Conference paper
Wardle, M., Taylor, R., Li, Q., Li, S. and Black, L. (2009) *The effect of co-combusted biomass-coal fly ash on the behaviour portland cement.* In: 29th Cement and Concrete Science Conference, 7 - 8 September 2009, Leeds.

The Effect of Co-Combusted Biomass-Coal Fly Ash on the Behaviour Portland Cement

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Abstract: This project has investigated the hydration behaviour of pfa-OPC blended cements, comparing conventional pfa with that obtained from co-firing of coal with biomass (palm kernel expeller). Calorimetry, thermal analysis and electron microscopy have been used to investigate the compositions and microstructures of the hydrated pastes. These have been used to explain the materials' engineering properties (strength development and workability). The results showed that, in the short term, the behaviour of the co-fired material is comparable with that of conventional pfa, there being no discernable differences between the two systems.

Aims and Objectives

Energy generators are committed to 10% production from renewable resources. These aims can be met by co-firing biomass with coal, earning the power companies Renewable Obligation Certificates. However, the pfa produced by co-firing coal and biomass does not always meet EN450[1]. This third year research project has investigated the hydration behaviour of a Portland cement–co-fired pfa mix and compared this with a conventional pfa. Conventional pfa was compared with a pfa obtained by co-firing coal and palm kernel expeller in terms of strength, shrinkage, phase composition and microstructure.

Experimental

The elemental compositions of the starting materials were determined by x-ray fluorescence. Mixes were prepared in the ratios OPC:sand:water 1:3:0.5, with replacement of the OPC by 40% of either the conventional or co-fired pfa where necessary. 40% replacement was chosen to exacerbate any differences between the two fly ash samples. The mortar samples were then investigated by the following methods; workability via the flow table method[2], compressive strength[3], scanning electron microscopy, thermal gravimetric analysis and isothermal calorimetry.

Results

Table 1 shows the elemental composition, as determined by XRF, of the materials used in this study. The LoI of the co-fired ash, at 12.36 is greater than the allowable limit of 5%. However, much of this loss on ignition was attributed to sulphate, since quantitative XRF, requiring that the sample be fused with lithium tetraborate at 1100^{o}C , gave a sulphate content of 0.1%. Other noticeable differences are that the co-fired pfa contains less aluminium and iron, and slightly more calcium. Visually, the co-fired pfa was very dark grey in colour, imparting a dark grey colour on the resultant mortars.
Table 2 shows the effects of pfa addition on workability, as determined by BS EN 12350-5. The addition of PFA improved the workability of the mortar. This supports previous work on PFA workability by Dhir *et al*[4]. The generally lower water demand for the fly ash represents a commonly observed advantage relative to pure OPC due to the porous spherical nature of the pfa

particles. Contrary to expectations, since higher LoIs are normally indicative of carbonaceous material, the co-fired pfa had an even lower water demand.

Table 1: Elemental composition of the materials used in this investigation.

Oxide	OPC (%)	PFA (%)	Co-fired PFA(%)
SiO_2	21.0	49.8	51.46
Al_2O_3	4.63	26.4	19.32
Fe_2O_3	2.26	9.3	5.49
CaO	65.6	1.4	4.29
MgO	1.18	1.4	1.71
SO_3	2.69	0.8	9.36
Na_2O	0.16	1.5	1.02
K_2O	0.78	3.5	2.34
Cl	0.01	0.01	0.04
LOI	0.99	4.9	12.36

Table 2: Mix specifications and workability data.

	OPC (g)	Sand (g)	PFA (g)	Co-fired PFA (g)	Water (g)	Flow Diameter (mm)
Control	224	673	0	0	112	109
Mix 1	135	673	89.8	0	112	120
Mix 2	135	673	0	89.6	112	135

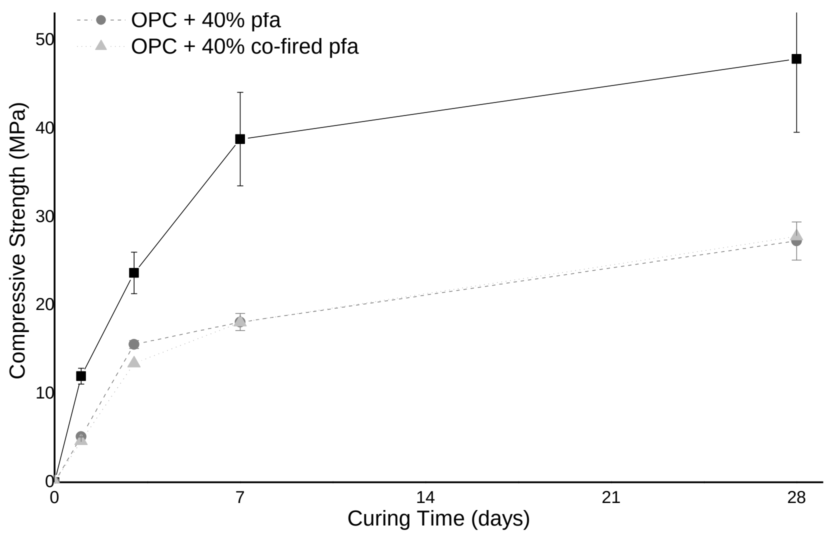

Figure 1: Compressive Strength Development of the Various Mixes.

Figure 1 shows the strength development of the three mixes. Whilst the OPC mortar was considerably stronger, there were no discernable differences between the two pfa-containing mixes. There were however slight changes seen in the calorimetry data (Figure 2 and Table 3). The addition of pfa appeared to delay the hydration, and led to reduced heat evolution over the first 70 hours. There was also the appearance of a distinct second peak at about 16 hours. These results support previous research by Bai and Wild[5] suggesting that PFA substituted cement retards the overall reaction rate. The drop in relative heat output was attributed to the reduction in OPC content, a dilution effect, and the negligible contribution from pozzolanic activity by the

PFA. The consequences of this are that the mortar/concrete will be subjected to much less thermal expansive stresses, thus decreasing the chance of cracks forming and ultimately improving the durability of the concrete. The co-fired pfa delayed hydration slightly less than the conventional pfa, possibly due to the increased levels of sulphate and calcium in this material.

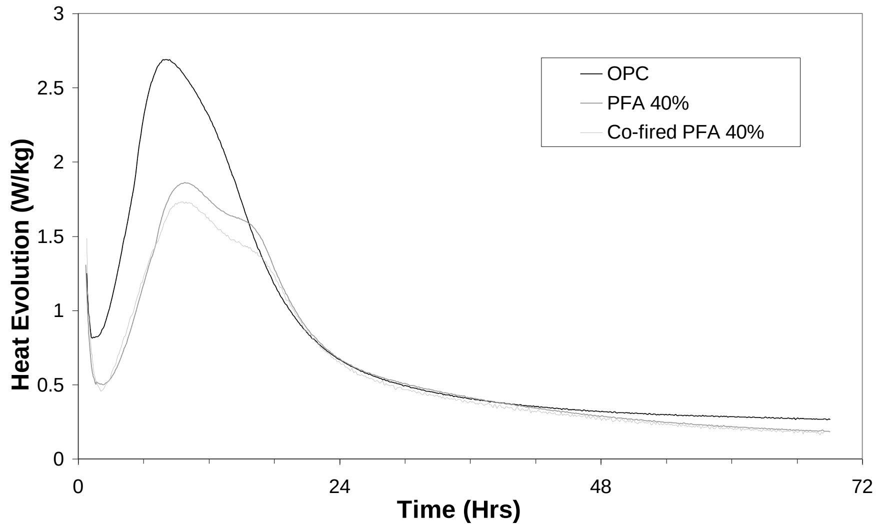

Figure 2: Isothermal Calorimetry Data for the Various Mixes

Table 3: Total Heat Evolution, Rate of Evolution and Time of Maximum Heat Evolution for the Various Mixes.

	Total Heat Evolved (kJ/kg)	Max rate (W/kg)	Time of max. rate
OPC	195.42	2.686	8 h 22 min
PFA	158.67	1.859	9 h 47 min
Co-PFA	149.22	1.733	9 h 17 min

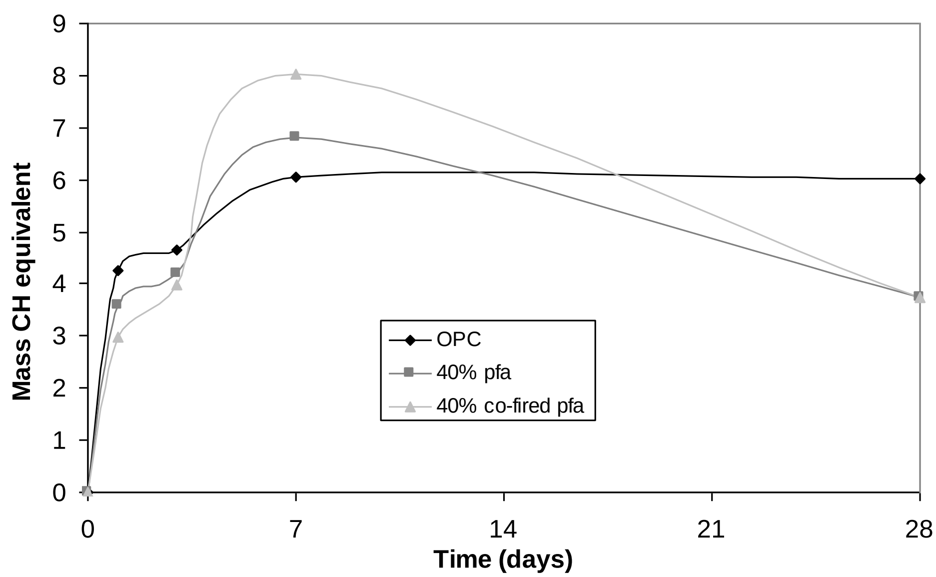

Figure 3: Amount of portlandite detected in the various pastes by TGA.

Thermal analysis was then used to determine the quantities of portlandite present in the hydrated pastes. The portlandite is a product from the hydration reaction of the calcium silicates from the cement. It is clear from Figure 3 that portlandite is produced rapidly upon hydration. Portlandite production in the OPC mortar soon levels off, whilst the levels of portlandite in the blended cements started to diminish beyond 7 days as the portlandite is consumed in the pozzolanic reaction. Comparing the two fly ashes, the results are not too dissimilar. However, the co-fired ash exhibits slightly higher levels of portlandite after 7 days, perhaps reflecting a slightly reduced mid-stage reactivity.
Figure 4 shows SEM images obtained from the two blended cements. The figure on the left contains co-fired pfa whilst that one the right contains conventional pfa. There is little difference between the samples, with similar sized spherical pfa particles distributed throughout the matrix. However, in the image from the sample containing co-fired pfa there are a number of dark features, possibly due to the slightly elevated levels of carbonaceous material in the pfa.

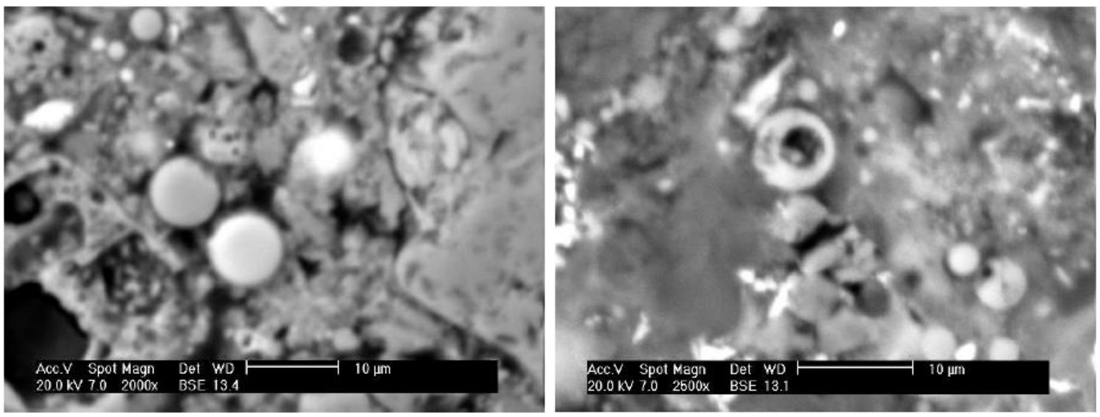

Figure 4: SEM Micrographs of the Blended Cement Mortars,
(Co-fired pfa lef,t Conventional pfa right)

Conclusions

This study has shown that co-fired pfa performs similarly to conventional pfa in OPC mortars. There is negligible difference in terms of compressive strength, microstructure and hydration behaviour. However, the co-fired ash did increase workability, and it is important to note that no long term durability tests were performed.

References

[1] EN450 (Fly ash for concrete — Part 1: Definition, specifications and conformity criteria)

[2] BS EN 12350-5

[3] BS EN 12390-3

[4] R K Dhir, *et al*. ‘Contribution of PFA to workability and strength development’, Cem. Conc. Res. (1988). 18, 277-289.

[5] J. Bai, S. Wild, ‘Investigation of the temperature change and heat evolution of mortar incorporating PFA and metakaolin’, Cem.Conc. Comp., (2002), 24, 201–209