

25 Mar 2002

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Recommended Citation

K. T. Stanton et al., "Thermal Analysis of Fly Ashes Sourced from European Non-Blended Coals," *Journal of Chemical Technology and Biotechnology*, vol. 77, no. 3, pp. 246 - 250, Wiley; Society of Chemical Industry, Mar 2002.

The definitive version is available at <https://doi.org/10.1002/jctb.582>

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Thermal analysis of fly ashes sourced from European non-blended coals[†]

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Abstract: Fly ashes exist as a mixture of major amorphous phases and minor crystalline phases. For commercial applications, such as in concretes and for the production of zeolites, it would be desirable to be able to predict the reactivity of fly ashes. The amorphous phase dominates degradation behaviour, because glasses have a higher potential energy than the equivalent crystal structure and the variation of bond angles and distances in a glass make the bond breakage easier. Despite the large quantities of fly ash produced annually by coal-burning power plants, there have been very few studies investigating the microstructure and composition of the amorphous component. In particular, there has been little research undertaken in measuring the glass transition temperature (T_g), which can be directly correlated to the chemical reactivity of the glass phase. Thirteen European fly ashes were used for the present study. Differential scanning calorimetry (DSC) was employed to determine the presence of transition temperatures and any other thermal events (exotherms or endotherms) in the glassy phase of the fly ashes. Several different but distinct behaviours were evident in the DSC traces with T_g values visible for six of the ashes. The results suggest that thermal analysis has potential as a technique for fly ash characterisation.

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Keywords: fly ash; differential scanning calorimetry (DSC); glass transition temperature (T_g)

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 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 the 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 the 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 should form on cooling. The principal crystalline phases present in fly ash formed by combustion of bituminous coals are mullite, quartz, magnetite/haematite and lime, whilst the crystalline phases in high-calcium lignite-based coals are quartz, lime,

anorthite, mullite and anhydrite. 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 heterogeneous dissolution of elements in the fly ash and this does not occur in practice. Furthermore, the ternary phase diagram is only pertinent under equilibrium conditions and even then will only approximate crudely to the multi-component fly ash compositions so detailed analysis on the basis of the phase diagram is not possible.

Evidence for the view that crystalline phases form by crystallisation of an amorphous melt is supported by the spherical shape of many fly ash particles,² which suggests that the particles have gone through a viscous fluid state. This latter view emphasises the amorphous nature of fly ashes. It is the amorphous glassy phase present in fly ash that will dominate pozzolanic behaviour as well as the degradation behaviour under both alkaline and acid conditions. 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.

Despite the large tonnage of fly ash produced

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[†] Paper presented at the PROGRES Workshop: Novel Products from Combustion Residues, 6–8 June 2001, Morella, Spain

Contract/grant sponsor: BRITE-EURAM; contract/grant number: BRPR-CT98-0801

(Received 4 July 2001; revised version received 12 November 2001; accepted 20 November 2001)

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	Al ₆ Si ₂ O ₁₃
Illites	K ₂ O·3Al ₂ O ₃ ·6SiO ₂ ·2H ₂ O	Mullite	Al ₆ Si ₂ O ₁₃
Pyrite	FeS ₂	Haematite, magnetite, iron sulfide	Fe ₂ O ₃ , FeO, FeS
Calcite	CaCO ₃	Lime, anhydrite	CaO, CaSO ₄
Siderite	FeCO ₃	Haematite, magnetite	Fe ₂ O ₃ , FeO

annually by coal-burning power plants, there have been few studies investigating the microstructure and composition of the glass component. Whilst thermal techniques have been employed both to measure the reactivity of char to oxygen³ and to quantitatively determine carbonaceous matter in fly ashes,⁴ there has been little research measuring fly ash reactivity by determining the transition temperature (T_g) of the glassy phase. Fly ash reactivity is important in diverse applications such as acting as a pozzolan in concrete and for the production of zeolites.⁵

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 make a great contribution to its chemical reactivity. It should be borne in mind, however, that absolute understanding of the glass in a given fly ash will be hindered because of the complex inter- and intra-particle heterogeneity in these materials.⁶

A characteristic of any glass is its glass transition temperature. The lower the T_g of a glass, the greater its reactivity. If the amorphous component of fly ash approximates to a single glass composition or a range of closely related glass compositions then it should possess a single experimentally observable glass transition temperature. Conversely, if fly ashes consist of a range of particles each comprising a different glass composition then each particle will have a different glass transition temperature; and since there would be many thousands of such particles in a single differential scanning calorimetry (DSC) crucible, the experimentally determined glass transition temperature will become 'washed out' and will disappear.

MATERIALS AND METHODS

Thirteen fly ashes from different pulverised coal-fired powder plants were selected for this study. These ashes have a broad range of chemical and mineralogical compositions. The samples were supplied by various Spanish power generation facilities and Contento Trade (Udine, Italy). Details of the power stations sampled are given 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.

Fly ash characterisation

Major, minor and trace element concentrations were determined in the fly ash samples, (by Inductively Coupled Plasma Mass Spectrometry and Atomic Emission Spectroscopy (ICP-MS and ICP-AES)) using a special two-step digestion method devised for the analysis of trace elements in coal and combustion wastes.⁷ Silica contents were determined by X-ray fluorescence (XRF). By using these techniques, the fly ash compositions in wt% could be determined and are shown in Table 3.

Thermal analysis

A high temperature Stanton Redcroft DSC 1500 (Rheometric Scientific, Epsom, UK) Differential Scanning Calorimeter was used for thermal analysis. This technique uses 50-mg samples contained within platinum/rhodium crucibles. The DSC is run in oxygen-free nitrogen to prevent oxidation of any carbon and iron that may be present in the sample. Preliminary heating rates from 10 to 40 °C min⁻¹ were

Table 2. Fly ashes sourced in this study, with the indication of the power plant, the power capacity, the power company and the plant location, when known

Power station	Power (MW)	Power company	Location
Teruel	1050	ENDESA	North-east Spain
Escucha	160	FECSA	North-east Spain
La Robla	625	Union FENOSA	Northern Spain
Compostilla	1312	ENDESA	Northern Spain
Meirama	550	Union FENOSA	Northern Spain
Narcea	569	Union FENOSA	Northern Spain
As Pontes	1400	ENDESA	North-west Spain
Puertollano	220	ENECO	Central Spain
Espiel	938	ENECO	Southern Spain
Los Barrios	550	SE	Southern Spain
Soto de Ribena	672	IBERDROLA	Northern Spain
Monfalcone	336	ENELSPA	Italy
Lignite	Unknown	AMYNTATON-LKPA	Greece

Fly ash	Component							
	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
Escucha	49.5	26.7	12.3	2.3	0.9	0.3	1.9	0.2
La Robla	41.1	23.2	14.3	8.9	1.8	0.3	2.6	0.8
Compos	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
Narcea	54.3	23.3	6.9	4.0	2.5	0.7	3.8	0.3
As Pontes	41.4	30.1	12.6	5.6	1.6	0.6	1.9	0.2
Puerto	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
Barrios	42.3	35.6	2.6	8.4	2.1	0.3	0.6	1.7
Sribera	48.6	30.6	7.2	3.0	1.6	0.6	3.9	0.1
Monfalcone	49.0	33.4	6.4	2.4	0.8	0.4	0.7	0.3
Lignite	27.3	17.9	8.4	27.3	3.8	0.2	1.0	0.3

Table 3. Fly ash compositions in weight percent

used in a flowing 60 cm³ min⁻¹ dry nitrogen atmosphere. A final heating rate of 40 °C min⁻¹ was employed to exacerbate the thermal characteristics of the samples.

RESULTS

It was not possible to detect a clear glass transition temperature in all of the fly ash samples. One of several notable exceptions was the Meirama ash, which was run at three heating rates; 10 °C min⁻¹, 20 °C min⁻¹ and 40 °C min⁻¹. The DSC traces may be seen to be reasonably reproducible for a given sample by simple comparison of the traces given in Fig 1 which overlays the DSC traces of Meirama fly ash at the three heating rates. However, an increased heating rate can exacerbate the thermal characteristics of a particular material and it may cause an upward shift in the recorded temperature of a transition, as can also be seen in Fig 1.

DSC trace analysis

When analysing the traces, T_g will be seen as a change in the gradient of the base line, whilst exotherms will

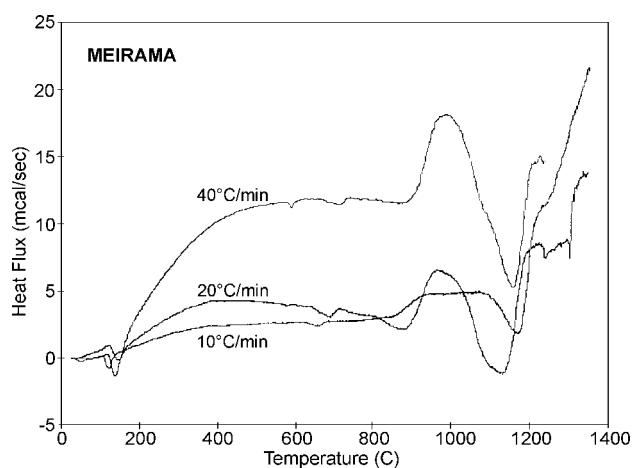


Figure 1. DSC traces for Meirama fly ash as determined using heating rates of 10, 20, and 40 °C min⁻¹.

be seen as peaks and endotherms as troughs. One of the disadvantages of the DSC equipment is that the readings are not valid below approximately 200 °C, thus none of the peaks or troughs evident below this temperature have been noted. The positions of all thermal events, so far as can be determined, are given in Table 4.

By considering the traces individually, the following statements can be made. Teruel has no discernible T_g which may be due to the glass phase being present in slightly different compositions, leading to a 'washed out' T_g . However, the trace does exhibit two small exotherms, probably due to the onset of crystallisation of the glass present in the system. There is a sharp endotherm at 851 °C.

The trace for Escucha fly ash exhibits a T_g at 500 °C, but has no clear exotherms or endotherms.

La Robla exhibits an exotherm at 1106 °C, but there is little other thermal activity.

Compostilla exhibits a T_g at 530 °C, slightly higher than that for Escucha. There is a very sharp trough at 855 °C. The cause of this is currently unknown.

Meirama gives a relatively simple trace with a T_g at 686 °C, a large exotherm at 993 °C and an endotherm at 1160 °C.

Table 4. DSC trace analysis of the fly ashes

Fly ash	T_g (°C)	Exotherm (°C)	Endotherm (°C)
Teruel	–	405, 478	851
Escucha	500	–	–
La Robla	410	1106	–
Compostilla	530	–	855
Meirama	686	993	150, 1160
Narcea	–	1143	–
As Pontes	–	576, 734	711, 911
Puertollano	–	–	1050
Espiel	806	1030	–
Los Barrios	–	433, 749, 1000	713, 897, 1115
Soto de Ribera	–	–	1197
Monfalcone	486	653, 815	965
Lignite	–	767, 918, 1010	–

Narcea exhibits a trace similar to La Robla, although the exotherm is at the slightly higher temperature of 1143 °C.

As Pontes exhibits a clear T_g at 470 °C, an exotherm at 734 °C and endotherms at 711 °C and 910 °C. It is likely that some of the smaller peaks and troughs are due to either base-line shift or small changes in composition (eg the remaining coal combusting). The endotherm at 711 °C appears to be superimposed on the exotherm at 734 °C (leading to the asymmetric appearance of the latter). If this is the case, then the endotherm is probably deeper than it appears to be on the trace.

Puertallano exhibits a very flat thermal trace, similar to that of Narcea and La Robla. A single exotherm is present at 1050 °C.

Espiel exhibits a T_g at 806 °C, with a small exotherm at 1030 °C, probably due to the glassy phase crystallising.

Los Barrios has a trace similar to that of As Pontes and exhibits the same endotherm/exotherm pair at temperatures within the margin of error for the DSC data acquisition and trace analysis (taken to be ± 10 °C). In this case they are observed at 713 °C (endotherm) and 749 °C (exotherm).

Soto de Ribena has a similar trace to Puertallano, in that there is very little change in thermal history over the temperature scale. It is very likely that any glass present in this system is of such a heterogeneous nature that transition and crystallisation peaks are washed out.

Monfalcone exhibits sharp endotherms and exotherms. This trace is similar to what would be expected for a homogeneous glass produced under laboratory conditions, rather than a fly ash, which is effectively a mix of glass, minerals, un-combusted coal particles, grit and other detritus. The sharp exotherm is due to the onset of crystallisation of the glassy phase (which has a transition temperature of 486 °C). The sharp endotherm at 965 °C may be due to reactions in the FeO–FeS system. This is usually evident at 930 °C, but the high heating rate may result in some thermal characteristics being shifted upwards in temperature.

Lignite exhibits exotherms at 767 °C, 918 °C and 1010 °C. This could be related to the high calcium content of this ash. There is some evidence of a T_g at around 430 °C.

The influence of the FeO–FeS system on thermal analysis

The lowest temperature melting phase in fly ashes concerns the presence of iron particles containing oxygen and sulfur. This FeO–FeS system has a eutectic point at 930 °C.⁸ The fly ashes that exhibit endotherms around this temperature are As Pontes and Monfalcone. Their Fe₂O₃ and SO₃ contents are given in Table 5.

The eutectic melting point in the FeO–FeS system is of critical importance in slagging processes in coal firing plants. The FeO–FeS particles melt and bind the

fly ash particles together, leading to the formation of slag deposits. These deposits inhibit heat transfer, cause corrosion, and reduce the efficiency of the power plant, whilst also increasing the down time whilst the deposits are chipped away. This research has inferred that the tendency of a certain fly ash to produce such deposits can be determined by thermal analysis. Thus, a plant could reduce costs and inefficiency by being able to choose coals for burning which are less likely to form slag deposits.

CONCLUSIONS

The amorphous phase of fly ash dominates degradation behaviour because glasses have a higher potential energy than the equivalent crystal structure and the variation of bond angles and distances in a glass make the bond breakage easier. If the amorphous component approximates to a single glass composition or a range of closely related glass compositions then it should possess a single experimentally observable glass transition temperature; the lower the glass transition temperature, the more degradable is the glass. The results obtained in this preliminary study suggest that thermal analysis can ascertain the relative reactivity of a series of fly ashes by determining the transition temperature of the glassy phase. Six of the fly ashes, Escuscha, Compostilla, Meirama, As Pontes, Espiel and Monfalcone, exhibit transition temperatures in their glass phase. The absence of clear T_g values in the other fly ashes may be the result of three factors:

- the fly ash particles present have widely different glass compositions with correspondingly different T_g values resulting in a 'washing out' of the transition;
- the fly ash particles contain a heavily cross-linked glass composition (the glass transition reduces in magnitude on increasing the cross-linking in the glass);
- the fly ash particles are highly crystalline with little amorphous content.

The fact that T_g proved to be so readily observable for many of the ashes is important considering that it is directly related to the degradability of the glass phase. Thermal analysis may well prove to be a simple check of relative reactivity for a given ash for pozzolanic applications.

Also of interest in the study is that, despite the wide variety in composition, there were several distinct types of behaviour observed. These ranged from very little thermal activity across the temperature range (eg

Table 5. Fe₂O₃ and SO₃ contents of fly ashes that exhibit endothermic troughs at or around 930 °C

Fly ash	wt% Fe ₂ O ₃	wt% SO ₃
As Pontes	12.6	1.4
Monfalcone	6.4	0.3

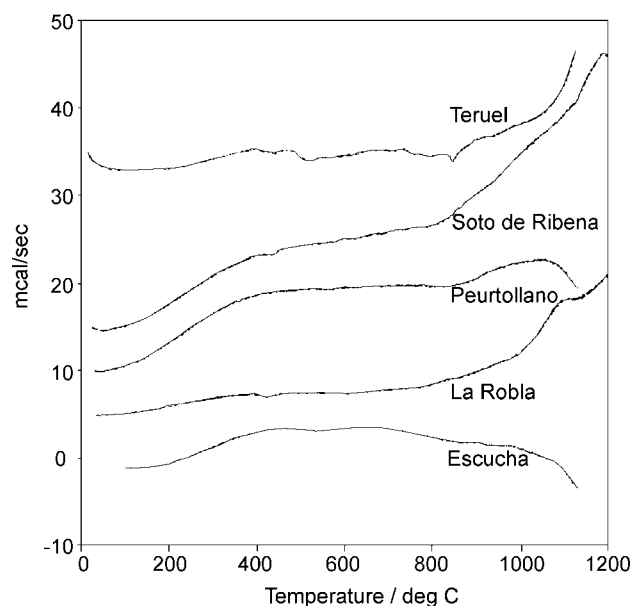


Figure 2. DSC traces for Escucha, La Robla, Puertollano, Soto de Ribena and Teruel fly ashes.

Escucha, La Robla, Puertollano, Soto de Ribena and Teruel; Fig 2) to very dramatic activity (eg Los Barrios, As Pontes and Monfalcone; Fig 3). Some samples showed an endotherm/exotherm pair (Los Barrios and As Pontes) and further research is required to quantify this.

This research has implied that the tendency of a fly ash to produce slags when combusted can be determined by thermal analysis. Thus, a plant could reduce costs and inefficiency by being able to choose coals for burning which are less likely to form slag deposits.

ACKNOWLEDGEMENTS

The present study was supported by the BRITE-EURAM Program from the 4th Framework of R&D of the European Union (SILEX, BRPR-CT98-0801). We would also like to express our gratitude to the power generation companies AMYNTATON-LKPA, ENDESA, ENECO, ENEL-SPA, IBERDROLA, FECSA and Union FENOSA for supplying the fly ash samples.

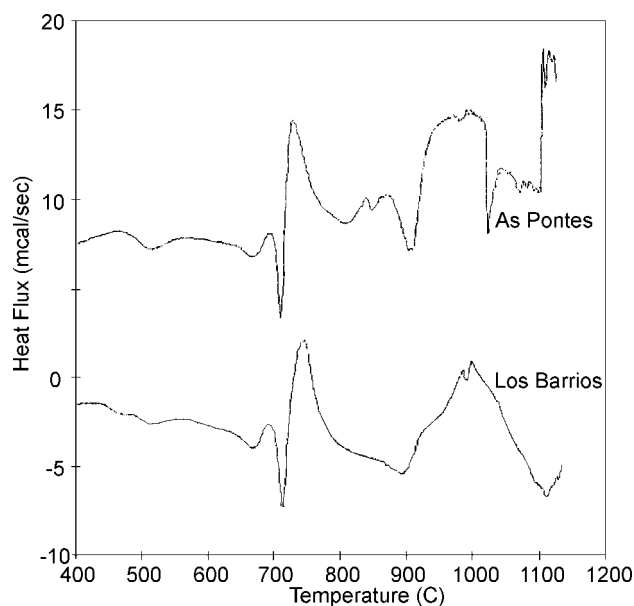


Figure 3. DSC traces for Los Barrios and As Pontes fly ashes.

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