

Contents lists available at ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp



Resistance of mortar containing unprocessed pulverised fuel ash (PFA) to sulphate attack

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ARTICLE INFO

Article history: Received 23 November 2007 Received in revised form 1 March 2010 Accepted 2 March 2010 Available online 6 March 2010

Keywords: Resistance of mortar Sulphate attack Tensile strength Pulverised fuel ash (PFA) Paste

ABSTRACT

An investigation was carried out to establish the physical, mechanical and chemical characteristics of an unprocessed pulverised fuel ash (PFA) from a former landfill site at the Power Station Hill near Church Village, South Wales, United Kingdom. This was aimed at establishing the suitability of the ash in road construction (embankment and pavement) and also in concrete to be used in the construction of a proposed highway.

This paper reports on mortar blends made using the unprocessed PFA as cement replacement. The resistance of the mortar was tested by observing sulphate attack during soaking in a standard BS sodium sulphate solution, for soaking periods of up to 504 days. Mortar cylinders of various mix designs were subjected to splitting tensile strength tests, after curing in water for up to 28 days. Thermogravimetric and derivative thermogravimetric (TG/DTG) analyses were carried out on the unhydrated ingredients, in order to assess the degree of hydration and rate of, and portlandite formation in the cement paste after soaking in either water or sodium sulphate solution environment.

The binary PC-PFA mortar shows good sulphate resistance under a sulphatic environment with the exception of one trial pit ash (Trail Pit No. 6). The tensile splitting strength decreases as the cement replacement increases.

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1. Introduction

The use of industrial waste and by-products materials is now widely recognised as one of the major preferred options towards the achievement of sustainable development. The prevailing environment policies require the waste to be treated before going to landfill. Treating waste in a manner that it can be used in construction is more economical, particularly where the wastes are already on site. Fly ash or pulverised fuel ash (PFA) is a by-product of coalfired power stations, collected from the flues of the furnaces by electrostatic precipitators. Research on blended PC-PFA binders in mortar and concrete has been conducted by many researchers [1,2] including researchers at the University of Glamorgan [3,4]. However, unprocessed PFA may perform differently when used to partially replace Portland cement (PC) in mortar.

The service life of mortar and concrete depends principally on its durability. Bonen and Cohen, [5] reported that many of the destructive and corrosive processes affecting mortar and concrete involving chemical reactions can be attributed to the aggressive actions of sulphate in solution. Cement mortars or concretes subjected to sulphate attack in sulphate-bearing environments can

undergo a progressive and profound reorganisation of their internal microstructure. For example, cement mortar or concrete subjected to sulphate attack is often found to suffer from expansion, cracking, scaling or shelling of the surface layer and decrease in strength. According to Al-Amoudi [6] sulphate attack leads to the conversion of hydrated products of the cement or mortar to ettringite, gypsum and other phases, and also to the destabilisation of the primary strength providing amorphous calcium–silicate–hydrate (C–S–H) gel. The expansion seen in hardened cementitious materials is thought to mainly result from this formation of ettringite and gypsum [6], although the exact mechanisms continue to be subject to discussion.

One approach to preventing this attack is to use mineral admixtures or supplementary cementing materials because they may improve durability of the paste in various mechanisms [1,7]. Previous research by Monteiro and Kurtis [8] observed that the partial replacement of low C_3A cement with 25% and 45% fly ash showed less expansion than comparable mixtures containing no pozzolans [8]. Their results also indicated that a water/cement ratio lower than 0.45 and an unhydrated C_3A content lower than 8% were required for the long term durability of the concrete. Research by one of the current authors has indicated that a PC replacement level of 30% with PFA is required to achieve a good sulphate resistance [4]. The use of pozzolans to combat sulphate attack has

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been demonstrated by other researchers, such as Santhanam et al. [9], who have reported that in sodium sulphate solution the expansion of mortar bars is drastically reduced by incorporating pozzolans in the cementitious mixtures.

Table 1 Chemical properties of Portland cement used.

Oxide	Composition (%)
SiO ₂	20.69
AI_2O_3	3.80
CaO	62.99
Fe_2O_3	2.12
MgO	2.62
K_2O	0.55
Na ₂ O	0.13
SO_3	3.10
Chemical (%)	
Cl	0.03
Free lime	1.32
Bogue's compositions (%) ^a	
Tricalcium aluminate (C ₃ A)	6.48
Tricalcium silicate (C ₃ S)	70.58
Dicalcium silicate (C ₂ S)	6.09
Tetra-calcium alumino-ferrite (C ₄ AF)	6.45
Other properties (%)	
LOI – loss on ignition	4.36

Experimentally determined.

In this paper the sodium sulphate attack of mortar and splitting tensile strength development, for mortar cases where the PC has been replaced with unprocessed pulverised fuel ash (PFA) at 0%, 10% and 40% replacement levels are reported. Thermogravimetric and derivative thermogravimetric (TG/DTG) analyses were also carried out on the unhydrated ingredients, in order to assess the degree of hydration and rate of, and portlandite formation in, the cement paste after soaking in either water or sodium sulphate solution environment. The main characteristics to be established by this investigation are the resistance of mortar to sulphate attack and the physical, mechanical and chemical properties.

2. Materials

2.1. Portland cement

A single batch of blue circle cement in accordance with BS EN 197-1 [10], supplied by Lafarge, was used throughout this research programme. Data on the oxide compositions and properties of the cement, including phase composition, are shown in Table 1.

2.2. Pulverised fuel ash (PFA)

2.2.1. Background

The proposed construction of the Church Village Bypass will comprise a dual carriageway, 7.3 m wide and approximately 6.5 km long. At the Power Station Hill landfill site (see Fig. 1) the

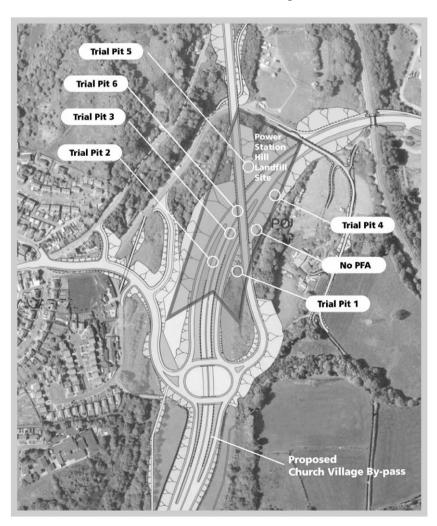


Fig. 1. An aerial photograph showing Trial Pits on the Power Station Hill landfill site-near Church Village, South Wales, United Kingdom.

^a Bogue's compositions [13].

PFA would have to be removed to allow the construction of the Church Village Bypass. The options available for the waste removed during the construction of the carriageway, either re-use or disposal, were investigated.

The Power Station Hill landfill site, which is no longer operational, was located at the Northern end of the scheme. The Upper Boat coal-fired power station became operational in 1902 [11] and PFA collected from the flues of the furnaces was deposited in the landfill site situated between two railway lines. The power station closed in 1972 [11] and demolished on 14th December 1976 [12]. In the early 1980's the site was purchased by the current owner, who has used the site for scrap vehicle storage and a recycling/reclamation business [11].

2.2.2. Sample collection and preparation

The researcher team endeavoured to structure the conditions of the laboratory investigations to mirror the anticipated real-time construction scenario. Consequently, rather than oven drying the

Table 2 Properties of unprocessed PFA.

	Composi	tion (%)			
Oxide ^a	CERAM			Bodycote	
	Trial Pit 2	Trial Pit 3	Trial Pit 5	Trial Pit 6	Trial Pi 6
SiO ₂	35.02	35.11	41.78	31.67	32.00
AI_2O_3	21.01	19.59	18.19	19.73	19.30
CaO	1.01	1.12	2.57	0.80	0.87
Fe_2O_3	4.81	5.36	12.61	5.36	5.48
MgO	0.81	0.88	1.33	0.67	0.67
Mn_3O_4	0.05	0.06	0.20	0.04	0.05
K ₂ O	2.48	2.34	2.03	1.87	1.84
Na ₂ O	0.45	0.42	0.41	0.37	0.35
TiO ₂	0.70	0.65	0.61	0.62	0.62
P_2O_5	0.51	0.42	0.44	0.59	-
Cr_2O_3	0.02	0.02	0.02	0.02	-
ZrO ₂	< 0.02	< 0.02	< 0.02	< 0.02	-
HfO ₂	< 0.01	< 0.01	< 0.01	< 0.01	-
PbO	< 0.02	< 0.02	< 0.02	< 0.02	-
ZnO	0.03	0.02	0.03	0.03	-
BaO	0.14	0.12	0.11	0.14	-
SrO	0.10	0.08	0.08	0.13	-
SnO ₂	< 0.01	< 0.01	< 0.01	< 0.01	-
CuO	0.02	0.02	0.03	0.03	-
SO ₃ remaining	< 0.05	<0.05	<0.05	<0.05	-
Chemical (%) ^b					
Insoluble residue	95.60	95.90	92.70	95.70	96.50
Soluble silica	0.70	0.79	1.39	0.71	0.33
Soluble calcium oxide	0.52	0.61	1.07	0.38	0.32
Soluble AI ₂ O ₃	0.72	0.61	0.79	0.73	0.40
Soluble MgO	0.11	0.14	0.22	0.07	0.05
Soluble Fe ₂ O ₃	0.32	0.37	1.40	0.43	0.18
Sulphate as SO ₃	< 0.01	< 0.01	0.03	0.01	< 0.01
Carbon dioxide from carbonates	0.18	0.22	0.81	0.11	0.37
Cl	< 0.01	< 0.01	< 0.01	0.02	0.01
Free lime	< 0.05	<0.05	< 0.05	<0.05	0.02
Other properties (%)					
LOI – loss on ignition	32.95	33.71	19.85	38.20	37.60
Fineness (m ² /kg)	246	157	70	155	155
Particle density p_s (Mg/m ³) ^c		1.63	1.87	1.62	1.62
Maximum dry density (Mg/ m ³) ^d		0.908	1.282	0.786	0.786
Optimum moisture content (%) ^d	58.2	46.5	22.5	60.3	60.3
Moisture content (%)e	55.6	34.7	17.1	58.1	58.1

Experimentally determined.

- ^a Oxides by XRF.
- ^b Analysis in accordance with BS 1881.
- ^c Density bottle method.
- ^d BS compaction test light hammer.
- e Air dried PFA (average of 3 tests).

PFA for the laboratory investigations, it was decided to air-dry it for 3 days, bag it in polythene bags and then use this material for all laboratory work. This procedure was aimed at simulating the stripping of top soil on site, the excavation of the material and subsequent stockpiling before utilisation on the Bypass, during the relatively drier months of the year. However, as this may happen either in the dry or during relatively wetter months, a 3 day air drying was estimated as the best way of striking a balance in the anticipated working conditions using the PFA. An initial investigation of the wet PFA showed it to be freely draining during the initial hours of stock piling, and that contributed to the settlement for the 3 day drying period. Seven Trial Pits (see Fig. 1) were dug using a Joseph Cyril Bamford (JCB) excavator, in order to establish the depth of the landfill material, and also to obtain a representative working sample of the PFA. The samples were air-dried in the laboratory as already described.

2.2.3. Physical properties

Laboratory work on the properties of the unprocessed PFA have been reported in earlier publications [14,15] and was carried out using PFA from Trial Pits 2, 3, 5 and 6. The properties of the PFA are reproduced in Table 2. It is clear that the PFA collected from Trial Pit 5 has different properties of lower fineness and lower moisture content, higher particle density and higher maximum dry density when compared to the PFA from the other three Trial Pits. The particle size distributions of the PFA from Trial Pits 2, 3, 5 and 6 using a Mastersizer 2000 particle size analyser are shown in Fig. 2. Results from all the Trial Pits indicate closely identical well-graded particle size distribution.

2.2.4. Microstructure

Scanning electron microscopy (SEM X-ray) was carried out using a scanning electron microscope fitted with an X-ray spectrum analyser, on samples of PFA that were dried at 40 °C using silica gel. Fig. 3 shows SEM scans for Trial Pits 2, 3, 5 and 6. The visual display shows the shape of the individual PFA particles and relative particle size. The element data showed significantly higher values of silicon content when the electron beam was focussed on the rounded spheres (indicated by an arrow) than on any other particles, strongly suggesting that these spheres were of PFA. The apparently molten structures in Trial Pit 5 (indicated by a triangle) were unique and were very low in silicon. Trial Pit 5 was also observed to have unique chemical and particle characteristics. In general, the SEM scans appear to back up the observations made on chemical analysis, particle size and visual inspection of the PFA on site. The specific surface of the particles from Trial Pit 5 was relatively low indicating that the particles are larger than the particles from the other Trial Pits (with higher specific surface).

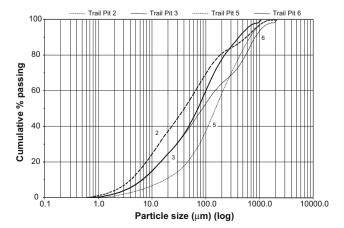
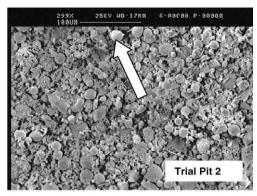
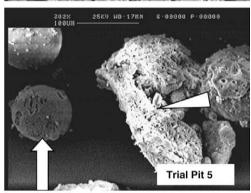


Fig. 2. Particle size distribution of unprocessed PFA from Trial Pits 2, 3, 5 and 6.







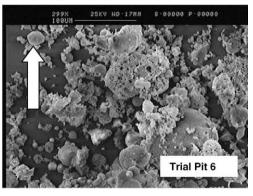


Fig. 3. SEM scans of unprocessed PFA from Trial Pits 2, 3, 5 and 6.

2.2.5. Chemical properties

A full chemical analysis and the determination of the oxide content of the PFA were carried out at two different United Kingdom Accreditation Service (UKAS)-accredited laboratories. The majority of the analyses (samples from Trial Pits 2, 3, 5 and 6) were carried out by CERAM Research Limited in Stoke-on-Trent, England. In order to validate the results from CERAM, a separate analysis was carried out on the sample from Trial Pit 6, by Bodycote Materials

Table 3Typical chemical composition of processed PFA.

Oxide ^a	Before 27/01/00	After 27/01/00
SiO ₂	49.10	47.60
AI_2O_3	26.40	26.20
CaO	1.40	2.40
Fe ₂ O ₃	9.30	9.40
MgO	1.40	1.42
K ₂ O	3.50	3.02
Na ₂ O	1.50	1.10
Na ₂ O Equivalent	3.81	3.09
SO ₃	0.80	0.86
TiO ₂	1.00	1.03
Chemical (%) Cl	0.01	0.01
CI	0.01	0.01
Other properties (%) LOI – loss on ignition	4.90	4.96

Experimentally determined.

Testing of Somerset, England. Table 2 shows a summary of the results from both CERAM and Bodycote [14,15]. Results for Trial Pit 6 from both companies show a very close agreement, with a silica content of 32% as the main oxide in the Power Station Hill PFA, followed by an alumina content of just over 19%. Results from the other Trial Pits also show these two oxides as the key components, with the variation across all the Trial Pits as follows:

Silica (SiO₂): 32–42% Alumina (Al₂O₃): 18–21%.

Other oxide compositions in the PFA (above 1% in content) include ferric oxide (Fe₂O₃) (about 5.0-5.5%, with only Trial Pit 5 showing a relatively higher value of 12%), and potassium oxide (K_2O) (2.0–2.5%). Table 3 shows typical oxide analyses from two samples of standard PFA from the United Kingdom Quality Ash Association ((UKQAA) formerly Ash Resources Limited), which the current research team has used in research work for more than 10 years [4,16]. A comparison of Tables 2 and 3 shows both ashes to be low calcium (Type F) PFAs, with considerable differences in the relative distribution of the four main oxides (SiO₂, Al₂O₃, Fe_2O_3 and K_2O). On average, with the exception of the 12% Fe_2O_3 content in Trial Pit 5, the Power Station Hill PFA is slightly lower in the composition of all these key oxides. This is most probably due to the raw nature of the PFA as no processing has been undertaken, as confirmed by the very high loss on ignition (LOI) for the Power Station Hill PFA (average value 32%) compared with 4.9% for PFA from UKQAA.

From Table 2 it is clear that most of the silica in the Power Station Hill PFA is not acid soluble, suggesting that a relatively low level of pozzolanic activity can be anticipated from this PFA compared with the PFA from UKQAA. From the $\rm K_2O$ and Sodium oxide ($\rm Na_2O$) levels in the PFA from both sources, the Power Station Hill PFA shows a marginally lower alkalinity (pH) compared with processed PFA. The Power Station Hill PFA is also much lower in sulphate ($\rm SO_4$) ($\rm <0.05\%$ compared with about 0.8%). All these parameters appear to suggest differences between the PFA from the two sources but these small changes in the properties, combined together, may result in significant differences in engineering behaviour.

3. Experimental procedure

3.1. Mix proportions and specimen preparation

3.1.1. Mortar

Mortar containing binders at two PC replacement levels using unprocessed PFA at 10% and 40% replacement level by mass of

^a Oxides determined by XRF (source: UKQAA).

Table 4 PC-PFA mortar mix proportions at water/binder ratio 0.5.

PC	PFA	Total replacement (%)	kg/m ³			
			PC	PFA	Sand	Water
100	0	0	300	0	900	150
90	10	10	270	30	900	150
50						

the PC, from Trial Pits 2, 3, 5 and 6, were investigated together with a PC control mortar (Table 4). Nine mortar mixes were investigated, each containing a total binder content of 300 kg/m^3 . The ratio of binder to sand was 1:3, with water to binder ratio of 0.5. The mortar was used to produce six $20 \text{ mm} \times 20 \text{ mm} \times 160 \text{ mm}$ bars for durability studies and one $100 \text{ mm} \times 200 \text{ mm}$ cylinder for splitting tensile strength per mix proportion.

The binder and sand were first pre-mixed dry in a pan mixer for 1 min to ensure homogeneity. Wet mixing was carried out in accordance with EN 196-1 [17], with a total mix time of $3^1/2$ min. The mortar was cast into steel moulds and covered with cling film to maintain the moisture content of the specimens. The mortar specimens were demoulded after 24 h, wrapped in cling film and moist cured in a closed container with water maintained at the bottom of the container, so as to ensure a near 100% relative humidity at 20 ± 1 °C.

After 14 days of moist curing, three mortar bars were immersed in tap water in a plastic container and the water was topped-up regularly but not renewed. These bars soaked in tap water were treated as control specimens, to compare performance with the bars soaked in sodium sulphate solution.

After 14 days of moist curing, three mortar bars were immersed in a 5% sodium sulphate solution at 20 ± 2 °C, for a period of 72 weeks. Small plastic containers were used to store each individual set of three $20~\text{mm}\times20~\text{mm}\times160~\text{mm}$ mortar bars. The solution was prepared in accordance with pr ENV 196-X [18] with the 11 of solution per container that was renewed every 28 days [18].

3.1.2. Testing for resistance to sodium sulphate attack

Each $20 \times 20 \times 160$ mm mortar bar was measured on a comparator every 4 weeks, to determine any linear changes occurring in the mortar to the nearest 0.002 mm. Weight changes were also recorded at this time. When the bars had expanded to such an extent that they could not fit into the comparator or had lost their physical form, they were deemed to have failed and were discarded.

3.1.3. Testing for splitting tensile strength

The mortar cylinders were tested after a total curing period of 28 days, in accordance with BS EN 12390-1: Part 6 [19]. The splitting tensile strength was carried out using an Avery-Denison compression-testing machine, at a constant loading rate of 127 kN/min.

3.1.4. Paste

In order ensure a homogeneous mixture the PC and PFA powders were blended by hand until a uniform colour was achieved. Five PC-PFA paste mixes, including the PC control paste, were investigated, each containing 890 g of total binder at a water binder ratio of 0.3 (see Table 5). A lower water to binder ratio, compared with the water/binder ratio adopted for mortar, was found necessary in order to produce a workable paste mixture. Mixing was carried out in accordance with BS EN 196-1: [17], for a total mixing time of $3^{1}/_{2}$ min, using a KM250 Kenwood Chef Major mixer. The pastes were compacted in 25 mm \times 25 mm \times 25 mm perspex moulds, vibrated using a vibrating table, to make 21 paste cubes. The moulds were covered with cling film to maintain the moisture content of the specimens.

Table 5 PC-PFA paste mix proportions at water/binder ratio 0.3.

PC	PFA	Total replacement (%)	kg	kg		
			PC	PFA	Water	
100	0	0	0.89	0.00	0.27	
90	10	10	0.8	0.09	0.27	
60	40	40	0.53	0.36	0.27	

The paste specimens were demoulded after 24 h and wrapped in cling film. They were then moist cured in a closed container, in a similar manner to the mortar bar specimens. Three of the paste cubes from each paste mix composition were tested for compressive strength after moist curing for 7 days. After 14 days of moist curing, half of the remaining cubes were soaked in water in a plastic container at 20 ± 2 °C, where the water was never renewed, but a constant water level was maintained by topping-up when necessary. The remaining nine cubes were soaked in sodium sulphate solution, which was renewed every 28 days. The paste cubes were tested for compressive strength after a total curing period of 28, 90 and 180 days. The compressive strength data is not reported in this paper but the paste fragments were used for thermogravimetric analysis (TGA).

3.1.5. Thermogravimetric analysis (TGA)

The current TGA work was carried out using a TGA 2950 hi-res thermogravimetric analyser, fitted with a TA5000 Thermal Analysis controller. The heating rate was chosen as 10 °C per minute, up to a maximum of 1000 °C. The samples were firstly dried to constant weight at the low temperature of 40 °C, so as to preserve any phases that are combustible above this temperature. A carbondioxide absorbing compound (carbosorb) was used during drying, so as to minimise any sample carbonation that is common in most systems containing hydrated lime (Ca(OH₂). Drying was accelerated by using silica gel. After drying, each sample was ground for 20 s to a fine powder using a Grasslin Mixermill 2000. During the TGA, a sample size of approximately 10 mg was used, and heating carried out in alumina pans fitted with a lid. The heating was carried out in an inert gas-argon-atmosphere. Weight loss and temperature increase were logged during the test and plots of the TGA weight loss (%) and the derivative weight loss (DTG) (dw%/ dt °C) produced with respect to temperature. In the current work TGA was used to assess the degree of hydration and rate of portlandite formation of the cement paste upon curing in either water or sulphate solution environment.

4. Results and discussion

4.1. Resistance to sodium sulphate attack

One hypothesis for the sulphate attack mechanism is that the expansion of mortar bars exposed to sodium sulphate occurs in two stages [9]. In stage one the expansion is very low, and is due to the pore spaces being gradually filled with the expansion products (shown by weight gain). This stage can thus be referred to as the 'induction period'. At the end of this induction period the expansion increases rapidly and proceeds at a steady rate until the specimen disintegrates. This second stage occurs because the total volume of gypsum and ettringite (the by-products of soaking in sodium sulphate) is over that which can be accommodated by the pore structure.

4.1.1. Expansion of PC-PFA mortar

Figs. 4a and b show the changes in expansion of binary PC-PFA mortar at a water/binder ratio of 0.5, with 0%, 10% and 40% PC

replacement using the unprocessed PFA, upon various exposure periods to sodium sulphate solution for up to 504 days. The bars soaked in water (control) showed nominal expansive traits (>0.05%), and so their trends are not reported in this paper. At the 10% replacement level Trial Pit 6 shows rapid expansion after approximately 200 days in sodium sulphate solution. The bars fail at approximately 1 year after rapid expansion. The authors suggest that a low total silica (SiO₂) content and a high LOI (5% more than Trail Pits 2 and 3 as shown in Table 2, suggesting high organic content), may partly be the cause of the rapid expansion for PFA from Trail Pit 6. This trend follows the mechanism proposed by Santhanam et al. [9] to explain why the initial expansion is low followed by a rapid expansion till failure of the specimen. Previous research [4] has indicated that a PC replacement level of at least 30% with PFA is required to achieve a good sulphate resistance. It is not therefore surprising that at 10% PC replacement, some mortar bars expanded due to low sulphate resistance.

4.1.2. Expansion with respect to weight change of PC-PFA mortar

Fig. 5 shows the changes in expansion with respect to weight change of binary PC-PFA mortar at a water/binder ratio of 0.5, with 0%, 10% and 40% PFA replacement levels, upon various exposure periods to sodium sulphate solution for up to 504 days. There is a substantial weight increase prior to any significant expansion occurring. This is followed by very substantial expansion occurring with only minor weight increase. The initial weight increase without expansion is indicative of pore filling by sulphate-containing reaction products whereas the subsequent marked expansion accompanied by relatively small weight increase is indicative of

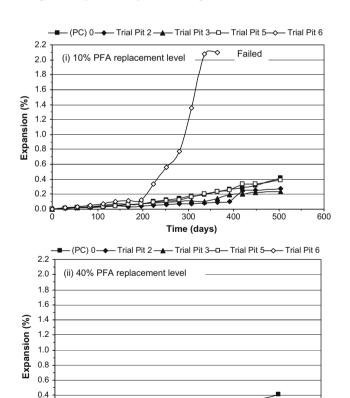


Fig. 4a. Expansion of binary PC-PFA mortar bars (water/binder ratio of 0.5) at PC replacement levels of: (i) 10% and (ii) 40%, versus exposure time in sodium sulphate solution for a total soaking period up to 504 days (moist curing for the first 14 days).

300

Time (days)

200

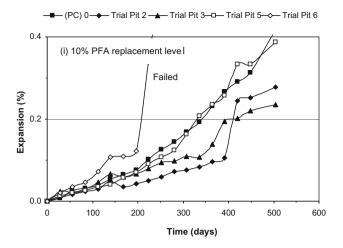
500

600

0.2

0.0

100



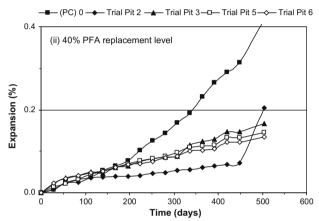


Fig. 4b. Expansion of binary PC-PFA mortar bars (water/binder ratio of 0.5) at PC replacement levels of: (i) 10% and (ii) 40%, versus exposure time in sodium sulphate solution, for a total soaking period up to 504 days (moist curing for the first 14 days).

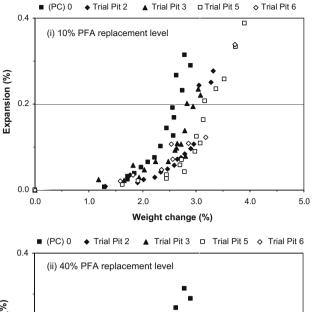
completion of pore filling and generation of expansive pressure by further reaction product formation.

The substantial expansion that follows the initial weight increase observed for the Trail Pit 6 PC-PFA mortars only occurs at the lower replacement levels (Fig. 4a). This suggests that at lower replacement levels the PFA has not reduced sufficiently the portlandite content and/or modified the pore structure to significantly reduce the permeability of the hydrated cement paste. This is not the case at higher 40% replacement level where the capacity of the sulphate ions to penetrate deeper into the mortar and attack the portlandite has been diminished [6]. According to Al-Amoudi [6] sodium sulphate (NS) attacks the portlandite (CH) produced when Portland cement in concrete hydrates, thus altering the chemistry of the system. The gypsum, formed by reaction between NS and CH, reacts with monosulphate and other alumina-bearing phases to form secondary ettringite as shown in the following reactions [6]:

$$CH + NS + 2H \rightarrow CSH_2 + NH \tag{1}$$

$$C_3A + 3CSH_2 + 26H \rightarrow C_6AS_3H_{32}$$
 (2)

The gypsum (CSH₂), produced in Eq. (1), will react with the hydration products (calcium aluminate hydrate (C_4AH_{13}), monosulphate (C_4ASH_{12}) and/or calcium aluminate (C_3A)) to produce secondary ettringite. Ettringite is expansive in nature with a lower density of 1.73 g/cm³ when compared to an average of 2.50 g/cm³ for other hydration products [6]. Also at higher replacement level



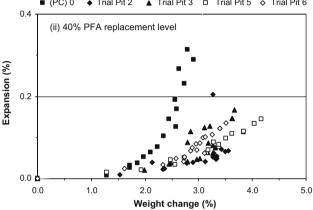


Fig. 5. Expansion with respect to weight change of binary PC–PFA mortar (water/binder ratio 0.5) at PC replacement levels of: (i) 10% and (ii) 40%, upon exposure in sodium sulphate solution for a total soaking period up to 504 days (moist curing for the first 14 days).

the pozzolans decrease the C_3A content (dilution effect) of the mortar thus reducing the aluminate-bearing phases [6], and also the relative quantity of CH available is lowered. The other Trial Pits show low expansion levels at or below 0.4%, and these compositions could be used for structures placed in sulphatic soils.

4.2. Splitting tensile strength of PC-PFA mortar

Fig. 6 shows the changes in splitting tensile strength of binary PC-PFA mortar at a w/b ratio 0.5 and at 0%, 10% and 40% PC

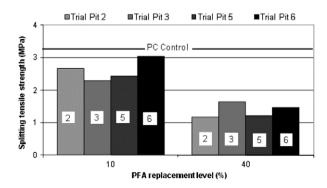


Fig. 6. Tensile splitting strength of PC–PFA mortar (water/binder ratio of 0.5) at PC replacement levels of: (i) 10% and (ii) 40% upon exposure in tap water for a total curing period up to 28 days (moist curing for the first 14 days).

replacement levels, after moist curing for 14 days and then soaking in tap water for 14 days. For all the individual Trial Pits, the strength development at all PC replacement levels was lower than that of the PC control (3.22 MPa). The splitting tensile strength (like the compressive strength reported in an earlier paper [20]) decreases as the PC replacement level increases. This is thought to be due to the typically low pozzolanic activity of the PFA, which delays strength development. The low pozzolanic activity is attributed to, among other factors, the high proportion of insoluble silica content, as suggested by the low soluble silica content in the range of 0.33–1.39%, and the high insoluble residue in the range of 92.7–96.5% (see Table 2).

4.3. Thermogravimetric (TG) analysis of pore structure deposits

Fig. 7 shows the TG curves of pore deposits for paste specimens using ash from Trial Pit 2 at PC replacement level of 10% PFA, after exposure to water for up to 180 days. The associated trends are not

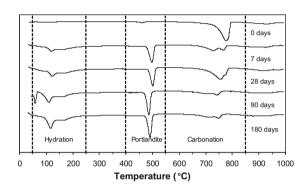


Fig. 7. TG curves of paste test specimens at a PC replacement level of 10% PFA for Trial Pit 2 upon exposure in tap water for a total curing period of up to 180 days (moist curing for the first 14 days).

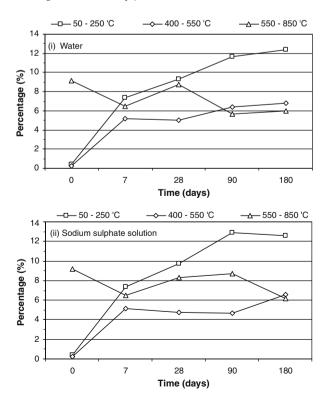


Fig. 8. Ignited weight loss of paste test specimens at a PC replacement level of 10% PFA for Trial Pit 2, versus exposure time in water and sodium sulphate solution for a total soaking period of up to 180 days (moist curing for the first 14 days).

evident from these TG curves displayed in this format. However the trends can be observed when weight losses for the main weight

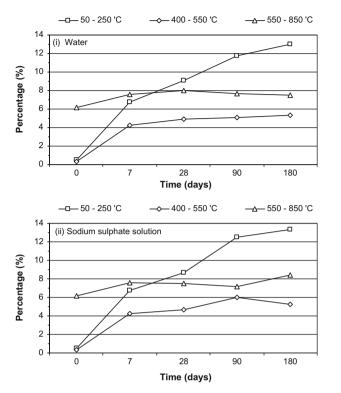


Fig. 9. Ignited weight loss of paste test specimens at a PC replacement level of 40% PFA for Trial Pit 2, versus exposure time in water and sodium sulphate solution for a total soaking period of up to 180 days (moist curing for the first 14 days).

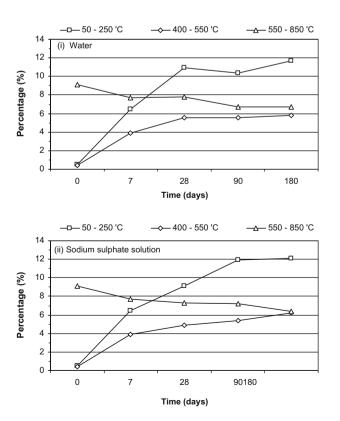


Fig. 10. Ignited weight loss of paste test specimens at a PC replacement level of 10% PFA for Trial Pit 5, versus exposure time in water and sodium sulphate solution for a total soaking period of up to 180 days (moist curing for the first 14 days).

losses at the three temperature ranges (50–250 °C, 400–550 °C and 550–850 °C), are plotted against time.

These plots are shown in Figs. 8 and 9 where the ignited weight losses are displayed at the three temperature ranges for Trial Pit 2. The % wt losses plots at zero time represent the dry blended powders before they are mixed with water to produce paste. For both curing environments (in water and in a sodium sulphate solution), it is difficult (based on the weight loses within 50-250 °C), to make any differences between the degree of hydration for the two cementitious systems with PC replacement levels of 10% and 40%. However, from the rate of portlandite formation (weight loses within 400-550 °C), it is fairly consistent that at 10% PC replacement level, the formation of portlandite continues beyond the curing period of 90 days (Fig. 8). For 40% PC replacement level, there is no significant increase in portlandite formation beyond 90 days of curing (Fig. 9). In the sulphate system, the level of portlandite actually drops after 90 days at 40% PC replacement (Fig. 9), probably due to its consumption in the formation of sulphate-bearing C-S-H phases.

Figs. 10 and 11 shows the ignited weight losses displayed at three temperature ranges for Trial Pit 5. For Trial Pit 5, the scenario is different from that for Trial Pit 2 in that overall, the degree of portlandite formation is lower for Trial Pit 5. For the specimens cured in water, specimens with PFA from Trial Pit 5 clearly show a higher degree of hydration at 10% PC replacement. Also, the formation of portlandite (at 10% PC replacement) stops after 28 days, in contrast with its continued formation for Trial Pit 2. At 40% PC replacement, and also in contrast with Trial Pit 2, the formation of portlandite continues beyond 90 days of curing.

Results from both Trial Pits are indicative of accelerated PC hydration at low PC replacement with PFA. This phenomenon has been observed by some researchers [21], where acceleration of PC hydration at low replacement levels using PFA has been reported.

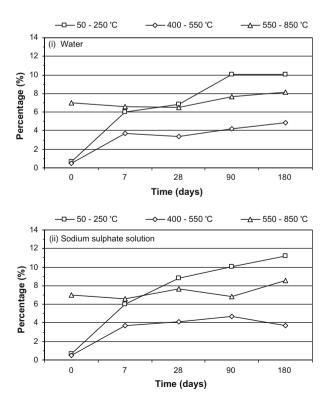


Fig. 11. Ignited weight loss of paste test specimens at a PC replacement level of 40% PFA for Trial Pit 5, versus exposure time in water and sodium sulphate solution for a total soaking period of up to 180 days (moist curing for the first 14 days).

5. Conclusion

The main conclusions than can be drawn from this experimental study may be summarised as follows:

With the exception of the unprocessed PFA from one Trial Pit (Trial Pit No. 6), mortar made using PC–PFA binder using the unprocessed ash shows good sulphate resistance under a sulphatic environment despite the variations in the chemical and oxide compositions of the PFA from the different Trial Pits.

The splitting tensile strength (like the compressive strength reported in an earlier paper) decreases as the PC replacement with PFA increases. This is typical behaviour of strength development observed by researchers who have worked on replacement of PC with processed PFA. The decrease in both compressive and splitting tensile strength is thought to be due to combined effect of PC dilution and the low pozzolanic activity of the PFA used. By maintaining low PC replacement levels (up to 40% for processed PFA and possibly up to 20% in the unprocessed PFA), the strength may be controlled to levels close to those desired in practice.

Thermogravimetric and derivative thermogravimetric (TG/DTG) analysis of hydrated paste specimens made with PC diluted with the unprocessed PFA in the current study showed that the formation of portlandite from the finer PFA (Trial Pit No. 2) continued beyond 90 days of curing. In contrast, the formation of Portlandite with the coarser PFA (Trial Pit No. 5) stopped after 28 days. This appears to confirm that there were significant variability in the PFA reactivity and thus explains the variability in performance.

The unprocessed PFA used in this study has a chemistry with considerable differences from that of the processed PFA, especially in terms of the proportions of the four major oxides – CaO, SiO₂, Al₂O₃ and Fe₂O₃. The samples made using unprocessed PFA from closely located test pits within the Power Station Hill landfill site indicated variations in terms of their physical properties and also in their chemical and oxide compositions. The authors suggest that the effects cumulatively result in poor performance, relative to the processed PFA when the unprocessed PFA was used to replace Portland cement (PC).

Acknowledgments

The authors would like to acknowledge funding from the Glamorgan Engineering Consultancy (GEC) Ltd., a joint venture of three County Borough Councils from South Wales, United Kingdom – Bridgend, Merthyr Tydfil and Rhondda Cynon Taff County Borough Councils, and the contribution made to the field work by Ms. Shin-Ru Chang, a research student at the time. The current research is part of a larger study to investigate the available options

for waste tyres and waste pulverised fuel ash removed from the Power Station Hill landfill and other landfill sites during the construction of the Church Village Bypass in South Wales, United Kingdom.

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