

Table 4 : Expansion of Bars containing Beltane Opal

Mix Ref No:	Expansion in Microstrain			
	14 Days	2 Months	6 Months	12 Months
2011B	88	139	164	172
2021B	84	172	216	236
2031B	120	235	295	304
2041B	276	493	529	528
2051B	144	189	200	200
2061B	112	152	159	152
2071B	109	140	153	156
2311B	112	238	262	264
2321B	127	293	337	324
2331B	160	368	416	396
2341B	129	219	251	268
2351B	121	223	247	248
2361B	109	224	239	244
2371B	92	223	252	224

Table 6 : Alkali Contents of Bars containing Beltane Opal

Mix Ref No.	Density kg/m ³ *	Na ₂ O _{eq} kg/m ³ **	*** Analysis of Bar			*** Analysis of liquid below each bar		
			%Na ₂ O	%K ₂ O	Na ₂ O _{eq} kg/m ³	%Na ₂ O	%K ₂ O	Na ₂ O _{eq} kg/m ³
			2011B	2070	6.30	0.113	0.314	6.62
2021B	1980	6.00	0.109	0.295	6.00	0.001(5)	0.004(3)	0.086
2031B	1910	5.77	0.098	0.286	5.47	0.001(7)	0.006(7)	0.117
2041B	2180	6.65	0.089	0.251	5.54	0.009(1)	0.025(3)	0.561
2051B	2180	6.65	0.098	0.280	6.15	0.005(0)	0.014(1)	0.311
2061B	2170	6.62	0.102	0.275	6.14	0.003(2)	0.008(5)	0.191
2071B	2160	6.59	0.105	0.292	6.42	0.003(4)	0.008(6)	0.196
2311B	2070	3.10	0.147	0.386	8.30	0.003(9)	0.009(8)	0.214
2321B	1970	2.94	0.140	0.372	7.58	0.002(6)	0.006(4)	0.134
2331B	1890	2.81	0.148	0.395	7.71	0.001(7)	0.006(1)	0.108
2341B	2140	3.21	0.128	0.337	7.48	0.008(9)	0.020(2)	0.475
2351B	2120	3.18	0.140	0.352	7.88	0.005(4)	0.013(7)	0.306
2361B	2120	3.18	0.138	0.353	7.85	0.005(6)	0.012(8)	0.297
2371B	2130	3.20	0.139	0.359	7.99	0.004(6)	0.010(7)	0.248

* As determined at time of chemical analysis
 ** Calculated using the alkali content of the Portland cement
 *** Expressed with respect to the mass of each bar

EFFECT OF SILICA, PFA AND SLAG ADDITIVES ON THE COMPOSITION OF CEMENT PORE FLUIDS

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The pore fluid of a moderately low alkali cement with and without additives has been analyzed after 30 and 90 d cure. During this time, typical PFA's are not sufficiently reactive at ~18°C to affect significantly the aqueous phase composition and pH, but slag and a chemically-produced SiO₂ do exhibit significant reactivity. These data are assessed with a view to designing long-term experiments relevant to elucidating the chemical evolution of the aqueous phase in real cement-based systems.

Pore fluid, PFA, Slag.

1. INTRODUCTION

Slag, PFA and other pozzolanic addition appear to be helpful in controlling the extent to which alkali-aggregate reaction occurs in set cements. These materials might act by effectively removing alkali from the aqueous pore fluid, thereby lowering the alkalinity of the system. Once setting has occurred, it is difficult to sample directly the pore fluid composition, although this has been partly surmounted by the development of powerful squeezers which can extract a sample of the pore fluid even from set cements. Using squeezer designs developed elsewhere /1,2/ we report on exploratory studies on the role of pozzolans in controlling the pore fluid composition.

2. MATERIALS

A cement having a moderately low alkali content was selected. Additives used include (i) a chemically reactive, high surface area silica produced by flame hydrolysis of SiO₂ and sold commercially by Degussa (FK 320) (ii) ground iron blast-furnace slag, containing > 98% glass, ex Ravenscraig (iii) a suite of five British PFA materials consisting of a siliceous glass and having a variable content of crystalline materials (e.g., mullite, spinel, quartz, feldspar) and (iv) a natural Italian pozzolan, consisting largely of crystalline phases. Each sample was analyzed for Na and K contents by flame emission, following LiBO₂ fusion with the results shown in Table 1.

Table I: Alkali Contents.

Material	(wt %) Na ₂ O	K ₂ O
OPC	0.19	0.48
Degussa SiO ₂	0.88	< 0.02
Slag	0.37	0.64
PFA		
Barony	0.33	3.04
Eggborough	1.14	3.73
Fiddler's Ferry	0.81	3.43
Ironbridge	0.84	2.83
Longannet	0.28	1.39
Natural Pozzolan	0.59	2.67

The cement has a moderate-to-low alkali content with K₂O > Na₂O. The flame hydrolysis silica also has a substantial alkali content, especially of Na, relative to the cement. Slag, while normally considered to be low in alkali also has a comparatively high alkali content while the PFA materials, as well as the natural pozzolan, all have a high alkali content such that K₂O > Na₂O. Thus the total alkali content of the reactive components of composite materials made with these additives is likely to be raised or at least maintained, relative to neat cement. In the examples studied the additives, if reactive, do not dilute the alkali content of the system.

of reliable measurement; a target value of the displaced pH of 11 - 12 was selected, and the apparent original solution pH calculated from the displaced pH and the quantities of reactants used. The validity of this procedure is discussed subsequently. Finally, the solution pH was calculated from the independently-determined Na and K contents, assuming both to be present as fully-dissociated $M^+ OH^-$. Table 3 shows the results obtained from the 90 d extracts. The presence of PFA makes little difference to the pH, relative to the OPC control. Slag-cement falls towards the upper end of the range of observed pH's, but Degussa silica composites, with their considerable sorptive potential for K, give markedly lower pH values. The pH's determined by the acid-displacement method and those calculated agree within limits of experimental error.

Table 3. Solution pH's.

OPC and -	corrected for acid	calc. from (Na+K) conc.
no additives (neat)	13.43	13.42
Degussa silica	13.10	13.13
Slag	13.54	13.50
PFA		
Barony	13.47	13.45
Eggborough	13.50	13.46
Fiddler's Ferry	13.45	13.45
Ironbridge	13.48	13.46
Longannet	13.43	13.43
Natural Pozz.	13.61	13.52

the composites, relative to the OPC control. The portlandite content was determined by TGA. The results after 90 d are shown in Table 4. The neat cement yielded 22.84% $Ca(OH)_2$; however, having been diluted by 15% material inert in the special sense that it will not produce $Ca(OH)_2$ upon hydration, the equivalent portlandite content would be 19.41%. This value, shown in (), should be compared with other 15% additions. The PFA's are seen to have undergone little reduction in $Ca(OH)_2$ content. This is interpreted as indicating that the pozzolanic reactor is still at an early stage. Slag, and to an even greater extent, active silica, have substantially reduced the free $Ca(OH)_2$ content thereby indicating their greater reactivity. The natural pozzolan - the mineralogy of which is largely unknown - gives a strongly alkaline reaction upon mixing with water and it is not therefore surprising to see an enhanced $Ca(OH)_2$ content.

Table 4. Portlandite Contents

Sample, OPC and -	% $Ca(OH)_2$ by weight
No additive (with 15% inert diluent)	22.84 (19.41)
Degussa silica	7.49
Slag	17.53
PFA	
Barony	19.29
Eggborough	19.22
Fiddler's Ferry	19.22
Ironbridge	19.24
Longannet	19.46
Natural pozzolan	22.53

5. DISCUSSION

Limitations of space precludes a complete discussion, and we therefore highlight several key points. In the course of 90 d, pozzolanic reactions have only just begun for less-active pozzolans such as PFA. It is therefore not surprising that they have not yet had time to modify appreciably the aqueous phase composition. The more active pozzolans (slag, and especially high-surface SiO_2) have, however, undergone appreciable reaction. Their influence on the aqueous phase differs. The slag contains about 1% total alkali, rather more than the cement, and this leads to an actual rise in the pore fluid alkali, relative to neat cement. Apparently neither slag or its hydration products exhibit strong sorption for alkali. High-surface area SiO_2 , on the other hand, produces a strong sorption for K. Complimentary

3. METHODS

Cylinders 42 mm diameter and typically weighing 200 g were made to a w/c ratio = 0.60. These were aged at 16 - 18°C for 30 and 90 days at 100% RH in CO_2 -free conditions. After ageing, the cylinders were pore-squeezed, resulting in the collection of 2 - 6 ml of fluid which was used for pH determinations, and then acidified to permit storage without precipitation occurring until analyses could be done. The solid was used for determination of residual water by drying at 105°C and analyzed quantitatively for $Ca(OH)_2$ by TGA.

4. RESULTS

4.1 Chemistry of the pore fluids

Table 2 records the Na_2O and K_2O contents of the pore fluids after 30 and 90 d. To facilitate subsequent calculations, these concentrations are given in units of molarity as elemental Na or K, rather than as oxides Na_2O or K_2O . Contrasting the behaviour of samples with and without additives, it may be seen that the addition of Degussa silica has a strong effect in reducing the K content of the aqueous phase. This SiO_2 , which has a surface area by N_2 sorption of 170 m^2/g , is known to exhibit strong sorption for monovalent cations; in alkaline solution, its sorptive effect increases in the order $Na < K < Cs$ with the result that the K content is more markedly influenced by its

Table 2. Analyses of Pore Fluids

Sample: OPC and additive	Molarity in:-				Conc., $\mu g/ml$.	
	Na		K		Ca	Al
	30 d	90 d	30 d	90 d	90 d	90 d
None	0.058	0.064	0.222	0.200	110	2
Degussa SiO_2	0.058	0.070	0.065	0.063	120	3
Slag	0.076	0.098	0.247	0.219	80	4
PFA (Barony)	0.052	0.063	0.209	0.220	71	9
" (Eggborough)	0.063	0.081	0.215	0.207	85	8
" (Fiddler's Ferry)	0.059	0.072	0.217	0.207	77	11
" (Ironbridge)	0.066	0.081	0.215	0.207	71	4
" (Longannet)	0.059	0.075	0.217	0.195	67	6
Natural Pozzolan	0.076	0.088	0.253	0.246	85	6

addition than Na. Many of the PFA materials have some sorptive capacity for Na and especially K, but are also themselves relatively rich in alkali, which is potentially liable to release in the course of pozzolanic reaction. The net result of these two opposing tendencies - release of alkali during pozzolanic reaction, and removal by sorption on the pozzolan and its hydration products - are roughly in balance at 90 d. Slag, natural pozzolan and the most reactive of the PFA's give increased Na concentrations while natural pozzolan increases somewhat the aqueous-phase K concentrations, all relative to neat cement. The relatively high alkali content of the aqueous phase helps significantly to reduce the Ca content, from ca 120 - 70 $\mu g/ml$. At the same time the alkali contents, typically 0.1 - 0.2 M (Na + K), are not yet sufficiently high to enhance significantly the solubility of Al, which remains very low.

4.2 pH of the pore fluids

The pH was measured using a conventional electronic pH meter/electrode combination. These electrodes are subject to considerable error and drift, particularly at $pH > 13$ and the resulting measurements are unreliable. Therefore, the pH was not measured directly, but instead measured after addition of a standard quantity of acid sufficient to bring the solution pH into the range

studies, made using radiocaesium /3/ confirm that this mechanism is one of sorption, at least during the initial stages of reaction. This alkali removal leads to a lowering of the pH of the solution, relative to the control.

Experiments designed to demonstrate the effect of less-reactive pozzolans at "normal" temperatures will clearly have to extend over periods longer than 90 d, and probably over several years, in order to determine what, if any chemical control these materials exert on the pore-fluid chemistry. Elevated temperatures may, within limits, be useful to accelerate reaction thereby compressing the time scale required to assess the effect of specific additives.

These preliminary experiments are, it is felt, instructive, because not only do they give some indication of how the more reactive materials behave, but they also give insight to the chemical nature of the alkaline pore fluid. Both Na and K evidently contribute equally to the alkalinity; thus a "fully ionized" model is appropriate to describe the chemical state of the major components at least up to ionic strengths of 0.2M. Further work with a high alkali cement would be desirable to determine whether this simple description extends to pore fluids of still higher ionic strength in which, moreover, A₂ may be increasingly soluble.

We also find these preliminary studies helpful to indicate how an internal 'alkali balance' can be constructed using experimentally - attainable data. The objective of the alkali balance model will be to explain the partition of alkali between unreacted constituents (clinker, pozzolan), aqueous phase, cement hydration products and a potentially reactive aggregate. Much of the oral presentation will centre about the development of this 'alkali balance' model, its data input and its assumptions.

6. ACKNOWLEDGEMENT

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7. REFERENCES

- 1/ LONGUET, P., BURGLIN, L., and ZELWER, A. Rev. Mater. Construct. 1973 No. 676, 34 - 41.
- 2/ BARNEYBACK, Jr R.S., and DIAMOND, S. Cement Concr. Res. 1981, 11, 279 - 285.
- 3/ GLASSER, F.P., RAHMAN, A.A., CRAWFORD, R.W., McCULLOCH, C.E., ANGUS, M.J. Immobilization and Leaching Mechanisms of Radwaste in Cement Based Matrices. Report DOE/RW/82-108 (Nov. 1982).

SUMMARY

This discussion concerns some adventitiously occurring variations in the physical and chemical composition of fly ashes which are derived from different coals and which receive different preparative and combustion treatments.

In addition some difficulties encountered in producing and controlling the performance characteristics of blended cements are mentioned briefly along with some problems which may occur in concrete when blended cements are substituted for straight portland cements.

Although fly ash additions may improve some properties of concrete and reduce the magnitude of some problems, they should not be regarded as an assured universal cure-all for all the defects of portland cement concrete.

INTRODUCTION

The general upward trend in electricity demand and in mining and industrial activities throughout the world has accentuated the need for the effective disposal of increasingly large quantities of waste materials such as mine tailings, washery residues, furnace slags, fly ashes, alumina refinery red muds etc. All of these waste products have potential uses. Economic considerations will of course determine the extent of their utilization and such factors as an assured supply of suitable quality material, its processing cost, its proximity to processing plants and markets and the market acceptance of waste products must be evaluated against the costs of alternate methods of transport and disposal and the availability of dumping sites. The imposition of increasingly restrictive environmental protection limitations on waste disposal will inevitably promote the utilization of such materials.

The future trend towards the increased use of pulverized coal in place of oil for electricity generation will accentuate certain operational problems in the production, handling, combustion and safe storage of pulverized solid fuel simultaneously with the need to handle and dispose of increasingly large quantities of fly ash. At its power station source fly ash has a negative value since it must be handled and transported to a dumpsite. Consequently, the use of fly ash as a portland cement replacement, especially in pre-mixed concrete, is becoming increasingly prevalent. Fly ash may be dispensed directly into the mixer as a separate component of the concrete mix or it may be interground with portland clinker and gypsum to produce a blended portland-fly ash cement which is somewhat comparable to other types of blended cements such as portland-pozzolan and portland-granulated blast furnace slag cements.

The present paper therefore discusses the desirable properties and preferred quality of fly ash and the production and performance of blended portland-fly ash cements and blended cement concretes under normal working conditions. In addition the mechanism of fly ash reaction and the behaviour of fly ash reaction products are discussed together with some of their effects on the properties and performances of concrete.

PROPERTIES AND QUALITY OF FLY ASH

Fly ashes possess chemical and physical properties which are largely influenced by the characteristics of the raw coal ash. Inorganic residues which occur naturally as lenses or narrow bands in coal can have variable chemical and mineralogical compositions. The physical state of ash inclusions is first modified by the preparatory treatment of raw coal and secondly to a somewhat