



Quantitative evaluation of minerals in fly ashes of biomass, coal and biomass–coal mixture derived from circulating fluidised bed combustion technology

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ABSTRACT

The chemical and mineralogical composition of fly ash samples collected from laboratory scale circulating fluidised bed (CFB) combustion facility have been investigated. Three fly ashes were collected from the second cyclone in a 50 kW laboratory scale boiler, after the combustion of different solid fuels. Characterisation of the fly ash samples was conducted by means of X-ray fluorescence (XRF), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Quantitative analysis of the crystalline (mineral) and amorphous phases in each ash sample was carried out using the Rietveld-based Siroquant system, with an added spike of ZnO to evaluate the amorphous content. SiO₂ is the dominant oxide in the fly ashes, with CaO, Al₂O₃ and Fe₂O₃ also present in significant proportions. XRD results show that all three fly ashes contain quartz, anhydrite, hematite, illite and amorphous phases. The minerals calcite, feldspar, lime and periclase are present in ashes derived from Polish coal and/or woodchips. Ash from FBC combustion of a Greek lignite contains abundant illite, whereas illite is present only in minor proportions in the other ash samples.

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1. Introduction

In spite of the fact that combustion of solid fuels using conventional pulverised fuel (PF) technologies is and will probably continue to be an important part of the world's heat and power generation systems, combustion of solid fuels using more environmentally friendly technologies, such as circulating fluidised bed (CFB) combustion, continues to gain ground. This technology has another important advantage in comparison with PF technologies; it is able to burn low quality coal, lignite, and alternative fuels such as biomass (wood chips), as well as blends of such fuels.

A result of the continued development of CFB technologies is that the amount of ash and other combustion by-products from such sources is steadily increasing. Fly ash can be regarded either as an industrial waste material and an ecological nuisance, or as a valuable raw material. For the latter purpose, the ash properties need to be evaluated and controlled, so that a uniform and reproducible material can be supplied. This paper describes a comprehensive study of some CFB fly ash samples, with the aim of elucidating their chemical, physical, mineralogical and technical properties as an incentive to their utilization.

2. Materials and analytical methods

2.1. Materials

Three fly ashes, identified as FA1, FA2 and FA3, were produced from the combustion of different solid fuels in laboratory scale CFB boiler. The samples had been collected from the ash collection system in the boiler, without any flue gas desulphurisation or other treatment. The combustion experiments were carried out in the 50 kW lab scale boiler operated by VTT (the Technical Research Centre of Finland), following the flow chart as indicated in Fig. 1.

Combustion experiments were conducted using (a) coal from Katowice region, Poland, which hosts one of the main fossil fuel deposits of Central Europe, (b) xylite/lignite originating from the Florina Basin, which hosts the most significant fossil fuel deposits of Greece, (c) wood chips produced in Sweden from conifers as biomass, (d) blends of those fuels at different rates [1]. The results of proximate and ultimate analyses on a dry basis for the fuels used, determined following ASTM procedures, are presented in Table 1.

The Greek lignite is a low rank coal, with typical characteristics that include low fixed carbon, high moisture and (in the present study) high ash yield. The biomass has a higher calorific value and lower ash yield than the Greek lignites. However, the oxygen content of the biomass is higher than that of the lignite. This indicates

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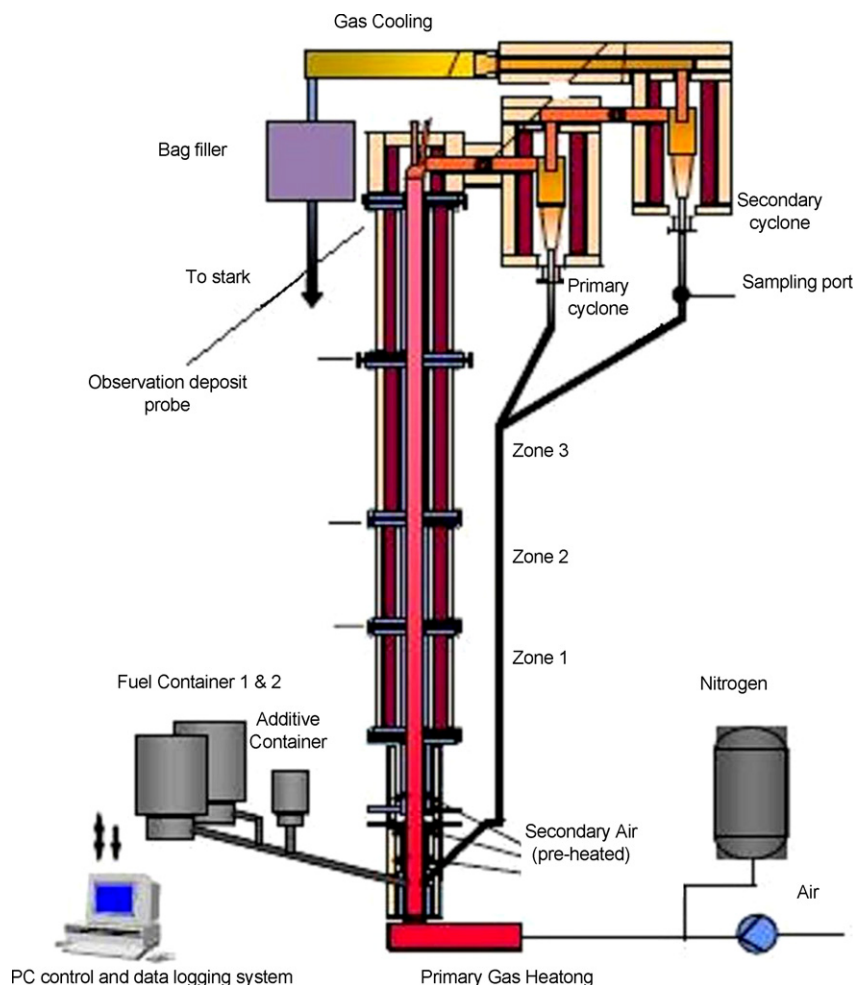


Fig. 1. Schematic diagram of the fluidised bed test facility.

that biomass material would have a higher thermal reactivity than the lignite [2].

During the experiments, fly ash samples were collected from the second cyclone in the test system. The combustion experiments were conducted at a temperature of 900 °C, without the use of limestone to absorb any sulphur oxides released by the combustion process. The samples and the fuels combusted in each case are indicated in Table 2.

Analysis of the fly ashes was carried out by means of XRF, XRD and SEM techniques. The present paper lays particular emphasis on

the use of the Rietveld-based Siroquant XRD system to evaluate the percentages of the crystalline mineral phases and the proportion of non-crystalline (amorphous or glassy) material in fly ash samples derived from combustion of lignite, coal and biomass using CFB technology.

2.2. Chemical analysis of ash samples

The major elements present in the ashes were determined using a Spectro X-Lab 2000 energy dispersive X-ray fluorescence (XRF) spectrometer, with the samples analysed in pressed powder form. The loss on ignition percentages were obtained by heating each sample to 850 °C, initially in nitrogen and then in an oxygen atmosphere, using a LECO TGA 501 thermogravimetric analyser [1]. Although the loss on ignition (LOI) is commonly used as a measure of the unburned carbon content of coal ashes, it may also represent losses in mass from some of the minerals in the ash, such as portlandite ($\text{Ca}(\text{OH})_2$), calcite (CaCO_3) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) [3].

Table 1
Average characteristics and energy contents of the feed fuels.

Parameter	Polish coal	Greek lignite	Wood chips
Proximate analysis (wt.% dry basis)			
Moisture	1.9	36.5	4.6
Volatiles	29.33	41.67	80.10
Ash	12.96	38.36	1.14
Fixed carbon	57.71	19.97	18.76
Ultimate analysis (wt.% dry basis)			
Carbon	68.42	32.29	48.77
Hydrogen	3.91	3.42	5.85
Nitrogen	1.32	1.33	0.45
Oxygen	12.69	17.96	43.79
Sulphur	0.7	1.64	0.02
Gross heating value d.b. (kJ/kg)	29,171	17,887	25,154
Net heating value d.b. (kJ/kg)	28,330	17,150	23,899

Table 2
Fuels used to produce fly ash samples.

Sample	Composition of fuels
FA1	100% Greek lignite
FA2	50% wood chips–50% Polish coal
FA3	100% wood chips

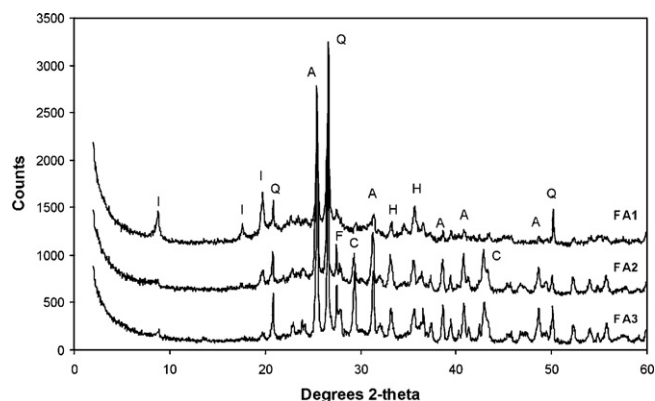


Fig. 2. X-ray diffractograms of fly ash samples, showing key peaks for principal mineral phases: A = anhydrite, C = calcite, F = feldspar, H = hematite, I = illite, Q = quartz.

2.3. X-ray diffraction (XRD) analysis

X-ray diffraction (XRD) has long been used as a definitive technique for identifying minerals and other crystalline phases in a wide range of materials [4], including coal ash [5–7]. It is especially useful where the individual particles are too small to be reliably identified by microscopic techniques.

The fly ash samples collected from the second cyclone were powdered by grinding in a pestle and mortar, and each powder was subjected to XRD analysis using a Phillips X'pert diffractometer system with Cu K α radiation. Scans were run from 2° to 60° 2 θ with increments of 0.04° and a counting time of 2 s per step. The resulting data (Fig. 2) were used to identify the mineral phases present. Duplicate samples of each fly ash were spiked with known proportions of crystalline ZnO, and diffractograms obtained using the same operating conditions.

2.4. Scanning electron microscopy

The morphology of the solid residues was observed using a JSM-6300 JEOL scanning electron microscope (SEM), operated with a typical accelerating voltage of 20 kV. The microscope was equipped with an Oxford Link ISIS energy dispersive X-ray spectrometer system. The XRF and SEM analyses were carried out in the laboratories of the Centre for Research and Technology Hellas (CERTH). The mineralogical analyses of the fly ash samples were carried out in the School of Biological, Earth and Environmental Sciences in the University of New South Wales.

3. Results and discussion

3.1. Chemical composition

The chemical analysis data (Table 3) show that the ash samples are rich in CaO [values ranging between 5 and 20%] and that the sum of Al₂O₃, SiO₂ and Fe₂O₃ ranges between 50 and 70%. Based on ASTM Standard C618 [8], fly ash is classified according to the content of its major elements (Si, Al, Fe and Ca). According to this Standard sample FA1 can be classified as a class F [SiO₂-rich] ash, whereas ashes FA2 and FA3 meet the requirements of class C [CaO-rich] ash material.

Al₂O₃ occurs in relatively high proportions in all samples (Table 3), which is also in accordance with information from literature review [9]. The proportions of SiO₂ and Al₂O₃ are higher in FA1 than in FA2 or FA3, whereas the percentage of CaO is lower in FA1 relative to the other ash samples. There is also slightly less Fe₂O₃ in FA2 and FA3, compared to FA1.

Table 3

Chemical composition (wt%) of the fly ash samples as determined by XRF analysis [1].

	FA1	FA2	FA3
SiO ₂	47.80	28.05	29.20
Fe ₂ O ₃	9.06	7.70	8.89
Al ₂ O ₃	24.12	15.11	14.63
TiO ₂	0.98	0.48	0.39
CaO	5.73	14.19	19.59
MgO	3.64	5.00	5.70
SO ₃	3.80	9.65	13.23
P ₂ O ₅	0.50	0.73	1.03
Na ₂ O	0.28	1.46	1.95
K ₂ O	3.13	2.23	2.96
LOI	1.19	16.24	2.64
Total	100.23	100.84	100.24

The fly ash from combustion of wood chips (FA3) is slightly richer in phosphorous than the fly ash derived from the Greek lignite (FA1) or the fly ash derived from wood chips and Polish coal (FA2). The phosphorous in FA2 and FA3 probably originated mainly from the biomass (wood chips) used [9]. Calcium is also an important component in wood, and, as might be expected, the CaO levels in the ashes from combustion of the wood chips (FA3) are higher than those from co-combustion of wood with coal (FA2) or from the Greek lignite material. It was also noticed that when the proportion of wood in the coal–wood mixture was increased, the concentration of alkali (Na) was also elevated.

3.2. Mineralogical characteristics of fly ash

Determination of the relative abundance of the different phases in ash and similar materials, described as mineralogical analysis, is an essential complement to the chemical analysis process. The use of XRD as a quantitative tool has been considerably enhanced in recent years following development of purpose-specific computer processing systems based on the principles of full-profile XRD analysis developed by Rietveld [10]. One of these is the SiroquantTM technique, developed in Australia by Taylor [11].

From the mineralogical viewpoint, fly ash can be regarded as essentially consisting of three types of components: crystalline minerals, unburnt carbon particles and non-crystalline aluminosilicate and other oxides glass. The samples were expected to contain significant proportions of amorphous material, and for this reason the diffractograms obtained from the spiked samples were processed and quantified using Siroquant [12]. The results are indicated in Table 4.

Based on Rietveld principles, the Siroquant method uses full profile fitting routines to generate a synthetic pattern that can be systematically adjusted by a user-friendly interface to best match the observed XRD profile of the sample under analysis. The scaling factors developed in this process are then used to evaluate the percentages of the different crystalline phases or minerals present [11]. Up to 50 different minerals can be incorporated in the analysis. The system also incorporates a routine that allows calculation of the proportion of amorphous material (glass) in the original sample, based on the weighed-in proportion of the spike component [12]. Comparison with other methods [13] shows that Siroquant provides results consistent with other indicators and by inference a reliable mineralogical analysis, even when amorphous material is present.

Table 4 indicates that all three samples contain quartz, anhydrite, hematite, illite and amorphous material. Samples FA2 and FA3 contain calcite, feldspar, lime and periclase. A trace of rutile may be present in sample FA1.

Table 4
Mineralogy of fly ash samples by X-ray diffraction and Siroquant.

ZnO Spiked XRD	FA1		FA2		FA3	
	Weight %	Error of fit	Weight %	Error of fit	Weight %	Error of fit
Quartz (SiO ₂)	12.3	0.3	13.6	0.2	13.9	0.2
Anhydrite (CaSO ₄)	8.1	0.3	19.6	0.3	18.4	0.3
Hematite (Fe ₂ O ₃)	2.1	0.2	10.0	0.3	5.2	0.1
Calcite (CaCO ₃)			2.0	0.2	5.2	0.2
Illite (K,H ₃ O)(Al,Mg,Fe) ₂ (Si,Al) ₄ O ₁₀ [(OH) ₂ ,H ₂ O]	29.3	0.6	5.9	0.5	4.4	0.3
Feldspar (CaAl ₂ SiO ₈)			4.0	0.5	12.6	0.4
Lime (CaO)			0.7	0.1	1.1	0.1
Periclase (MgO)			4.3	0.2	3.1	0.2
Rutile (TiO ₂)	0.1	0.2				
Amorphous	48.1	1.2	39.7	1.1	36.1	0.8

Minerals in coal ash may be divided into three categories: primary minerals, secondary minerals and ternary minerals. The primary minerals originate from the initial components of the combustion fuels. The secondary minerals originate from phases that were formed during combustion and finally the ternary minerals originate from material formed during hydration of the fly ash.

Quartz, which is present in all samples, is considered as a primary mineral. Due to its high fusion temperature, it is often regarded as essentially non-reactive in combustion processes, at least if it is present as relatively large monomineralic particles. It is also a hard mineral and it is often represented by angular (fragmented) to rounded grains [14]. Quartz is commonly also found as cell and pore infillings in the organic matter of coal, a mode of occurrence that clearly indicates an authigenic precipitation process [15].

Anhydrite is also present in all three ash samples, and is typically found as plate, needle or wedge-shaped crystals. It is usually formed by dehydration of bassanite (CaSO₄·1/2H₂O) or gypsum (CaSO₄·2H₂O), some of which may in turn be formed by calcite-pyrite reactions at temperatures higher than 300 °C. Alternatively, the anhydrite and its precursor minerals may be formed by reactions between Ca and S liberated from the organic matter, especially in low-rank coals [14,16], as well as between sulphuric acid (generated during sulphide oxidation) and Ca carbonates in the coal, or by pore-water crystallization [17].

The ash samples derived from the combustion of 50% wood chips–50% Polish coal and 100% wood chips contain twice as much anhydrite as the sample from the combustion of 100% Greek lignite. This is attributed to the lower concentrations of sulphur and calcium in the lignite sample. As might be expected, the proportion of sulphur (SO₃) in the ash tends to increase with increasing anhydrite content. Retention of SO₃ in the ash is probably due to the abundance in the fuel of calcium; calcium reacts with sulphur and the sulphur that combines with the calcium remains in the ash and does not escape as sulphur oxides with the flue gases. Anhydrite may also react with water to form gypsum or ettringite, the latter being an undesirable mineral in cement or concrete production.

All of the samples contain hematite. This is an iron oxide mineral that is rare in coals, but may be produced from oxidation of other iron minerals, such as pyrite or siderite, during combustion processes. The combination of high Fe and high S in the Polish bituminous coal (Table 1) suggests pyrite as the source of the relatively abundant hematite in FA2, in comparison with the Greek lignite and the wood chips. Hematite may also be formed from iron that is bound in some way with the organic matter [16,17], especially for the lignite and the wood ash materials. Hematite can be considered as a secondary mineral, since it can be formed the oxidation of pyrite or marcasite, decarbonation of siderite or ankerite.

Calcite and lime are present only in samples FA2 (combustion of 50% wood chips–50% Polish coal) and FA3 (100% wood

chips). Their abundance, along with that of anhydrite, is consistent with the high concentrations of CaO in FA2 and FA3. Lime may come from the decomposition of calcite or dolomite (which are common minerals in coal) or from Ca incorporated into the organic matter [17]. Calcite may be transformed to its polymorphs aragonite and vaterite with increasing temperature, and decomposes to form lime at around 900 °C. Calcium may also interact with aluminosilicate materials at the high temperatures associated with coal combustion to form anorthite and similar feldspar minerals.

Illite is present in all of the ash samples, and is especially abundant in the ash from the Greek lignite (FA1). It is a potassium aluminum silicate hydroxide clay mineral, with a chemical formula of (K,H₃O)(Al,Mg,Fe)₂(Si,Al)₄O₁₀[(OH)₂,H₂O]. The abundance of illite in the lignite ash is also consistent with the high concentration of SiO₂ and Al₂O₃ in FA1, relative to the other ash samples.

Rutile is the natural mineral form of titanium dioxide (TiO₂) in plutonic and metamorphic rocks. In ash it is a mineral of secondary origin. Sample FA1 seems to contain rutile in a very small, almost negligible concentration; it is not present in measurable quantities in the other ash samples.

The fly ash samples from the combustion of 50% wood chips–50% Polish coal and those coming from the combustion of 100% wood chips contain a feldspar mineral, processed by Siroquant as anorthite. Anorthite (CaAl₂SiO₈) is an end member of the plagioclase series; it is found in a number of coal ashes and slag deposits [18], where it appears to form at relatively high temperatures.

Anorthite by definition must contain no more than 10% sodium and no less than 90% calcium in the sodium/calcium position within the crystal structure. The XRD patterns of the members of the plagioclase series are all very similar, and the composition of the material in the samples of the present study need not necessarily be a pure anorthite component. The increased abundance of Na₂O in FA2 and FA3 may also suggest some involvement of the sodium-bearing end member, albite, in the actual feldspar present.

Another mineral which is present in FA2 and FA3 is periclase. This may be formed from the decomposition of dolomite, CaMg(CO₃)₂, through magnesite; however, in the case of the wood chips it may represent a residue of Mg incorporated into the organic matter. Periclase does not appear in samples which originate from 100% Greek lignite, which suggests that neither dolomite or organically-bound Mg are present in that material.

All three fly ash samples contain amorphous material, representing components without a definite crystalline structure. Most amorphous minerals are unstable and may tend to dissolve rather easily. The amorphous material in the present samples may include metakaolin, produced from decomposition of kaolinite in the feed coal is broken up at moderate temperature (around 450–500 °C). In Portland cement-based mortars or concretes, metakaolin and hydrated lime are combined to form a hydraulic binding agent.

3.3. Unburned carbon content

The loss on ignition (LOI), which is usually taken as a measure of the amount of the unburned carbon remaining in the fly ash, is one of the most significant chemical properties of the samples analysed. The maximum LOI determined in these experiments, shown in Table 3, was for FA2 (16.24%), derived from the combustion of Polish coal and wood chips. In general, low-carbon ashes are required because carbon may interfere with air entrainment by adsorbing entrainment additives, although the carbon content does not always have this effect [19].

In addition to unburned carbon, the LOI may also partly represent material released from different minerals in the ash when the material is subjected to the high temperatures associated with LOI determination [3]. The minor proportion of calcite in samples FA2 and (especially) FA3 may represent a source of some of the loss on ignition associated with those samples, but otherwise most of the LOI in the present study, especially the high LOI value for sample FA2, probably reflects the unburned carbon content.

3.4. Scanning electron microscopy (SEM)

The three ash samples were analysed by SEM EDX. This technique gives the location of elements in the region being scanned, allowing the distribution of each element to be evaluated in the fly ash samples.

Each sample was mounted into specimen holders, carbon coated and analysed from backscattered electron as well as secondary electron images. The chemical composition of the particulates and the homogenous groundmass was determined from the analysis of energy dispersive spectra (EDX) produced by X-rays generated from the particles by the electron beam.

Morphology, texture and chemistry of the samples were analysed. Examination under the scanning electron microscope showed that the fly ash samples are different in comparison with conventional fly ash. The morphology of conventional fly ashes, such as the presence of cenospheres and plerospheres, varies within the examined fly ashes. Moreover, most of the quartz crystals remain intact, and are present as angular particles due to the relatively low temperature in the circulating fluidised bed furnace. In addition many of

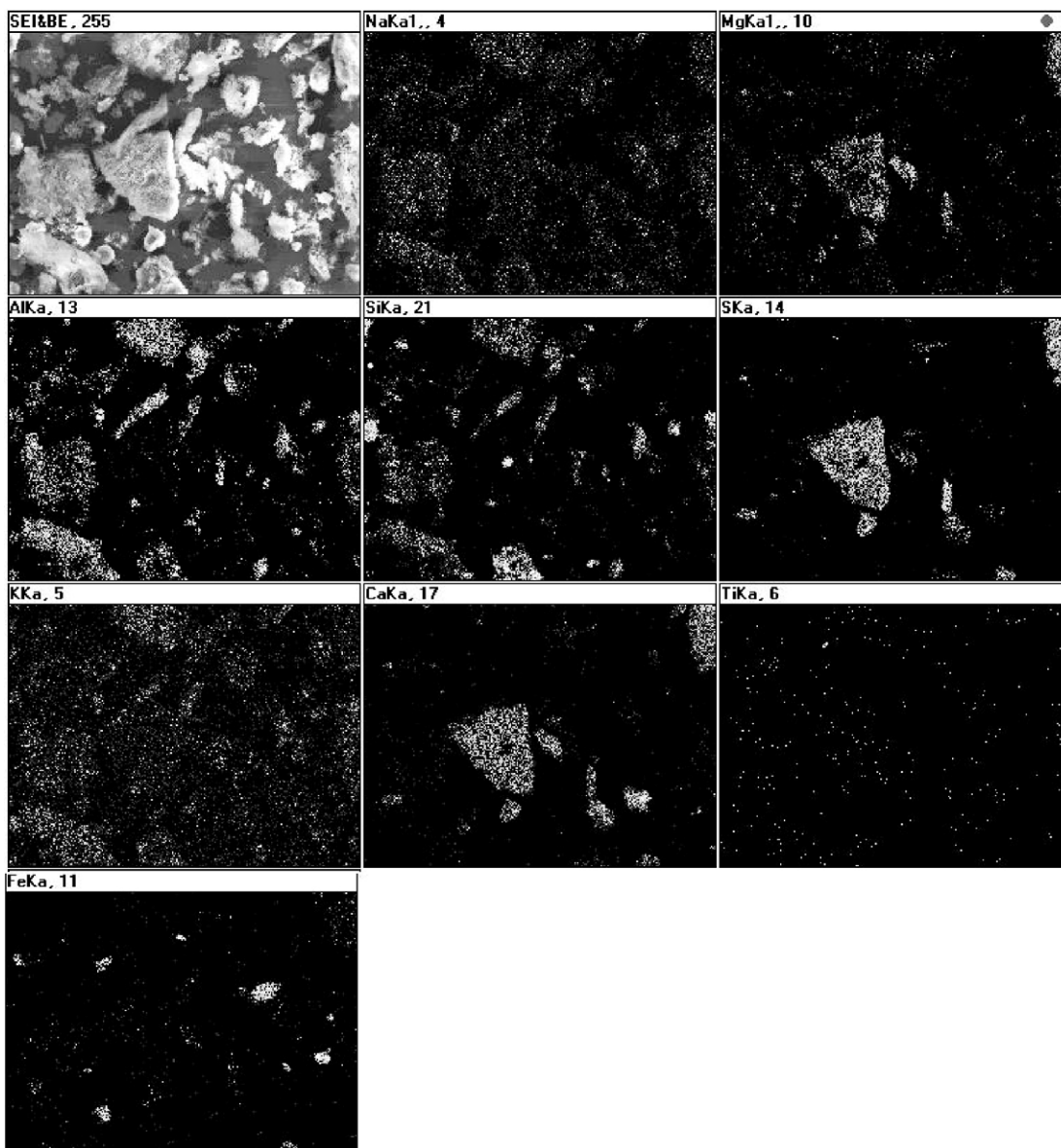


Fig. 3. Mapped region of fly ash sample FA2.

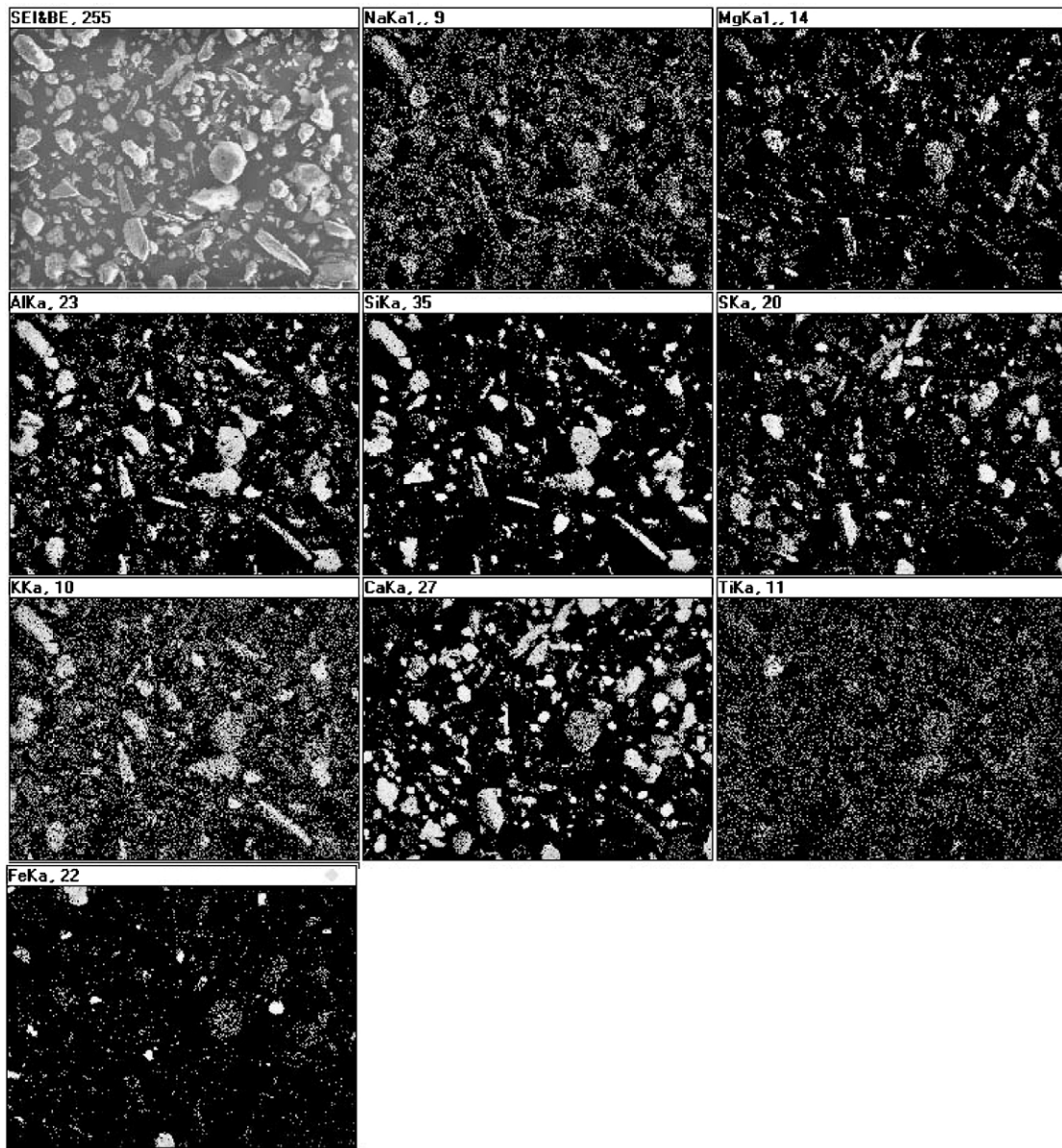


Fig. 4. Mapped region of fly ash sample FA3.

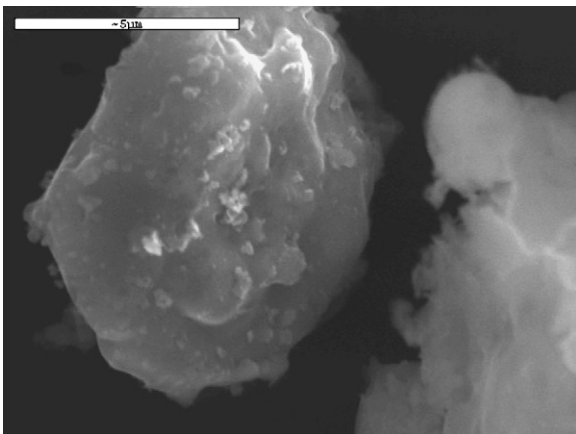


Fig. 5. Mineral phase in sample FA2, Si–84.74%, Al–6.5%.

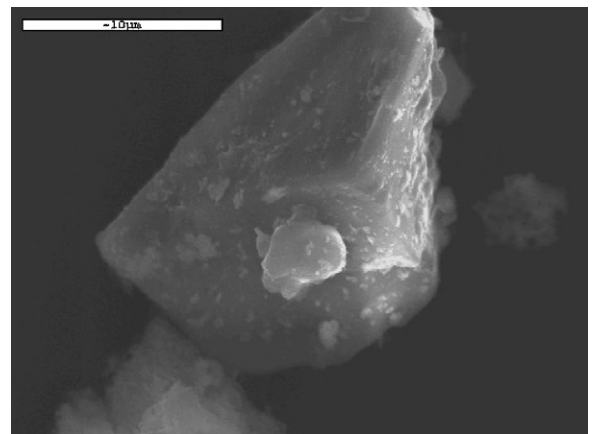


Fig. 6. Mineral phase in sample FA3, Si–84.64%, Al–3.02%, Ca–5.59%.

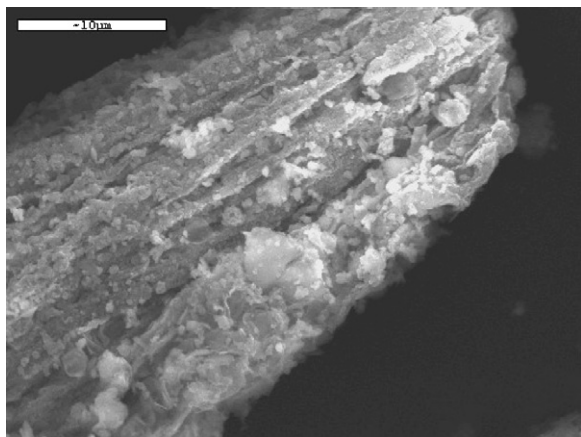


Fig. 7. Mineral phase in sample FA1, Ca–34.97%, S–29.12%, Si–9.02%, Al–7.33%.

the particles in the CFB fly ashes are present in sub-angular form, as they contain bi-mineral and multi-mineralogical phases, and quartz is mixed with calcium and aluminosilicate phases.

Figs. 3 and 4 each show a secondary electron image of a typical mapped region in each ash, followed by maps of nine elements (Na, Mg, Al, Si, S, K, Ca, Ti and Fe) chosen such that the fly ash particles could be identified in the SEM photos.

Comparing the above images, fly ash derived from the combustion of blends (biomass and coal) is poorer in elements such as K, Na and Ca than the fly ash derived from the biomass combus-

tion. Also, minerals that were identified by XRD were confirmed by the SEM study. Some representative figures with minerals or multi-mineralogical phases are presented with their chemical analyses. Quartz is shown in Figs. 5 and 6, and a particle of anhydrite in Fig. 7. More complex multi-mineral phases are presented in Fig. 8a–c.

3.5. Utilization of the fly ashes

ASTM Standard C618-99 [8], which is usually taken as the industry benchmark, has an upper limit of 6% loss on ignition for fly ash utilization as a pozzolan in Portland cement. Based on the ASTM specification, good results were obtained for the fly ash samples originating from Greek lignite and the wood chips (samples FA1, FA3). However, the LOI from co-combustion of Polish coal and woodchips exceeded this value (Table 3).

The same ASTM Standard also indicates that the SO_3 content of ash used in pozzolanic applications should be lower than 5%. Only sample FA1, derived from Greek lignite, meets this requirement for the fluidised-bed combustion process used in the present study. Sample FA1 also has less than the maximum value of 1.5% Na_2O for ash used in pozzolanic applications.

4. Conclusions

Compared to fly ash from combustion of wood chips, the co-combustion ashes studied had lower proportions of iron, calcium, potassium, magnesium and sulphur. The admixture of coal to the wood fuel added silicon, aluminium and iron to the ash. On the other

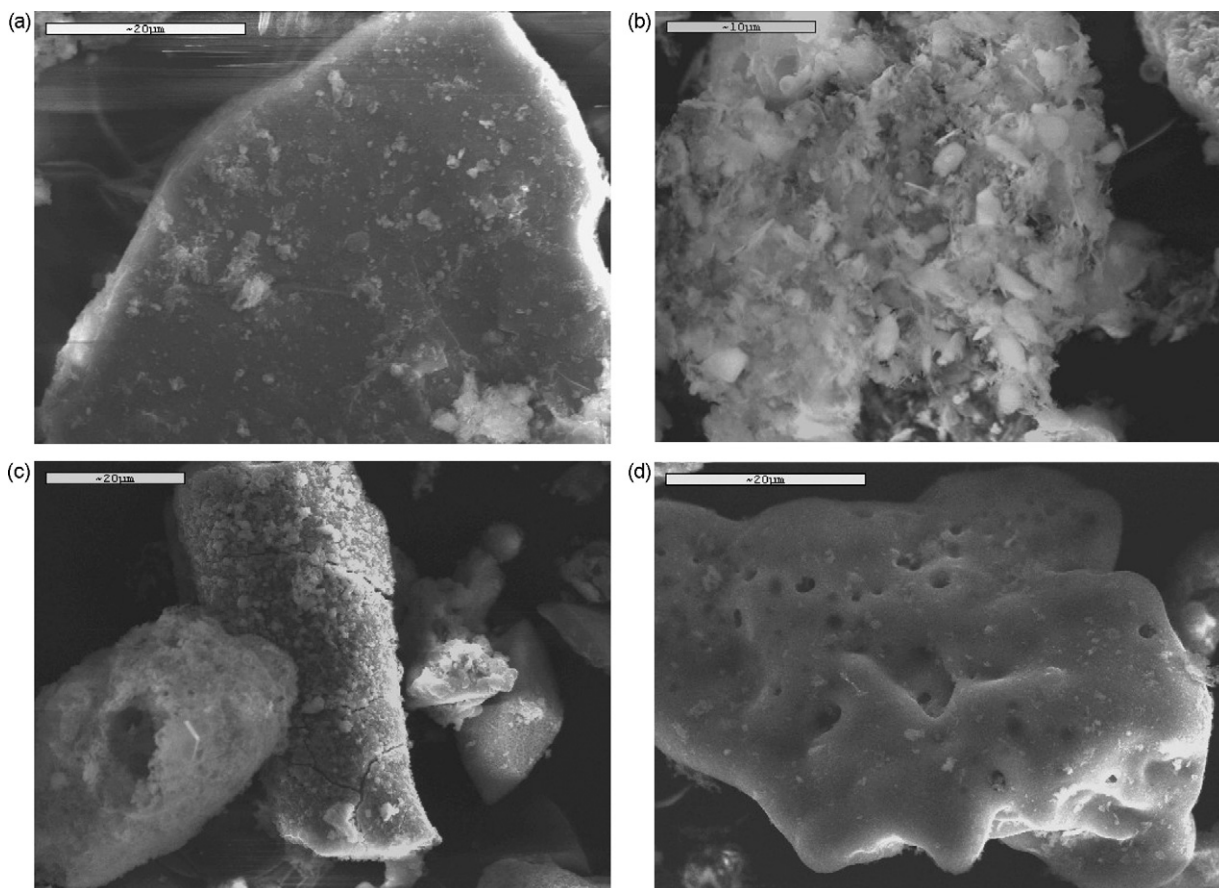


Fig. 8. a Multi-mineral phase in FA1, rich in Si, Al, K and Fe, b: Multi-mineral phase in FA2, rich in Ca, Si, S, Mg and Al. c: Multi-mineral phase in FA3 rich in Ca, S and Mg. d Multi-mineral phase in FA3 rich in Si, Al, K, and Na

hand fly ash derived from the combustion of pure Greek lignite and pure wood chips has a lower LOI level than that from Polish coal and wood chips. If the SO₃ content is taken additionally into account (SO₃ < 5%), then the most attractive fly ash to the cement industry is FA1 (Greek lignite), collected at the second cyclone.

Regarding the mineralogical composition of the fly ash samples, it appears that the composition of the samples depends both on the fuels used and the combustion temperature. The presence of minerals such as anhydrite is more likely when the fuels contain calcium; the fly ashes derived from the wood chips or wood chips co-fired with Polish coal have relatively high anhydrite percentages.

The addition of woodchips to the co-combustion process has significantly increased the proportions of Ca, S, Na and P in the ash, but at the same time has lowered the proportions of Si and Al. This in turn may have had the effect of increasing the combustion temperature in the boiler and of lowering the reaction temperature for some minerals, such as that required for the formation of anorthite.

Fly ash from co-combustion of wood with other fuels, such as Greek lignite or Polish bituminous coal, may have chemical characteristics depending on the furnace type and the combustion process, as well as the effectiveness of the cleaning system for the gases emitted. This is mainly because the combustion furnace type and the combustion process are closely related to the degree of coal combustion, the combustion temperature and combustion sufficiency.

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