

Comparative Performance of Beneficiated Run-of-Station Fly Ash as Cement

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KEYWORDS: run-of-station fly ash, air-cycloning, thermal processing, grinding, mortar, consistence, compressive strength development, initial surface absorption, porosity.

ABSTRACT

The overall aim of the work reported in this paper was to investigate different methods of enhancing the quality, in terms of its use as cement, of typical run-of-station, low-lime, bituminous fly ash from a large low SO_x/NO_x coal-fired power station. The key objective was to improve the particle size characteristics and reduce the amount of residual unburned coal material. In order to achieve this, three simple methods of enhancing fly ash properties, namely air-cyclone classification, thermal processing and grinding, were studied on laboratory scale. The study showed that all treatments led to enhanced properties (i) of the fly ash (particle size distribution, morphology and chemical composition) and (ii) of mortars containing the treated fly ash as a replacement for Portland cement (in terms of consistence, compressive strength development, initial surface absorption and porosity). However, significant differences were noted in the comparative performance of the fly ash produced by the different processing methods. Given the positive outcome, it is hoped that producers will be encouraged to adopt a policy of holistic utilisation of fly ash produced with different particle phases being used in the most appropriate manner.

INTRODUCTION

In the drive towards ever cleaner coal-fired power stations, producers in many countries have modified furnace conditions to reduce emissions of both SO_x and NO_x. Although this is both laudable and necessary, given government regulations, these changes generally have an adverse effect on the quality of fly ash (FA) produced (usually termed as run-of-station ash), particularly with respect to its premium outlet as a cement [1-8]. Generally, particle size is coarsened and/or residual carbon content increased, both of which impact significantly on the water reducing ability and reactivity of FA. In extreme cases, the run-of-station ash cannot be used as a cement component, without some form of beneficiation. Consequently, a number of such methods have been developed and are being adopted by an increasing number of producers to enhance ash quality and ensure outlet to the

cement market, with the concomitant economic benefits. However, whilst there has been a significant amount of research and development work on processing techniques themselves and the characteristics of the ash obtained, there is limited data on the comparative performance of these materials in cementitious mixes.

This paper considers a range of methods to control the physical and/or chemical characteristics of FA and the effect of these on the performance of processed FA in cementitious mortars. Three types of FA processing were investigated, namely (i) air-cyclone classification, (ii) thermal treatment at 600°C and 900°C and (iii) mechanical grinding. These treatments were selected as being among the simplest and most straightforward methods, with a potential for use at full-scale.

Processing effectiveness was determined by measuring their impact on key FA properties such as particle size distribution, morphology and chemical composition. In addition, the effect of changes in the characteristics of the processed fly ashes was assessed on mortars containing treated FA at 15%, 30% and 45% by mass cement. Measurements of consistence, strength development, surface absorptivity of water and porosity were made and compared with those of mortars containing untreated (raw) fly ash.

EXPERIMENTAL PROGRAMME

Test Materials and Mortar Specimen Preparation

The Portland cement (CEM I, denoted hereafter as PC) used in the study conformed to BS EN 197-1 [9]. A bituminous fly ash (FA) was obtained directly from a large coal-fired power station. This FA is typical of low emission power stations and, therefore, expected to be relatively coarse. The FA considered was used to replace PC at 15%, 30% and 45% levels by mass cement. However, the 45% replacement was not examined on the cycloned FA, due to limitations of material quantity. A water/cement ratio of 0.50 and a ratio of cement to natural sand ($G_F=85$, conforming to BS EN 12620 [10]) of 1:3 were used for all tests. Mixing of the mortars was carried out in accordance with the method described in BS EN 196-1 [11]. Mortar prisms, 160x40x40mm, were cast for strength tests and 40x25x25mm specimens for porosity measurements. All specimens were water-cured at 20°C until testing.

Processing Methodologies

Air-Cyclonic Separation

Processing FA by using an air cyclone is a simple method for improving FA quality by separating the coarse, heavy and/or non-spherical particles from the fine particle fraction [12]. Air-cycloning has the particular advantage of being able to be continuously fed, thereby allowing large quantities of ash to be treated in a fixed period of time. In this study, a Stairmand-type, tangential inlet high-efficiency type cyclone [13] was developed. In this case, the work concentrated on obtaining the finest fraction of particles from the raw ash, i.e. $<10\mu\text{m}$.

Thermal Processing (Carbon Burn Out)

Thermal processing was used to reduce the loss-on-ignition (LOI) of the raw FA, as this is generally considered to be detrimental to the quality of the material. This was carried out in a laboratory muffle furnace at 600°C (denoted TP600) and at 900°C (denoted TP900) (the raw FA was placed in a crucible with a bed depth of 10mm and then ignited for 3.5 hours at the specified temperature). Following ignition, the processed sample was placed in a desiccator for 24 hours to cool. This type of processing is obviously extremely slow and produced only small quantities of processed ash, as well as adding to the CO₂ emissions load.

Mechanical Grinding (Ball-Milling)

Grinding of the raw FA, is a simple, but rather crude, method of reducing the mean particle size. In this study, the raw FA was ground in a laboratory planetary ball mill, until the majority of particles, in this case >98% by volume, were finer than 45µm. Grinding required typically around 20 minutes for 200g of FA in a 500cm³ tungsten carbide container with six 15mm diameter tungsten carbide balls, which makes this a relatively slow process, compared to the continuous cyclonic separation. In addition, it does not reduce the residual carbon content and, indeed, is likely to increase its surface area.

Test Procedures

- A laser particle size analyser (Malvern Mastersizer Type E) was used to measure the particle size distribution of both raw and processed FAs [14].
- Particle morphology of the FAs was studied visually using scanning electron microscopy (SEM).
- X-ray Fluorescence Spectrometry (XRFS) was used to measure the bulk oxide composition of the raw and processed FAs, whilst calibration curves, derived from international standards, were used to enable quantification.
- The effect of processed FA on mortar consistence was determined with the mortar flow spread test [15,16].
- Strength development was measured in accordance with BS EN 196-1 [11] after 28, 90 and 180 days curing.
- The initial surface absorption specimens (150mm cubes) were oven-dried at 105°C till constant weight after 180 days water curing and tested on two faces using the standard ISAT apparatus.
- Bulk porosity was determined at 28, 90 and 180 days on oven-dried specimens (105°C for 72 hours) by measuring the volume of toluene absorbed after 180 minutes immersion in a vacuum chamber.

CHARACTERISTICS OF RAW AND PROCESSED FLY ASHES

Particle Size Distribution

The particle size distributions of the raw and processed fly ashes are given in Table 1 and Figure 1. As expected, the raw FA was relatively coarse with broadly distributed particle sizes. In contrast, the cyclone processed FA was found to be very fine, with a narrow, but well-distributed, particle size range. Virtually all particles were below 10 μ m in diameter, with in excess of 90% falling between 1 and 4 μ m, providing mean sizes of around 2 μ m.

Table 1 Effect of processing fly ash on particle size

FA Type / Processing Method	Fly Ash Particle Size Characteristics ¹					
	Mean size, μ m			Volume above, %		
	d(v,0.1)	d(v,0.5)	d(v,0.9)	10 μ m	20 μ m	45 μ m
Raw	1.9	19.2	76.8	64.7	49.0	24.2
Cycloned	0.9	2.0	4.5	0.2	0.0	0.0
Thermal TP600	1.9	16.6	79.0	61.7	45.5	23.2
Thermal TP900	3.5	18.4	72.8	70.1	47.1	20.5
Ground	1.3	8.4	26.9	44.3	19.5	1.2

¹ Based on laser particle size measurements

Thermal processing at 600°C (TP600) only marginally improved the particle size distribution. The mean size reduced from 19.2 to 16.6 μ m, while the volume of particles below 20 μ m increased. These increases were offset by the loss of particles over 45 μ m, which was due to the combustion of unburned coal residue within the FA. Thermal processing at 900°C (TP900) also reduced the mean particle size of the raw ash but surprisingly these improvements were not as great as those experienced at 600°C. Furthermore, the TP900 ash had much reduced contents of particles <10 μ m and significant increases in the d(v,0.1) values. Against this, were the large increases in particles between 10 and 20 μ m. This suggests that the finer particles may have partially melted and subsequently agglomerated. The TP900 processed ash also had a reduced number of particles coarser than 45 μ m, probably due to the ignition of residual coal fragments. As expected, the ground FA was much finer than the raw material, with only 1.2% of particles coarser than 45 μ m after processing.

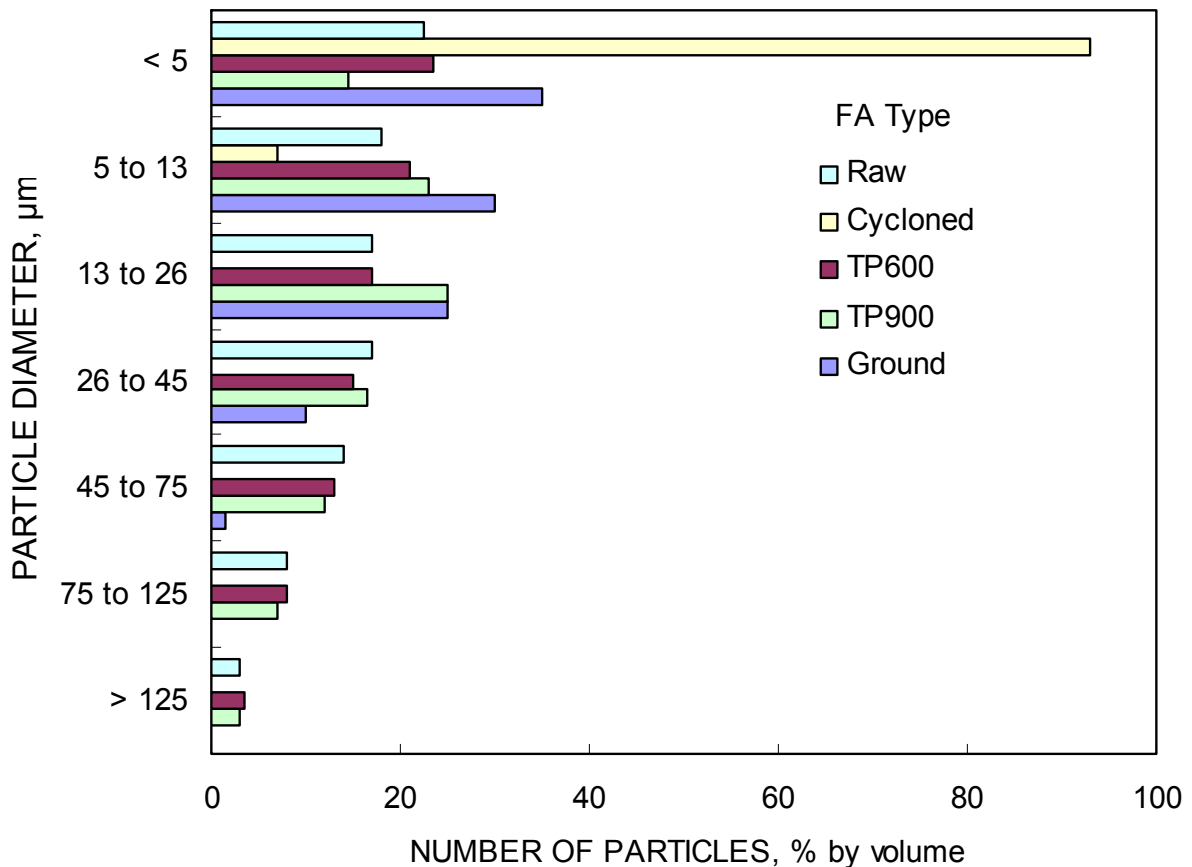


Figure 1 Effect of processing on the particle size distribution of the fly ashes

Particle Morphology

Representative SEM images of the raw and processed ashes are shown in Figure 2. As can be seen, the cyclone processed ash consisted of mainly small cenospheres, the TP900 ash showed a reduction in fine particles, as it is believed that these had formed agglomerations, and the ground ash consisted of fine cenospheres that were largely unaffected by ball-milling, suggesting both a high particle strength and resistance to the action of the grinding balls.

Chemical Composition

The cycloned and thermal processed FAs both had increased silica and alumina contents compared to the raw material, as shown in Table 2. This would appear to support the view that the removal of crystalline material results in an effective increased concentration of amorphous material [17]. The increased alumina content of the cyclone processed FA suggests that there is a high proportion of this component in the fine particles [18]. Iron content was greatly reduced in the air cycloned FA, as it was easily removed, given its higher density. The LOI of the cycloned FA was not reduced as much as perhaps expected from the removal of the

residual carbon. Indeed, the almost pure white colour of the air cycloned FA suggested that very little carbon could have been left in the processed material. It is, therefore, likely that the LOI value was due to components other than carbon [19].

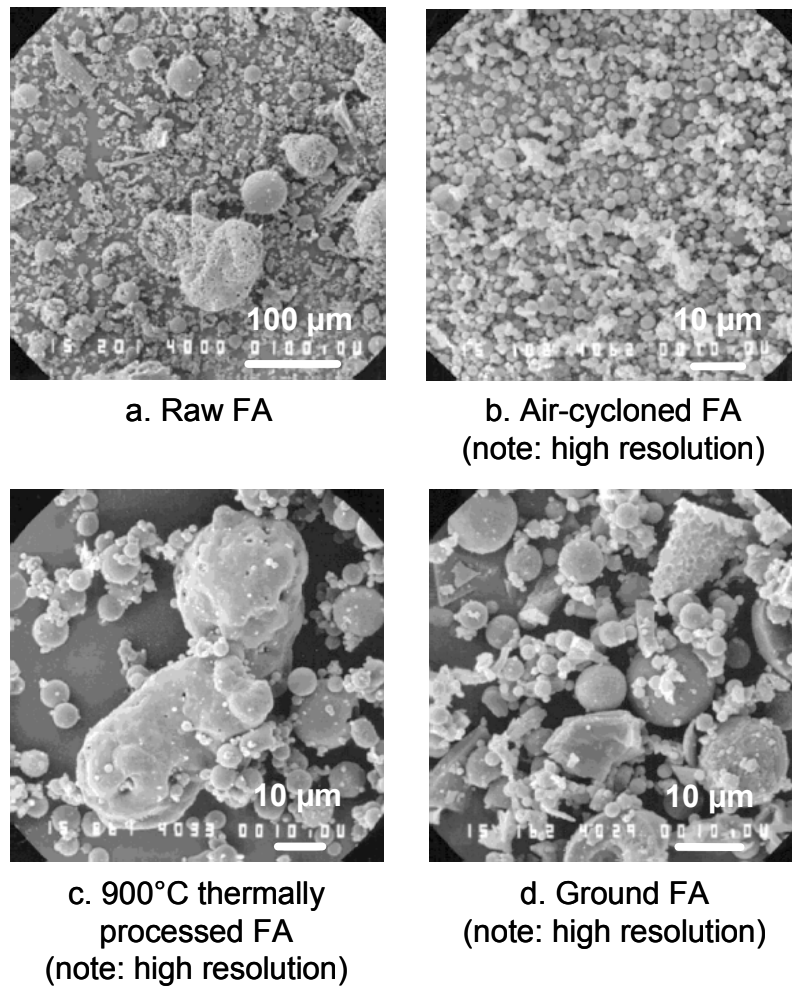


Figure 2 Typical microstructure of raw and processed fly ashes

Table 2 Effect of processing on FA bulk chemical oxide composition and LOI

Oxide/LOI	Bulk Oxide Composition and LOI, % wt				
	Raw	Cycloned	TP600	TP900	Ground
SiO ₂	42.6	44.0	47.6	48.3	42.6
Al ₂ O ₃	19.0	23.0	22.6	22.4	19.0
Fe ₂ O ₃	12.9	9.9	13.2	14.0	12.9
LOI	7.6	5.0	1.4	0.0	7.6

EFFECT OF PROCESSED FLY ASH ON THE PROPERTIES OF PC/FA MORTARS

Mortar Consistence

Figure 3 shows that all the processed ashes improved mortar flow spread compared to the raw ash. At 15% and 30% FA levels, the cycloned FA gave the largest increase in spread with over twice the flow spread of the PC mix at 30% FA, due to the high content of cenospheres and fine particles. The thermally processed ashes also enhanced the mortar flow, particularly at an addition level of 45%, as a result of the lack of irregular carbon particles. A similar performance occurred with the use of the ground FA, which has been observed previously [20].

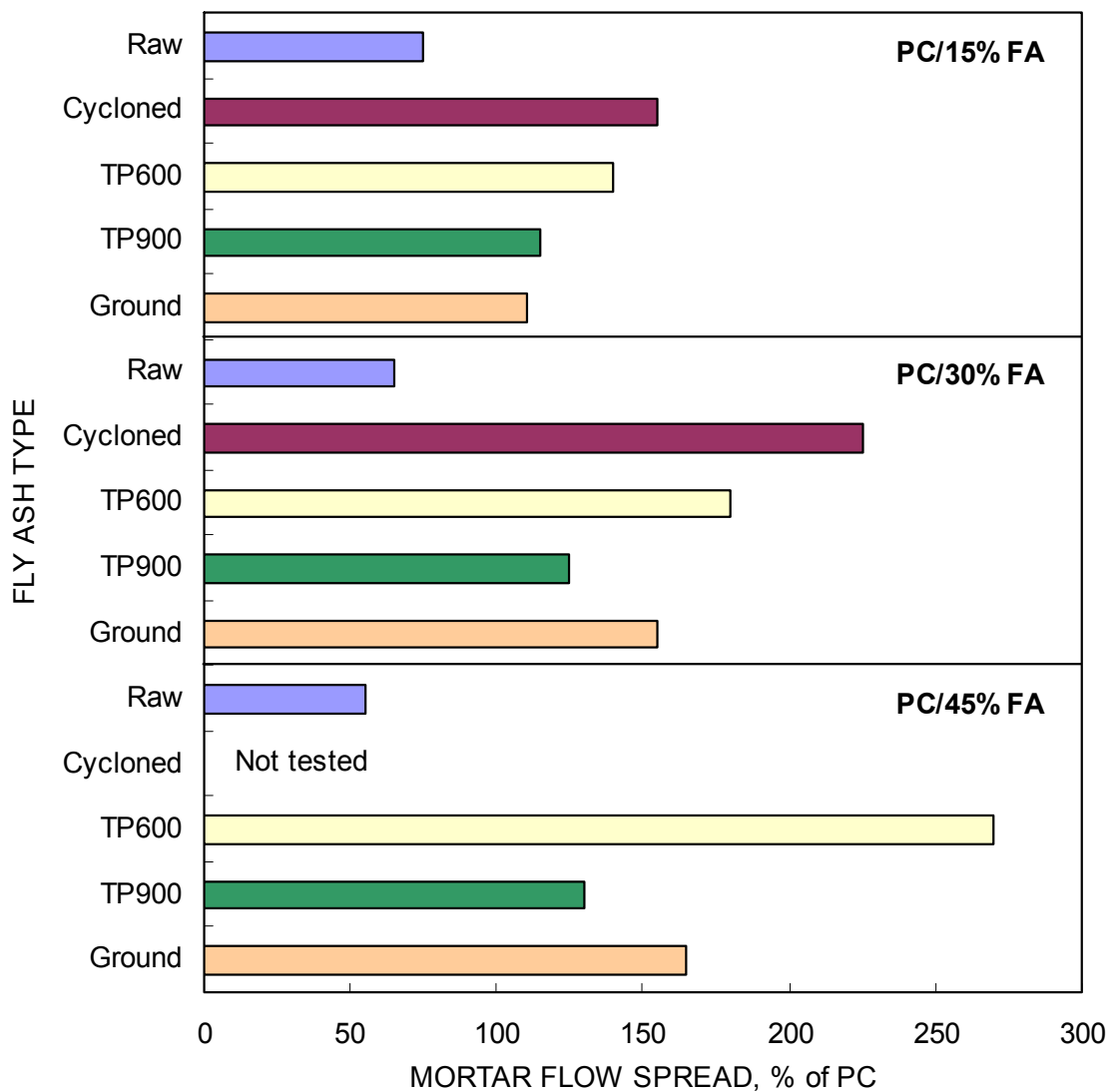


Figure 3 Effect of processed FA addition on mortar flow spread

Compressive Strength Development

From Figure 4 it can be seen that the processed FA mortars exhibited higher strengths than those containing the raw materials throughout the 180 day test period. The greatest improvements in strength were noted with the cycloned FA, whilst the least enhancement in performance was observed on the TP900 specimens at all FA addition levels. Furthermore, the ground FA performed better than both thermally treated ashes at 30% and 45% levels.

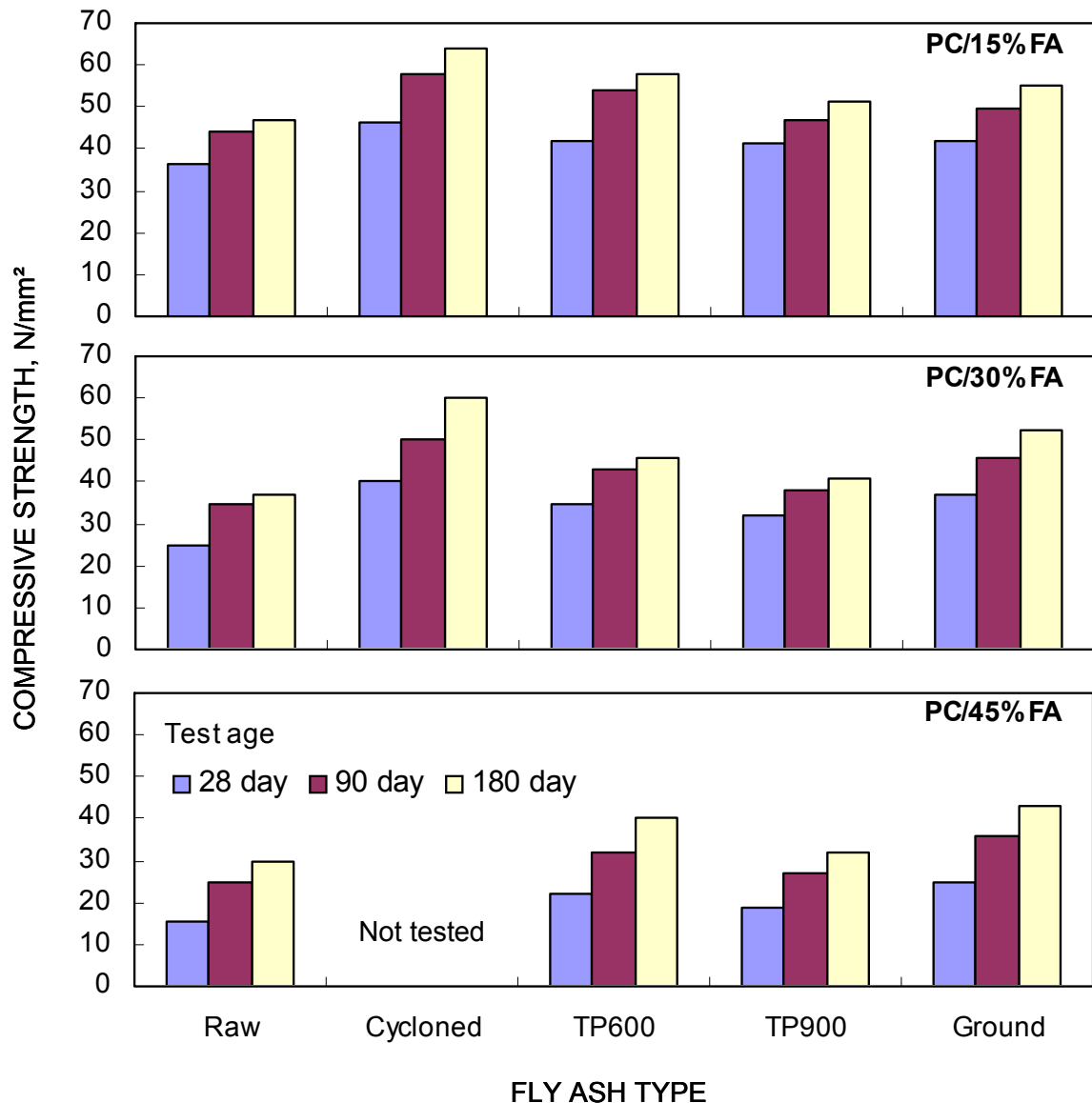


Figure 4 Comparison of strength development of mortars with processed fly ashes

Since it is the products of the pozzolanic reaction which provide the long-term strength improvements, strength was used as an indication of FA reactivity. The increased strengths of the processed FA mortars are, therefore, indicative of enhanced FA reactivity. This is particularly apparent for the cycloned FA due to its

high cenosphere content, fine particle sizes, increased surface area and increased Al_2O_3 content. Furthermore, this has been shown in previous work [21], whereby the cycloned FA consumed high quantities of $\text{Ca}(\text{OH})_2$ and increased the heat produced from cement hydration. The thermally processed FA indicated higher reactivity, in line with the increased silica and alumina contents observed. The ground FA could only increase reactivity through increased surface area available for reaction. Thus, it can be suggested that the ground FA, as for the cycloned FA, improved the strength characteristics significantly by encouraging early cement hydration through providing nucleation sites and cement grain dispersion [22].

Initial Surface Absorption

The initial surface absorption (ISA) values obtained on the mortars after 10 minutes are given in Figure 5. As can be seen, the processed FAs improved the initial surface absorption properties of the mortars in comparison to that of the raw FA specimens. The greatest reduction in surface absorption was achieved by the cycloned FA, suggesting the highest densification of the paste matrix and increased capillary pore tortuosity. The same appears to have occurred to the other processed FA mortars, but to a lesser degree. Although this is possibly due to improvements in the packing density characteristics of the mortar through the enhance FA particle size characteristics for the cycloned and ground materials, a further reason may be the reduction in capillary continuity due to pore blockage [23].

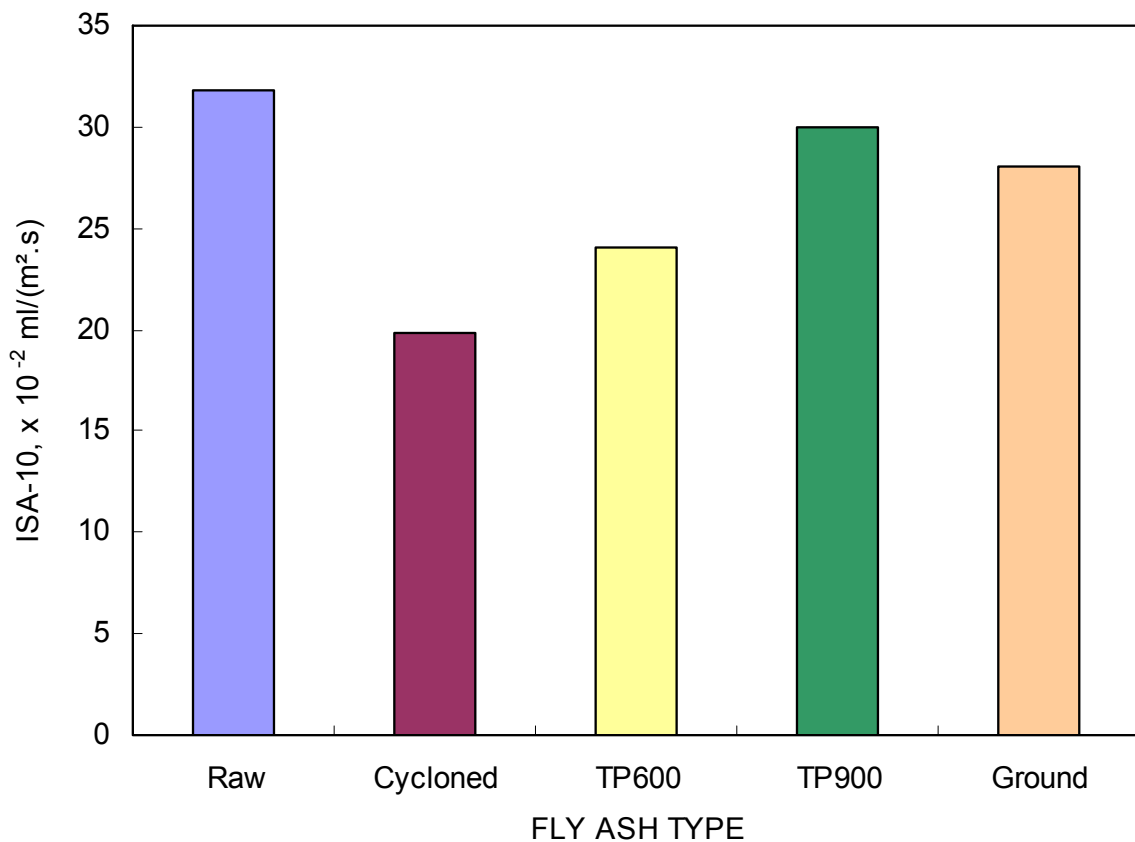


Figure 5 Effect of fly ash type on surface absorption of mortars after 10 minutes

Bulk Porosity

In line with all other mortar properties, the processed FAs also resulted in improved mortar porosity, compared to the raw materials. As can be seen in Figure 6, the cycloned FA produced the mortar with the least porosity at both 15% and 30% FA levels (less than 6% by volume, compared with 8.5% of the raw FA specimens). At 45% FA, the least porosity was observed on the TP600 mortar throughout the 180 day test period, while the FA achieving the least enhancement in porosity was that subjected to thermal treatment at 900°C.

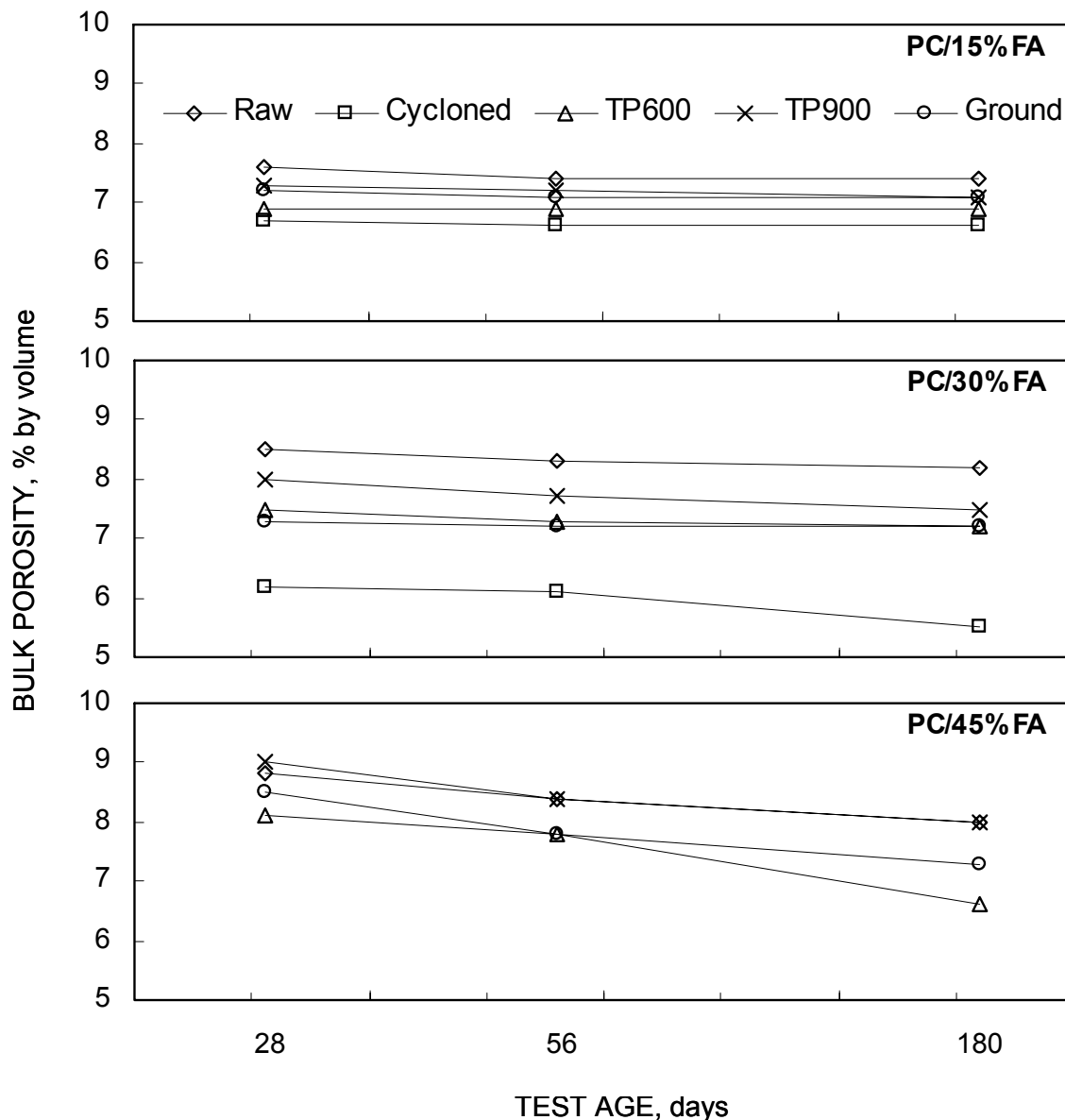


Figure 6 Change in bulk porosity of mortars with processed fly ashes

CONCLUDING REMARKS

The overall conclusions from this study can be summarised as follows:

1. Cyclone processing separated FA into (i) a material with a very fine particle size distribution, high cenosphere content and increased Al_2O_3 content and into (ii) oversize, dense and non-spherical particles. When added to mortars, the cycloned FA increased flow spreads and compressive strength, whilst reducing initial surface absorption and porosity.
2. Thermal processing of FA reduced the LOI significantly, thereby resulting in an increased proportion of amorphous material per unit weight. The fresh and hardened mortar properties were improved greatly, compared to mortar made with the raw FA. It was found, however, that at 900°C , sintering and binding of the finer particles occurred, which reduced the ash quality and thus, processing at 600°C is recommended. However, the feasibility of full-scale thermal treatment is questionable, given the additional cost involved.
3. Grinding the FA was found to increase ash fineness and improve the overall performance (i.e. consistence, strength, initial surface absorption and porosity) of PC/FA mortars. As with the thermal processing, however, there are significant cost implications of this type of processing method at full-scale.
4. The improved mortar properties observed when utilising the cycloned and ground FAs are mainly due to the enhancement of the packing density of the fresh mixture. This densification of the hardened paste matrix is due to the increased number of nucleation points for cement hydration by the high fine particulate content. The thermally processed FA removed the angular shaped carbon particles and possibly altered the surface texture characteristics of the particles, thereby increasing mortar consistence.

ACKNOWLEDGMENTS

The Authors wish to acknowledge the Engineering and Physical Sciences Research Council (EPSRC) for funding the work.

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