the risk of asr and doubtless this was largely due to its low alkali content. Nonetheless, the expansions of the 350 and 450  $\text{kg/m}^3$  binder content prisms made from the 50/50 blend do suggest that what alkali was present in the slag had supported the asr. Eg, the alkali content of the 450  $\text{kg/m}^3$  mix from the Portland cement alone was only  $2.56 \text{ kg/m}^3$  and this would be quite insufficient to produce an expansion of 0.32%.

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TABLE 2 - Expansion Results

Cement	Slag	Slag %	Binder Content $\text{kgm}^{-3}$	Concrete Effective Alk. Level $\text{kgm}^{-3}$		Expansion		
				$k_s = \frac{1}{2}$	$k_s = 1$	Start days	Ult. days	Ult. %
B	-	0	450	3.87	3.87	90	330	0.32
	L	30	450	3.14	3.59	130	720	0.33
	P	30	450	3.13	3.55	160	720	0.30
	L	40	450	2.90	3.49	160	730	0.33
	L	50	450	2.66	3.40	270	>1300	0.34
	P	50	450	2.63	3.33	300	>1400	0.21
	L	60	450	2.42	3.29	390	> 800	>0.20
B	-	0	350	3.03	3.03	170	350	0.11
	L	30	350	2.46	2.80	180	680	0.12
	P	30	350	2.44	2.77	220	560	0.10
	L	40	350	2.28	2.74	210	600	0.12
	L	50	350	2.09	2.66	440	1000	0.09
	P	50	350	2.06	2.61	-	-	0.005
	L	60	350	1.89	2.58	780	>1100	>0.10
B	-	0	325	2.80	2.80	160	320	0.07
B	-	0	275	2.37	2.37	-	-	0.008
	L	30	275	1.94	2.21	-	-	0.003
	P	30	275	1.92	2.18	-	-	0.003
A	N	50	450	3.01	3.47	350	>1300	>0.32
	-	0	350	4.01	4.01	70	240	0.31
	N	50	350	2.36	2.72	600	>1300	0.05
	-	0	275	3.16	3.16	140	260	0.08
	N	50	275	1.86	2.14	-	-	NIL
	-	0	225	2.57	2.57	-	-	0.01
C	-	0	450	3.01	3.01	100	400	0.25
	P	30	450	2.53	2.95	230	520	0.22
	-	0	350	2.36	2.36	-	-	0.03
	P	30	350	1.97	2.30	-	-	0.002
	-	0	275	1.85	1.85	-	-	NIL
D	-	0	450	3.05	3.05	120	310	0.21
	P	30	450	2.55	2.97	250	970	0.23
	-	0	350	2.39	2.39	-	-	0.009
	P	30	350	2.01	2.33	-	-	0.008
B	T	50	450	3.24	4.56	170	1020	0.41
	T	60	450	3.11	4.69	280	1030	0.33
	T	30	350	2.73	3.36	120	400	0.26
	T	50	350	2.54	3.57	200	1020	0.26
	T	60	350	2.44	3.66	400	1030	0.21
	T	30	275	2.15	2.64	250	400	0.05

Chemical tests

In the previous paper (3) it was speculated that the slag P might have a greater capacity for reducing the calcium hydroxide level in the concrete on account of its lower basicity. This might reduce the availability of  $\text{Ca(OH)}_2$  and thus alter the nature of the alkali-silica reaction and its potential to cause expansion. To examine this idea tests were carried out on cement pastes.

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TABLE 3 - Percentage Calcium Hydroxide in Paste calculated on Ignited Paste, w/s = 0.40

Cement	Slag	% Slag	Age of Paste, weeks					
			4	13	26	52	104	
B	L	30						
		50	5.6	6.5	6.3	9.4	7.1	
		60	6.1	4.5	4.1	5.9	6.3	
B	P	30						
		50	8.3	8.6	8.4	9.4	7.1	
		60	6.2	6.3	6.3	7.5	8.2	
B	T	50	7.3	7.1	6.9	6.5	7.1	
		60	5.4	5.2	5.2	5.5	6.0	
A	N	50	6.5	8.7	7.2	5.0	4.7	

Table 3 gives calcium hydroxide contents of pastes expressed as mass percentage on the ignited paste. Results are available so far up to two years only but these are in broad agreement with those obtained by Hinrichs and Odler (9) where the  $Ca(OH)_2$  contents of slag cement pastes slowly diminished with increasing age from a few days after mixing. A few slightly erratic variations with time occurred in the present work, similar to those observed by Luke and Glasser (10).

The P slag  $Ca(OH)_2$  contents do not differ much from those of the other slags and do not yet show any tendency to become exhausted.

The potassium content of the unhydrated slag in each paste at each age is given as a percentage of the anhydrous slag's content in Table 4. These determinations are subject to experimental errors of several percent, but the results suggest that after six months or so three of the slags are less rich in potassium than the original material. It follows that the regions of a slag particle richer in potassium hydrate more readily than the leaner regions, and since it is also the glass phase which hydrates and which also holds the bulk of the potassium (11), the overall result is likely to be genuine.

The exception is slag P which seems to be reluctant to release its potassium.

Table 4 - Potassium content of Unhydrated Slag in each Paste as a Percentage of the content of the Original Slag

Cement	Slag	% Slag	Age of Paste, weeks				
			4	13	26	52	104
B	L	30					
		50	90	101	99	74	
		60	97	91	105	90	78
B	P	30					
		50	100	102		92	
		60	93	97	97	96	90
B	T	50	87	93	91	74	72
		60	88	95	96		84
A	N	50	103	87	99	76	67

DISCUSSION

Table 2 clearly shows that in the majority of slag cement concretes with a total alkali content greater than  $2.5 \text{ kg/m}^3$  the slag has made a positive contribution to asr expansion. While this also applies to some extent to the slag P at 50% replacement, this slag has usefully reduced concrete expansion below that of the corresponding opc concrete. There are at least three factors which can contribute to the P slag's performance. First, it hydrates more slowly than the other slags, as shown by concrete cube strengths (3), and this provides more opportunity for leaching of alkalis from the concrete. Second, the part of the slag which hydrates in the first few years does not seem to be particularly rich in potassium. Third, it has a lower sodium/potassium quotient than the other slags and sodium is known usually to be more asr aggressive than potassium, mole for mole.

The reason why many test programmes have shown slags to be very effective in eliminating or reducing asr expansion while other work including that with cfc has found otherwise is not fully understood. It may be that cfc reacts at a slightly lower level of alkalinity than most natural aggregates, but two further factors are probably of greater significance. First, a large proportion of the tests done with natural aggregates used very rich mixes of  $700 \text{ kg/m}^3$  or so and the lower water/cement quotients of these mixes may not have provided sufficient water to hydrate the slag fully and extract the alkalis. The consequent trivial or absent expansion would not be a result which could be fairly related to the usual field concretes. Second, the work done with cfc employed dense coarse aggregate, which maximises asr expansion. Where more porous coarse aggregates have been used in tests with natural reactive sands, some alleviation of expansion would have occurred as discussed by Collins and Bareham (12).

A major problem encountered in long term asr expansion tests at  $20^\circ\text{C}$  is finding a means to allow the concrete to imbibe water while preventing leaching of alkalis. In current UK practice the prism is wrapped in wet towelling and the assembly sealed in a plastics bag. Although no reactants escape from the bag, they do enter the towelling lowering their concentrations inside the concrete. Concentrations might fall below the threshold values for silica attack and terminate reaction earlier than would be the case with no leaching.

The test specimens of the present paper were placed bare on shelves in a fog room. A limited amount of testing has shown that leaching takes place, but almost certainly at a significantly slower rate than that associated with towelling.

It is possible that cfc produces significantly different asr expansion test results to some natural reactive aggregates. Nevertheless, the results reported in this paper do show that under certain conditions slags are capable of releasing the majority of their alkali metal ions into the pore solution and that this may cause the pH to rise sufficiently to continue or regenerate the alkali silica reaction.

CONCLUSIONS

1. Under the test conditions described, it is clear that three of the slags positively contributed well over 50% of their alkalis to asr at the 30% and 50% levels of cement replacement. However, one of these three had a low alkali content and considerably reduced the risk of asr when blended with a high alkali Portland cement. The fourth slag, a pelletized product of moderate alkali content, also contributed to asr but to a lesser extent and offered some degree of asr-alleviation.
2. The partial replacement of Portland cement by slag delayed both the onset and completion of expansion; the latter, sometimes by a few years.

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3. When an expansion test is carried out on a concrete prism over a period of some years, thought should be given to arrangements for preventing leaching of the specimen during moist storage.

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Figure 1 Influence of Slag Content on Ultimate Expansion

