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Determining suitability of a fly ash for silica extraction and zeolite synthesis

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Abstract: Zeolitic material is obtained from fly ash both by direct conversion of the ash or from SiO₂ extracts obtained from fly ash. This study focuses on determining the suitability of a fly ash for SiO₂ extraction and for zeolite synthesis by direct conversion. The SiO₂ extraction experiments from different fly ashes show that the main parameters governing the SiO₂ extraction are: (a) a high bulk SiO₂ content (>52%, for obtaining an extraction yield of 100 g SiO₂ kg⁻¹) in the starting fly ash, (b) a high proportion (>55%) of the bulk SiO₂ present in the degradable glass matrix and the highly soluble opaline fraction, and (c) a high bulk SiO₂/Al₂O₃ ratio (>2.0) of the fly ash. The results from experiments of zeolite synthesis by direct conversion demonstrate that the most important criteria for the selection of a fly ash for this process are: (a) a high content of Al₂O₃ and SiO₂ (>65%) (b) a high glass content (>63%) and (c) relatively low SiO₂/Al₂O₃ ratio (<2.0). Multivariate analysis confirms the importance of the above-mentioned variables and shows some additional variables that have influence on ash behaviour under alkaline conditions. It quantifies the use of those variables for determining the suitability of ashes for SiO₂ extraction and zeolite synthesis and is able to distinguish between the two.

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Keywords: fly ash; zeolite synthesis; SiO₂ extraction

INTRODUCTION

The direct conversion of coal fly ash into a zeolitic material has been widely studied at laboratory^{1–7} and at pilot plant scale.^{8–9} All these methodologies are based on a direct alkaline hydrothermal activation that differs in the molarity of the alkaline reagents (mainly KOH and NaOH), solution/fly ash ratio, temperature (80–200 °C), time (3–48 h) and pressure (vapour pressure at the different temperatures tested). In addition, microwave- or ultrasound-assisted processes have been tested to reduce the activation time down to the scale of minutes.¹⁰ All these conversion procedures have the drawback that the final product is a mixture of zeolites and residual non-reacted fly ash components. For this reason, a new process was introduced by Hollman *et al.*,¹¹ which synthesised 'pure zeolites' using a two-step procedure based on an initial SiO₂ extraction from fly ash, followed by the synthesis of pure zeolites by combining the leachates with high-Al solutions. This method allows a product to be obtained with >99% of zeolite content. Moreno

and Colleagues^{12,13} improved SiO₂ extraction yields and obtained simultaneous zeolite synthesis of the residue. These studies fixed the conditions for pure zeolite synthesis from SiO₂ extracts (with a cation exchange capacity, CEC, of 5 meq g⁻¹) as follows: (a) gelification at 60 °C for 15 min of a mixture of reactants with the following molar ratios: Na₂O/SiO₂ = 1.3, SiO₂/Al₂O₃ = 1.7 and H₂O/Na₂O = 41.0, and (b) crystallisation at 90 °C for 8 h.

SiO₂ and Al₂O₃ in fly ash are found in the dominant aluminosilicate glassy matrix, in opaline SiO₂ and various crystalline phases such as mullite, quartz, and feldspar. Other species present in fly ash such as unburned carbon, magnetite, haematite, lime and Ca-sulfates are considered as impurities for the present work as they do not contribute to zeolite formation. The SiO₂ and Al₂O₃ bearing phases may be classified according to their solubility potential (in the alkaline environment) as follows: glass = opaline silica > tridymite – cristobalite > quartz > feldspar > mullite.¹⁴

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In addition to this inherent solubility gradient, the following factors may influence the SiO_2 and Al_2O_3 extraction process:

- The dissolution of SiO_2 and Al_2O_3 from fly ash particles is favoured by using alkaline extractants. Using extractants with $\text{pH} > 10$, both SiO_2 and Al_2O_3 may be extracted from fly ash particles.¹⁵ However, Querol *et al*⁸ indicated that for high NaOH or KOH/fly ash ratios the formation of sodalite or cancrinite in the residue is favoured, both with little industrial applicability. Thus, if the residue is intended to be used as a low efficiency ion exchange material, such high ratios must be avoided in order to form high CEC zeolites in the residues.
- Similar limitations are considered for temperature (T). The dissolution of SiO_2 and Al_2O_3 phases increases with temperature, but if $T > 120^\circ\text{C}$ then increased Al_2O_3 dissolution and over-saturation of the extracts results. Also, the energy input is much higher than the zeolite activation energy and provokes excessive zeolite formation. In addition, the probability of synthesising low CEC products (analcime, sodalite, cancrinite) is enhanced at $T > 150^\circ\text{C}$ and at high alkaline concentrations.⁸ The process has to focus on the high $\text{Al}^{3+}/\text{Si}^{4+}$ zeolite synthesis in order to obtain high CEC zeolites.
- The use of high alkaline solution/fly ash (L/S) ratios may also enhance the extraction yield. However, on the basis of economic criteria, this ratio should be kept at 2–3 dm^3 per kilogram of fly ash.
- The extraction time has also an important influence on the extraction¹³ yield of SiO_2 and Al_2O_3 . Obviously, the extraction or conversion time for high glass fly ashes will be lower than that needed for obtaining the same extraction/conversion yields with high mullite and/or quartz fly ashes.

Comparison of experimental data from direct conversion/zeolite synthesis and SiO_2 extraction experiments using a wide variety of coal fly ashes with known characteristics are used in this study to investigate the major parameters governing the suitability of a given fly ash for either direct conversion or SiO_2 extraction.

METHODOLOGY

Selection of fly ashes

Twenty-three fly ashes from different European pulverised coal-fired (PC) power plants were selected for this study (Table 1). This selection covered most of the types of PC fly ash produced in the EU, from the high calcium Tertiary lignite fly ash produced at several Greek power plants, the high sulfur sub-bituminous Cretaceous coal and lignite fly ashes produced in several plants in Spain, to the more common Permo-Carboniferous bituminous and anthracite fly ash. Full characterisation of these fly ashes was undertaken^{12,16} and Table 1 summarises the results. Samples were considered to be representative of the production at

each power plant fly ash and were supplied by the power generation company.

SiO_2 extraction and zeolite synthesis tests

The SiO_2 extraction tests were carried out with the following extraction procedures:

- Closed heated system in 60 cm^3 Savillex PFA reactors. The experiments were carried out at 90°C . This process was repeated up to three times with the solid residue resulting from the extraction test to determine the theoretically maximal SiO_2 extraction.
- Closed heated system using a 2 dm^3 Parr 4843 autoclave reactor with continuous stirring, and temperature and pressure controls. This system has the facility of direct sampling of the reactants without stopping the extraction process. Samples of the extractants and the solid residue were obtained hourly for the first 9 h. The reaction was also sampled at the end of the 24 h experiment.
- SiO_2 extraction with microwave assistance. The extraction tests were carried out in a Milestone MLS-1200 MEGA laboratory microwave oven.

The experimental conditions selected for this study were: (a) for conventional extraction: stirring, temperature at 90 and 120°C , reaction time from 2 to 24 h, 2 and 3 mol dm^{-3} NaOH with an alkaline solution/fly ash ratio between 2 and 3 $\text{cm}^3 \text{g}^{-1}$, and (b) for microwave extraction: 1000 W, temperature between 140 and 185°C , reaction time from 3 to 8 min, and NaOH/ Na_2CO_3 solutions with an alkaline solution/fly ash ratio between 4.4 and 8.6 $\text{cm}^3 \text{g}^{-1}$. Although the preliminary SiO_2 extraction experiments were applied to all fly ashes in this study, the optimisation of the extraction and the direct conversion processes focused on five selected fly ashes. This selection covered the whole range of SiO_2 contents in the vitreous phase, as well as the selection of fly ashes containing highly soluble opaline silica. The following fly ashes were selected: Alkaline (47.0% of the glass phase composed of SiO_2); Meirama (50.9% of glass composed of SiO_2 and 4.5% of opaline silica); Neutral (53.7% of glass composed of SiO_2); Monfalcone (54.4% of glass composed of SiO_2 and 0.5% of opaline silica), and Puertollano (65.5% of glass composed of SiO_2).

The presence of zeolitic material in the solid residue obtained in all the SiO_2 extraction experiments was investigated. Furthermore, the different zeolite synthesis yields in direct conversion experiments were investigated under the following conversion conditions: NaOH 3 mol dm^{-3} , 125°C , 8 h and alkaline solution/fly ash ratio of 2 $\text{dm}^3 \text{kg}^{-1}$.

Analysis

The concentrations of Si, Al, Na and other major and trace elements in the extraction solutions were determined by Inductively Coupled Plasma Atomic

Table 1. Fly ash selected and sampled in this study alongside details of the power plant capacity, the power company and the power plant location, and major chemical and mineralogical composition

Power station	Power (MW)	Power company (location)	Chemical composition (wt%)										Mineralogical composition (wt%)					Composition of glass fraction (wt%)				
			SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	MnO	SO ₃	Glass	Mullite	Quartz	Opal	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	SO ₃
Acid	600	EPZ (The Netherlands)	51.3	28.9	8.4	1.8	1.0	0.5	2.5	0.2	1.5	0.02	0.5	83.1	9.1	6.0	<0.3	51.0	26.8	9.4	2.2	0.6
Alkaline	450	EPZ (The Netherlands)	46.8	24.8	9.0	6.8	3.7	1.2	2.0	0.7	0.9	0.10	1.0	63.1	20.1	11.2	<0.3	47.4	16.4	13.0	8.1	0.3
Amer-8	600	Amer Centrale (The Netherlands)	45.2	26.5	7.1	6.1	1.6	0.8	1.2	1.1	1.3	0.04	1.1	77.8	8.2	6.9	<0.3	46.3	26.5	8.4	6.1	1.4
Amer-9	600	Amer Centrale (The Netherlands)	52.4	25.8	7.0	5.6	1.6	0.7	1.4	0.9	1.3	0.05	0.6	77.4	9.1	12.5	<0.3	48.1	24.8	8.6	6.5	0.8
As Pontes	1400	ENDESA (NW Spain)	41.5	30.1	12.6	5.6	1.6	0.6	1.9	0.2	0.6	0.10	1.4	51.8	29.4	6.2	<0.3	48.0	15.8	13.7	8.7	0.6
Barrios	550	ENDESA (S Spain)	42.6	35.6	2.6	8.4	2.1	0.3	0.6	1.7	1.6	0.10	0.6	48.4	40.4	3.4	<0.3	55.4	13.1	4.7	14.0	<0.1
CCB	600	Centrale Borssele (The Netherlands)	59.6	27.0	3.3	0.5	0.9	0.3	2.9	0.1	1.4	0.02	0.2	80.1	9.8	9.4	<0.3	59.1	24.9	4.1	0.6	0.2
Compostilla	1312	ENDESA (N Spain)	51.2	25.5	7.5	2.8	2.0	0.8	3.9	0.4	0.9	0.10	0.6	88.8	3.2	3.1	<0.3	53.2	26.1	7.4	3.0	0.5
Escucha	160	ENDESA (NE Spain)	49.5	26.7	12.3	2.3	0.9	0.3	1.9	0.2	0.9	0.03	0.3	55.5	24.4	9.6	<0.3	59.5	16.5	15.9	3.5	<0.1
Espiel	938	ENECO (S Spain)	52.3	28.5	5.9	2.0	1.5	0.5	4.0	0.4	1.0	0.10	0.1	85.7	7.4	2.7	<0.3	55.4	27.1	5.4	2.3	0.1
Fusina	980	ENEL spa (Italy)	48.2	25.9	8.8	2.3	1.5	0.5	2.6	0.3	1.3	0.05	0.6	71.6	17.4	6.4	<0.3	51.5	18.7	12.2	1.7	0.8
Hermweg-8	600	Centrale Amsterdam (The Netherlands)	53.2	26.0	8.6	2.4	1.6	0.5	2.7	0.3	1.3	0.05	0.6	83.9	6.6	7.8	<0.3	51.9	25.3	9.5	2.3	0.7
Lignite	Not available	Amyntaion and LKPA (N Greece)	28.5	17.9	8.4	27.3	3.8	0.2	1.0	0.3	1.0	0.04	8.6	61.5	<0.3	9.2	<0.3	31.4	29.1	8.0	24.4	<0.1
Meirama	550	Unión FENOSA (N Spain)	49.2	17.6	10.4	11.8	2.0	0.4	0.4	0.2	0.5	0.10	2.2	62.5	19.6	6.9	4.5	50.9	5.4	12.6	17.2	1.1
Montfalcone	336	ENEL spa (Italy)	50.8	33.4	6.4	2.4	0.8	0.4	0.7	0.3	2.6	0.02	0.3	73.1	25.9	3.2	0.5	54.4	20.3	8.3	3.3	0.4
Narcea	569	Unión FENOSA (N Spain)	55.2	23.3	6.9	4.0	2.5	0.7	3.8	0.3	0.9	0.10	0.4	85.6	3.8	6.6	<0.3	55.4	23.9	6.9	3.7	0.3
Neutral	600	EPZ (The Netherlands)	53.3	26.1	7.4	3.1	0.6	0.1	0.6	1.5	1.8	0.06	0.5	80.1	10.9	7.1	<0.3	53.7	22.8	8.5	3.9	0.6
Nijmegen	600	Centrale Gelderland (The Netherlands)	45.3	25.0	8.8	6.4	1.4	0.8	1.1	1.0	1.3	0.04	1.3	82.2	4.9	6.1	<0.3	46.0	26.1	9.9	6.6	1.6
Puertollano	220	ENECO (Central Spain)	58.6	27.4	7.3	0.8	1.0	0.3	2.4	0.1	0.7	0.10	0.2	64.7	20.7	10.4	<0.3	65.5	19.4	7.6	1.2	0.3
Robla	625	Unión FENOSA (N Spain)	44.1	23.2	14.3	8.9	1.8	0.3	2.6	0.8	0.9	0.10	1.1	84.9	4.2	1.7	<0.3	47.8	23.6	13.8	7.5	0.3
Sardagna	Not available	ENEL SpA (Italy)	41.7	29.0	3.8	10.0	2.4	0.5	0.8	1.5	1.7	0.08	0.9	74.0	14.5	4.0	<0.3	45.0	24.7	4.9	9.8	1.1
Soto Ribera	672	IBERDROLA/EBierzo (N Spain)	48.9	30.6	7.2	3.0	1.6	0.6	3.9	0.1	0.8	0.00	0.3	74.4	18.4	5.0	<0.3	52.0	23.4	8.8	4.0	0.4
Teruel	1050	ENDESA (NE Spain)	48.3	23.9	16.0	5.4	1.0	0.2	1.4	0.2	0.8	0.04	0.8	62.7	19.4	8.6	<0.3	54.6	15.9	14.7	7.6	<0.1

Emission Spectrometry (ICP-AES) and the crystalline phases present in the solid residue resulting from each experiment (both direct conversion and SiO₂ extraction tests) were analysed by means of X-ray diffraction (XRD). After identification of major crystalline phases, including neomorphic zeolite phases, the normalised intensity values of major XRD reflections (proportional to its content in the sample) were obtained from each phase to compare the efficiencies of dissolution of the original phases and zeolite synthesis yields from the different experiments.

Multivariate analysis, using the extraction and synthesis yields, as well as selected chemical and mineral patterns, was conducted to identify the main fly ash patterns controlling the silica extraction and zeolite synthesis yields.

RESULTS AND DISCUSSION

Silica extraction

From all results obtained from the SiO₂ extraction experiments, the following optimal conditions for the selected fly ashes, using a conventional single extraction step procedure were obtained: 120 °C, 3 mol dm⁻³ NaOH, liquid/solid ratio 3 dm³ kg⁻¹ and from 2 to 10 h, depending on the fly ash (7 h for Alkaline, 2 h for Meirama, 5 h for Monfalcone, 10 h for Neutral and 9 h for Puertollano). The SiO₂ extraction yields reached: 87, 179, 186, 166 and 405 g kg⁻¹ fly ash for Alkaline, Meirama, Monfalcone, Neutral and Puertollano fly ashes, respectively (Table 2). The fastest SiO₂ extraction was obtained from the Meirama fly ash with 180 g SiO₂ kg⁻¹, equivalent to 540 g of 4A zeolite kg⁻¹, reached in only 2 h; most likely due to the presence of soluble opaline phases. Furthermore, these optimal extraction conditions also favour the

crystallisation of neomorphic zeolites in the solid residue. Crystallisation of these zeolites consumed all dissolved Al₂O₃ and consequently also part of the dissolved Si, but when the soluble portion of the ash has an excess of SiO₂ over Al₂O₃, this results in both SiO₂ extraction and zeolite formation. This is a key result since a high SiO₂ extraction and a zeolitised residue are obtained in a relatively short time using a single step process.

Using microwave-assisted extraction procedures, very high extraction yields were reached during the experimental optimisation of the process. Extractions of 138–358 g SiO₂ kg⁻¹ fly ash were attained in a very short time (3–8 min, Table 2). However, the limitations of the process are: (a) high water consumption (from 4 to 9 dm³ kg⁻¹), (b) the high NaOH and Na₂CO₃ concentrations needed results in a high Na/Si ratio in the extracts (and so low CEC zeolitic materials may be obtained from these leachates), and (c) the costs of scaling up the laboratory reactor for industrial SiO₂ extraction.

When the optimal conditions determined for direct zeolite conversion were used for the SiO₂ extraction experiments, very low extraction yields (<25 g SiO₂ kg⁻¹) were obtained for most conditions of synthesis. This is due to the incorporation of most of the SiO₂ into zeolite in the solid residue.

Although a wide data scatter was noticed when relating the results of SiO₂ extraction yields to the ash properties found during characterisation of the fly ashes, the results allowed the identification of the following decisive factors favouring the SiO₂ extraction process:

- The first parameter to be considered is the bulk SiO₂ content in the fly ash. A high correlation with the SiO₂ extraction yields obtained for the optimal

Table 2. Optimised SiO₂ extraction parameters for the selected fly ashes using conventional extraction procedures and the microwave-assisted method

Conventional	T (°C)	t (h)	L/S (dm ³ kg ⁻¹)	NaOH (mol dm ⁻³)	SiO ₂ extr (g kg ⁻¹)	
Puertollano	90	9	3	2	140	
Meirama	90	4	3	2	111	
Monfalcone	90	4	3	2	99	
Neutral	90	9	3	2	99	
Alkaline	90	5	3	2	51	
Puertollano	120	9	3	3	405	
Meirama	120	2	3	3	179	
Monfalcone	120	5	3	3	186	
Neutral	120	9	3	3	166	
Alkaline	120	7	3	3	87	
Microwave	T (°C)	t (min)	L/S (dm ³ kg ⁻¹)	NaOH (mol dm ⁻³)	Na ₂ CO ₃ (mol dm ⁻³)	SiO ₂ extr (g kg ⁻¹)
Puertollano	174	8	5.8	5.0	1.5	358
Meirama	148	5	8.6	3.5	1.0	239
Monfalcone	159	5	6.7	5.0	2.0	226
Compostilla	185	5	6.5	7.0	2.0	183
Alkaline	143	3	4.4	7.0	2.0	138

extraction conditions for each of the five selected fly ashes is found (Fig 1(a) and Table 2). The linear relationship between the bulk SiO_2 content ($\text{SiO}_{2\text{bulk}}$, in %) and the SiO_2 extraction yield (EY_{Si} , in $\text{g SiO}_2 \text{ kg}^{-1}$ fly ash) for the different extraction conditions are:

$$90^\circ\text{C} \quad EY_{\text{Si}} = 6.0 \times \text{SiO}_{2\text{bulk}} - 211 (R^2 = 0.71)$$

$$120^\circ\text{C} \quad EY_{\text{Si}} = 24.4 \times \text{SiO}_{2\text{bulk}} - 1055 (R^2 = 0.85)$$

$$\text{Microwave} \quad EY_{\text{Si}} = 17.1 \times \text{SiO}_{2\text{bulk}} - 650 (R^2 = 0.84)$$

From these equations it can be concluded that to obtain an extraction yield of $100 \text{ g SiO}_2 \text{ kg}^{-1}$, the bulk SiO_2 content of the starting fly ash has to be at least >52 and $>47\%$ when using optimal extraction conditions at 90 and 120°C , respectively or $>44\%$

when using an optimised microwave extraction (140 – 185°C , depending on the fly ash).

If the 23 fly ashes are considered for the starting extraction (90°C , 2 mol dm^{-3} , liquid/solid ratio $3 \text{ dm}^3 \text{ kg}^{-1}$, 6 h, with multiple consecutive extraction steps, Table 3 with the residue), the following relationship is found (Fig 1(c)):

$$EY_{\text{Si}} = 5.7 \times \text{SiO}_{2\text{bulk}} - 188 (R^2 = 0.65)$$

- Fig 1(b) shows that, in addition to the bulk SiO_2 content, the SiO_2 in ‘reconstituted’ glass content (%) is another parameter that significantly controls the SiO_2 extraction potential. The value for ‘% SiO_2 in glass + SiO_2 as opal’ is only different from % SiO_2 in glass for the Meirama and Monfalcone ashes since these are the only ashes having opaline silica in amounts detectable by XRD (Table 1). The opaline phase has been formed after sampling as a devitrification product of the glass.^{12,16} This means that for Meirama the original quantity of glass was not 62.5% but $62.5 + 4.5 = 67 \text{ g}/100 \text{ g}$ (assuming equal density for opaline silica and glass).

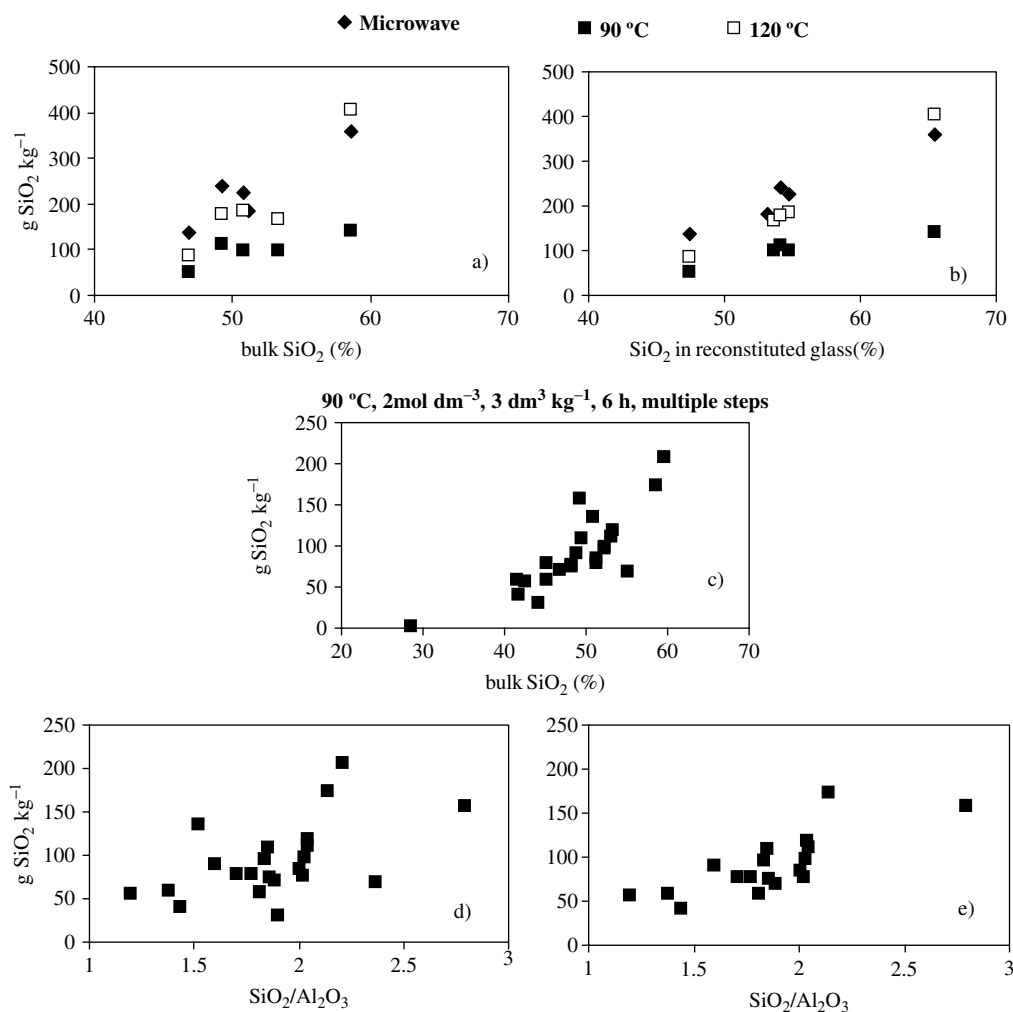


Figure 1. Top, correlation between the SiO_2 extraction yields obtained under optimised conditions for the selected fly ashes and the bulk SiO_2 content in fly ash (a) and the SiO_2 content of glass+ the opaline SiO_2 (b). Middle, correlation between the SiO_2 extraction yields, for the all fly ashes (c), obtained at 90°C , 2 mol dm^{-3} , liquid/solid ratio $3 \text{ dm}^3 \text{ kg}^{-1}$, 6 h, with consecutive extraction steps with the residue and the bulk SiO_2 content in fly ash. Bottom, correlation between $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in bulk fly ashes and SiO_2 extraction yields obtained with the all fly ashes (d) and excluding Narcea, Monfalcone, CCB and Robla (e), at 90°C , 2 mol dm^{-3} , liquid/solid ratio $3 \text{ dm}^3 \text{ kg}^{-1}$, 6 h, with multiple consecutive extraction steps.

Table 3. Continued steps of SiO₂ extraction with stirring fixed conditions at NaOH 2 mol dm⁻³, 90 °C, 6 h and solution/fly ash ratio of 3 dm³ kg⁻¹ (values are Na con (calculated Na consumption in the process with respect to the original NaOH extractant input), extraction yields, equivalent potential pure A zeolite and XRD normalised intensities (counts per second) of major reflections of crystalline phases in the solid residue and XRD background at 22 and 29° 2θ (representing the amorphous phase))

Fly ash	Step	Extraction yields				Solid residue XRD intensity (counts s ⁻¹)					
		Na con (%)	SiO ₂ (g kg ⁻¹)	Al ₂ O ₃ (g kg ⁻¹)	A zeo (g kg ⁻¹)	Glass	Quartz	Mullite	A Zeo	NaP1	Herschelite
Acid	I	42	47	<0.1	142	375	42	36	6	122	<1
	II	19	31	—	94	360	51	48	5	218	<1
Alkaline	I	31	48	—	145	363	59	25	<1	118	<1
	II	28	11	0.4	32	349	68	32	<1	154	<1
	III	20	11	0.7	33	341	94	26	<1	161	<1
Amer-8	I	31	61	<0.1	185	294	42	18	<1	91	<1
	II	7	17	—	52	382	79	55	<1	153	<1
Amer-9	I	32	76	<0.1	230	336	88	29	6	131	<1
	II	23	22	—	67	356	87	48	4	180	<1
As Pontes	I	40	40	—	120	313	30	22	<1	92	<1
	II	4	13	0.5	40	273	36	30	<1	128	<1
	III	12	6	1	19	300	37	38	<1	145	<1
Barrios	I	33	42	—	128	404	17	74	<1	103	<1
	II	24	9	0.5	27	420	25	84	<1	137	<1
	III	2	5	1.1	15	402	20	95	<1	133	<1
CCB	I	15	126	2	382	583	76	42	<1	<1	<1
	II	23	81	—	245	420	119	69	<1	201	<1
Compostilla	I	30	38	—	116	458	35	15	27	<1	<1
	II	35	31	0.3	95	362	35	<0.3	35	131	<1
	III	15	15	0.5	46	369	40	17	48	177	<1
Escucha	I	26	62	—	188	354	70	42	<1	91	<1
	II	19	33	0.4	99	374	93	50	<1	168	<1
	III	7	14	0.6	42	347	79	46	<1	180	<1
Espiel	I	30	27	—	82	446	8	<0.3	39	<1	12
	II	35	40	0.4	120	534	14	19	49	127	<1
	III	15	29	0.4	88	332	12	32	52	185	<1
Fusina	I	32	61	<0.1	185	428	53	52	<1	116	<1
	II	8	14	<0.1	42	404	64	65	<1	157	<1
Hemweg	I	26	56	1	170	464	62	30	<1	98	<1
	II	25	54	—	164	313	71	37	<1	211	<1
Lignite	I	24	1	6	3	252	49	<0.3	<1	<1	<1
	II	6	2	—	6	319	57	<0.3	<1	<1	<1
Meirama	I	27	98	—	297	365	56	4	<1	79	<1
	II	20	50	—	152	371	44	2	<1	114	<1
	III	4	9	0.7	27	369	35	3	<1	113	<1
Monfalcone	I	29	99	<0.1	300	373	38	100	<1	114	<1
	II	12	37	<0.1	112	328	31	121	<1	175	<1
Narcea	I	50	34	—	103	349	39	11	37	82	<1
	II	33	22	0.4	66	394	46	19	23	160	<1
	III	14	13	0.6	38	375	42	5	40	177	<1
Neutral	I	42	83	<0.1	251	395	62	50	15	115	<1
	II	12	36	—	109	255	22	23	6	129	<1
Nijmegen	I	44	38	<0.1	115	465	64	41	9	158	<1
	II	7	20	—	61	404	52	48	<1	209	<1
Puertollano	I	30	124	—	376	610	74	31	<1	<1	<1
	II	64	49	0.1	148	450	82	34	<1	156	<1
	III	25	5	0.3	16	370	85	45	<1	247	<1
Robla	I	49	13	—	39	340	10	10	<1	82	<1
	II	14	12	0.7	35	298	13	8	<1	123	<1
	III	15	6	1.5	18	359	10	6	<1	142	<1
Sardegna	I	40	21	<0.1	64	417	46	52	<1	103	<1
	II	7	20	—	61	404	32	58	<1	140	<1
Soto Rib	I	34	42	—	128	520	36	39	<1	100	<1
	II	18	36	0.3	109	321	28	28	<1	160	<1
	III	18	12	0.6	37	371	37	40	<1	230	<1
Teruel	I	37	40	—	122	279	52	15	<1	94	<1
	II	26	24	0.5	73	304	66	23	<1	166	<1
	III	10	13	0.6	38	264	45	20	<1	171	<1

This glass then contained 31.8 g of SiO₂ plus the 4.5 g from the opaline silica. This adds up to 36.3 g, and gives a reconstituted SiO₂ content for the glass of $(36.3/67) \times 100 = 54.2\%$. For Monfalcone the result of a similar calculation will give 54.8%. The linear relationship between the SiO₂ in glass (reconstituted) and the SiO₂ extraction yield for the different extraction conditions are:

$$90^\circ\text{C} \quad EY_{\text{Si}} = 4.6 \times \text{SiO}_{2\text{in glass (reconstituted)}} - 154 \quad (R^2 = 0.88)$$

$$120^\circ\text{C} \quad EY_{\text{Si}} = 18.0 \times \text{SiO}_{2\text{in glass (reconstituted)}} - 790 \quad (R^2 = 0.98)$$

$$\text{Microwave } EY_{\text{Si}} = 12.3 \times \text{SiO}_{2\text{in glass (reconstituted)}} - 450 \quad (R^2 = 0.96)$$

From these equations it can be concluded that to obtain an extraction yield of 100 g SiO₂ kg⁻¹, in addition to the requirements on bulk SiO₂ contents in the starting fly ash, the following limiting values have to be considered: (a) >55% SiO₂ in glass (reconstituted) using optimal extraction conditions at 90 °C, (b) >50% SiO₂ in glass (reconstituted) using optimal extraction conditions at 120 °C and (c) >45% SiO₂ in glass (reconstituted) using optimised microwave assisted extraction conditions (140–185 °C).

Furthermore, high opaline silica contents in the fly ash (as in Meirama) favours the SiO₂ extraction in such a way that higher yields than those expected from the bulk SiO₂ contents may be obtained.

• A low SiO₂/Al₂O₃ in the extract may cause the fast precipitation of zeolites in the extraction residue with the consequent reduction of the SiO₂ extraction yields. Consequently, the SiO₂/Al₂O₃ ratio of the fly ash is the third parameter influencing the SiO₂ extraction process (Fig 1(d)). Figure 1(e) shows that if CCB, Monfalcone, Narcea and Robla fly ashes are excluded, the SiO₂ extraction yields may be predicted from the SiO₂/Al₂O₃ ratios in bulk fly ash based on the following equation:

$$90^\circ\text{C} \quad EY_{\text{Si}} = 76 \times \text{SiO}_2/\text{Al}_2\text{O}_3 - 50 \quad (R^2 = 0.60)$$

From this correlation it may be concluded that a SiO₂/Al₂O₃ (%wt) ratio in bulk fly ash >2.0 was measured in the fly ash yielding extraction values >100 g SiO₂ kg⁻¹, in at least 19 of the 23 fly ashes studied.

The different degree of correlation between the extraction yields and the above parameters points to the following order of importance concerning the influence on the SiO₂ extraction:

SiO₂ in glass reconstituted (R^2 : 0.88–0.98) > bulk SiO₂ content (R^2 : 0.71–0.85) > SiO₂/Al₂O₃ (R^2 : 0.60).

Direct conversion

The synthesis of zeolites (as identified by XRD analysis) such as NaP1 (Na₄[(AlO₂)₆(SiO₂)₁₀].15H₂O),

herschelite (Na₄[(AlO₂)₄(SiO₂)₈].11H₂O) or A zeolite (Na₁₂[(AlO₂)₁₂(SiO₂)₁₂].27H₂O) took place in the residue arising from extraction tests carried out on several fly ashes. Most fly ashes exhibited NaP1 growth in the first extraction step, indicating that simultaneous dissolution of SiO₂ and Al₂O₃ occurred, and that an excess of SiO₂ over Al₂O₃ relative to the zeolites found resulted in a net SiO₂ extraction. In the second extraction step, the NaP1 zeolite content increased for most fly ashes (15 out of 23). Consequently, for most fly ashes, in this second extraction step the SiO₂ dissolution still continued, but the simultaneous Al₂O₃ dissolution accounts both for the limitation of the SiO₂ extraction and also the precipitation of zeolite. In the third step, the zeolite content was further augmented but the SiO₂ extraction yield did not considerably increase (Table 3).

Based on the relationship between the results of direct conversion experiments and fly ash characteristics, two fundamental factors must be taken into account when investigating the suitability of fly ashes for direct conversion.

- The first parameter for the selection of a fly ash for direct conversion is a high content of Al₂O₃ and SiO₂, since these represent the zeolitisable fraction of the fly ash. The conventional conversion processes have been optimised for fly ash having >65% of Al₂O₃ + SiO₂ with good results.^{8,17} Above this limit (the higher the Al₂O₃ + SiO₂ content), a higher zeolite content may be obtained for the final product. Approximately 65 % of zeolite content in the final product has been reached from a pilot plant scale (2.2 tonnes in one batch for 8 h) using a fly ash with 78% Al₂O₃ + SiO₂.¹⁸
- The direct zeolite synthesis from coal fly ashes is based on the dissolution of SiO₂ and Al₂O₃ bearing phases followed by the fast precipitation of zeolites. Consequently, one of the basic parameters for obtaining high conversion yields is the high content of easily degradable SiO₂ and Al₂O₃ phases such as glass. If SiO₂ and Al₂O₃ are mainly present in more insoluble phases, such as quartz and mullite, the dissolution rate will be low and the conversion yield will be reduced. The loss of Na from the extraction solution may be used as a direct indicator of the amount of zeolites or zeolite precursors formed in the extraction residue. Using the optimal conditions for SiO₂ extraction, a good correlation was determined between the glass content of five selected fly ashes (63% Alkaline, 63% Meirama, 73% Monfalcone, 80% Neutral and 65% Puertollano) with respect to the Na consumption (7, 4, 15, 27 and 12%, respectively) according to the following relationship (Fig 2):

$$\text{NaOH consumption}(\%) = 1.11 \text{ glass content}(\%) - 63.5 \quad (R^2 = 0.92)$$

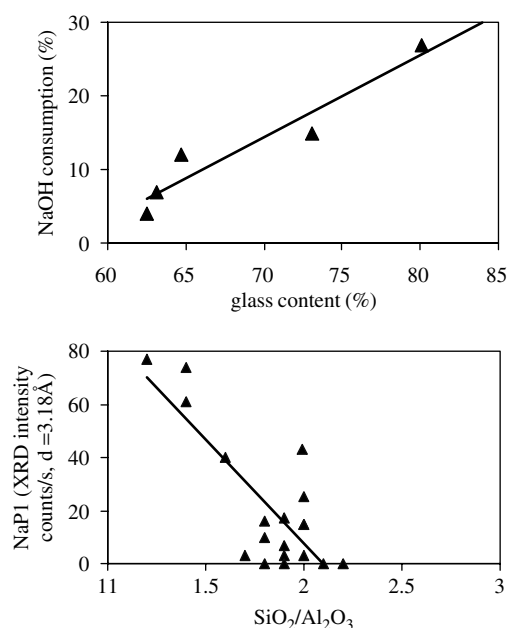


Figure 2. Top, correlation between: the glass content with the NaOH consumption (proportional to the conversion efficiency) under the optimal SiO_2 extraction conditions for each selected fly ash (Table 2). Bottom, correlation between $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in bulk fly ashes and NaP1 synthesis yield by direct conversion (125°C , 2 dm^3 of a 3 mol dm^{-3} NaOH per kg of fly ash, 8 h) for 20 of the 23 studied fly ashes (excluded are Lignite, Monfalcone and Meirama).

This shows that one of the basic parameters for the selection of a fly ash for the direct conversion process is based on a high glass content and that, under this condition, in theory no significant zeolite synthesis (detected by NaOH consumption) is present when the glass content is $<63\%$. However, zeolitic products have been obtained from fly ashes having very different glass contents (ie 86 and 63% for Narcea and Teruel respectively). In the case of the high glass fly ash, 65% of zeolite content is reached in the final product after 8 h.¹⁸ However, only 45% of zeolite content is reached in the low glass fly ash after 24 h.⁸ Therefore, the conversion yields of low glass fly ashes may be improved by increasing temperature, but there is a limit due to the fact that above 200°C , low CEC zeolites are easily formed.

- The third parameter having a major influence on the efficiency of the conversion processes is the bulk $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. For the synthesis of zeolites, the Si/Al/Na ratios of the starting solutions are the basic parameters for consideration. Figure 2 shows that high CEC zeolites such as NaP1 zeolite are preferentially obtained from fly ashes having an $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of <2.0 . Thus, conversely to the SiO_2 extraction, low Si/Al rates are more suitable for direct conversion.

Factor analysis

Multivariate analysis confirmed the relationships between SiO_2 extraction, synthesis yield and the above fly ash properties. The following nine fly ash

Table 4. Top: Factor loadings matrix for the first three factors after applying a biquartimax rotation. Bottom: Correlation coefficients (R) of factor scores and the three alkaline treatment variables (bold figures are significant at the 95% confidence level)

	F1	F2	F3		
% of Total variance	61.8	16.3	11.8		
Loadings:					
SiO ₂ bulk	0.84	0.25	0.44		
CaO + MgO bulk	−0.96	−0.22	0.03		
Na ₂ O + K ₂ O bulk	0.29	0.75	−0.08		
SO ₃ bulk	−0.93	−0.15	0.07		
SiO ₂ /Al ₂ O ₃ bulk	0.15	0.15	0.95		
Glass	0.12	0.91	0.22		
SiO ₂ in glass	0.92	−0.11	0.21		
CaO in glass	−0.85	−0.46	0.06		
SiO ₂ in glass + opal	0.60	0.65	0.40		
	F1	F2	F3	F1 + F2	F1 + F3
SiO ₂ extraction	0.65	−0.13	0.53	0.37	0.83
Zeolites in residues	0.79	0.46	0.00	0.89	0.56
Total SiO ₂ mobilised	0.78	0.04	0.43	0.58	0.86

properties were selected for evaluation: bulk SiO_2 , bulk CaO + MgO, bulk $\text{Na}_2\text{O} + \text{K}_2\text{O}$, bulk SO_3 , bulk $\text{SiO}_2/\text{Al}_2\text{O}_3$ rate, glass content, SiO_2 content in glass, CaO in glass and SiO_2 in glass + opaline SiO_2 . Factor analysis grouped these patterns in the following three factors (Table 4): Factor 1 (F1) is mainly defined by high bulk and glass SiO_2 contents and low bulk SO_3 and CaO + MgO. Factor 2 (F2) is characterised by high bulk glass and $\text{Na}_2\text{O} + \text{K}_2\text{O}$ contents. Factor 3 (F3) is characterised by a high bulk $\text{SiO}_2/\text{Al}_2\text{O}_3$ rate.

To correlate these grouped fly ash properties with the yields of SiO_2 extraction and zeolite synthesis, the factor scores for each fly ash were determined for F1 to F3. Subsequently the correlation coefficients of these factor scores with three alkaline treatment results (yields of SiO_2 extraction and zeolite synthesis and the total SiO_2 mobilised) from the extraction test (90°C , 2–3 consecutive extraction stages, NaOH 2 mol dm^{-3} , liquid/solid ratio $3 \text{ dm}^3 \text{ kg}^{-1}$ of fly ash, 6 h) were determined. The results (Table 4, bottom) allowed the correlation of F1 properties with SiO_2 extraction and zeolite formation and therefore with total SiO_2 mobilised. F2 scores correlate rather poorly but significantly with zeolite formation and not with SiO_2 extraction, whereas F3 scores do the opposite. Thus, F1 properties may be the tracers of a general SiO_2 mobility behaviour, F2 as an indicator of a zeolite formation potential, and F3 as a specific SiO_2 extraction factor. By adding F1 and F3 scores an optimised SiO_2 extraction indicator is created and the same applies for F1 and F2 scores for zeolite formation potential. The correlations with the above alkaline treatment variables are now $R = 0.83$ and 0.89 as shown in Table 4. Plots of F1 + F3 scores against SiO_2 extraction and F1 + F2 scores against zeolites in residues for all 23 fly ashes show that the

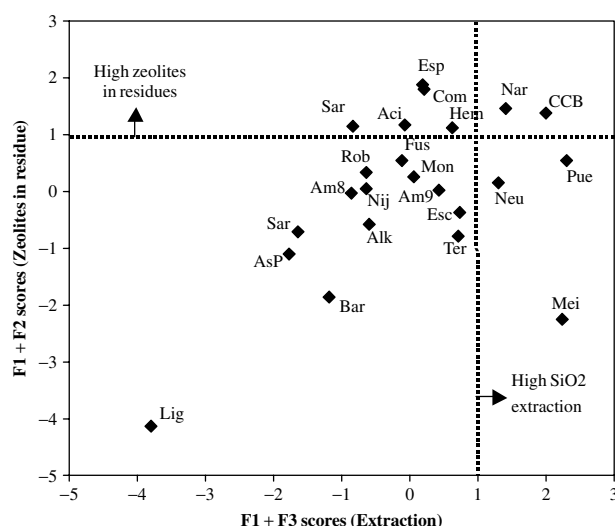


Figure 3. F1 + F2 scores plotted against F1 + F3 scores allow to classify ashes as being suitable for SiO₂ extraction or zeolite formation or both. Lines at F1 + F2 = 1 and F1 + F3 = 1 are drawn arbitrarily and ashes are indicated by their first three letters (see Table 1 for full name and origin).

SiO₂ extraction yield (EY_{Si}) can now be expressed as:

$$EY_{Si} = 27.8 \times (F1 + F3) + 90 (R^2 = 0.69)$$

and that the tendency to form zeolites in the residues (Z_{res}), expressed as the sum of the main XRD peaks of observed zeolites (in counts per s, measured under standard conditions), can be predicted by:

$$Z_{res} = 33.8 \times (F1 + F2) + 173 (R^2 = 0.79)$$

The latter variable is rather semi-quantitative as far as the absolute amount of zeolites formed is concerned. However, the sums of F1 + F2 and F1 + F3 scores may be very useful for classifying ashes in terms of suitability for synthesis of zeolites or silica extraction, respectively, as shown in Fig 3.

From this plot it is concluded that the Meirama and Puertollano ashes are the most suitable for SiO₂ extraction, Espiel and Compostilla the best for zeolite synthesis and that CCB and Narcea ashes may be used for both purposes. This is in good agreement with that found during experiments on extraction and synthesis of zeolites.

CONCLUSIONS

The experiments on silica extraction carried out with 23 coal fly ashes confirm that the main parameters governing the SiO₂ extraction are: (a) a high bulk SiO₂ content, (b) a high proportion of the bulk SiO₂ present in the degradable glass matrix and the highly soluble opaline fraction, and (c) a high bulk SiO₂/Al₂O₃ ratio. In addition, the results on synthesis of zeolites by direct conversion demonstrate that the most important criteria for the selection of a fly ash for this process are: (a) a high content of Al₂O₃ and SiO₂, (b) a high

glass content and (c) relatively low SiO₂/Al₂O₃ ratio. From this plot it is concluded that the Meirama and Puertollano ashes are the most suitable for SiO₂ extraction, whereas Espiel and Compostilla the best for zeolite synthesis and that CCB and Narcea ashes may be used for both purposes.

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