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Characterisation of the glass fraction of a selection of European coal fly ashes

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Abstract: Fly ash largely consists of the inorganic content of coal that remains after combustion. The crystalline phases present in fly ash may form upon cooling of a molten aluminosilicate glass. This view is supported by the spherical shape of many fly ash particles, inferring that they have gone through a viscous fluid state. The amorphous content in fly ash is believed to dominate reactivity behaviour, under both alkaline and acid conditions, because glasses have a higher potential energy than the equivalent crystal structure and the variation of bond angles and distances in a glass makes the bond breakage easier. It is the degradation behaviour under alkaline conditions, and the subsequent release of silica from the glass phase, that is important in the use of fly ash for conversion to zeolites and for pozzolanic applications in cement. This research comprehensively studies the composition, quantity and stability of the glass phase in a series of nine fly ashes sourced from Spanish and Italian power plants. The quantitative elemental composition of the glass phase in each fly ash was determined. Samples of the ashes then underwent a series of tests to determine the internal structure of the ash particles. Heat treatment of most of the ashes results in mullite crystallising from the glass phase; this is the crystalline phase that is predicated to form by both the relevant phase diagrams and also by NMR spectroscopy. In the ashes, mullite is present as a spherical shell, tracing the outline of the particle but in some specific cases the mullite skeleton is made up of coarse crystals reach also the internal parts of the particles. The morphology and density of the mullite crystals in these shells varies greatly. This work has supported the view that some crystalline phases present in fly ashes, such as mullite, form upon cooling of the amorphous glass melt as opposed to direct conversion from existing mineral phases in the coal during the combustion process.

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Keywords: fly ash; mullite; thermal analysis; X-ray diffraction; solid-state NMR

INTRODUCTION

Fly ashes consist largely of the inorganic content of coal left behind after the combustion process. They have a complex microstructure, with a mixture of amorphous (usually predominant) and crystalline phases. Table 1 summarises the principal phases found in various coals and the phases formed after combustion. The crystalline phases are widely regarded as forming by direct solid-state reaction from the mineral phases present in the coal.¹ The types of crystal phase, the amount present and their distribution therefore directly reflect the mineral content of the original coal and the combustion technology. This is the accepted view.¹ An alternative view is that some crystalline phases present in fly ashes may form, not directly by solid-state reaction, but upon cooling by crystallisation of a largely amorphous glass melt. In this case, equilibrium phase diagrams could be employed to make predictions as to what crystalline phases could form on cooling. The principal phases present in fly ash formed by combustion of most coals are mullite,

quartz, magnetite/haematite and lime. These phases are the ones predicted from the CaO–SiO₂–Al₂O₃ and Fe₂O₃–SiO₂–Al₂O₃ phase diagrams upon cooling the ash from the molten state. However, the ternary phase diagrams are based on homogeneous dissolution of elements in the fly ash and this does not occur in practice. Furthermore, the ternary phase diagram is only applicable under equilibrium conditions and even then will only approximate crudely to the multi-component fly ash compositions. This means that detailed analysis on the basis of the phase diagram is not possible.

Evidence for the view that certain mineral phases, such as mullite, form by crystallisation of an amorphous melt is supported by the spherical shape of many fly ash particles,² which strongly suggests that the particles have gone through a viscous fluid state upon cooling, so the particles become spherical in order to minimise surface area and therefore surface energy per unit volume, at temperatures where the viscosity is low enough to allow this to happen. It is

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Table 1. The principal phases found in coals and the phases formed after combustion

Common coal minerals	Chemical formula	Phases formed after combustion	Chemical formula
Quartz	SiO ₂	Quartz	SiO ₂
Kaolinite	Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O	Mullite	3Al ₂ O ₃ ·2SiO ₂ ·2O 13
Illites	K ₂ O·3Al ₂ O ₃ ·6SiO ₂ ·2H ₂ O	Mullite	3Al ₂ O ₃ ·2SiO ₂ ·2O 13Al ₆ Si ₂ O ₁₃
Pyrite	FeS ₂	Haematite, Magnetite, Iron Sulphide	Fe ₂ O ₃ , Fe ₂ O ₃ ·FeO, FeS
Calcite	CaCO ₃	Lime, Anhydrite	CaO, CaSO ₄
Siderite	FeCO ₃	Haematite, Magnetite	Fe ₂ O ₃ , Fe ₂ O ₃ ·FeO

this residual glass phase that will dominate pozzolanic behaviour as well as the degradation behaviour under both alkaline and acid conditions. Glasses, described as 'inorganic products of fusion which have been cooled to a rigid condition without crystallising'³ have a higher potential energy than the equivalent crystal structure and the variation of bond angles and distances in a glass makes the bond breakage easier, making them more reactive than the equivalent crystalline phases.

It is only in the last 15 years that attempts have been made to understand the chemical nature of the glass phase.^{4–7} Whilst the mechanisms of fly ash reactivity are not fully understood, factors including glass content, glass composition and the physical state of the glass will contribute heavily to its chemical reactivity. It should be borne in mind, however, that absolute understanding of the glass in a given fly ash is currently hindered by the perceived inter- and intra-particle heterogeneity of these materials.⁸

It is the objective of this paper to study the extent of homogeneity in the glass phase of a selection of fly ashes produced from burning coals sourced from different locations. This study will involve characterisation of the fly ashes by a series of different techniques:

1. Mineralogy and morphology analysis by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray spectroscopy (EDX), respectively.
2. Determining the tetrahedral or octahedral occurrence of aluminium by solid-state Nuclear Magnetic Resonance (NMR).
3. The study of mullite skeletons by HF dissolution.

If certain crystalline phases form upon cooling of a largely amorphous glass melt then the principal crystalline phases present in fly ash would be mullite, quartz, magnetite/haematite and lime (as predicted by the CaO–SiO₂–Al₂O₃ and Fe₂O₃–SiO₂–Al₂O₃ phase diagrams). This work will use solid-state NMR to determine whether the remaining glass would be likely to convert to mullite by heat treatment; should this be the case it will reinforce the hypothesis that mineral phases form from the glass melt.

The intractable nature of fly ashes means that there are only a few techniques with which it is possible to analyse their complex structure; solid-state NMR

spectroscopy is one of these. As far as is known, there have only been two reported studies of fly ash being examined by NMR,^{9,10} though there has been another report using NMR to examine zeolites synthesised from fly ash material.¹¹ The first report was on ²⁹Si MAS/NMR on a fly ash obtained from a French power station fed mainly by a bituminous coal-type. This spectrum was taken on material extracted from the fly ash using an extraction/demineralisation procedure with hydrofluoric acid. From the spectra, it can be seen that there were four overlapping peaks and these are assigned and compared with the mullite spectrum.

It is hypothesised that there is a physical barrier that inhibits the release of the glassy phase silica to a greater extent in some of the fly ashes than others, thereby limiting the degradability of some ashes for pozzolanic applications. The morphology, density and orientation of the mullite crystals in the skeleton may provide this barrier, ie the greater the packing of the acicular mullite crystals in the skeletons observed in these fly ashes, the more difficult it would be to degrade and release the glass component. The outer shell of the fly ash particles will be analysed to determine whether a physical barrier exists, such as an outer layer of mullite, which could inhibit degradation of the glassy phase.

It is the objective of this work to determine whether certain crystalline phases present in fly ashes may form, not directly by solid-state reaction, but upon cooling by crystallisation of a largely amorphous glass melt. This will be achieved by using a series of different characterisation techniques, some of which are rarely used for fly ashes (such as thermal analysis). This will allow the identification of certain characteristics of the glass phase of the fly ashes, including glass transition temperatures (T_g), which could be related to the reactivity of the ashes, and thermal events that are most likely due to the crystallisation of a phase from the glassy material. Silicon can be extracted from the glass phase of fly ashes in order to synthesise zeolites. The quality of the zeolite synthesised is dependent upon the purity of the silicon extracted. Unfortunately, when extracting silicon from the glass phase, a certain amount of alumina is also extracted. A technique is needed where the alumina can be locked away so more pure silicon can be extracted.

MATERIALS AND METHODS

Nine fly ashes were chosen from pulverised coal-bed power plants in Spain and Italy, as shown in Table 2. The fly ashes were sampled at the electrostatic precipitators, with the exception of As Pontes fly ash which is made up of a mixture of fly ash and molten slag. The ashes have a broad range of chemical and mineralogical compositions.¹² The fly ashes were fully characterised by conventional techniques. Details of the characterisation procedures used are available elsewhere.¹³

Nuclear magnetic resonance

A series of fly ash samples was examined by solid-state NMR spectroscopy (Bruker DSX-200 NMR spectrometer, Bruker, Coventry, UK). The frequency was 52.1 MHz for ²⁷Al, the number of scans was 20 000–100 000, the recycle delay was 2s, and the 90° pulse was 4 μs. The samples were recorded without magic angle spinning using a solid echo pulse sequence (90°_x–τ–90°_y–acq) as spinning made no improvement on the line width of the spectra. All samples of fly ash were investigated as received. No demineralisation process (eg HF treatment) was carried out on the samples. All samples were externally referenced to Al(H₂O)₆³⁺.

Acid dissolution

In order to determine the extent of the barrier present in each fly ash, samples of all the ashes were subjected to a process that would dissolve the glass phase. An etchant (15% HF + 25% HNO₃) was added to the fly ash and the solution was then agitated on a weekly basis for 1 month. The etchant was removed by decanting and the remaining material was washed and dried.

To ensure that only the mullite phase remained after etching, samples of the etched ashes were analysed using X-ray powder diffraction. A Phillips X'pert X-ray powder diffractometer (MPD) was utilised with Cu-Kα radiation and a scan time of 50 min over an angular range of 10 to 70° 2θ. Scanning electron microscopy (JEOL JSM 840) and energy dispersive X-ray analysis was used to inspect the etched materials. Samples were mounted on a carbon-backed adhesive and sputter coated with gold prior to analysis in secondary electron imaging mode.

Table 2. Fly ashes selected and sampled in this study

Power station	Power (MW)	Power company	Location
Los Barrios	550	ENDESA	S Spain
As Pontes	1400	ENDESA	NW Spain
Monfalcone	336	ENEL	Italy
Puertollano	220	ENDESA/VIESGO	Central Spain
Meirama	550	Union FENOSA	N Spain
Soto de Ribera	672	IBERDROLA	N Spain
Espiel	938	ENDESA/VIESGO	S Spain
La Robla	625	Unión FENOSA	N Spain
Narcea	569	Unión FENOSA	N Spain

Heat treatment of fly ashes

Samples of each of the fly ashes had previously been analysed by thermal techniques to determine their relative reactivity.¹³ High temperature Differential Scanning Calorimetry (DSC) experiments were conducted in a Stanton and Redcroft DSC 1500 (Rheometric Scientific, Epsom, UK). Samples weighing 50 mg were analysed in matched pairs of platinum–rhodium (90–10) crucibles. Identical weights of calcined analar grade Al₂O₃ reference and fly ash samples were investigated in a flowing dry nitrogen atmosphere.

To determine whether mullite is crystallising out of the glass phase when heated, samples of each fly ash were heat treated to the temperature of the thermal event and held at the temperature for 1 h. This was conducted in a dental porcelain furnace (Dekema Austromat 3001) and heating rates of 40 °C min⁻¹ were used throughout. To determine whether mullite had been formed as a result of these heat treatments, quantitative XRD was performed upon both the heat-treated and the as-supplied samples.

Quantitative X-ray diffraction

Quantitative X-Ray Diffraction (QXRD) was performed using the method described by Klug and Alexander.¹⁴ In this method, a reference (10 wt% of calcium fluoride) is mixed with various proportions of reference grade mullite (Zed Mark Refractories, Earlsheaton, UK) along with powdered soda-lime silica glass as a bulking agent. The area of a characteristic reflection of the mullite XRD spectrum (15–17.5° 2θ) and the internal standard calcium fluoride (46–48° 2θ) diffraction patterns were then measured. The integrated areas of these peaks, as a function of the weight percent mullite present, produced a calibration plot. Using this plot, the mullite contents of both non-heat-treated and heat-treated fly ashes could be determined. Thus, the crystallisation hold temperature and the amount of mullite obtained at each temperature could be quantified.

RESULTS

The chemical compositions of the fly ashes are supplied in Table 3. Details of the characterisation procedures used are available elsewhere.¹³

The quantitative elemental composition of the glass phase in each fly ash was determined by subtracting the contribution of the mineral phases (as determined by qualitative XRD) from the overall elemental composition of the fly ashes. The resultant elemental compositions of the glass phases are supplied, in mole fractions, in Table 4.

Nuclear magnetic resonance

The spectra from ²⁷Al NMR each show a broad signal because of the presence of considerable amounts of paramagnetic iron in each sample. In fact, there is a direct correlation between line widths in each sample and the iron content recorded by microanalysis

Table 3. Fly ash composition in wt%

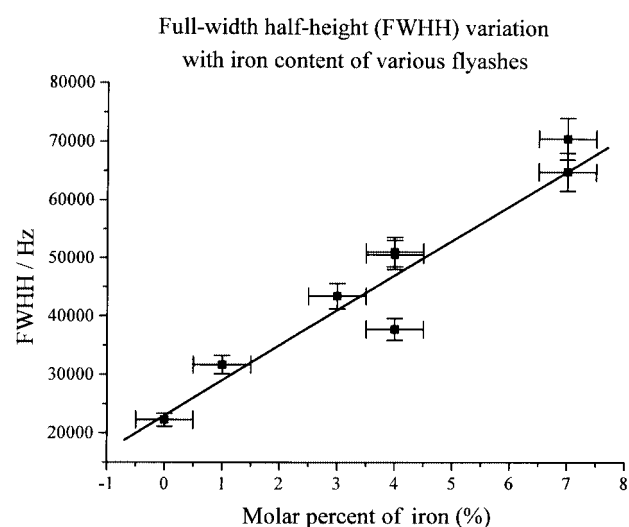
Fly Ash	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅
Teruel	48.0	23.9	16.0	5.4	1.0	0.2	1.4	0.2
La Robla	41.1	23.2	14.3	8.9	1.8	0.3	2.6	0.8
Compostilla	49.2	25.5	7.5	2.8	2.0	0.8	3.9	0.4
Meirama	50.2	17.6	10.4	11.8	2.0	0.4	0.4	0.4
As Pontes	41.4	30.1	12.6	5.6	1.6	0.6	1.9	0.2
Puertollano	58.4	27.4	7.3	0.8	1.0	0.3	2.4	0.1
Espiel	51.7	28.5	5.9	2.0	1.5	0.5	4.0	0.4
Soto de Ribera	48.6	30.6	7.2	3.0	1.6	0.6	3.9	0.1
Barrios	42.3	35.6	2.6	8.4	2.1	0.3	0.6	1.7
Monfalcone	49.0	33.4	6.4	2.4	0.8	0.4	0.7	0.3

Table 4. Amended glass compositions in weight fraction after correction for mineralogical contribution

Fly Ash	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅
Teruel	0.68	0.12	0.07	0.10	0.02	<0.01	<0.01	<0.01
La Robla	0.61	0.17	0.06	0.10	0.04	<0.01	0.02	<0.01
Compostilla	0.65	0.20	0.03	0.04	0.04	<0.01	0.03	<0.001
Meirama	0.63	0.04	0.06	0.22	0.04	<0.01	<0.01	<0.01
As Pontes	0.62	0.12	0.07	0.14	0.03	<0.01	0.01	<0.01
Puertollano	0.78	0.14	0.03	<0.01	0.02	<0.01	0.02	<0.01
Espiel	0.68	0.20	0.02	0.03	0.03	<0.01	0.03	<0.01
Soto de Ribera	0.71	0.19	0.04	<0.01	0.03	<0.01	0.03	<0.01
Los Barrios	0.64	0.09	0.02	0.17	0.06	<0.01	<0.01	0.01
Monfalcone	0.65	0.14	0.15	0.03	0.01	<0.01	<0.01	<0.01

(Fig 1). This shows how the line widths are broadened by paramagnetic relaxation and are related to the level of iron present.

However, at lower levels of iron content it is possible, with a good enough signal-to-noise ratio, to see some features on these spectra. These samples, which have substantially narrower peaks, show either a distinct splitting or more often, a flattened top to the ²⁷Al signal present. These are indicative of chemically different sites present in the lattice, and the splitting or flattening may be indicative of overlapping broad Gaussian/Lorentzian line shapes of these sites.

**Figure 1.** Comparison of Full-Width Half Height (FWHH) of ²⁷Al NMR peaks against iron content.

Despite the very large chemical shift distribution (+400 to -400 ppm), it is possible, from previous chemical shift studies, to deconvolute the peaks into two Gaussians, the left hand and right hand peaks representing tetrahedral (AlO₄) and octahedral sites (AlO₆) respectively. This would imply that there is approximately an equal number of both tetrahedral and octahedral sites present in these materials. Though it is difficult to discern accurately (especially in the high iron content samples), there appears to be a consistent ratio of the octahedral to tetrahedral sites throughout the range of samples. This implies that any aluminium-silicate material present in the coal (eg kaolite or α -quartz) gets converted into mullite-type mineral matter.

Acid dissolution

Examples of the type of material presented to the diffractometer are shown in Fig 2. Two samples, Monfalcone and Los Barrios, are known to have high mullite contents in their raw form. X-ray powder diffraction results for the residues arising from glass dissolution of these two ashes are given in Figs 3 and 4.

The match for mullite with the JCPDS standard (card #15-0776) is excellent and there are few extraneous peaks. There is also little evidence of the amorphous halo associated with the presence of residual glass. Thus, XRD suggests that mullite is the only crystal phase present in significant amounts.

To determine how the physical state of the ashes changes by dissolution in HF/HNO₃, samples of both the raw and etched materials were analysed using

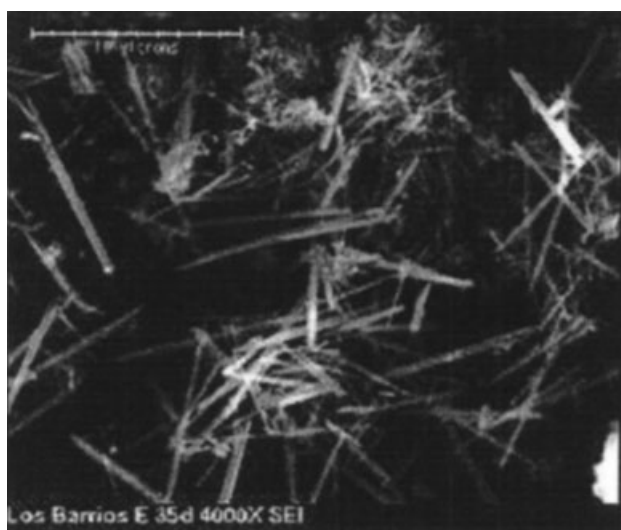


Figure 2. Needles of mullite from etched Los Barrios ($\times 4000$).

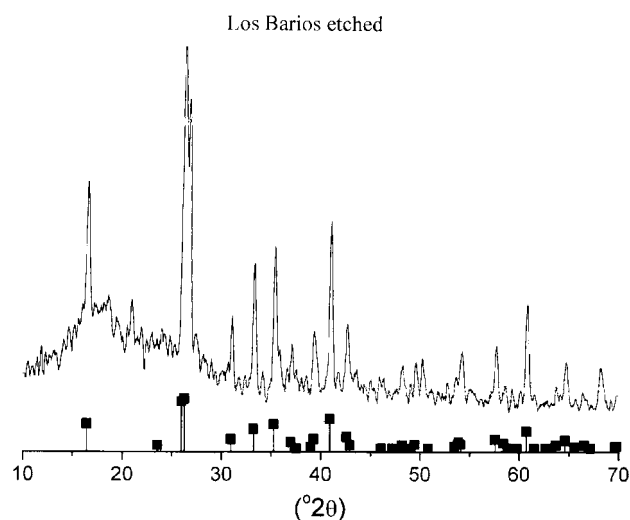


Figure 3. X-ray diffraction pattern for acid-etched Los Barrios fly ash which includes the JCPDS standard (card #15-0776) used to identify the presence of mullite.

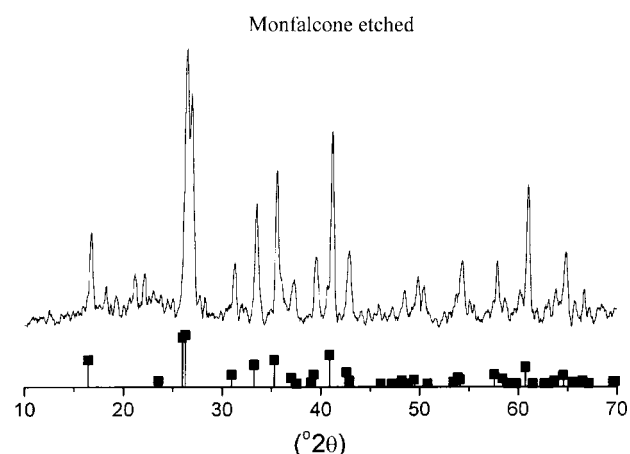


Figure 4. Powder X-ray diffraction pattern for acid-etched Monfalcone fly ash which includes the JCPDS standard (card #15-0776) used to identify the presence of mullite.

SEM. Examples using Monfalcone fly ash are supplied in Figs 5 and 6. In the etched samples, the mullite

appears as a spherical shell, tracing the outline of the original particle. The etched Monfalcone particle (Fig 6) shows an open structure that appears hollow. It is likely that such a structure would offer only minimal physical resistance to the release of silica.

The micrographs (Figs 7 and 8) show the effect of the HF dissolution on the Los Barrios ash. The etching has left only the mullite needles (Fig 8) but they are arranged in a more compact manner than in the Monfalcone particle (Fig 6). There also appears to be another mullite-based spherical structure within the exoskeleton. This more complex structure may account for the lower levels of silica release/reactivity.

Energy Dispersive X-ray spectroscopy (EDX), performed upon the surface of this etched Los Barrios particle (Fig 9), confirms that the exoskeleton contains mainly aluminium and silicon and, as such, is likely to be pure mullite.

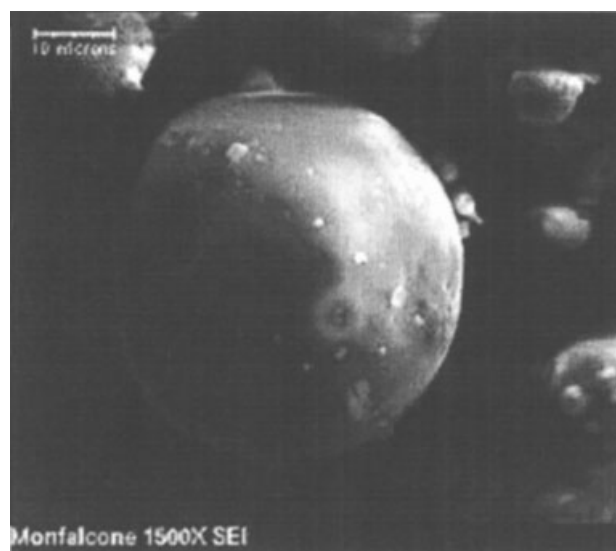


Figure 5. Raw Monfalcone particle ($\times 1500$).

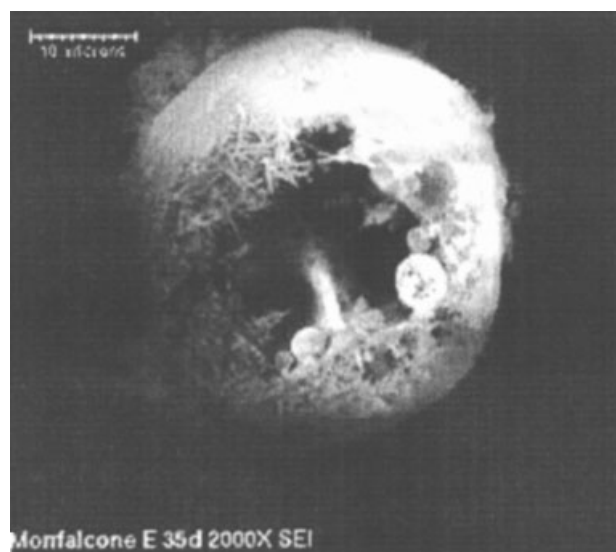


Figure 6. Etched Monfalcone particle ($\times 2000$).

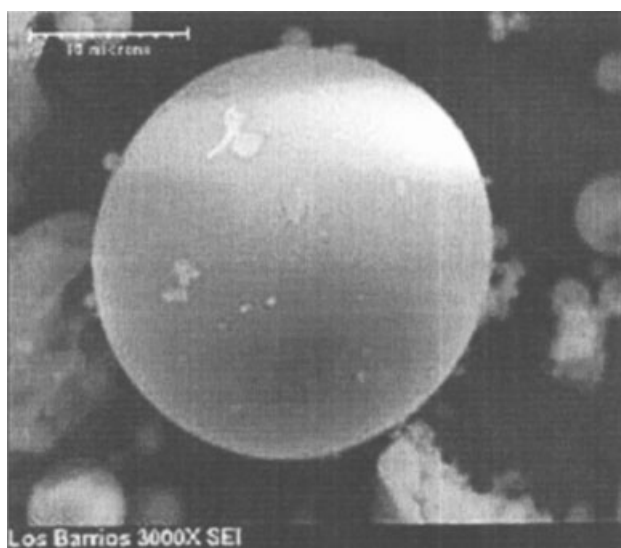


Figure 7. Raw Los Barrios particle ($\times 3000$).

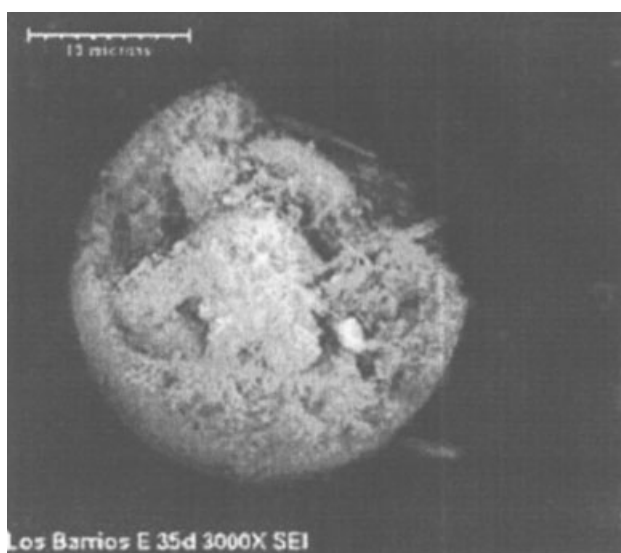


Figure 8. Etched Los Barrios particle ($\times 3000$).

Heat treatment of fly ashes

The thermal characteristics obtained by DSC are shown in Table 5.¹³ Several of the fly ashes

Table 5. Thermal characteristics obtained from DSC trace analysis of the fly ashes¹³

Fly ash	T_g ($^{\circ}\text{C}$)	Exotherm ($^{\circ}\text{C}$)	Endotherm ($^{\circ}\text{C}$)
Los Barrios	—	433, 749, 1000	713, 897, 1115
As Pontes	—	576, 734	711, 911
Monfalcone	486	653, 815	965
Puertollano	—	—	1050
Meirama	686	993	150, 1160
Soto de Ribera	—	—	1197
Espiel	806	1030	—
La Robla	410	1106	—
Narcea	—	1143	—

(Los Barrios, Meirama, Espiel, La Robla, Narcea) showed an exothermic peak at approximately 1000°C ($\pm 100^{\circ}\text{C}$).¹³ This peak corresponds to the crystallisation of mullite, as identified by XRD results (Figs 3 and 4).

The mullite content is calculated for both non heat-treated and heat-treated fly ash samples. The analysis was performed twice and the mullite contents were found to be within acceptable tolerances (5%). The results were averaged and the mean value is represented in Table 6.

The application of different heat treatments results in a significant amount of mullite being crystallised; the amount increasing significantly with heat treatment temperature and time, the exception being the La Robla ash. However, the reduction in mullite for this material is very low and as such is likely to be within the boundaries of experimental error.

The results could assist in the refinement of procedures for silicon extraction from fly ashes. Furthermore, the results of this investigation could be used to select certain fly ashes, which may be exploitable, in terms of cheap and easily producible low-grade mullite ceramic components.

CONCLUSIONS

This work has employed novel characterisation techniques in order to further the understanding of ash formation by coal combustion.

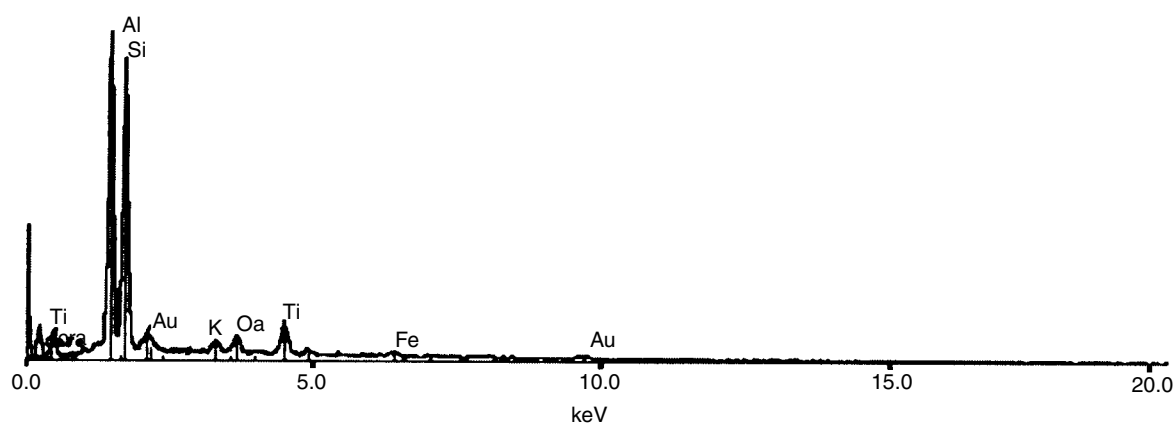


Figure 9. EDX spectrum of surface of spherical particle in Los Barrios fly ash.

Table 6. QXRD results of various fly ash materials heat treated to temperatures mirroring thermal events

Sample	Heat treatment (HT °C)	Area of mullite peak	Area of CaF ₂ peak	Ratio of peak areas	wt% mullite	Difference
Los Barrios	Non-heat-treated	7	17	0.40	37	—
	HT = 1000 °C	10	14	0.73	41	4
Meirama	Non-heat-treated	2	26	0.09	9	—
	HT = 993 °C	5	12	0.44	41	32
Espiel	Non-heat-treated	9	99	0.09	9	—
	HT = 1030 °C	6	30	0.21	19	10
La Robla	Non-heat-treated	9	73	0.13	12	—
	HT = 1106 °C	2	22	0.11	10	-2
Narcea	Non-heat-treated	2	42	0.06	5	—
	HT = 1143 °C	3	10	0.34	32	26

Analysis of the etched samples has implied that the release of silica from fly ashes through the alkaline attack (both in Si extraction and in pozzolanic reactions) is not only dependent upon the silica available in the glass phase, but is also related to the ease with which the silica can escape its physical constraints.

This work has also shown that certain characterisation techniques which have rarely been used for fly ash analysis, can offer significant information about how the glass phase forms. For example solid-state ²⁷Al NMR has been shown to be a suitable technique for determining the propensity of the glass phase of a fly ash to crystallise to mullite but it is only really suitable for ashes with low iron contents. Thermal analysis has proven to be a suitable technique for determining the onset of crystallisation of mullite from the glass phase of ashes and could be used to ascertain a suitable temperature for heat treatments that would allow for the extraction of silica without alumina, hence, purer silicon extraction yields may be attained.

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