Characterisation and use of biomass fly ash in cement-based materials

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ABSTRACT

This paper presents results about the characterisation of the biomass fly ashes sourced from a thermal power plant and from a co-generation power plant located in Portugal, and the study of new cement formulations incorporated with the biomass fly ashes. The study includes a comparative analysis of the phase formation, setting and mechanical behaviour of the new cement–fly ash formulations based on these biomass fly ashes. Techniques such as X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), thermal gravimetric and differential thermal analysis (TG/DTA), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and environmental scanning electron spectroscopy (ESEM) were used to determine the structure and composition of the formulations. Fly ash F1 from the thermal power plant contained levels of SiO_2, Al_2O_3 and Fe_2O_3 indicating the possibility of exhibiting pozzolanic properties. Fly ash F2 from the co-generation plant contained a higher quantity of CaO ($\sim$25%). The fly ashes are similar to class C fly ashes according to EN 450 on the basis of chemical composition. The hydration rate and phase formation are greatly dependant on the samples' alkali content and water to binder (w/b) ratio. In cement based mortar with 10% fly ash the basic strength was maintained, however, when 20% fly ash was added the mechanical strength was around 75% of the reference cement mortar. The fly ashes contained significant levels of chloride and sulphate and it is suggested that the performance of fly ash–cement binders could be improved by the removal or control of these chemical species.

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1. Introduction

In recent years, pressures on global environment and energy security have led to an increasing demand on renewable energy sources, and diversification of Europe's energy supply. Among these resources the biomass could exert an important role, since it is considered a renewable and CO_2 neutral energy resource, once the consumption rate is lower than the growth rate, and can potentially provide energy for heat, power and transports from the same installation.

The EU research priorities on biomass for electricity, heating and cooling, and their corresponding objectives, are included in the Seventh Framework Programme. The objective is to develop technologies for electricity, heating and cooling from biomass. This research aims at increasing overall conversion efficiency, achieving cost reductions, further reducing the environmental impact and optimising the technologies in different regional conditions.

A broad range of research topics are considered including biomass availability and logistics, conversion technologies, such as combustion, co-firing and gasification, emission abatement and land use [1].

Among the technologies, the solid biomass combustion is a proven technology for heat and power production, where the technologies of fluidised bed and grate furnace combustion are mainly used [2,3]. One of the problems associated to biomass combustion is related with the ash, in the thermal conversion process itself (for example, slagging and fouling phenomena), and also its environmental management.

The quantity and quality of ashes produced in a biomass power plant are strongly influenced by the characteristics of the biomass used: agriculture wastes or herbaceous biomass, wood or bark [2,4]. Combustion of wood generates fewer amounts of ashes to be managed, because herbaceous biomass, agriculture wastes and bark have higher ash content when compared to wood.

The biomass combustion technology used influences the amount and characteristics of the ash produced in a power plant. For example, in a grate furnace the biomass ashes are subjected to higher temperatures (the maximum fuel bed temperature can

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be as high as 1000–1200 °C) in comparison to a fluidised bed (less than 900 °C). In consequence, this influences the amount of organic species (several salts and heavy metals) that volatilise in the furnace, and consequently the relative composition of bottom and fly ashes. This difference in operating temperature in the furnace also influences the degree of slagging and fouling in the furnace and boiler, because of the relatively low melting temperature characteristic of biomass ashes and consequently the composition of slag formed [2,5,6]. Also, the hydrodynamics of the furnace influences the biomass ash fractions collected. In a grate furnace the amount of bottom ashes is dominant compared to multi-cyclone or filter (bag filter or electrostatic precipitator) fraction, whereas in the case of a fluidised bed the fly ash are quantitatively dominant. The concentration of ecological relevant heavy metals (for example, Zn, Cd, Pb, Hg) and organic contaminants (PCDD/F, PAH) increases from the bottom to the fly ash [2,6,7]. Consequently it is not recommended the mix of those ashes fluxes, in particular the filter fly ashes with bottom ashes, since they must follow distinct management strategies, in order to minimize environmental impacts.

Currently, most of the biomass ash produced in thermal power plants is either disposed of in landfill or recycled on agricultural fields or forest, and most times this goes on without any form of control. However, considering that the disposal cost of biomass ashes are raising, and that biomass ash volumes are increasing worldwide, a sustainable ash management has to be established. Besides, for a sustainable biomass to energy strategy it is essential to close the material fluxes and to integrate the biomass ashes within the natural cycles [7].

Due to its high level of contaminants the filter fly ashes should not be recycled in the environment, and should be disposed off or treated as an industrial waste, according to some European guidelines and practices [2]. A possibility for the management of this fly ash fraction includes its incorporation in construction materials, as a component of lightweight aggregates, a component of cement blends and mortars [8], as also performed with coal fly ashes [2], ashes from municipal wastes incineration [9], and ashes from hospital waste incineration [10].

Biomass ashes differ from coal ashes, in particular in what concerns to its chemistry and mineralogy. The characteristics of ashes from biomass combustion vary widely and are influenced by: (i) biomass characteristics (for example, herbaceous material, wood or bark), (ii) combustion technology (for example, fixed bed or fluidised bed), (iii) the location where the ashes are collected (for example, bottom ashes or fly ashes) [2,3,7].

Extensive research has been conducted on industrial by-products and other waste materials which are suitable for use as binder substitutes in cement formulations. The use of these materials brings a number of benefits including reduced cost and a reduction in the environmental impacts caused by waste disposal and cement production. The cement industry is responsible for a significant proportion of carbon dioxide (CO_2) released into atmosphere. Utilisation of industrial by-products substitutes for natural resources and provides an alternative for natural minerals [11–15].

Many researchers have studied the use of agricultural waste ashes as constituents in concrete, including rice–husk ash, sawdust ash, bagass ash and palm oil fuel ash [16–20]. Those agro-waste ashes, containing a large amount of silica in amorphous form, have potential for use as pozzolanic materials replacing cement.

Typically, fly ash from neat biomass combustion contains more alkali metals—sodium and potassium (Na, K) and less alumina (Al_2O_3) than coal fly ash, traditionally used as a pozzolanic additive in cement formulations. Wang et al. [8] compared the properties of biomass fly ashes from co firing (herbaceous with coal), pure wood combustion, and blended (pure wood fly ash blended with coal fly ash) to those of coal fly ash in concrete. Their results imply that fly ashes from co-firing biomass with coal within a certain blending ratio (25%) should be considered in concrete. However, for the time being, biomass fly ash is excluded from addition in concrete according to the standards because of its non-coal origin.

Currently Portugal has two thermal power plants dedicated to electricity production and connected to the national electric grid; both installations use forestry biomass as their main fuel. In addition to these, nine co-generation power plants are installed in forestry sector industries, which use biomass for combined heat and power production. There are also a wide range of other industrial consumers of biomass for heat production, although in at lower scale. In the very near future 17 new biomass thermal power plants are scheduled to join with the existing ones, according to the energy policy of the Portuguese Government [21]. This will result in an increase of generation of several thousand of tonnes of biomass ashes per year requiring proper monitoring and management.

There is a clear need for guidelines for a sustainable management of biomass ash (bottom ash and fly ash) from thermal power plants. The biomass ashes from thermal power plants are classified as an industrial waste, with code 100101 or 100103 according to the European List of Wastes [22] and should be managed accordingly. Nevertheless, some current practices include the utilisation of biomass ashes in agriculture or in road construction. There are also some ongoing studies about the mixing of biomass ashes with other wastes, as for example sewage sludge and green parts of gardens maintenance, in order to produce a compost to be used in forestry and agriculture [23].

The present work aims to study the characterisation and the incorporation of fly ash from biomass combustion in a thermal power plant (grate furnace) and co-generation plant (bubbling fluidised bed) in cement based formulations, as a possible future use of this waste stream.

2. Experimental procedure

The biomass fly ashes samples used were collected from the electrostatic precipitator of a biomass thermal power plant and of a co-generation plant, both located in Portugal. Both plants use forest wastes as main fuel (mainly eucalyptus wastes, resulting from logging and wood processing activities).

The fly ash F1 was collected from a biomass thermal power plant dedicated to electricity production, which uses forest residues for energy production. The fuel is burnt in a boiler with a water cooled vibrating grate, and nominal thermal capacity of 30 MWth. Whenever needed natural gas is also used for maintaining proper temperatures in the boiler. Typical temperatures in the furnace are around 1000 °C. These biomass fly ashes were black in colour, indicating significant carbon content.

The fly ash F2 was collected from a biomass co-generation plant, from a pulp and paper industry. The fuel is burnt in a boiler with fluidised bed technology, and nominal thermal capacity of 90 MWth. Typical temperatures in the furnace is around 800 °C. These biomass fly ashes were medium grey in colour.

Ordinary Portland cement (OPC) type I (42.5 R) was used in the present study to prepare pastes and mortars. Siliceous sand was sieved through a 2.18 mm mesh before using in the mixture as an aggregate. Excess moisture was removed by heating in an oven at 60 °C for 24 h prior to use.

The fly ashes samples (F1 and F2) collected from the plants were also dried in a laboratory oven at 60 °C to remove excess moisture. In order to reduce the agglomeration of particles, the fly ashes were sieved through a 75 μm mesh prior to incorporation in cement pastes and mortars.

The particle size distributions of the fly ashes were studied using a Coulter LS particle size analyser (LS230FM). The real densities of the fly ash particles were determined using a picnometer and the surface area by the BET (Brunauer, Emmett, and Teller) method.

X-ray diffraction (XRD) patterns of the fly ashes were taken using an X-ray diffractometer (RIGAKU-Geigerflex, power 40 kV/30 mA, scan mode continuous/speed-3°2(/min). Thermal gravimetric and differential thermal analyses (TG/DTA) of the fly ashes were performed up to 1000 °C with a heating rate of 10 °C/min, in a simultaneous TG/DTA (STA 409 EP). The fly ashes were sieved to remove particles larger than 75 μm and dried at 120 °C before performing the thermal analysis (TG/DTA). The chemical composition of the fly ashes was studied using X-ray fluorescence spectroscopy (XRF). The pozzolanicity of the ashes was determined using the procedure described in the Standard EN 196-5:2005 [24]. According to this standard, pozzolanicity was determined by measuring the concentration of CaO and OH^- ions in the reacted solution of the test material with high grade cement. The concentrations of ions were determined by titration methods. The appropriate amounts of the test material, high grade cement and double distilled water were mixed in a plastic bottle and were kept in an oven at about 40 °C. After 14 days the solution was filtered and titrated against HCl and EDTA solutions to find out the OH^- and CaO concentrations, respectively. The microstructure of the ash samples was studied using a scanning electron microscope (SEM) (Hitachi S2300 SEM with EDX25KV).

The chloride and sulphate contents of the fly ashes were determined by the Argentometric method (CHLORIDE, 4500-Cl^-; Standard Methods Committee, 1997) and the Gravimetric method (SULFATE, 4500-SO_4^{-2}; ignition of residue, Standard Methods Committee, 1997), respectively.

Cement pastes and cement mortars were prepared by replacing OPC with different amounts of biomass fly ashes (10%, 20% and 30% by weight of cement) in dry condition. The cement pastes were prepared with a water content ranging from 30% to 46% of the binder weight. The consistency was determined by the VICAT consistency needle penetration method following EN 196-3:2005 [25]. The consistency of cement is given by the paste water content at the moment when the VICAT consistency plunger enters the sample down to a depth 5 mm above the bottom surface.

The heat of hydration of pastes in terms of the temperature was measured using a quasi-adiabatic calorimeter. The cement pastes were put in thermally isolated boxes and the temperatures of the mixes were recorded continuously with the help of thermocouples and computer aided data loggers.

The cement mortars were prepared with 0.55–0.65 water/binder (w/b) weight ratio. The cement to aggregate ratio was taken as 1:3, and for the standard mortar sample the water to binder (w/b) ratio was taken as 0.55. The components were weighed and mixed thoroughly in a laboratory mixer (CONTROLS, 65-LS). The mixing procedure includes: (i) addition of water to the dry powder mix; (ii) mixing for 1 min at a low rotation speed of (~60 rpm); (iii) stopping for 1 min to gather the mix into the centre; (iv) mixing again for 2 min at a higher rotation speed (~120 rpm). No dispersing agent or plasticizer was used in either pastes or mortars.

Mortar workability was measured with the slump method and expressed as a spread diameter in mm. Slump measurements were performed according to EN 1015-3:1999 [26]. The mortar sample spread diameter measured before and after 15 strokes (1 stroke per second) represents slump values. The w/b ratio was selected to have a minimum slump value of 120 ± 10 mm. The density was obtained from geometrical measurements. The fresh state relative density was evaluated through the weight determination of a specific mortar volume. Setting time was evaluated by the VICAT apparatus. The mortar samples for mechanical tests were prepared with the standard dimensions 16 cm × 4 cm × 4 cm. The moulds were covered well with plastic sheets to avoid water loss and stored in a curing chamber at a temperature of 20 °C and a relative humidity of 65%. After 24 h, the blocks were removed from the moulds and immersed in tap water for curing for 28 days. The mechanical strength was evaluated by compression and flexural tests carried out according to EN 1015-11:1999 [27], on three samples of each composition, using a Standard Universal Testing Machine (Shimadzu). The prisms were first mechanically tested in three-point bending mode, after which each part was tested in compression.

XRD and TG/DTA of the cement pastes were taken after 28 days to check the composition. The hydration in the cement-based pastes was studied using an Electroscan 2020 environmental scanning electron microscope (ESEM) equipped with a Peltier cooling stage. Images were obtained at an accelerating voltage of 20 kV and filament current of 2.5 A. The microscope was operated in wet mode, using water vapour as the imaging gas. A gaseous ion detector was used with a sample chamber pressure of 5 Torr for imaging and 14 Torr when flooding. The hydration process was monitored at 4 h, 24 h, 7 days and 30 day intervals.
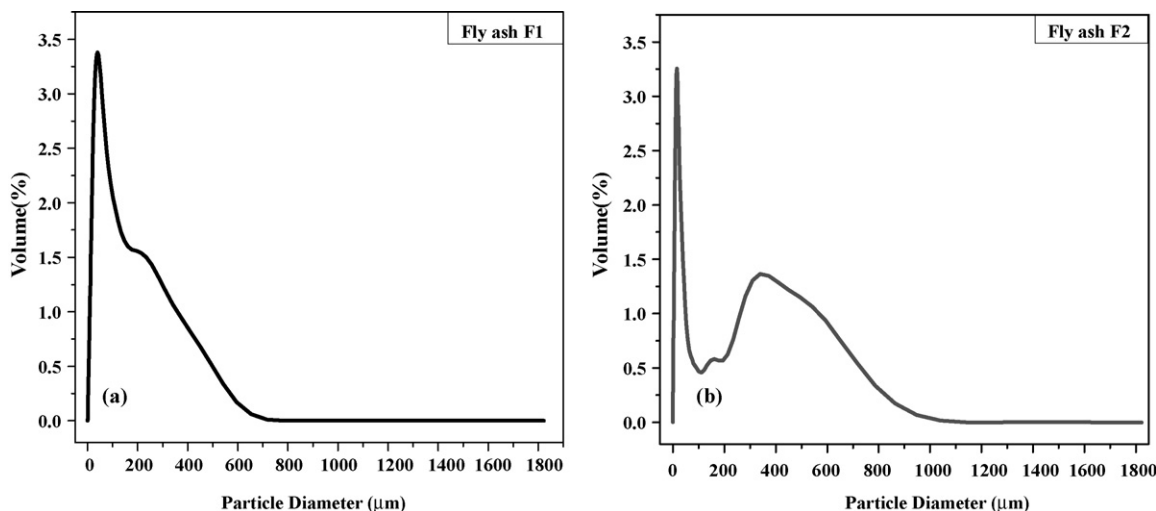

Fig. 1. (a) Particle size distribution of fly ash F1 and (b) particle size distribution of fly ash F2.
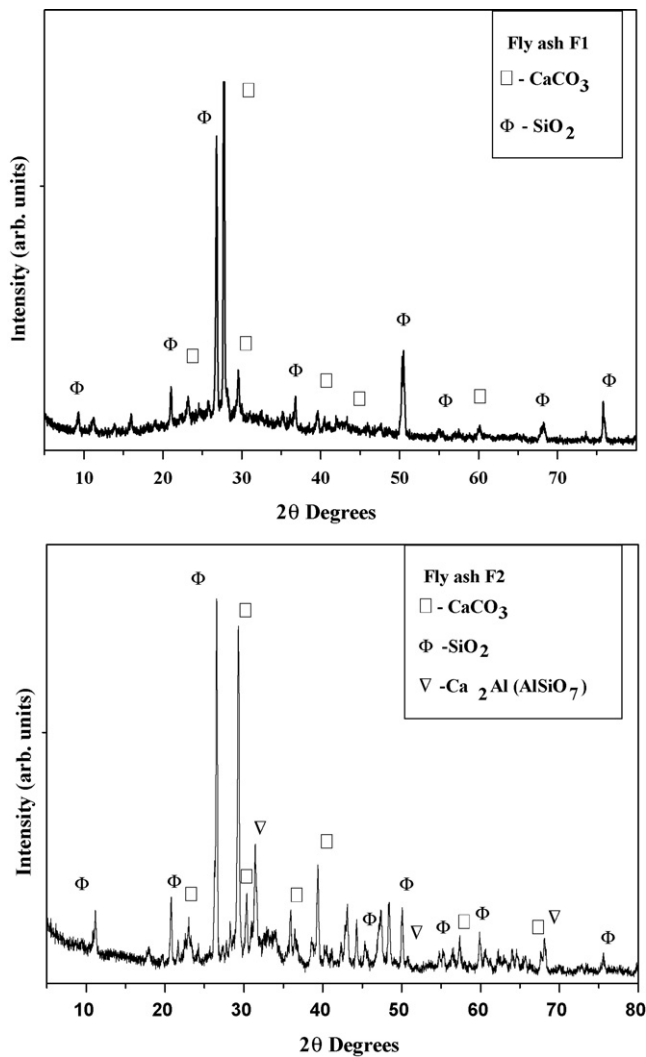
Fig. 2. XRD patterns of the biomass fly ashes.

Table 1
XRF analyses of fly ashes.

Element	F1 (wt. %)	F2 (wt. %)
SiO_2	41	28
Al_2O_3	9.3	6.2
Fe_2O_3	2.6	2.2
CaO	11.4	25.4
MgO	2.3	5.0
Na_2O	0.9	3.3
K_2O	3.9	3.2
TiO_2	0.4	0.3
MnO	0.3	0.7
P_2O_5	0.9	0.9
Cd	1.0 mg/kg	1.3 mg/kg
Pb	191 mg/kg	12 mg/kg
Cu	99 mg/kg	27 mg/kg
Cr	47 mg/kg	73 mg/kg
Hg	<1 mg/kg	<1 mg/kg
Ni	35 mg/kg	27 mg/kg
Zn	376 mg/kg	34 mg/kg

3. Results and discussion

3.1. Characterisation of fly ashes

The particle size distribution analysis of the ashes is shown in Fig. 1a and b. The fly ash F1 was cut at 500 μm to remove the elongated particles which were found to reduce the measurements accuracy significantly. Fly ash F2 was cut at 1 mm. The particle sizes of the ashes were typically below 50 μm. Broad peaks indicating agglomeration of particles were observed in both ashes (especially in fly ash F2). Both ashes were sieved to remove particles greater than 75 μm before using in cement formulations.

The real densities of the ashes F1 and F2 were 2.59 and 2.54 g/cm³ respectively, both significantly lighter than that of the cement powder which was 3.035 g/cm³. The BET surface areas of the fly ashes F1 and F2 were 40.29 and 7.922 m²/g respectively. The higher surface area value for fly ash F1 can be explained by irregular particle shape and also due to the presence of some unburnt organic matter indicating an inefficient burning of the biomass in the boiler.

The X-ray diffraction patterns of the biomass fly ash are shown in Fig. 2. The main components of the ashes were SiO_2 and Calcite. The loss on ignition test to determine the organic matter content in the biomass fly ashes gave the values around 14% and 7% for the fly ashes F1 and F2, respectively. The test was done by combusting the fly ashes for around 3 h at 525 °C (ISO 1762:2001) [28].
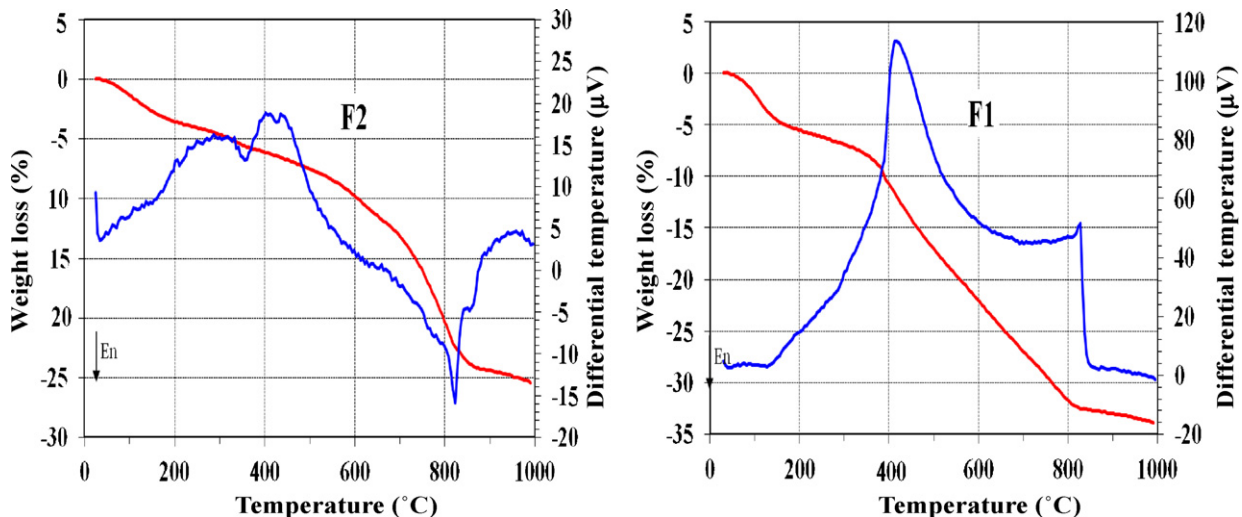

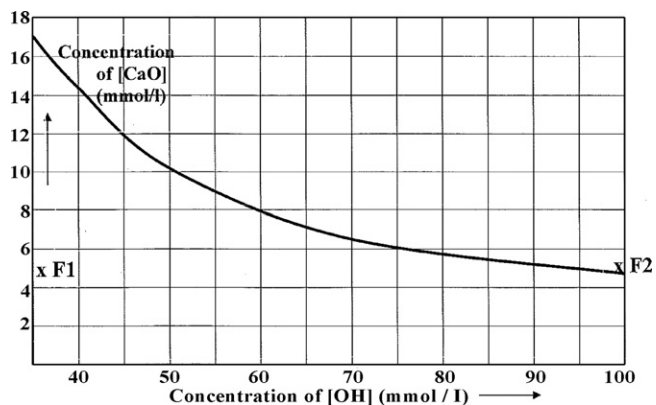**Fig. 3.** TG/DTA analyses of fly ash F1 and fly ash F2.

**Fig. 4.** Pozzolanicity diagram for the biomass fly ashes.

Two major variations in weight were seen in the TG/DTA in the range of 300–600 °C and at around 800 °C in both ashes indicating the presence of organic matter and calcite (Fig. 3). The combustion of the organic matter in the biomass materials occurs in the range 300–600 °C and the thermal decomposition of $CaCO_3$ (calcite) occurs at 800 °C. The calcite peaks indicate that fly ash F2 con-

tained more calcite compared to F1. The TG/DTA also gives values around 14% and 7% if the weight loss is evaluated at a temperature around 525 °C thus corresponding to the organic matter content. The TG/DTA curves indicated that fly ash F1 contained more organic matter than fly ash F2, so explaining its higher loss on ignition. In fact, although the biomass is burnt under sufficiently high temperature (750–1000 °C) in the furnace, there is always some inefficiency on carbon conversion due to kinetic and mass transfer limitations. Consequently, the fly ashes present some amount of organic matter.

The major chemical analysis of the fly ashes obtained using X-ray fluorescence spectroscopy is shown in Table 1. Fly ash F1 contained the pozzolanic material SiO_2, Al_2O_3 and Fe_2O_3. Fly ash F2 contained 25% CaO and would be expected to react hydraulically. Both fly ashes were similar to a class C fly ash (EN 450-1:2005) [29].

CaO and OH^- concentrations obtained from the pozzolanicity test were plotted on the pozzolanicity diagram shown in Fig. 4. The saturation curve is that of cement without pozzolans. Fly ash F1 is positioned significantly below the saturation curve (marked as "x") indicating strong pozzolanicity, whereas fly ash F2 is positioned slightly above the saturation curve indicating a negative pozzolanicity result.

Fly ash F1 contained a chloride content of 1.42 g/L and sulphate content 1.30 g/L, and fly ash F2 a chloride content of 3.74 g/L and
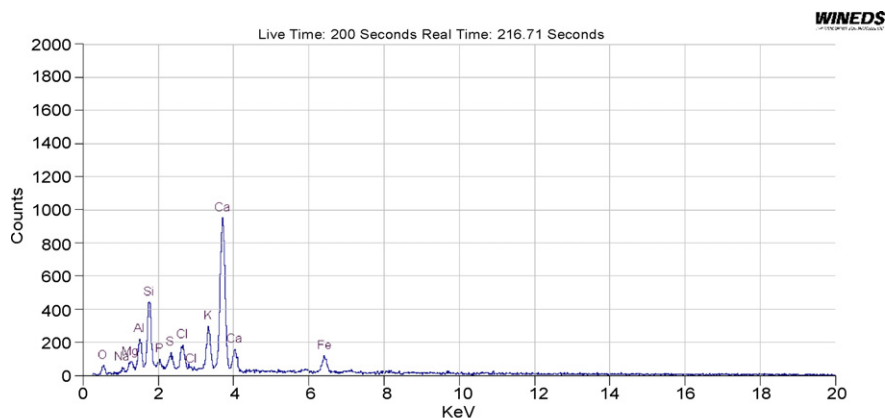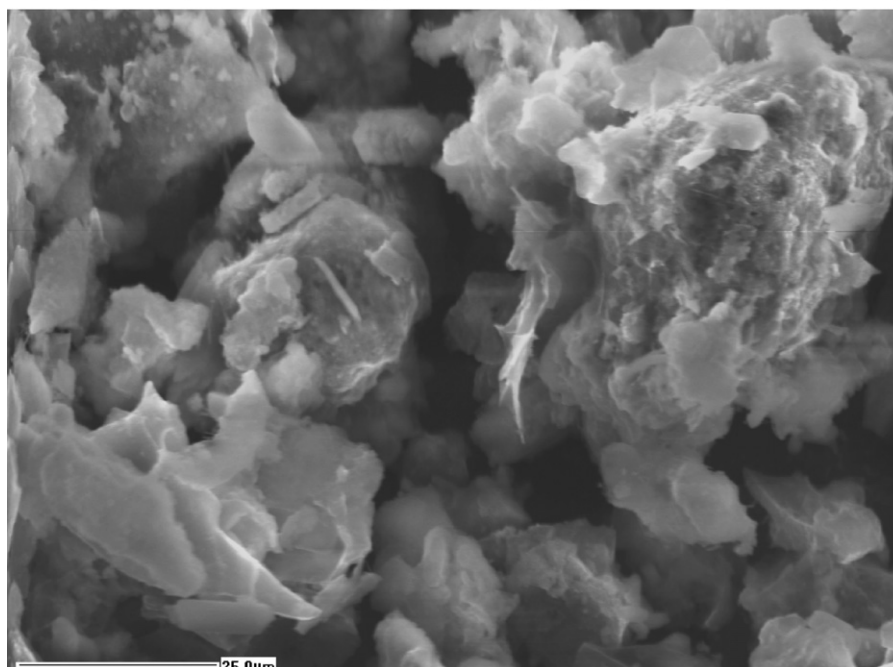

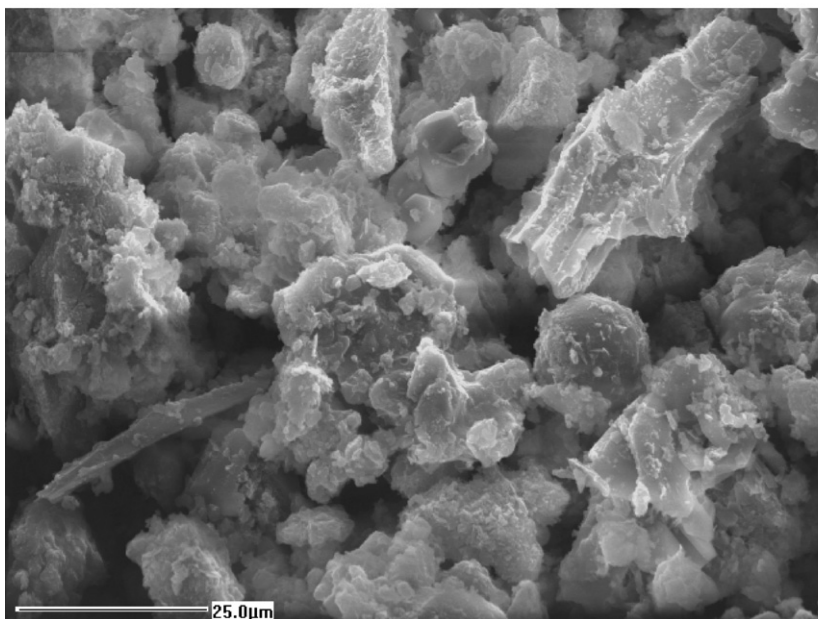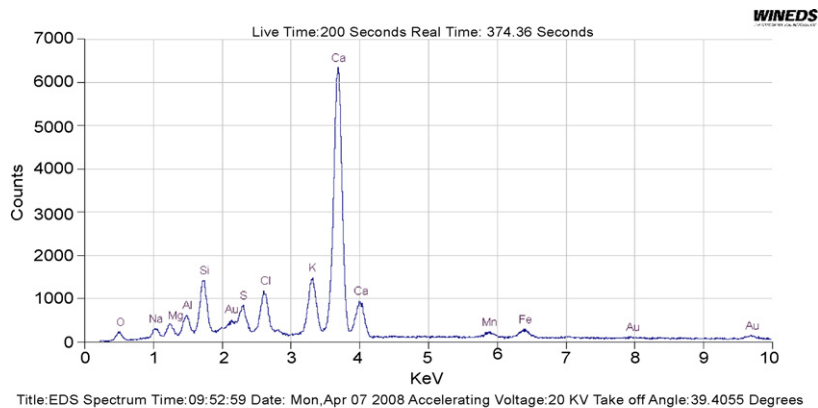**Fig. 5.** SEM images of (a) fly ash F1 and (b) fly ash F2.

Fig. 5. (Continued).

sulphate content of 2.60 g/L. As noted later, the presence of chlorides and sulphates in cementitious materials can reduce durability by deterioration of the microstructure.

A quantitative elemental analysis of the cement and ash particles determined by XPS analysis is shown in Table 2. Significant amounts of Ca, Si, Al and Mg were present on the ash surfaces compared to that of cement. The carbon content was high for the fly ashes. The amount of chlorine as chloride was also high in the fly ashes: 1.9 and 3.0% for fly ash F1 and fly ash F2, respectively. A significant amount of alkali metals Na, K were also present in the fly ashes.

The microstructure of fly ashes sieved to remove particles greater than 75 μm was characterized using SEM (Fig. 5). It was observed that the fly ash particles were irregular in shape. Fly ash F2 was more homogenous than F1. The particle size of the fly ashes was typically below 50 μm and in agreement with the particle size

analysis results (Fig. 1). According to Energy Dispersion X-ray spectroscopy (EDX) analysis at the SEM (Fig. 5), the major elements in both fly ashes were Ca, Si and Al. The presence of Na, K, Cl and S was also evident in the ashes.

3.2. Cement–ash formulations

3.2.1. Calorimetric analysis

The effect of fly ash on the hydration behaviour of cement pastes was investigated using calorimetric analysis. The water content required to prepare distinct fly ashes compositions ranged from 30% to 46%, as given in Table 3.

Results of calorimetric experiments conducted on the cement pastes are shown in Fig. 6. The highest temperature of hydration, ~40 °C, was observed in the pure cement paste after a period

Table 2
Summary of XPS analysis done on the surface of the cement and the fly ash samples.

Sample	(atomic %)									
	C	O	Na	Mg	Al	Si	S	Cl	K	Ca
Cement	23.5	38.8	0.4	0.9	2.4	6.3	2.0	1.5	1.6	22.8
F1	41.6	27.5	0.5	2.0	5.3	8.8	0.6	1.9	3.7	8.1
F2	38.7	29.0	1.0	2.5	3.6	6.9	0.9	3.0	2.2	12.1

Table 3
Relative amount of water used in the cement–fly ash pastes and corresponding consistency given by the VICAT needle.

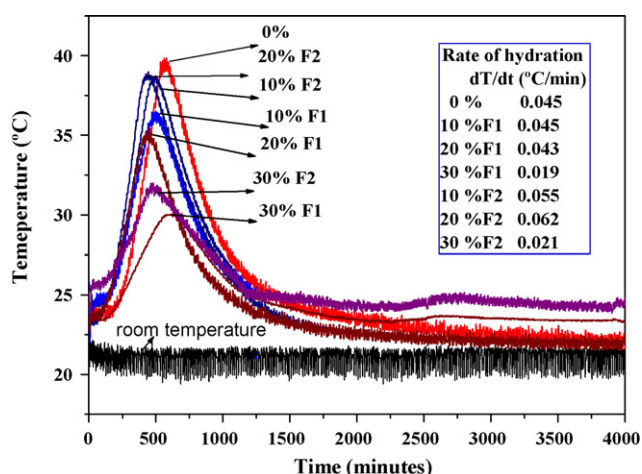| Sample	Percentage of water (%) (wt. % of cement)	VICAT apparatus scale value (mm)
Cement	30	7
10 F1	33	8
10 F2	33	7
30 F1	46	9
30 F2	42	8

Fig. 6. Calorimetric evaluation of the hydration process of cement–fly ash pastes.

of approximately 10 h. The hydration process in all the samples reached a steady state temperature of around 24 °C within 3 days. It was observed that the time taken to reach the hydration peak was less for the ash replaced cement pastes. As the amount of ash content was increased, the heat of hydration decreased indicating a reduction in the hydrating phases in the ash replaced cements. However, 10 and 20 wt. % F2 fly ash replaced cements showed a slight increase in the heat of hydration with respect to that of pure cement paste. From Fig. 6 it was also evident that the rate of hydration for fly ash F1 substituted cement pastes was less compared to that of fly ash F2 substituted cement pastes. The difference in the hydration rate and the shift in hydration peak are probably influenced by the alkalis and chlorine present in the fly ashes [30].

3.2.2. Fresh and hardened state properties of ash incorporated cement mortars

The mechanical properties of the freshly prepared and hardened mortars containing fly ashes F1 and F2 are listed in Table 4 . Both fly ashes affected the mechanical properties of the mortars in a similar way, but the fly ash F1 required more water to maintain the same slump value. The fresh density (apparent density) of the cement–fly ash mixtures was more or less similar in all the samples. The slight variations are influenced by the compactness degree obtained upon the sample preparation, and the different w/b ratios.

The setting time varied with the different w/b ratio. In 30% fly ash F1-cement mortar the setting time was reduced by 60 min even though the w/b was increased by 0.1 ($w/b = 0.65$) to maintain the slump value. This indicated that fly ash F1 absorbs more water, probably due to its higher content of organic matter in the fly ashes. The fly ash F2-cement mortar also required increased water content on substituting the higher amounts of fly ash, though less than that needed for the mixture containing fly ash F1. Here also the organic

Table 5
Weight loss of the fly ash–cement pastes as a function of temperature.

Temperature range (°C)	Weight loss (%)				
	Cement	10 F1	10F2	30F1	30F2
135–185	3.89	3.95	3.98	4.19	4.91
525–575	1.81	1.27	1.46	0.43	0.92
800–850	1.39	2.11	1.42	3.18	2.17

matter in the fly ash absorbs the water in the mortar and in effect the setting time is reduced due to this water consumption. But on 10% substitution of both fly ashes in cement the setting time was increased unexpectedly. This may be because of the dominating effect of fineness of the ashes over the organic content effect in regulating the setting time. For fly ash F2 compositions up to 20% the w/b was constant ($w/b = 0.55$) and with 30% there was used excess water to keep up the workability ($w/b = 0.60$). So the setting time is increased for 30% fly ash F2 substituted cement mortars. All these results indicate that the water absorbed by the organic matter in the fly ash is available for hydration during the setting process. Considering the w/b ratios fly ash F2 was more beneficial than fly ash F1 for the cement formulations.

The 30% replacement of cement by both the fly ashes in mortars showed a decline in strength, as compressive strength was around 60% of the reference mortar while the 10% and 20% replacement mixes showed smaller deterioration. From this, the limit of biomass fly ash replacement in cement can be set at 20% to ensure the quality of the mortars.

3.2.3. XRD and thermal analysis

XRD patterns of cement–ash pastes cured in water for 28 days are shown in Fig. 7. The main peaks observed are from calcium hydroxide, calcium aluminium hydrate and calcium silicate. Peaks from ettringite, calcite and silica were also found. The XRD patterns gave a preliminary idea of the fly ashes influence on the phase formation in the paste samples. The patterns indicate that the calcium silicate peaks are more intense in cement and in 10% fly ash added samples compared to those in the 30% fly ash added samples. The ettringite formation is expected to be enhanced in the cement–fly ash paste samples, specially on substitution of higher amounts of fly ash, due to the presence of alkalis and increased water content, eventhough its not possible to quantify due to the low intensities of the peaks. The intensities of all other peaks were comparable.

Fig. 8 shows the TG and DTA curves of the cement paste and of the cement–fly ash pastes after 28 days of curing in water. There were 3 endothermic peaks in the DTA curves, located within the temperature ranges 135–185 °C, 525–575 °C and 800–850 °C. The decomposition of calcium silicate hydrate and ettringite both occur within the temperature range 135–185 °C. The peak at 525–575 °C is due to calcium hydroxide (CH) decomposition. The intensity of the CH peaks were reduced in the fly ash-containing pastes, com-

Table 4
Mechanical properties of fly ash substituted cement mortars (w/b = water–binder ratio, taken in weight, the standard variations are shown in brackets).

	w/b	Fresh mortar properties			28th day curing		
		Slump (mm)	Setting time (min)	Density (g/cc)	Flexural strength (MPa)	Compression strength (MPa)	Density (g/cc)
F1 ash (wt. %)							
0	0.55	130	180	3.17 (0.01)	6.98 (0.12)	41.48 (1.17)	2.19 (0.01)
10	0.55	120	197	3.06 (0.03)	4.96 (0.15)	43.31 (1.49)	2.52 (0.02)
20	0.60	110	150	3.10 (0.01)	4.16 (0.24)	32.53 (0.37)	2.11 (0.01)
30	0.65	110	120	3.11 (0.01)	3.39 (0.65)	22.59 (1.20)	2.07 (0.02)
F2 ash (wt. %)							
10	0.55	120	212	2.94 (0.06)	4.23 (0.16)	35.76 (1.35)	2.07 (0.01)
20	0.55	110	121	3.00 (0.01)	4.31 (0.34)	30.13 (0.49)	2.08 (0.01)
30	0.60	120	221	3.17 (0.02)	3.14 (0.38)	26.72 (0.57)	2.21 (0.02)

pared to that of pure cement paste. Fly ash, F2-based pastes showed a higher amount of CH compared to fly ash F1. The weight losses of the pastes obtained from the TGA data corresponding to the different temperature ranges are shown in Table 5. The amount of CH produced is a function of the relative amounts of alite and belite present in the cement. Therefore, it follows that the variation in CH indicates the amount of calcium silcate hydrate (CSH) gel formed. A contribution from the pozzolanic effect of fly ashes is also expected. The pozzolanic reaction primarily occurs between amorphous siliceous materials and portlandite, as a simple acid-base reaction between (CH), and silicic acid (H_4SiO_4) or $Si(OH)_4$, to form calcium silicate hydrate of general formula ($CaH_2SiO_4 \cdot 2H_2O$)

or CSH. The ratio Ca/Si, or C/S, and the number of water molecules can vary according to the stoichiometry of the components in the reaction. The peak after 800 °C is related to the thermal decomposition of $CaCO_3$. The thermal analysis is in good agreement with the mineralogical characterisation obatined from XRD studies.

3.2.4. Microstructural analysis

ESEM images of the fly ash incorporated cement pastes were taken after 4 h, 24 h, 7 days and 30 days are shown in Figs. 9–12, respectively. The phases were identified by EDX analysis. The ESEM images of pastes taken after 4 h of hydration were in the beginning of the acceleration period after the initial hydration of the C_3A
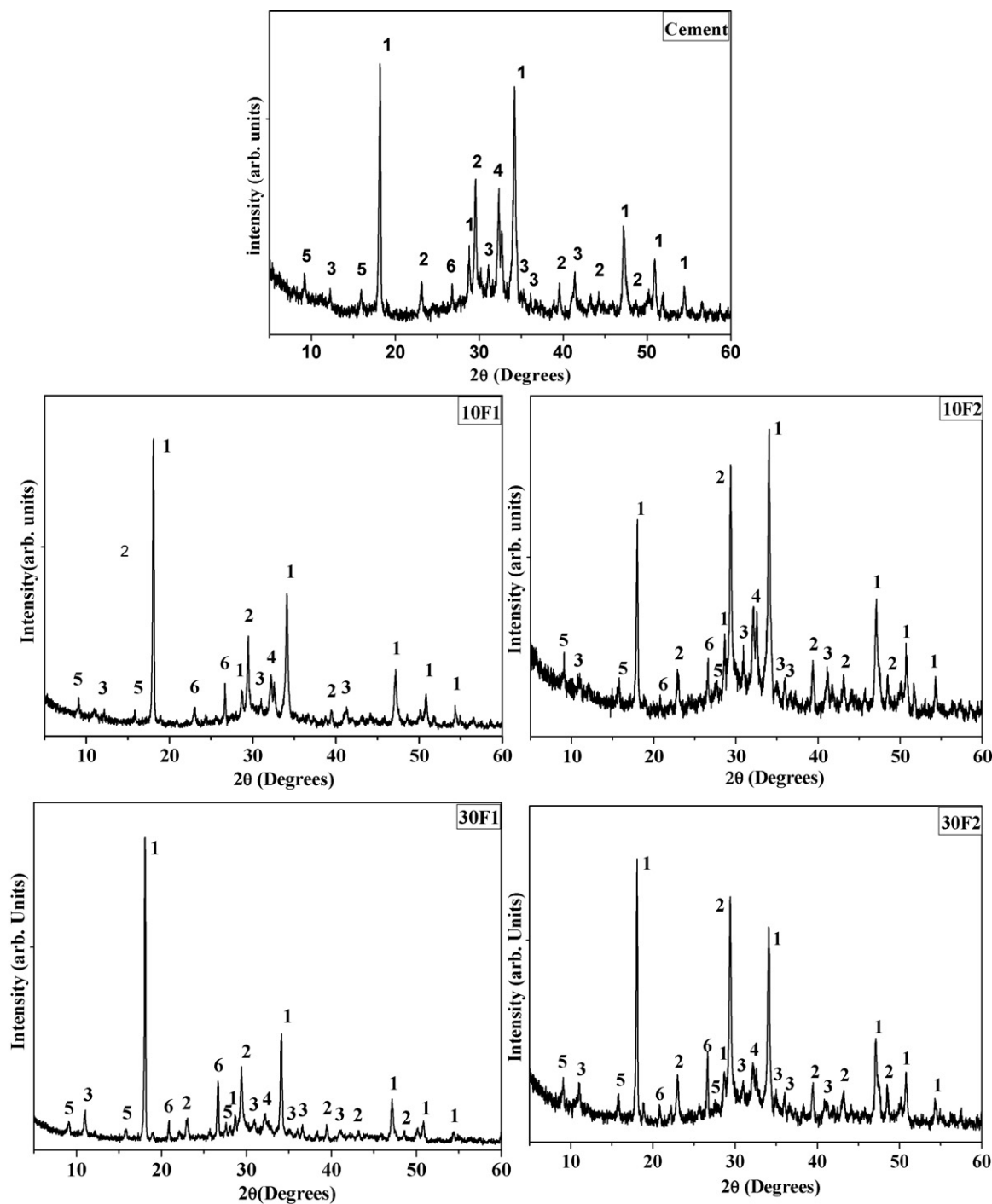

Fig. 7. XRD patterns of 28 days cured cement–fly ash pastes. The phases identified were (1) $Ca(OH)_2$, (2) $CaCO_3$, (3) $Ca_2Al(OH)_2 \cdot xH_2O$, (4) Ca_2SiO_4, (5) Ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$), and (6) SiO_2.

phase. The C_3A phase reacted with water to form an aluminate rich gel and, following further reaction with sulphate ions within the water, ettringite in colloidal form with CH was formed. The ESEM images in Fig. 9 show a gel-like structure around the cement grains identified as the amorphous CH gel.

The water content and the pH of the hydrating medium are the two major factors affecting the hydration mechanism in cements. The fly ash contained Na^+ and K^+ ions, together with Cl^- in amounts expected to influence the pH level. In addition, the higher percentage of fly ash replacement required increased amounts of water. These are the main factors affecting the hydration behaviour in the investigated samples. The Na^+ ions decelerate hydration, whereas K^+ and Cl^- ions accelerate the hydration process. After 24 h of hydration the cement and 10% fly ash substituted pastes showed

extensive CSH growth. Ettringite needles were visible in 30% fly ash F1 substituted cement paste (Fig. 10).

After 7 days, a well-formed network of CSH crystals in the pastes covering the fly ash particles was visible (Fig. 11), in addition to large portlandite crystals. The CSH network was well-defined in the pure cement and 10% fly ash F1 substituted pastes.

Analysis after 30 days of curing indicated that the hydration reaction was almost finished (Fig. 12). The cement–fly ash pastes showed the silicate hardening phases and ettringite needles were observed in cements containing 30% fly ash substitution. This was attributed to the presence of sulphate ions in the fly ashes and the high water content of the pastes.

On reviewing the chemical analyses for the fly ashes and fly ash–incorporated cement formulations, two major issues have
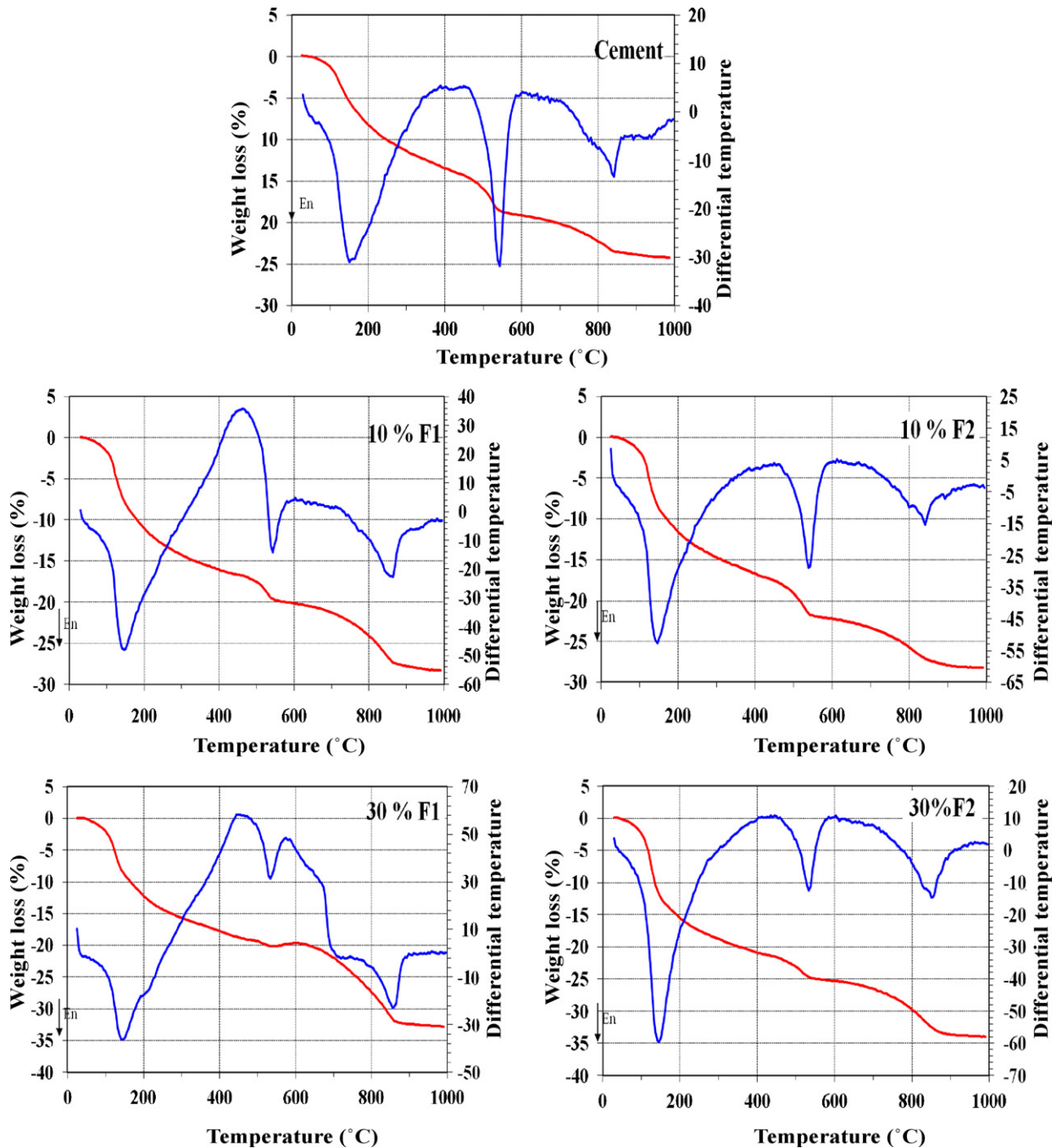

Fig. 8. TG/DTA curves of (a) cement paste; (b) 10% fly ash F1 substituted cement–fly ash paste; (c) 10% fly ash F2 substituted cement–fly ash paste; (d) 30% fly ash F1 substituted cement–fly ash paste; (e) 30% fly ash F2 substituted cement–fly ash paste after 28 days of curing.
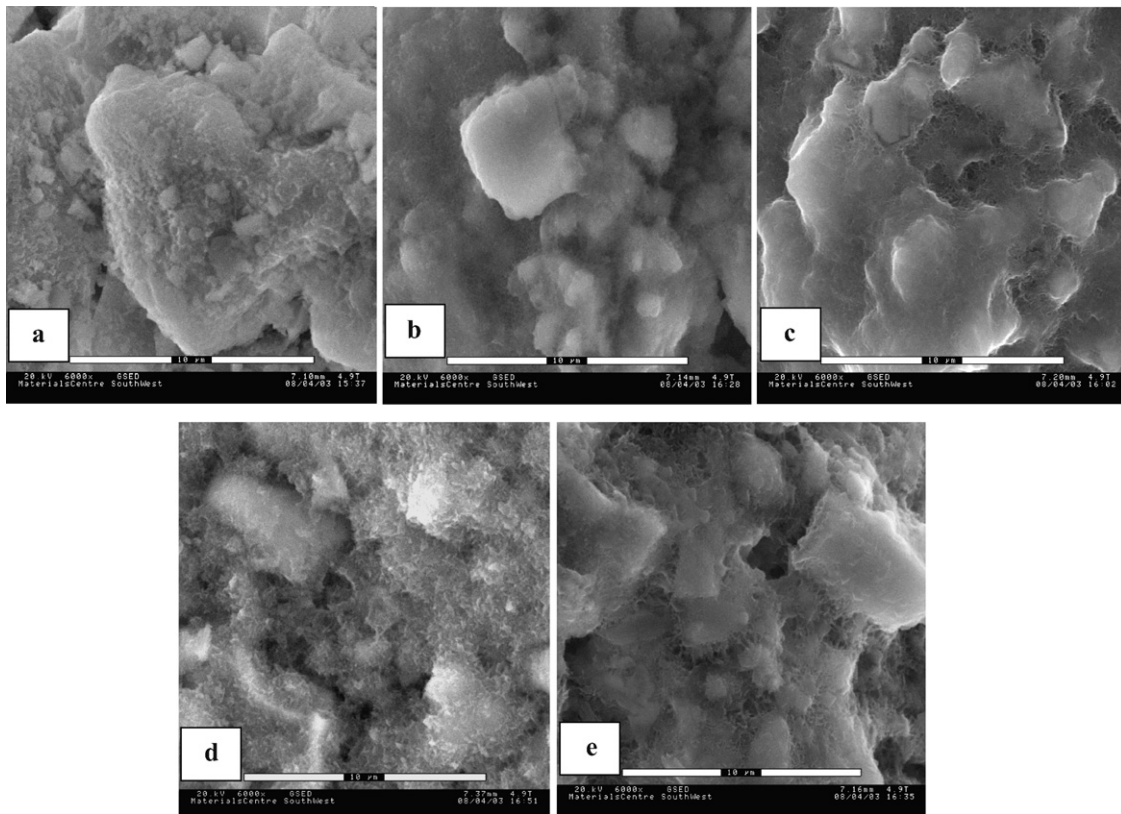
Fig. 9. Microstructure of cement–fly ash pastes after 4 h of hydration: (a) 0% ash, (b) 10% fly ash F1, (c) 10% fly ash F2, (d) 30% fly ash F1, and (e) 30% fly ash F2.
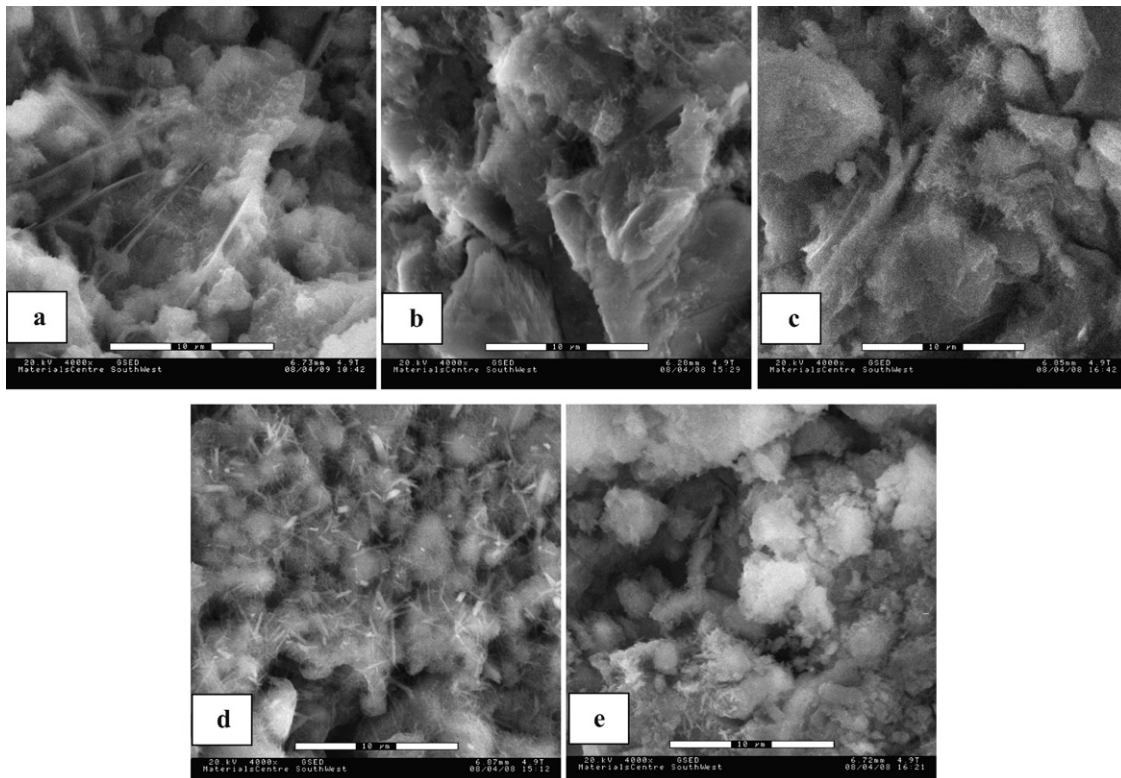

Fig. 10. Microstructure of cement–fly ash pastes after 24 h of hydration: (a) 0% fly ash, (b) 10% fly ash F1, (c) 10% fly ash F2, (d) 30% fly ash F1, and (e) 30% fly ash F2.
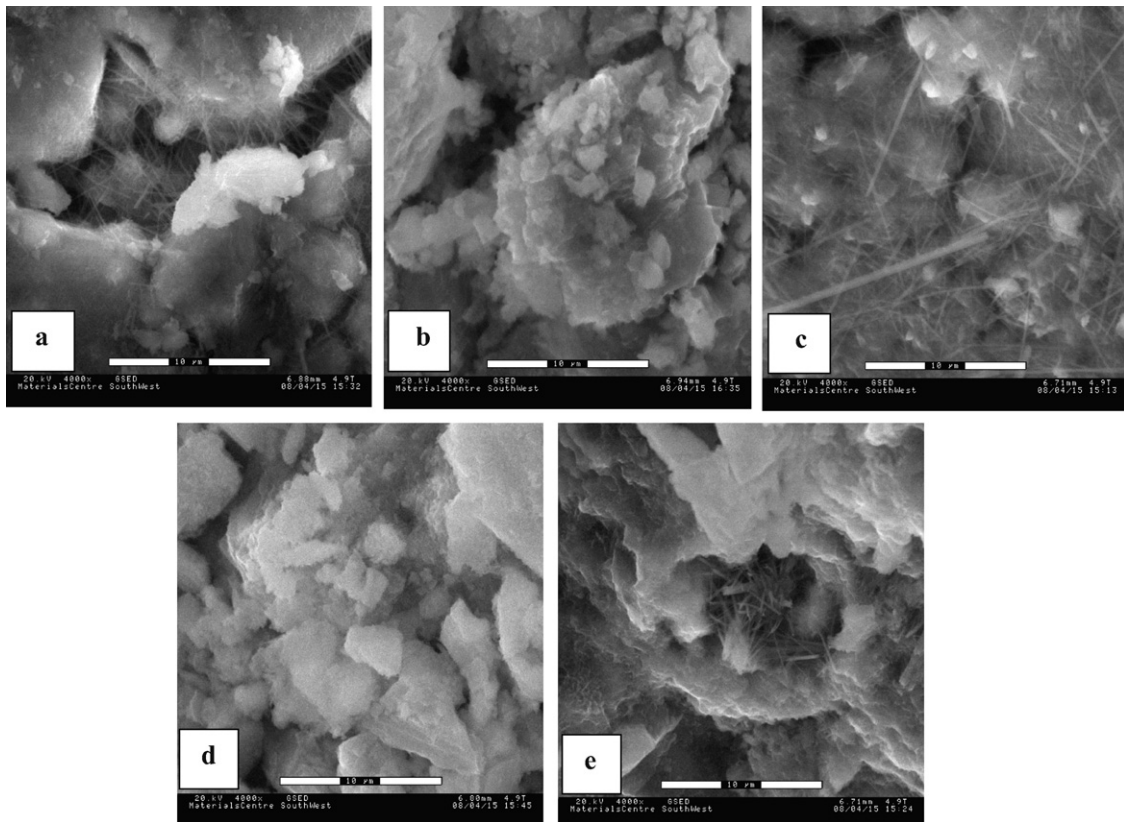
Fig. 11. Microstructure of cement–fly ash pastes after 7 days of hydration: (a) 0% fly ash (b) 10% fly ash F1, (c) 10% fly ash F2, (d) 30% fly ash F1, and (e) 30% fly ash F2.
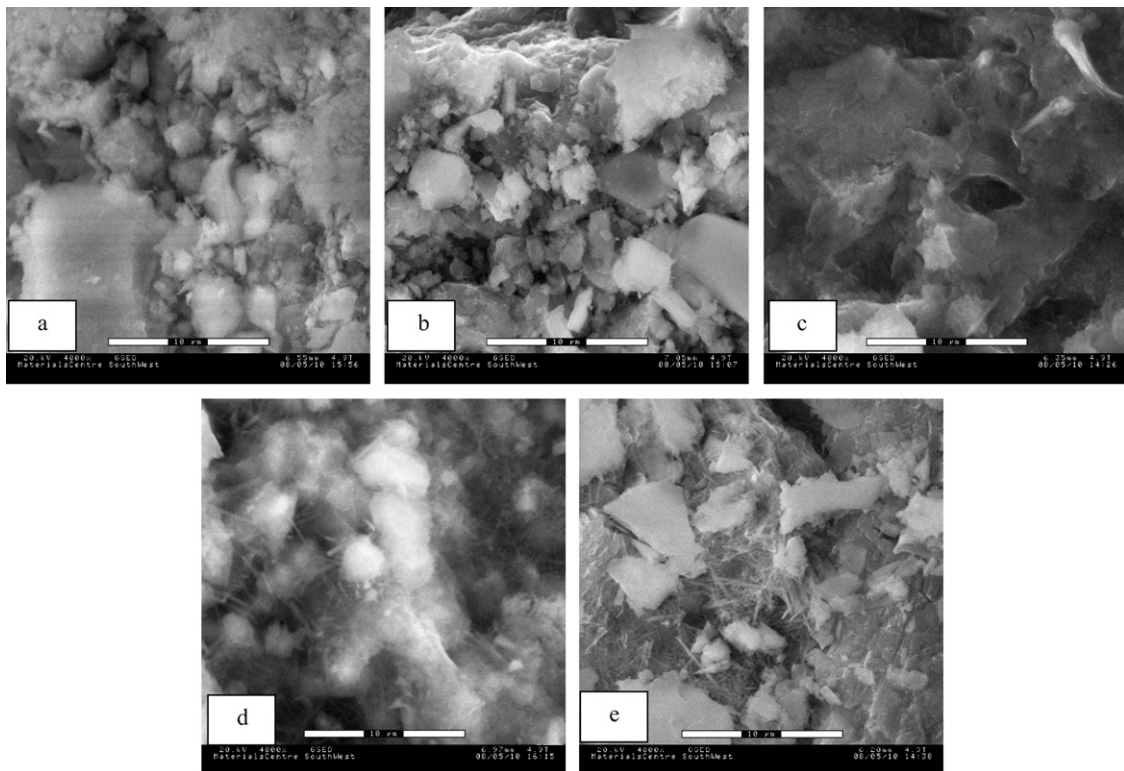

Fig. 12. Microstructure of cement–fly ash pastes after 30 days of hydration: (a) 0% fly ash, (b) 10% fly ash F1, (c) 10% fly ash F2, (d) 30% fly ash F1, and (e) 30% fly ash F2.

been identified which should be solved before the investigated biomass fly ashes can be used in applications requiring long term structural integrity. These are related to the fly ash carbon, chloride and sulphate concentration. An efficient burning of biomass in the furnace is the way to reduce the carbon content of the fly ashes while washing of the ashes could be effective in removing salts, especially chlorides. Further detailed investigations are in progress to address the application of these biomass fly ashes and to provide data for appropriate fly ashes. These include the tests of chemical strength/durability for obtaining sustainable biomass fly ash cement formulations.

4. Conclusions

The data presented in this paper has demonstrated a good potential for the utilisation of biomass fly ash in cement formulation. The main observations obtained are listed below.

(1) The biomass fly ashes are similar to class C fly ashes according to EN 450 on the basis of chemical composition.
(2) The calorimetric experiments indicated that fly ash F2 formulations containing lower amounts of fly ash hydrated faster, with a similar heat of hydration to pure cement paste.
(3) It can be concluded that up to 20% fly ash could be incorporated as cement replacement in cement-based mortars in order to maintain an acceptable mechanical strength. The strength is deteriorated rapidly on adding higher amounts of fly ashes.
(4) It is worth mentioning however that this study has clearly demonstrated that to maintain the highlighted benefits it is necessary to control the carbon, chloride and sulphate content of the employed biomass fly ashes.

Acknowledgement

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