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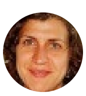
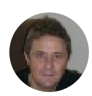


Natalia Moreno

Spanish National Research Council



Xavier Querol

Spanish National Research Council, in Barc…

Jose Manuel Andrés

Spanish National Research Council

Kenneth T Stanton

University College Dublin

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Physico-chemical characteristics of European pulverized coal combustion fly ashes

N. Moreno[a,*], X. Querol[a], J.M. Andrés[a], K. Stanton[b], M. Towler[b], H. Nugteren[c], M. Janssen-Jurkovicová[d], R. Jones[e]

[a]Institute of Earth Sciences 'Jaume Almera', CSIC, C/Lluis Solé Sabarís, s/n, 08028 Barcelona, Spain
[b]Materials and Surface Science Institute, University of Limerick, National TechnologicalPark, Limerick, Ireland
[c]DelftChemTech, Particle Technology Group, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands
[d]KEMA, Section of Environmental Affairs, Utrechtseweg, 310, 6800 ET Arnhem, The Netherlands
[e]Department of Civil Engineering, University of Dundee, DD1 4HN Dundee, Scotland, UK

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Abstract

Fly ashes sourced from European pulverised coal burning power plants (from Spain, The Netherlands, Italy and Greece) were characterised in terms of their chemical composition, mineralogy and physical properties. The amount and composition of the glass present in the ashes were also determined. The materials analysed have very different compositions and were selected with a view to determining their suitability for different applications and for further studies on applications. The results were compared to the literature to determine their similarities to UK coal fly ashes. Chemical analysis has enabled the categorisation of the ashes based on their oxide contents. Devitrification of the glass phase has been effected using suitable heat treatments and crystal phases formed are used as an indicator of glass reactivity. Based on leaching tests, certain ashes were identified as having limitations for some further uses due to the relatively high levels of leachable trace elements. A wide range of physical properties such as density were observed and these are related to factors such as mineralogical content and particle morphology.

Keywords: Fly ash; Characterisation; Mineralogy; Trace elements; Grain size

1. Introduction

Over 100 million tons of coal fly ash (CFA) are produced annually in the USA and EU. CFA is used mainly in the concrete and cement manufacturing industries [1]. However, CFA may have other uses, such as ceramic applications [2–4], synthesis of high cation exchange capacity (CEC) zeolites [5–11], additives for immobilization of industrial and water treatment wastes [12–13], land stabilization in mining areas [14], sorbents for flue gas desulfurization [15], filter material for the production of different products [16], 'slash' (fly ash/sludge blend) production for soil amendment [17] and as reservoirs for valuable metals, such as Al, Si, Fe, Ge, Ga, V, Ni [10,18,19].

For each of these applications it is necessary to undertake a complete characterization of the CFA involved. In this study, 23 CFAs from different European pulverised coal-fired power plants were selected with the aim of determining their chemical, mineralogical and physical properties. Furthermore, this data was compared with that for UK-fly ashes by McCarthy, et al. [20] and UKQAA [21].

Investigations were undertaken within the framework of an EU R+D project [22]. The major objective of the project was a study of a full range of CFAs that are produced in the EU with a view to determining their potential for silica extraction and zeolite synthesis. The major purpose of silica extraction is the liberation of SiO_2 into an alkaline solution that can be used subsequently after separation from the ash residue with an external Al source, for the synthesis of pure

* Corresponding author. Tel.: +34 934095410; fax: +34 934110012.
E-mail address: nmoreno@ija.csic.es (N. Moreno).

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zeolites [11] Characterisation was undertaken to determine the suitability of these ashes for silica extraction and conventional zeolite synthesis in a direct conversion process. The results may also serve to evaluate the suitability of the CFAs for alternative applications.

2. Experimental

2.1. Fly ash selection

Twenty-three CFAs from European pulverised coal-fired power plants were selected for this study. Details of the power stations from which the ashes were sampled are given in Table 1. All samples were collected 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.

This selection covered most of the fly ash types produced in the European Union, from the high calcium lignite fly ash produced by many Greek power plants, to the sub-bituminous coal fly ash produced in one Spanish plant, to the more common bituminous and anthracitic fly ashes. The selection of this large number of fly ashes is required to ensure that wide ranges of Si, Al, Ca, K, Fe, glass, mullite and quartz contents are included in the study.

Table 1
Fly ashes selected and sampled in this study including the power plant source, power capacity, Power company and location

Power station	Power capacity (MW)	Power company	Location
Narcea	569	Unión FENOSA	N Spain
Barrios	550	SE	S Spain
Escucha	160	FECSA	EN Spain
Meirama	550	Unión FENOSA	N Spain
Teruel	1050	ENDESA	EN Spain
Espiel	938	ENECO	S Spain
Compostilla	1312	ENDESA	N Spain
La Robla	625	Unión FENOSA	N Spain
As Pontes	1400	ENDESA	NW Spain
Soto Ribera	672	IBERDROLA/E. Bierzo	N Spain
Puertollano	220	ENECO	Central Spain
Alkaline	450	EP2	The Netherlands
Nijmegen	600	Centrale Gelderland	The Netherlands
Neutral	600	EPZ	The Netherlands
CCB	600	Centrale Borssele	The Netherlands
Acid	600	EPZ	The Netherlands
Amer-8	600	Amer Centrale	The Netherlands
Amer-9	600	Amer Centrale	The Netherlands
Hemweg-8	600	Centrale Amsterdam	The Netherlands
Lignite	Not available	AMYNTAION and LKPA	N Greece
Fusina	980	ENEL S.p.A.	Italy
Monfalcone	336	ENEL S.p.A.	Italy
Sardegna	Not available	ENEL S.p.A.	Italy

2.2. Characterisation of fly ashes

2.2.1. Chemical characterisation

Major, minor and trace element concentrations were determined in the CFAs. The samples were acid-digested by using a special two-step digestion method devised for the analysis of trace elements in coal and combustion wastes by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) [23]. This is based on a first HNO_3 extraction in closed PFA reactors under 90 °C during 6 h to extract the volatile metals, followed by the digestion of the solid residue (isolated with centrifugation) with $HF:HNO_3:HClO_4$. Finally, the dissolution is driven to dryness and the soluble residue re-dissolved using HNO_3. The fly ash international reference material NBS 1633[b] was also digested to check the accuracy of the analytical and digestion methods. Silica contents were determined directly in solid samples by X-ray Fluorescence (XRF), but the other elements were analysed in the acid digestions by means of ICP-MS and ICP-AES using the analytical conditions determined by Querol et al. [23] and Tait and Ault [24]. Finally, C and N contents where determined by conventional LECO elemental analysers.

2.2.2. Mineralogical characterisation

The mineral composition of the fly ashes was determined by X-ray diffraction (XRD) using a SIEMENS D501 powder diffractometer with a graphite monochromator, NaI(Tl) detector and Cu Kα radiation. Final quantitative XRD analysis was performed using the Reference Intensity Method (RIM) described by Chung [25,26]. Scans were performed between 2θ values of 10–70° with a step size of 0.02°. CaF_2 was used as an internal standard.

2.2.3. Physical characterisation

The physical characterisation of fly ash included proximate analysis (moisture content and loss on ignition), density, porosity, BET surface area determinations and particle size analysis. These parameters were selected as they have an important influence on the reactivity of fly ash for zeolite synthesis as well as for other structural and chemical applications.

The moisture and volatile (loss on ignition, LOI) contents were determined at 105 and 1050 °C, respectively. The particle size distributions of the CFAs were determined by means of laser diffraction particle size analysis (Malvern MASTERSIZER/E®). The true density (d_t) values of the samples were obtained by means of a helium pycnometer (MICROMERITICS 1330). The apparent density (d_a) values were measured by means of the standard NLT-176/74, which is based on the sedimentation of powdered materials in toluene. The porosity values (P) were obtained from the d_a and d_t measurements [27] from the following equation: $\%P = 100\times(1-d_a/d_r)$. The BET surface area was measured with a multi-point volumetric apparatus

(MICROMERITICS model ASAP 2000) by adsorbing and desorbing nitrogen on samples previously dried and outgassed (150 °C, 12 h under a vacuum of 0.1 mm Hg). The morphologies of the particles were investigated by a JEOL JSM 840 Scanning Electron Microscope.

2.2.4. Glass composition

The glass composition was computed from the chemical–mineralogical mass balance. The potential Si excess over Al and the glass reactivity was investigated by de-vitrification of the glass fraction induced by thermal treatment (1100 °C). The mineralogical composition of the thermally treated fly ashes was investigated and compared with the original mineralogy. If an aluminium–silicate glass matrix has an excess of SiO_2 over Al_2O_3, thermal treatment will give rise to de-vitrification processes that will result in the crystallisation of cristobalite [28,29], otherwise only mullite will crystallise.

2.2.5. Leaching tests

To determine the potential mobility of trace elements from the fly ashes, the leaching test DIN 38414-S4 was applied. This DIN method requires the mixing of 100 g of solid material (dry weight) with a liter of distilled water in 2 l bottles during 24 h [30]. The major and trace element contents in the leachates determined by means of ICP-AES and ICP-MS.

3. Results and discussion

3.1. Chemical characterisation

The composition of fly ash samples selected for this study is shown in Table 2, which also includes the range determined for UK-fly ashes in UKQAA [21]. According to the classification of the American Society for Testing and Materials (ASTM C618-92a, [31]) the following fly ashes groups may be distinguished:

- F group. Most of the fly ashes investigated in the present study should be included in the class. This group have pozzolanic properties and are characterised by (a) $SiO_2+Al_2O_3+Fe_2O_3>70\%$, (b) $SO_3<5\%$, (c) moisture content $<3\%$ and (d) loss on ignition (LOI) $<6\%$. Nijmegen, Sardegna, Fusina and Amer8 fly ashes show all the specifications for Class F with the exception of LOI contents that show values from 7.5 to 8.1% for these fly ashes.
- C group. This group have $SiO_2+Al_2O_3+Fe_2O_3<70\%$. Lignite fly ash is the only ash from the study to fit in this group. Class C fly ashes show cementitious properties and are characterised by (a) $SiO_2+Al_2O_3+Fe_2O_3>50\%$, due to the high Ca and Mg contents (27 and 3.8%, respectively). Class C fly ash can be used as a Portland cement replacement ranging from 20–35% of the mass of cementitious material.

Depending on major oxide contents the fly ashes may also be classified as follows:

- Sialic-fly ash type. Soto de Ribera, Acid, Espiel, Monfalcone, Puertollano and CCB fly ashes contain very high alumina and silica contents (80–87 wt%) and very low contents of major impurities (Fe, Ca, S). The Soto de Ribera, Espiel, Compostilla and Narcea fly ashes are characterised by a relatively high K_2O content (4%).
- Robla and Meirama fly ashes have low $SiO_2+Al_2O_3$ contents (around 67 wt%).
- Ferro-calco-sialic fly ash type. The other fly ashes have very similar contents of alumina and silica ($SiO_2+Al_2O_3$ 70–79 wt%) and different concentrations of impurities.
- Escucha, As Pontes Teruel and Robla fly ash samples are characterised by a relatively high Fe content, whereas Meirama, Sardegna, Robla and Barrios fly ashes have relatively high Ca content. Levels of Mg or Mn are also relatively high due to the similar atomic radii.

The range of major oxides obtained for the 23 selected fly ashes in this study are very similar to those determined for UK-fly ashes [21], with the exception of Na_2O and K_2O, which have higher concentration in the UK-fly ashes (0.8–1.8 wt% Na_2O and 2.3–4.5 wt% K_2O, compared to 0.2–1.2% Na_2O and 0.7–3.9% K_2O for the rest of the European fly ashes).

The N contents (Table 2) are very low in all samples, ranging from 0.02 (Puertollano and Teruel) to 0.14 wt% (Fusina).

Concerning the C content (Table 2), the following classifications can be made: (a) High C samples (6.2–7.6 wt% C): Fusina, Amer-8, Sardegna and Nijmegen; (b) intermediate C samples (2.3–4.6 wt% C): Escucha, Barrios, Neutral, CCB, Acid, Compostilla Espiel Amer-9 and Hemweg; and (c) low C samples: the remaining fly ashes (0.6–1.9 wt% C). These C contents are well correlated with the LOI values, with the exception of the Meirama fly ash. In this case the relatively high LOI values are probably due to the loss of sulphate. Similar LOI values were reported for UK fly ashes [20].

Table 3 shows the trace element concentrations of the fly ashes studied. Based on these data, the following fly ashes may have limitations when used for direct conversion because of their high heavy metal contents:

- Puertollano fly ash has the highest Pb, Zn, Sb and Ge contents (1075, 924, 120 and 61 mg kg^{-1}, respectively), and relatively high As and Cd contents (140, 5 mg kg^{-1}, respectively).
- Sardegna fly ash has the highest Ba and Sr contents (3134 and 4406 mg kg^{-1}, respectively), and relatively high B and Cr contents (393 and 235 mg kg^{-1}, respectively).

Table 2
Major element concentrations, moisture and LOI values of the fly ashes

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	TiO_2	MnO	SO_3	N	C	Moist	LOI	SiO_2/Al_2O_3
Narcea	55.2	23.3	6.9	4.0	2.5	0.7	3.8	0.3	0.9	0.1	0.4	0.03	1.4	0.03	1.9	2.4
Barrios	42.6	35.6	2.6	8.4	2.1	0.3	0.6	1.7	1.6	0.1	0.6	0.05	3.4	0.01	3.8	1.2
Escucha	49.5	26.7	12.3	2.3	0.9	0.3	1.9	0.2	0.9	0.03	0.3	0.08	4.6	0.03	4.7	1.9
Meirama	49.2	17.6	10.4	11.8	2.0	0.4	0.4	0.2	0.5	0.1	2.2	0.03	0.7	2.4	5.2	2.8
Teruel	48.3	23.9	16.0	5.4	1.0	0.2	1.4	0.2	0.8	0.03	0.8	0.02	0.6	0.1	2.0	2.0
Espiel	52.3	28.5	5.9	2.0	1.5	0.5	4.0	0.4	1.0	0.1	0.1	0.03	2.4	0.1	3.7	1.8
Compostilla	51.2	25.5	7.5	2.8	2.0	0.8	3.9	0.4	0.9	0.1	0.6	0.04	3.2	0.1	4.3	2.0
La Robla	44.1	23.2	14.3	8.9	1.8	0.3	2.6	0.8	0.9	0.1	1.1	0.03	1.1	0.1	1.9	1.9
As Pontes	41.5	30.1	12.6	5.6	1.6	0.6	1.9	0.2	0.6	0.1	1.4	0.04	1.4	0.3	3.8	1.4
S. de Ribera	48.9	30.6	7.2	3.0	1.6	0.6	3.9	0.1	0.8	0.03	0.3	0.03	1.2	0.2	3.0	1.6
Puertollano	58.6	27.4	7.3	0.8	1.0	0.3	2.4	0.1	0.7	0.1	0.2	0.02	0.7	0.1	1.1	2.1
Alkaline	46.8	24.8	9.0	6.8	3.7	1.2	2.0	0.7	0.9	0.1	1.0	0.04	1.9	0.2	3.0	1.9
Nijmegen	45.3	25.0	8.8	6.4	1.4	0.8	1.1	1.0	1.3	0.03	1.3	0.09	6.2	0.2	7.5	1.8
Neutral	53.3	26.1	7.4	3.1	0.6	0.1	0.6	1.5	1.8	0.1	0.5	0.06	4.0	0.3	4.8	2.0
CCB	59.6	27.0	3.3	0.5	0.9	0.3	2.9	0.1	1.4	0.03	0.2	0.05	3.4	0.3	3.7	2.2
Acid	51.3	28.9	8.4	1.8	1.0	0.5	2.5	0.2	1.5	0.03	0.5	0.05	2.7	0.1	3.3	1.8
Amer-8	45.2	26.5	7.1	6.1	1.6	0.8	1.2	1.1	1.3	0.03	1.1	0.11	7.0	<0.1	8.1	1.7
Amer-9	52.4	25.8	7.0	5.6	1.6	0.7	1.4	0.9	1.3	0.1	0.6	0.04	2.3	0.1	2.8	2.0
Hemweg-8	53.2	26.0	8.6	2.4	1.6	0.5	2.7	0.3	1.3	0.1	0.6	0.04	2.3	0.2	2.7	2.0
Lignite	28.5	17.9	8.4	27.3	3.8	0.2	1.0	0.3	1.0	0.03	8.6	0.06	1.0	0.1	3.0	1.6
Fusina	48.2	25.9	8.8	2.3	1.5	0.5	2.6	0.3	1.3	0.1	0.6	0.14	7.6	0.1	7.9	1.9
Monfalcone	50.8	33.4	6.4	2.4	0.8	0.4	0.7	0.3	2.6	0.03	0.3	0.04	1.6	0.1	1.9	1.5
Sardegna	41.7	29.0	3.8	10.0	2.4	0.5	0.8	1.5	1.7	0.1	0.9	0.08	6.5	0.2	7.6	1.4
UKQAA	48–52	24–32	7–15	1.8–5.3	1.2–2.1	0.8–1.8	2.3–4.5	ND	0.9–1.1	ND	0.3–1.7	ND	ND	ND	3.2	1.6–2.2
NBS 1633[b]	51.2	27.0	10.5	2.0	0.8	0.3	2.4	0.5	1.2	0.0	0.5	ND	ND	ND	ND	1.9
NBS 1633[b] certified	49.2	28.4	11.1	2.1	0.8	0.3	2.5	0.5	1.3	0.02	0.5	ND	ND	ND	ND	1.7

Concentrations are in %wt.

Table 3
Trace element concentrations (mg kg^{-1}) of the fly ashes

	As	B	Ba	Be	Cd	Co	Cr	Cu	Ge	Hg	Li	Mo	Ni	Pb	Rb	Sb	Se	Sn	Sr	Th	U	V	Zn
Narcea	98	98	1047	5	2	30	177	86	1	0.3	220	6	82	90	185	7	6	4	235	24	9	173	171
Barrios	22	407	1960	9	6	40	148	68	14	0.3	311	11	96	114	31	4	8	14	2267	55	19	179	154
Escucha	56	392	478	11	1	22	105	39	4	<0.01	247	7	69	77	118	4	3	9	438	24	10	169	222
Meirama	94	158	1601	4	1	20	47	44	3	0.4	37	5	49	40	26	1	7	4	757	20	6	154	112
Teruel	79	342	311	12	1	25	107	52	6	<0.01	256	15	85	65	90	4	3	8	523	21	20	206	174
Espiel	96	306	845	5	1	25	187	80	4	0.3	303	5	92	103	202	19	6	7	379	32	7	268	154
Compostilla	119	89	1029	6	2	35	137	90	2	0.2	210	11	98	129	197	21	4	7	289	28	8	202	173
Robla	162	117	619	5	1	41	148	81	3	0.2	190	22	126	145	150	7	7	10	388	28	18	287	189
As Pontes	129	340	1941	9	3	72	158	119	3	0.07	149	7	157	98	133	5	15	6	489	37	13	228	424
Soto Ribera	80	206	658	6	1	30	139	66	3	0.2	225	7	93	114	199	6	7	7	267	29	8	289	176
Puertollano	140	534	460	14	5	31	108	75	61	1.3	185	11	96	1075	139	120	7	10	131	30	15	202	924
Alkaline	48	289	2037	17	2	55	140	186	9	0.3	167	13	152	208	108	17	–	10	1189	34	25	325	200
Nijhegen	48	305	2215	9	2	34	161	81	16	0.4	162	13	90	69	63	4	11	11	2105	40	12	205	123
Neutral	55	178	2182	8	2	112	196	154	35	0.2	79	7	377	54	22	2	–	9	988	17	5	226	153
CCB	40	24	993	10	1	35	145	120	4	0.2	122	13	73	52	145	4	30	6	476	30	7	230	98
Acid	109	68	1757	34	1	72	171	254	25	0.1	268	14	136	102	127	9	–	10	1920	37	17	323	143
Amer 8	42	259	2074	8	2	34	159	75	15	0.2	168	11	89	67	57	4	12	10	1807	36	11	202	125
Amer 9	34	229	1787	7	2	29	162	70	11	0.4	150	12	80	59	64	3	18	8	1487	34	9	221	122
Hemweg 8	22	260	2313	8	1	35	133	93	10	0.3	329	16	156	80	42	8	14	10	2390	50	13	514	100
Lignite	33	51	402	3	2	25	281	135	2	0.05	36	11	220	44	60	2	8	4	338	25	25	234	76
Fusina	52	152	1302	12	1	47	172	117	14	0.2	139	13	117	93	149	7	15	8	757	31	13	266	160
Monfalcone	39	275	605	8	2	52	136	112	7	0.05	161	12	155	40	42	2	<5	8	1054	20	9	455	136
Sardegna	26	393	3134	13	2	48	235	89	18	0.7	377	12	112	59	33	3	<5	15	4406	65	29	268	70
UKQAA	4–109	5–310	<1–36000	–	<1–4	2–115	97–192	119–474	–	–	–	3–81	108–583	<1–976	–	1–325	4–162	933–1847	–	–	–	292–1339	148–918
1633[b]	141	142	690	13	2	46	182	107	12	0.1	163	80	120	71	136	6	11	8	971	25	9	296	199
1633[b] certif.	136	–	709	–	1	50	198	113	–	0.1	–	85	10	68	140	6	10	–	1041	26	9	296	210
Percentiles, minimum and maximum (mg kg^{-1})																							
Perc25	40	135	639	6	1	30	137	73	3	0.2	150	7	87	59	50	4	6	7	384	25	9	202	123
Median	55	259	1302	8	2	35	148	86	7	0.2	185	11	96	80	108	4	7	8	757	30	12	228	154
Perc75	97	323	1999	12	2	48	172	118	15	0.3	252	13	144	109	147	8	13	10	1647	37	18	278	175
Min	22	24	311	3	1	20	47	39	1	<0.01	36	5	49	40	22	1	3	4	131	17	5	154	70
Max	162	534	3134	34	6	112	281	254	61	1.4	377	22	377	1075	202	120	30	15	4406	65	29	514	924

- Monfalcone fly ash has the highest V content (455 mg kg^{-1}).
- Hemweg-8 fly ash has very high Ba, Sr and V contents (2313, 2390 and 514 mg kg^{-1}, respectively).
- The Acid fly ash has very high Ba, Cu and Sr contents (1757, 254 and 1920 mg kg^{-1}, respectively).
- The CCB fly ash has a high Se content (30 mg kg^{-1}).
- The UKfly ashes may have very high Ba contents (up to 36,000 mg kg^{-1}) and relatively high levels of Cu, Mo, Ni, Pb, Sb and Zn (up to 474, 81, 583, 976, 325 and 918 mg kg^{-1}, respectively [21]).
- Narcea and Compostilla fly ashes (and CCB excluding Se) have the lowest trace element contents.

25, 50 and 75 percentile values for the content of trace elements in EU fly ashes are given in Table 3.

3.2. Mineralogical characterisation

The major phases present in the fly ashes are aluminosilicate glass, mullite ($Al_6Si_2O_{13}$), quartz (SiO_2), magnetite (Fe_3O_4), anorthite/albite ($(Ca,Na)(Al,Si)_4O_8$), anhydrite ($CaSO_4$), ettringite ($3CaO\ Al_2O_3\ 3CaSO_4\ 32H_2O$), opaline SiO_2, hematite (Fe_2O_3) and lime (CaO).

A semi-quantitative estimation of the concentrations of these mineral phases is given in Table 4. The high glass contents (80–92 wt%) have been found in nine of the ashes. Glass contents below 65% were found in another eight.

The Barrios fly ash has a very high mullite content (40 wt%). This is of special interest for potential ceramic or refractory uses of these fly ashes, but it may have a negative impact on SiO_2 extraction. The Teruel, Escucha, Meirama, Puertollano, Alkaline, Soto de Ribera, As Pontes, Fusina, Monfalcone and Sardegna fly ashes have intermediate mullite contents (15–29 wt%), whereas the rest of fly ashes have relatively low mullite levels (3–10 wt%) and only the Lignite fly ash has no significant mullite content (<0.3 wt%).

Sixteen of the fly ashes have high quartz contents (6–2.5 wt%). The quartz levels in the other fly ashes are always below 5.0 wt%. The Meirama fly ash has relatively high levels of cristobalite. This probably originated from devitrification of the glass which indicates that the Meirama glass is very reactive.

The Lignite and Sardegna fly ashes show the highest lime contents (5.8 and 2.5 wt%, respectively). The Robla, Alkaline, Barrios, Nijmegen, Amer-8 and Fusina fly ashes also have traces of lime (1.0–1.9 wt%) which may result in high-alkaline solutions. With respect to the Fe impurities, the Escucha, As Pontes, Puertollano, La Robla, Teruel and Lignite fly ashes have the highest hematite or magnetite contents (from 3.5 to 7 wt%).

The Lignite fly ash has the highest anhydrite and calcite contents (15 and 0.7 wt%, respectively). The other fly ashes have very low anhydrite and calcite contents.

The UK-fly ashes show similar or slightly higher glass contents, lower mullite and quartz levels, and higher

Table 4
Mineralogical composition of fly ash samples

	Glass	Mullite	Quartz	Opaline SiO_2	Anhydrite	Calcite	Lime	Hematite	Magnetite	Feldspar	Ettringite
Narcea	86	3.8	6.6	<0.3	0.2	<0.3	0.7	<0.3	1.5	0.2	<1.0
Barrios	48	40.4	3.4	<0.3	1.3	<0.3	1.1	<0.3	0.5	1.5	<1.0
Escucha	56	24.4	9.6	<0.3	0.9	<0.3	<1.0	<0.3	5.0	<1.0	<1.0
Meirama	63	19.6	6.9	4.5	2.6	<0.3	<1.0	2.5	<0.3	0.7	<1.0
Teruel	63	19.4	8.6	<0.3	1.5	<0.3	<1.0	5.9	1.3	<1.0	<1.0
Espiel	86	7.4	2.7	<0.3	<0.3	<0.3	<1.0	<0.3	1.8	<1.0	<1.0
Compostilla	89	3.2	3.1	<0.3	0.3	<0.3	<1.0	<0.3	1.4	<1.0	<1.0
Robla	85	4.2	1.7	<0.3	1.5	<0.3	1.9	<0.3	3.8	0.9	<1.0
As Pontes	52	29.4	6.2	<0.3	1.0	<0.3	<1.0	5.5	<0.3	3.1	1.6
S. Ribera	74	18.4	5.0	<0.3	<0.3	<0.3	<1.0	<0.3	1.0	<1.0	<1.0
Puertollano	65	20.7	10.4	<0.3	<0.3	<0.3	<1.0	<0.3	3.5	<1.0	<1.0
Alkaline	63	20.1	11.2	<0.3	1.4	<0.3	1.1	<0.3	1.2	<1.0	<1.0
Nijmegen	82	4.9	6.1	<0.3	<0.3	<0.3	1.0	<0.3	1.0	<0.3	<1.0
Neutral	80	10.9	7.1	<0.3	<0.3	<0.3	<0.3	<0.3	0.9	0.2	<1.0
CCB	80	9.8	9.4	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	0.1	<1.0
Acid	83	9.1	6.0	<0.3	<0.3	<0.3	<0.3	<0.3	0.8	0.6	<1.0
Amer 8	78	8.2	6.9	<0.3	<0.3	0.6	1.0	<0.3	0.8	<0.3	<1.0
Amer 9	77	9.1	12.5	<0.3	<0.3	<0.3	0.6	<0.3	0.5	0.2	<1.0
Hemweg 8	84	6.6	7.8	<0.3	<0.3	<0.3	0.5	<0.3	0.9	<0.3	<1.0
Lignite	62	<0.3	9.2	<0.3	15.0	0.6	5.8	3.5	<0.3	<0.3	<1.0
Fusina	72	17.4	6.4	<0.3	<0.3	<0.3	1.1	<0.3	0.1	<0.3	<1.0
Monfalcone	73	25.9	3.2	0.5	<0.3	<0.3	<0.3	<0.3	0.5	<0.3	<1.0
Sardegna	74	14.5	4.0	<0.3	0.2	<0.3	2.5	<0.3	0.3	0.8	<1.0
UK (McCarthy, 1999)	74–90	1.2–8.3	1.5–10.8	–	–	–	–	2.5–8.6	0.8–4.1	–	–

Values are %wt as deduced from XRD analysis.

Table 5
Percentiles 10, 50 (median) and 90% of the grain size distributions of the selected fly ash samples (in micrometers)

	Perc 10	Median	Perc 90	d_t (g cm^{-3})	d_a (g cm^{-3})	Porosity (%)	BETSA (m^2 g^{-1})
Narcea	3.0	11.8	50.3	2.4	0.9	63.4	1.7
Barrios	4.6	24.6	84.6	2.3	0.7	72.0	2.6
Escucha	8.3	53.4	183.8	2.3	1.0	56.6	3.5
Meirama	8.9	40.5	248.0	2.4	0.7	71.6	12.4
Teruel	4.6	21.8	75.7	2.5	1.1	58.2	1.9
Espiel	3.8	21.0	99.5	2.3	1.0	55.6	1.8
Compostilla	4.2	17.3	77.4	2.5	1.0	58.9	3.1
La Robla	2.3	12.3	76.2	2.7	0.9	66.0	2.1
As Pontes	14.0	82.0	332.0	2.4	0.9	65.2	5.7
S. Ribera	7.5	43.8	221.0	2.2	1.0	57.0	1.8
Puertollano	4.7	26.2	123.8	2.2	0.7	68.6	2.7
Alkaline	4.5	26.1	114.1	2.0	0.7	64.3	2.0
Nijmegen	4.7	21.4	74.2	2.4	0.4	81.9	2.7
Neutral	3.9	18.8	85.8	1.8	0.5	70.0	1.8
CCB	7.6	53.2	173.5	1.3	0.8	65.9	1.3
Acid	2.6	13.7	43.8	2.4	0.7	71.3	1.7
Amer-8	4.6	25.9	151.8	2.4	0.7	72.2	2.5
Amer-9	3.1	18.6	63.9	2.4	0.8	66.7	1.5
Hemweg-8	4.7	21.9	69.9	2.4	0.6	76.9	3.6
Lignite	7.3	32.8	156.8	2.6	0.5	70.0	4.3
Fusina	6.5	29.3	171.2	2.4	0.5	81.7	3.3
Monfalcone	7.9	42.2	295.3	2.4	0.6	76.9	1.3
Sardegna	4.5	28.6	114.0	2.4	0.6	74.7	6.4

True density (d_t), apparent density (d_a), porosity and BET specific surface area (BETSA) of the fly ashes studied.

magnetite and hematite contents [20] than the European fly ashes studied here.

3.3. Physical characterisation

Due to the direct sampling of materials at the electrostatic precipitators, the moisture content of all fly ashes (Table 2) is very low (<1 wt%), with the exception of Meirama fly ash (2.4 wt%). The LOI values obtained (Table 2) show a wider range between 1.1 and 8.1 wt%. Although the volatilisation or the decomposition of inorganic species may have an impact on the LOI values, the majority of the volatile content is attributed to the oxidation of partially combusted coal particles. The different LOI values may reflect combustion efficiencies.

The As Pontes (mixture of fly ash and slag), Escucha, Meirama, Soto de Ribera, CCB and Monfalcone fly ashes have a coarser grain size distribution (median >40 μm and percentile 90 (p_{90})>180 μm, Table 5). The Narcea, Compostilla, Robla, Neutral, Acid and Amer-9 fly ashes show a finer grain size (median <20 μm and p_{90}<85 μm). The other fly ashes have an intermediate grain size.

The grain size distributions of these fly ashes may be grouped as follows (Fig. 1): (a) Normal-Gausian grain size distribution with modes around 10–30 μm were determined for fourteen fly ashes; (b) Asymmetric grain size distribution with modes close to 100 μm were obtained in only two fly ashes; and (c) Wide to bimodal grain size distribution with modes from 10 to 100 μm were found in seven ashes.

The true density (d_t) values range between 1.3 g cm^{-3} for CCB fly ash and 2.7 g cm^{-3} for the La Robla fly ash (Table 5). d_t values for typical ash particles with mullite and quartz inclusions range between 2.0 and 2.5 g cm^{-3} [32]. High-Ca glass particles have d_t values close or lower than 2.5 g cm^{-3}, whereas d_t values >2.6 g cm^{-3} are due to presence of free oxide phases such as lime, magnetite or hematite, or calcium salts such as anhydrite. In this study the highest d_t values were measured for those samples with the highest magnetite contents such as Teruel and La Robla fly

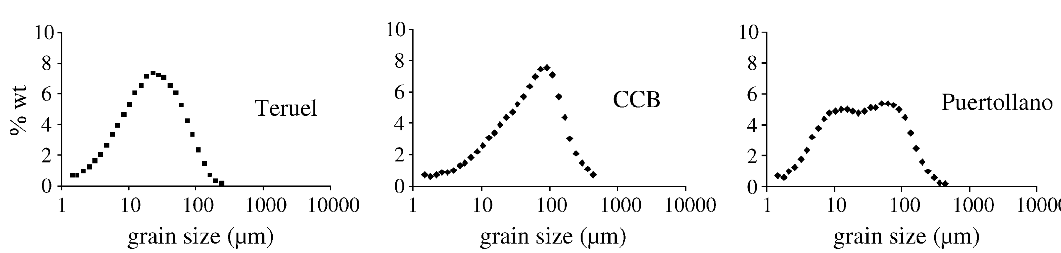

Fig. 1. Examples of normal (left) asymmetric (centre) and bimodal (right) grain size distributions.

ashes (2.5 and 2.7, respectively), and the Lignite fly ash which has high lime and anhydrite contents (2.6). d_t values between 2.2 to 2.4 g cm^{-3} were obtained for most of the fly ashes with intermediate Fe oxides and/or high Ca oxide contents and/or relatively high glass contents. The lowest d_t values (1.3–2.0 g cm^{-3}) were obtained for CCB, Neutral and Alkaline, but no discernable patterns were found that explained these low d_t values.

The apparent density (d_a) values range between 1.1 g cm^{-3} for the Teruel fly ash and 0.4 g cm^{-3} for Nijmegen fly ash (Table 5). The highest d_a values were obtained for high-Fe and glass fly ashes. Thus, the d_a values of the Escucha and Teruel fly ashes (12 and 16 wt% $Fe_2O\cdot_3$, respectively) and the Compostilla and Espiel fly ashes (94 and 96 wt% glass content) ranged between 1.0 and 1.1 gcm^{-3}. The lowest d_a values are probably due to a high cenosphere content as these structures tend to be hollow.

All these reported ranges on grain size distributions and density are similar than the results obtained by McCarthy et al. [20] for SIX UK fly ashes.

The highest porosity values (74.7–81.7%) were obtained for the Sardegna, Monfalcone, Hemweg and Fusina fly ashes (Table 5), whereas the lowest values (56%) were obtained for the Escucha and Espiel fly ashes.

The surface areas obtained from BET studies range between 1.3 and 12.4 m^2 g^{-1}, for CCB and Meirama fly ashes, respectively (Table 5). This range is in accordance with the usual surface area measurements in fly ashes [33]. The surface area values may be enhanced by several factors such as a high carbon content [34]. This is not the case for the Meirama and As Pontes fly ashes, since their carbon contents are very low (0.6 and 1.4 wt%, respectively). The irregular particle morphology in the Meirama fly ashes coupled with high particle porosity may account for the high surface area value. The other fly ashes do not show any apparent relationship between BET and C contents.

With the exception of the Meirama ash, all samples studied exhibited a conventional fly ash particle morphology (spherical particles of various sizes, cenospheres and plerospheres). However, the Meirama fly ash has a very high proportion of irregularly shaped particles with high micro-porosity, usually grouped in particle agglomerates.

3.4. Glass composition

The chemical and mineralogical data have been combined to elaborate a mass balance for the determination of the chemical composition of the glass matrix (Table 6). The results show that CCB, Escucha and Puertollano have the highest silica concentrations in the glass matrix (60–65 wt%), whereas Lignite has the lowest (31 wt%). The other fly ashes may be classified into two groups according to their silica content of the glass matrix: (a) Alkaline, Amer-8 and 9, Robla, Nijmegen and Sardegna (45–48 wt% silica); and (b) Acid, Barrios, Espiel, Fusina, Hemweg, Meirama, Montfalcone, Narcea, Neutral, Soto and Teruel (50–55 wt%).

Table 6
Chemical composition (major oxides in %) of the glass matrix as computed from the chemical and mineralogical data by using a mass balance over all detected phases

	Glass (%)				
	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3
Acid	51.0	26.8	9.4	2.2	0.6
Alkaline	47.4	16.4	13.0	8.1	0.3
Ameer 8	46.3	26.5	8.4	6.1	1.4
Ameer 9	48.1	24.8	8.6	6.5	0.8
As Pontes	48.0	15.8	13.7	8.7	0.6
Barrios	55.4	13.1	4.7	14.0	<0.1
CCB	59.1	24.9	4.1	0.6	0.2
Compostilla	53.2	26.1	7.4	3.0	0.5
Escucha	59.5	16.5	15.9	3.5	<0.1
Espiel	55.4	27.1	5.4	2.3	0.1
Fusina	51.5	18.7	12.2	1.7	0.8
Hemweg	51.9	25.3	9.5	2.3	0.7
La Robla	47.8	23.6	13.8	7.5	0.3
Lignite	31.4	29.1	8.0	24.4	<0.1
Meirama	50.9	5.4	12.6	17.2	1.1
Montfalcone	54.4	20.3	8.3	3.3	0.4
Narcea	55.4	23.9	6.9	3.7	0.3
Neutral	53.7	22.8	8.5	3.9	0.6
Nijmegen	46.0	26.1	9.9	6.6	1.6
Puertollano	65.5	19.4	7.6	1.2	0.3
Sardegna	45.0	24.7	4.9	9.8	1.1
Soto Rib.	52.0	23.4	8.8	4.0	0.4
Teruel	54.6	15.9	14.7	7.6	<0.1

The silica/alumina ratios of the glass matrices ranged from 9.4 and 4.2 for Meirama and Barrios, respectively to 1.7 and 1.0 for Nijmegen and Lignite, respectively. Most of the glass matrices showed a silica/alumina ratio of between 2.0 and 3.4.

Fig. 2 shows the high silica/alumina/calcium oxide ratio of the glass matrix in Meirama and Barrios and the low silica content of Lignite. The low silica content of Lignite is a consequence of the CaO enrichment of the glass matrix, whereas the high Si/Al ratio of the glass matrix of the Meirama fly ash (on the field of cristobalite in Fig. 2 explains the occurrence of opaline silica formed by devitrification processes. As expected from the common mullite occurrence in the fly ashes, the Si/Al/Ca ratios obtained for the glass matrix of the samples studied are within the phase field for mullite crystallisation (Fig. 2).

There is an upper limit of SiO_2/Al_2O_3 ratio for each glass content in the ash as is shown by the plot of these two properties in Fig. 3. Ashes with high glass content tend to have a low SiO_2/Al_2O_3 ratio. This may be caused by the crystallisation of mullite during the early stages of ash formation. When mullite is separated from an initially homogeneous amorphous phase by fractional crystallisation, the glass residue phase becomes enriched in SiO_2 and the quantity of glass will decrease. The only ash that violates this rule is the Meirama, and this falls outside the diagram ($SiO_2/Al_2O_3 = 9.3$). This limit is applicable because the line

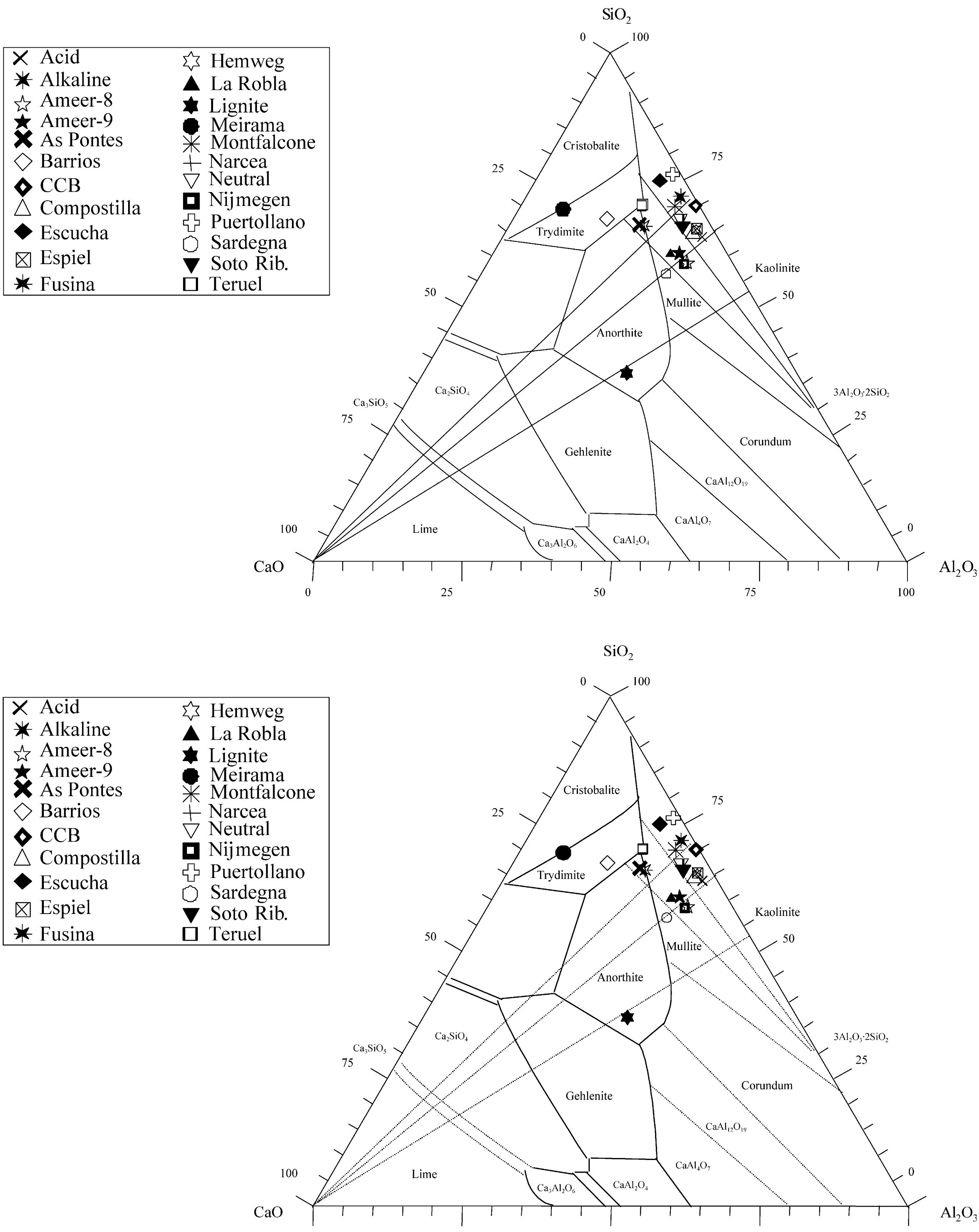

Fig. 2. Chemical composition of the glass matrix obtained from the chemical mass balance using chemical and mineralogical data.

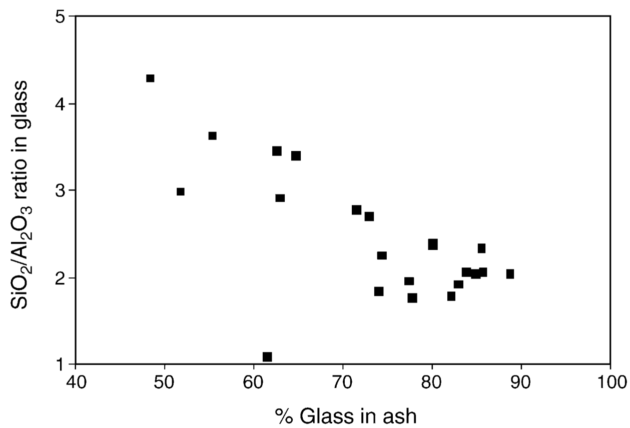

Fig. 3. Relationship between the content of glass in the ashes and the SiO_2/Al_2O_3 ratio in the glass. Note that the Meirama ash falls outside the diagram.

drawn in Fig. 3 intercepts the 100% ash axis at around 2, a value that coincides with the whole rock SiO_2/Al_2O_3 ratio as shown in Table 2 (equivalent to the ratio in glass when the ashes are completely vitrified).

3.5. Thermal de-vitrification

The potential Si/Al excess and the glass reactivity was investigated by de-vitrification induced by thermal treatment (1100 °C). If an aluminium–silicate glass matrix has an excess of SiO_2 over Al_2O_3, the thermal treatment will give rise to de-vitrification resulting in the crystallisation of SiO_2, whereas if the silica is equilibrated with alumina or with calcium or iron oxides, the crystallisation of mullite and anorthite or hercynite will take place. Thus, if the glass crystallises for a given fly ash and gives rise to high temperature silica, the suitability for silica extraction may be inferred due to the high SiO_2 content and high SiO_2/Al_2O_3 ratio of the glass. However, if the thermal treatment results in the crystallisation of mullite or anorthite, the suitability for direct conversion may be inferred because of the balanced SiO_2/Al_2O_3 ratio of the glass.

Furthermore, thermal treatment may enhance silica extraction due to the de-vitrification of relatively soluble silica; or the crystallisation of mullite (a highly insoluble phase) that may account for the immobilisation of alumina.

Table 7 shows the mineral contents of the fly ashes thermally treated at 1100 °C. The major mineral transformations induced in the original fly ash components due to the thermal treatment may be summarised as follows:

- Crystallisation of mullite ($Al_6Si_2O_{13}$) and cristobalite (SiO_2) from the aluminium–silicate glass in fly ash with low Ca contents. Barrios, Meirama, Teruel, Puertollano, Neutral, Fusina and Monfalcone fly ashes resulted in the crystallisation of cristobalite due to the high SiO_2 contents of the glass matrix. Consequently, these fly ashes have the potential for SiO_2 extraction due to the silica excess in the glass matrix.
- Crystallisation of anorthite ($(Ca,Na)(Al,Si)_4O_8$) from the aluminium–silicate glass and the original quartz in the fly ash with higher Ca content (mainly in Barrios, Meirama, Robla, Alkaline, Nijmegen, Amer8, Amer9, Fusina and Sardegna).
- Crystallisation of hercynite ($FeAl_2O_4$) from the alumino-silicate glass in the Soto de Ribera and Narcea fly ashes.
- Oxidation of magnetite (Fe_3O_4) to give hematite (Fe_2O_3).

Table 7
Mineralogical composition of thermally treated fly ash (1100 °C for selected fly ashes)

	Quartz	Cristobalite	Mullite	Feldspar
Narcea	21	10	12	46
Barrios	16	90	49	112
Escucha	22	10	20	9
Meirama	24	200	3	78
Teruel	28	60	24	45
Espiel	5	<1	51	<1
Compostilla	7	<1	18	19
Robla	9	23	5	72
As Pontes	3	19	30	57
Puertollano	48	78	9	<1
Alkaline	38	20	7	92
Nijmegen	22	40	16	80
Neutral	33	272	60	16
CCB	24	<1	37	<1
Acid	13	<1	53	<1
Amer 8	18	35	26	90
Amer 9	40	35	8	70
Hemweg 8	23	<1	29	9
Lignite	14	<1	<1	39
Fusina	19	79	40	112
Monfalcone	51	222	90	14
Sardegna	10	43	35	147

Values correspond to the integrated area of the XRD normalised intensity peaks for each mineral (proportional to the content of each mineral in the fly ash).

3.6. Leaching test

The results of the leaching experiments using the standard DIN-38414 are summarised in Table 8. The following trends are highlighted from the results obtained:

- pH values measured for the leachates ranged from 10.4 to 12.5 for most of the fly ashes in agreement with the free lime content. Acid, Neutral, As Pontes, Meirama and Compostilla gave rise to lower alkalinity leachates (pH from 8.3 and 9.7) and CCB and Puertollano gave rise to slightly acidic leachates (6.4 pH).
- The conductivity of the leachates ranged from 1300 to 1800 μS cm^{-1} for most of the fly ashes. The lowest conductivity values were obtained for Puertollano, Espiel, Acid and CCB (340–680 μS cm^{-1}), whereas Barrios, Alkaline, Lignite, Fusina and Sardegna reached

Table 8
pH, conductivity and leachable contents of major (μg g^{-1}) and trace (ng g^{-1}) elements from fly ashes using the DIN 38414-S4 leaching test

Fly ash	Narcea	Barrios	Escu-cha	Meira.	Teruel	Espiel	Compo.	Robla	As Po.	Soto	Puerto.	Alkalin.	Nij-meg.	Neutral	CCB	Acid	A-8	A-9	Hemwe	Lignite	Fusina	Mon-tfalc.	Sar-denga
PH	11.06	12.20	10.80	9.70	11.43	10.40	9.17	11.50	8.35	11.34	6.40	12.20	11.50	8.32	6.42	8.65	12.04	12.09	11.42	12.3	12.45	11.76	12.54
μS cm^{-1}	1460	4400	1030	2400	2200	430	1160	1600	1600	1410	340	4900	1780	1040	680	650	2800	2800	1500	5050	4800	1300	6600
μg g^{-1}																							
Al	38.3	0.1	218.2	0.2	5.2	114.8	129.1	1.2	87.4	35.9	37.6	0.5	1.5	43.3	5.2	26.3	2.4	2.8	271.0	<0.1	1.8	193.9	18.2
Ca	1648.5	7308.3	1712.6	6178.9	3127.9	618.1	1974.6	4378.3	4759.3	1660.4	537.8	6648.5	2783.5	1772.0	581.5	927.6	3131.5	3535.6	2566.5	7875.7	5680.9	1792.2	8791.6
Fe	3.1	<0.1	0.9	0.1	0.1	9.8	0.4	0.1	2.2	3.3	0.2	0.1	0.2	4.8	1.1	0.3	0.7	0.1	0.2	<0.1	0.3	0.1	2.4
Mg	0.2	0.5	0.8	17.7	0.1	4.8	10.4	0.6	15.4	<0.1	28.7	0.2	0.2	119.2	89.9	90.1	270.0	<0.1	0.1	0.4	0.7	<0.1	4.6
Mn	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1
Mo	3.2	2.8	3.2	0.4	6.7	1.0	3.0	4.7	2.5	3.4	5.1	3.0	4.8	2.6	5.8	3.8	4.2	3.7	6.3	3.3	4.6	6.1	2.2
Na	127.0	37.2	39.7	346.9	39.3	20.3	176.1	91.1	325.2	92.7	23.9	417.6	265.5	10.1	236.2	167.8	339.9	183.3	267.7	32.9	70.6	103.4	55.2
P	1.0	1.4	1.3	<0.1	2.6	2.7	3.7	<0.1	0.5	1.5	5.5	2.4	2.0	6.1	1.1	0.9	1.4	0.9	5.5	2.7	0.6	0.4	5.3
S	880.6	643.9	831.2	5419.2	1194.3	208.8	1799.2	2535.9	4341.8	821.5	415.2	2109.1	1465.1	1668.4	664.1	1059.9	1200.2	974.6	2013.9	3505.7	583.0	772.6	917.9
Si	49.0	35.8	25.0	410.3	52.7	139.5	34.9	67.5	44.4	92.5	43.9	51.1	69.9	35.0	35.2	23.7	56.9	53.1	41.7	19.9	37.9	35.5	53.4
ng g^{-1}																							
As	260	13	315	1211	212	685	415	107	890	304	12374	44	64	370	511	958	64	51	176	10	11	138	14
B	3796	1504	120486	13769	80860	35262	13250	3537	36860	16789	43548	19230	27781	51840	9839	25345	21056	32445	69056	1697	10083	106423	20209
Ba	2992	15251	2691	1271	2094	1083	204	3357	3746	1747	68	6370	7552	1878	1194	280	7870	14017	7958	3586	18435	5001	14076
Be	1	2	5	2	5	5	2	2	3	2	4	1	2	3	6	2	3	3	3	2	1	5	5
Cd	3	5	5	<1	13	<1	6	12	6	5	11	6	7	7	24	10	4	7	14	8	5	14	3
Co	7	27	8	23	15	14	9	18	21	8	4	36	11	27	119	6	17	19	13	37	28	9	53
Cr	9221	5039	410	202	2825	1834	2730	5702	249	3412	494	3112	3433	1727	17	1055	4134	2316	2184	9264	2524	1623	5310
Cs	32	17	6	3	6	23	20	23	28	13	8	157	36	1	5	7	40	9	20	148	12	6	20
Cu	37	45	35	97	44	55	88	70	97	36	43	57	43	341	55	38	46	42	75	93	42	31	94
Ga	292	7	477	4	303	159	152	37	164	491	191	8	47	361	3	296	17	227	1160	1	10	719	28
Ge	1	<1	11	2	1	57	5	1	19	4	1029	3	1	128	58	70	1	6	19	<1	<1	2	9
Hf	10	10	12	11	10	14	10	10	10	9	9	9	10	10	10	10	10	9	9	10	9	10	12
Li	11189	23559	10500	592	18201	7367	10743	12689	9736	9338	5895	9454	16232	4553	4983	17499	21984	14267	15674	2062	12663	11059	21475
Mo	2981	2740	3031	349	6441	952	2848	4497	2390	3201	4705	2899	4875	2431	5480	3594	4113	3755	6171	3264	4419	6558	2374
Nb	12	11	8	9	8	14	5	6	8	5	4	5	4	4	5	4	4	4	3	3	3	2	12
Ni	61	289	78	209	142	61	97	168	175	76	29	223	105	158	513	45	132	156	97	334	246	72	402
Pb	11	8	11	7	6	46	8	13	23	10	9	8	5	32	19	5	9	7	8	5	9	9	32
Rb	378	80	160	60	149	200	572	419	535	342	57	358	237	8	187	177	262	116	631	1833	70	85	71
Sb	195	10	101	20	10	449	474	9	113	50	5672	15	9	115	227	618	7	8	111	6	5	48	7
Sc	31	33	23	227	50	91	21	39	22	59	27	30	45	21	18	12	35	43	29	20	31	28	59
Se	208	45	384	216	171	948	258	254	1916	534	572	806	219	2097	3661	976	180	1654	2750	109	242	285	184
Sn	9	7	9	7	8	10	7	6	7	7	6	5	5	8	6	5	6	6	7	5	5	6	13
Sr	7699	144630	17368	35076	36714	2616	2595	21577	33167	8292	66	35809	92212	9201	12717	7746	95493	59735	19586	66096	169019	24406	269859
Th	11	11	8	8	11	16	11	8	9	9	7	9	10	10	10	9	11	7	7	8	8	10	18
Ti	180	129	141	793	243	1235	275	364	729	215	106	322	272	894	284	206	313	191	337	589	184	147	1670
Tl	2	2	2	3	3	7	1	8	1	2	1	3	4	1	19	23	1	4	5	4	3	3	4
U	2	5	4	4	7	11	6	1	12	3	4	2	4	2	8	7	<1	5	1	2	2	5	10
V	1950	51	1566	2698	1014	4062	865	611	1117	2476	1886	92	640	1048	1140	489	563	300	1084	163	358	2778	149
Zn	724	131	639	173	196	269	630	315	321	158	186	138	292	439	476	105	116	141	126	138	115	150	239

very high values (4400–6600 μS cm^{-1}). The conductivity values are directly related to the free lime (leachable Ca) and leachable sulphate. Thus leachable Ca contents ranged from 6000 to 9000 μg g^{-1} for the last group of fly ashes.

- The leachable Si contents were found in the range of <140 μg g^{-1} with the exception of Meirama (400 and 140 μg g^{-1}) due to the presence of soluble opaline phases.
- The elements with environmental importance, such as As, B, Ba, Cr, Mo, Se, Sr and V showed the highest mobility during the leaching tests. Thus, Puertollano contained 12 μg g^{-1} of soluble As. Escucha, Teruel, Hemweg and Montfalcone contained from 60 to 120 μg g^{-1} of soluble B. Barrios, Sardegna, Fusina and Amer 9 contained around 15 μg g^{-1} of soluble Ba, Lignite, Sardegna, Amer 8, Robla Barrios and Narcea contained from 4 to 9 μg g^{-1} of soluble Cr. Fusina, Montfalcone, Hemweg, CCB, Nijmegen, Puertollano, Robla and Teruel contained around 5μg g^{-1} of soluble Mo. Neutral, CCB, Ameer-9, Hemweg and As Pontes contained around 3 μg g^{-1} of soluble Se. Barrios, Nijmegen, Ameer 8 and 9, Lignite, Fusina and Sardegna contained from 60 to 270 μg g^{-1} of soluble Sr. Monfalcone, Soto, Meirama and Espiel contained around 3 μg g^{-1} of soluble V.

Based on these results, Puertollano, Montfalcone, Fusina, Lignite, Amer 8 and 9, Sardegna and Nijmegen may have limitations for direct zeolitisation due to the relatively high levels of leachable trace elements, however, this is not a concern for other applications (such as zeolite synthesis from silica extracts).

It may be concluded that these ranges of leached elements are representative of European fly ashes because they match the results of four UK fly ashes summarised previously [21].

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References

[1] Ecoba 2002, http://www.ecoba.com.

[2] Anderson M, Jackson G. The beneficiation of power station coal ash and its use in heavy clayware ceramics. Br Ceram Trans J 1983;82: 34–42.

[3] Stoch L, Kordek M, Nadachowski F. Processing of some non-conventional ceramic raw materials and by-products. Ceram Int 1986; 12:213–20.

[4] Queralt I, Querol X, López-Soler A, Plana F. Use of coal fly ash for ceramics: a case study for a large Spanish power station. Fuel 1997; 76:787–91.

[5] Höller H, Wirsching U. Zeolites formation from fly ash. Fortschr Miner 1985;63:21–43.

[6] Shigemoto N, Shirakami S, Hirano S, Hayashi H. Preparation and characterisation of zeolites from coal ash. Nippon Kagaku Kaishi 1992;5:484–92.

[7] Berkgaut V, Singer A. High capacity cation exchanger by hydrothermal zeolitization of coal fly ash. Appl Clay Sci 1996; 10:369–78.

[8] Querol X, Alastuey A, López Soler A, Plana F, Andrés JM, Juan R, et al. A fast method for recycling fly ash: microwave-assisted zeolite synthesis. Environ Sci Technol 1997;31:2527–33.

[9] Park M, Choi CL, Lim WT, Kim MC, Choi J, Heo NH. Molten-salt method for the synthesis of zeolitic materials. I. Zeolite, formation in alkaline molten-salt system. Micropor Mesopor Mater 2000;37:81–9.

[10] Park M, Choi CL, Lim WT, Kim MC, Choi J, Heo NH. Molten-salt method for the synthesis of zeolitic materials. II. Characterization of zeolitic materials. Micropor Mesopor Mater 2000;37: 91–8.

[11] Moreno N, Querol X, Plana F, Andrés JM, Janssen M, Nugteren H. Pure zeolite synthesis from silica extracted from coal fly ashes. J Chem Tech Biotech 2002;77:274–9.

[12] Andres A, Ortiz I, Viguri JR, Irabien A. Long-term behavior of toxic metals in stabilized steel foundry dusts. J Hazard Mater 1995;40: 31–42.

[13] Dirk G. Pulverized fuel ash products solve the sewage sludge problems of the wastewater industry. Waste Manage 1996;16:51–8.

[14] Jarvis ST, Brooks TG. The use of PFA: cement pastes in the stabilisation of abundant mineworkings. Waste Manage 1996;16: 135–44.

[15] Garea A, Viguri JR, Irabien A. Kinetics of flue gas desulphurization at low temperatures: fly ash/calcium (3/1) sorbent behavior. Chem Eng Sci 1997;52:715–32.

[16] Kruger RA. Fly ash benefication in South Africa: creating new opportunities in the market place. Fuel 1997;76:777–9.

[17] Reynolds KA, Kruger RA, Rethman NFG., The manufacture and evaluation of an artificial soil (SLASH) prepared from fly ash and sewage sludge. 1999 International ash utilization symposium, Lexington, KY, USA. p. 378–85.

[18] Pickles CA, Mclean A, Alcock CB, Nikolic RN. Plasma recovery of metal values from fly ash. Can Metal Q 1990;29:193–200.

[19] Font O, Querol X, Plana F, López-Soler A, Chimenos JM, March MJ, Espiell F, Burgos S, García F, Alliman C., Occurrence and distribution of valuable metals in fly ash from Puertollano IGCC power plant, Spain. 2001 International ash utilization symposium, 22nd–24th October, Hyatt Regency Lexington, Lexington, KY, USA.

[20] Mc Carthy MJ, Tittle PAJ, Dhir RK. Characterization of conditioned pulverized-fuel ash for use as a cement component in concrete. Mag Concrete Res 1999;51:191–206.

[21] UKQAA, Assessment of the leaching risk to the environment from the use of pulverised fuel ash (PFA); January 2003. p. 45.

[22] SILEX project, final report 2002: Recovery of major elements from coal fly ashes (BRPR-CT98-0801).

[23] Querol X, Whateley MKG, Fernández-Turiel JL, Tuncali E. Geological controls on the mineralogy and geochemistry of the Beypazari lignite, Central Anatolia, Turkey. Int J Coal Geol 1995; 33:255–71.

[24] Tait J, Ault L. Development of analytical procedures for the determination of major and trace elements in geological materials by ICP-ES. Analytical Geochemistry Series, Technical Report WI/92/8. British Geological Survey; 1992. p. 72.

[25] Chung FH. Quantitative interpretation of x-ray diffraction patterns of mixture iii: simultaneous determination of a set of reference intensities. J Appl Crystalogr 1974;7:17–19.

[26] Chung FH. Quantitative interpretation of x-ray diffraction patterns of mixture i and ii: matrix flushing method for quantitative multi-component analysis. J Appl Crystalogr 1974;7:519–31.

[27] Ramirez de Diego C., Características y Propiedades de Cenizas Volantes, alternativas para su uso. Memoria. CSIC-UB;1991. p. 130.

[28] Querol X, Fernández-Turiel JL, López Soler A. The behaviour of mineral matter during combustion of Spanish subbituminous and brown coals. Miner Mag 1994;58:119–33.

[29] Mollah MYA, Cocke DL, Promreuk S, Schennach R. Cristobalite formation from thermal treatment of Texas lignite fly ash. Fuel 1999; 78:1277–82.

[30] DIN 38414-S4. Institut für Normung, Berlin 1984.

[31] ASTM C618-92a. Standard specification for fly ash and raw or calcinated natural pozzoland for use as mineral admixture in portland cement concrete. American Society for Testing and Materials, Annual book of ASTM Standards, vol 04.02, Pennsylvania; 1994.

[32] Hemmings RT, Edwin E.B., Speciation in size and density fractionated fly ash. In: Fly ash and coal conversion by-products: characterisation, utilisation and disposal, vol. II. Materials research society symposia proceedings, 1985;65:91-104.

[33] Davini P. Investigation of flue gas desulfurization by fly ash and calcium hidroxide mixtures. Resour, Conserv Recy 1995;15: 193–201.

[34] Luxán MP, Sánchez de Rojas MI, Soria F., Characterisation and reactivity of Spanish fly ashes. Second international conference on the use of fly ash, silica fume, slag and natural puzzolans in concrete; 1986. p. 8.