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Pure zeolite synthesis from silica extracted from coal fly ashes†

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Abstract: Pure zeolites can be synthesised from silica extracted from fly ash by alkaline leaching. If the process is optimised the solid residue arising from this extraction may also contain a relatively high content of zeolitic material mixed with residual fly ash components. Both the pure and the impure zeolitic material have a high potential for application in waste-water and flue gas-cleaning technologies. The silica extraction potential of 23 European coal fly ashes covering most of the possible fly ash types is investigated in this study. Optimisation of leaching processes, by varying temperature, time and alkali/fly ash rates, permitted extraction yields up to 140 g of SiO_2 per kg using a single step process, but the extraction yields may reach up to 210 g kg^{-1} by applying thermal pre-treatments prior to the extraction. The solid residue arising from the silica extraction experiments shows a high NaP1 zeolite content. A high Si/Al ratio of the glass matrix, the occurrence of easily soluble silica phases in the original fly ash and a high reactive surface area were found to be the major parameters influencing silica extraction. High purity 4A and X zeolitic material was obtained by combining the silica extracts from the Meirama fly ash and a waste solution from the Al-anodising industry. The results allowed conversion of the silica extraction yields to an equivalent 630 g of pure 4A–X zeolite per kg of fly ash with a cation exchange capacity of 4.7 meq g^{-1}.

Keywords: fly ash; zeolite synthesis; silica extraction

INTRODUCTION

The synthesis of zeolite from coal fly ash was introduced by Höller and Wirsching[1] as a result of the compositional similarity of fly ash to some volcanic material, a precursor of natural zeolites. The conventional synthesis of zeolite from coal fly ashes is carried out by direct alkaline hydrothermal activation. The different methods used[2–6] differ in the molarity of the alkaline reagents (mainly KOH and NaOH), solution/fly ash ratio, temperatures (80–200 °C), time (3–48 h) and vapour pressure at the different temperatures tested. By varying these parameters, at least 15 different types of zeolites can be produced from a single fly ash. The conversion rate varies (usually 20–65%) as a function of the properties of the fly ash and the conditions of synthesis.[7] Microwave or ultrasound-assisted processes have been tested to reduce the activation time to minutes.[8] All these conversion procedures have the inconvenience that the final product is a mixture of zeolites and residual non-reacted fly ash components. This has an adverse effect on the CEC of the product. The residual fly ash fraction may also contain relatively high levels of leachable B, Mo, As, V, Cr and Se, which may limit the use of this zeolitic material.

A new process was introduced by Hollman *et al*[9] by synthesising 'pure zeolite' using a two-step procedure based on prior Si extraction from fly ash followed by the synthesis of pure zeolites by combining the leachates with high-Al solutions. This permitted the preparation of a product with a zeolite content >90%, with the solid residue from the extraction also being suitable starting material for the traditional conversion method to produce a lower quality zeolitic product.

This study focuses on the investigation of the relationship between the SiO_2 extraction potential and the characteristics of the fly ashes to optimise the process. The synthesis of pure zeolite by combining the silica extract with an Al-bearing waste solution from the Al-anodising industry is also investigated.

METHODOLOGY

Materials

Twenty-three European pulveised coal combustion fly ashes were selected for this study. Details on the origin

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Table 1. Fly ash selected for this study with the indication of the power plant source, power capacity and location

Power station	*Power (MW)*	*Location*
Acid	600	The Netherlands
Alkaline	450	The Netherlands
Amer-8	600	The Netherlands
Amer-9	600	The Netherlands
As Pontes	1400	North-west Spain
Los Barrios	550	Southern Spain
CCB	600	The Netherlands
Compostilla	1312	Northern Spain
Escucha	160	North-east Spain
Espiel	938	Southern Spain
Fusina	980	Italy
Hemweg-8	600	The Netherlands
Lignite	–	Northern Greece
Meirama	550	Northern Spain
Monfalcone	336	Italy
Narcea	569	Northern Spain
Neutral	600	The Netherlands
Nijmegen	600	The Netherlands
Puertollano	220	Central Spain
Robla	625	Northern Spain
Sardegna	–	Italy
Soto Ribera	672	Northern Spain
Teruel	1050	North-east Spain

of these fly ashes are given in Table 1. The Al source for the synthesis of pure zeolite was an etching bath residue from a Dutch Al-anodising plant (ALUMET), the residue containing 57.6 and 14.9 g dm^{-3} of Al and NaOH, respectively. This solution and the high-Si solution obtained from fly ashes were combined to obtain a pure zeolite product.

Silica extraction

Savillex PFA reactors (capacity 60 cm^3) and a 2 dm^3 Parr 4843 autoclave reactor allowing the on-line sampling of the process were used for the silica extraction experiments. Tests were carried out using 0.5–5 mol dm^{-3} NaOH solutions with a dose ranging from 3 to 12 dm^3 kg^{-1} of fly ash, at 50–200 °C for 1 to 24 h.

Based on the results of previous studies[10] thermal pre-treatments at 1100, 750, 550 and 200 °C were developed to increase the extraction yields by inducing the crystallisation of cristobalite.

The SiO_2 and Al_2O_3 extraction yields, the NaOH consumption and the composition of the extraction residue were determined for each extraction test.

Synthesis of pure zeolite

The synthesis of A4 and X zeolites followed the methodology of Sáez[11] using molar ratios of $Na_2O/SiO_2 = 1.3$, $H_2O/Na_2O = 38.93$ and $SiO_2/Al_2O_3 = 2.11$, a 0.5–2 h gelification stage at 80 °C, a 20–24 h room temperature aging, and a final 6–10 h crystallisation stage at 80 °C. Experimental conditions used by IQE SA (Industrias Químicas del Ebro SA) with molar ratios of $Na_2O/SiO_2 = 1.0$–2.0, $H_2O/Na_2O = 25.0$ and $SiO_2/Al_2O_3 = 1.9$, a 0.5–2 h single gelification step at 60 °C followed by a 2 h crystallisation stage at 80 °C were also tested.

The starting solutions were prepared by combining the 21.8 g Si dm^{-3} extract from the Meirama fly ash and the above mentioned etching bath solution.

Analysis

The silica contents in bulk fly ashes were determined by XRF. The analysis of the other major and trace components in the fly ashes and leachates was obtained by using ICP-MS and ICP-AES. The mineral composition of the fly ash, extraction residues and the pure zeolite material was determined by XRD (using CuK_α radiation). Final quantitative XRD analysis was obtained by the Reference Intensity Method (RIM) using CaF_2 as an internal standard.

The physical characterisation of fly ash included grain size determinations (using a laser light scattering-based particle size method), true density (with a helium pycnometer), apparent density (using the standard NLT-176/74), indirect determination of porosity (from apparent and true density values), N_2 BET surface area (with a multi-point volumetric instrument), and morphology (by SEM).

The cation exchange capacity (CEC) of zeolitic material was determined following the ISRIC methodology.[12]

RESULTS AND DISCUSSION

Fly ash characterisation

The more interesting properties of the fly ashes for application to SiO_2 extraction and zeolite synthesis are: (1) a high glass content, (2) a high SiO_2/Al_2O_3 ratio in the glass matrix and (3) a high SiO_2 content in the more reactive Si-bearing phase. Opaline silica has a high solubility, whereas mullite and quartz are more resistant to alkaline or acidic solvents.

The content of major oxides of the fly ashes is shown in Table 2. The results show that the Puertollano, CCB and Narcea fly ashes have very high SiO_2 contents (55–60%), coupled with a very high SiO_2/Al_2O_3 ratio (2–2.4). The Meirama fly ash shows the highest SiO_2/Al_2O_3 ratio (2.8). Most of these fly ashes exhibit also relatively low contents of major impurities such as S, Ca and Fe.

The highest aluminium-silicate glass contents (80–92%) were determined for Compostilla, Espiel, Narcea, Robla, Nijmegen, Neutral, CCB, Acid and Hemweg fly ashes. The Soto de Ribera, Amer-8, Amer-9, Fusina, Montfalcone and Sardegna have an intermediate glass content (70–78%). The other samples have a lower glass content (48–65%). The Los Barrios fly ash has a very high mullite content (40%), whereas the highest quartz contents (6.0–12.5%) were obtained for the Alkaline, Puertollano, Teruel, Meirama, Narcea, As Pontes, Escucha, Nijmegen, Neutral, CCB, Acid, Amer-8, Amer-9,

Fly ash	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	TiO_2	MnO	SO_3
Acid	51.3	28.9	8.4	1.8	1.0	0.5	2.5	0.2	1.5	0.02	0.5
Alkaline	46.8	24.8	9.0	6.8	3.7	1.2	2.0	0.7	0.9	0.10	1.0
Amer-8	45.2	26.5	7.1	6.1	1.6	0.8	1.2	1.1	1.3	0.04	1.1
Amer-9	52.4	25.8	7.0	5.6	1.6	0.7	1.4	0.9	1.3	0.05	0.6
As Pontes	41.5	30.1	12.6	5.6	1.6	0.6	1.9	0.2	0.6	0.10	1.4
Los Barrios	42.6	35.6	2.6	8.4	2.1	0.3	0.6	1.7	1.6	0.10	0.6
CCB	59.6	27.0	3.3	0.5	0.9	0.3	2.9	0.1	1.4	0.02	0.2
Compostilla	51.2	25.5	7.5	2.8	2.0	0.8	3.9	0.4	0.9	0.10	0.6
Escucha	49.5	26.7	12.3	2.3	0.9	0.3	1.9	0.2	0.9	0.03	0.3
Espiel	52.3	28.5	5.9	2.0	1.5	0.5	4.0	0.4	1.0	0.10	0.1
Fusina	48.2	25.9	8.8	2.3	1.5	0.5	2.6	0.3	1.3	0.10	0.6
Hemweg-8	53.2	26.0	8.6	2.4	1.6	0.5	2.7	0.3	1.3	0.10	0.6
La Robla	44.1	23.2	14.3	8.9	1.8	0.3	2.6	0.8	0.9	0.10	1.1
Lignite	28.5	17.9	8.4	27.3	3.8	0.2	1.0	0.3	1.0	0.04	8.6
Meirama	49.2	17.6	10.4	11.8	2.0	0.4	0.4	0.2	0.5	0.10	2.2
Monfalcone	50.8	33.4	6.4	2.4	0.8	0.4	0.7	0.3	2.6	0.02	0.3
Narcea	55.2	23.3	6.9	4.0	2.5	0.7	3.8	0.3	0.9	0.10	0.4
Neutral	53.3	26.1	7.4	3.1	0.6	0.1	0.6	1.5	1.8	0.06	0.5
Nijmegen	45.3	25.0	8.8	6.4	1.4	0.8	1.1	1.0	1.3	0.04	1.3
Puertollano	58.6	27.4	7.3	0.8	1.0	0.3	2.4	0.1	0.7	0.10	0.2
Sardegna	41.7	29.0	3.8	10.0	2.4	0.5	0.8	1.5	1.7	0.08	0.9
Soto de Ribera	48.9	30.6	7.2	3.0	1.6	0.6	3.9	0.1	0.8	<0.01	0.3
Teruel	48.3	23.9	16.0	5.4	1.0	0.2	1.4	0.2	0.8	0.04	0.8

Table 2. Major oxide contents (% wt) of the fly ashes

Hemweg, Lignite and Fusina fly ashes. The other samples have quartz contents of <5.0%. The Meirama fly ash has relatively high levels of opaline silica which probably originated from a late glass devitrification processes, indicating that the Meirama glass is very reactive.

Lignite and Sardegna fly ashes show the highest lime content (5.8 and 2.5%, respectively) whereas Escucha, As Pontes, Puertollano, La Robla, Teruel and Lignite have the highest haematite or magnetite content (3.5–7%). The Lignite fly ash has the highest anhydrite and calcite content (15 and 0.7% respectively).

Concerning trace elements, Narcea and Compostilla fly ashes have the lowest contents of potentially leachable trace elements, whereas Puertollano has the highest Pb, Zn and Sb (1075, 924, 120 mg kg^{-1}, respectively), and relatively high As, Cd and Ge (140, 5 and 61 mg kg^{-1}, respectively) contents. Other enrichments of environmentally relevant elements were found for the following fly ashes: Montfalcone (455 mg V kg^{-1}); Sardegna (3134 mg Ba kg^{-1} and 4406 mg Sr kg^{-1}), Hemweg-8 (2313, 2390 and 514 mg kg^{-1} of Ba, Sr and V, respectively), Acid (1757, 254 and 1920 mg kg^{-1} of Ba, Cu and Sr, respectively) and CCB (30 mg Se kg^{-1}).

A normal Gaussian grain size distribution with modes around 10–30 μm was obtained for most of the fly ashes (Narcea, Los Barrios, Teruel, Robla, As Pontes, Alkaline, Nijmegen, Neutral, Acid, Amer-8, Amer-9, Hemweg, Lignite and Sardegna), whereas the Meirama, Espiel, Compostilla, Soto de Ribera, Puertollano, Fusina and Montfalcone fly ashes show a bimodal grain size distribution (around 10 and 100 μm). The Escucha and CCB fly ashes have an asymmetric grain size distribution with modes close to 100 μm.

The true density values (d_t) range between 2.2 g cm^{-3} for the Puertollano fly ash and 2.7 g cm^{-3} for the La Robla fly ash. The highest d_t values were found for the high magnetite, lime or anhydrite fly ashes. The apparent density (d_a) values obtained range from 1.1 g cm^{-3} for the Teruel fly ash to 0.7 g cm^{-3} for Los Barrios fly ash. The highest d_a values were obtained for high-Fe and high-glass fly ashes. The lowest d_a values are probably due to higher cenosphere contents. The highest porosity values (72%) were obtained for the Meirama and Los Barrios fly ashes, whereas the lowest values (56%) were obtained for the Escucha and Espiel fly ashes. The high porosity value obtained for Meirama fly ash is probably due to both the fine grain size and the unusual irregular and porous morphology. The BET surface area values are <3 $m^2 g^{-1}$, with the exception of the Meirama fly ash (12.4 $m^2 g^{-1}$). The usual fly ash particle morphology (spherical particles of various sizes, cenospheres and plerospheres) was found for most fly ashes. However, the Meirama fly ash and, to a lower degree the CCB fly ash, have a very high proportion of irregularly shaped particles with high micro-porosity, usually grouped in particle agglomerates.

The results from the thermal pre-treatment of fly ashes indicated that Los Barrios, Meirama, Teruel, Puertollano, Neutral, Fusina and Monfalcone thermally-treated fly ashes evolved towards the crystallisation of cristobalite due to the high SiO_2 contents of the glass matrix. Consequently, these fly ashes have a potential application for SiO_2 extraction due to the excess of silica in the glass matrix.

Although initial silica extraction experiments were developed using all the fly ashes, the Meirama, Montfalcone, Puertollano and Neutral fly ashes were selected for optimisation of silica extraction, based on the results of their characterisation.

Silica extraction

Preliminary Si extraction tests were developed for the 23 European fly ashes using an extractant (2 mol dm^{-3} NaOH)/fly ash ratio of 3 $dm^3 kg^{-1}$, 90 °C, 6 h according to the optimal conditions of Hollman *et al.* [9] for the Si extraction from Dutch fly ashes. As expected from the chemical characterisation, the highest extraction yields were obtained for Puertollano, CCB, Meirama, Montfalcone and Neutral which resulted in 130, 126, 111, 98 and 80 g SiO_2 per kg, respectively. Conversely, Lignite, Espiel, Robla and Sardegna yielded very low extraction values (1–27 g $SiO_2 kg^{-1}$). No Si dissolution occurred in the tests of Lignite and Espiel, but the capture of dissolved Si by zeolite precipitation was deduced for Sardegna and Robla, from the relatively high NaP1 zeolite content of the extraction residue. High NaP1 zeolite contents were also measured in the residues arising from the extraction of Neutral, Montfalcone and Meirama.

The residue from the extraction tests was submitted to repeated extraction experiments to determine the maximum extraction for each fly ash. The extraction yields obtained with these two-step extraction experiments reached values of 207, 135, 162, 141 and 117 g SiO_2 kg^{-1} for CCB, Montfalcone, Puertollano, Meirama and Neutral. The solid residues arising from the second extraction step of these fly ashes contained between 40 and 75% of NaP1 zeolite. Consequently, using this two-step process, high Si-extraction yields coupled with zeolitisation of the solid residue may be obtained. The low extraction yields of the other fly ashes obtained by this two-step process were attributed to the fixation of the dissolved Si by precipitation of high amounts of NaP1 zeolite. In this case, both Al and Si from the glass matrix are dissolved at a similar rate giving rise to precipitation of zeolites, whereas in the first group of ashes a high Si/Al dissolution rate allowed high extraction for Si, without a high Al concentration in solution.

The Si extraction yields obtained with a single step test using thermally-treated (1100 °C) fly ashes reached values of 207, 200, 163 and 132 g SiO_2 kg^{-1} for Neutral, Puertollano, Montfalcone, and Meirama. These high yields were obtained as a consequence of the crystallisation of easily soluble cristobalite aggregates from the glass matrix and due to the fixation of Al by the crystallisation of phases with low solubility such as mullite and feldspars. Extraction after thermal treatment provided the highest extraction yields in a single step process. The zeolite content in the solid residue arising from this process reached values of 20–35%. The extraction yields obtained from thermally pre-treated fly ashes at 750, 550 and 200 °C were lower than at 1100 °C, but higher than the untreated fly ashes.

The time dependency of the Si-extraction yields varied as a function of the fly ash. A fast Si extraction was obtained for Meirama, with 100 g $SiO_2 kg^{-1}$ in only 3 h, due to the presence of soluble opaline phases. This allows the precipitation of zeolites during the initial stages of the process (first hour) but the extraction rate does not improve and may even decrease with time, due to the low solubility of the other silica-bearing phases. The Puertollano ash reached 140 g $SiO_2 kg^{-1}$ in 9 h, producing a solid residue with 40% NaP1 content (Fig 1) with around 2.0 meq g^{-1} CEC. The other fly ashes showed a delayed zeolite crystallisation parallel with a progressive Si-extraction rate in the first 6 h. In subsequent stages, the zeolite content of the solid residue increases without a major increase in the Si-extraction yield.

The optimisation of the extraction temperature (50–120 °C), allowed improvement of the extraction yields from 100 to 190 g $SiO_2 kg^{-1}$ for the Neutral, Montfalcone and Puertollano at 120 °C. Meirama yielded similar results with the 90 °C tests. The residue arising from the 120 °C extraction has a very high

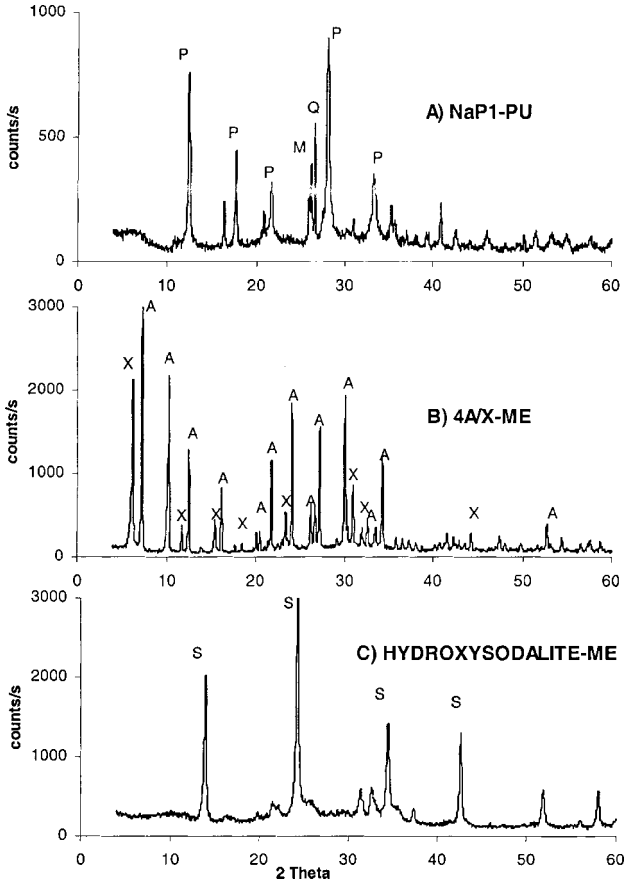

Figure 1. XRD patterns of (A) the solid residue arising from of the Si extraction using the Puertollano fly ash showing the presence of NaP1 zeolite mixed with fly ash phases; (B) pure 4A–X zeolite blend synthesised from the Si extracts of Meirama and the Al-etching bath solution using the conditions of Sáez;[11] and (C) idem with the IQE SA conditions (Q: quartz, M: mullite, P:NaP1 zeolite, X: X zeolite, A: 4A zeolite and S: hydroxysodalite).

NaP1 zeolite content (30–50%). Mass balance showed that at 120 °C the silica mobilisation varied from 57 to 76% of the bulk Si content in all the fly ashes studied.

The increase in the NaOH concentration of the extractant and the extractant/fly ash ratio does not increase the Si extraction due to the following causes: (a) an increase of the extractant/fly ash ratio accounted for the dissolution of Al-bearing phases with the subsequent fixation of Si in precipitated zeolitic material; (b) the increase of the NaOH content gave rise to the precipitation of sodalite, analcime and cancrinite (minerals without industrial interest) in the solid residue; and (c) the increase of the NaOH content gave rise to a high Na/Si ratio in the leachate,

Table 3. Mass balance of SiO_2 and Al_2O_3 obtained under the different experimental conditions using the Meirama and Puertollano fly ashes

	Extractable ($g\,kg^{-1}$)		*Fixed as zeolite* ($g\,kg^{-1}$)			*Total mobilised*			
						($g\,kg^{-1}$)		(% bulk)	
Experimental conditions	SiO_2	Al_2O_3	SiO_2	Al_2O_3	Na_2O	SiO_2	Al_2O_3	SiO_2	Al_2O_3
Meirama fly ash									
Two extractions 90 °C. 6 h, 2 M NaOH. 3 $dm^3\,kg^{-1}$	148	2.0	253	134	82	401	136	82	77
90 °C. 6 h. 1 M NaOH. 3 $dm^3\,kg^{-1}$	51	0.1	136	69	42	187	69	38	39
90 °C. 9 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	84	0.1	279	142	86	363	142	74	81
125 °C. 8 h. 3 M NaOH. 2 $dm^3\,kg^{-1}$	18	0.4	200	102	62	218	102	44	58
175 °C. 6 h. 1.3 M NaOH. 2 $dm^3\,kg^{-1}$	18	<0.1	112	57	35	130	57	26	32
125 °C. 10 h. 1.3 M NaOH. 2 $dm^3\,kg^{-1}$	18	0.2	84	43	26	101	43	21	24
125 °C. 6 h. 2.8 M NaOH. 2 $dm^3\,kg^{-1}$	26	0.6	185	94	57	210	95	43	54
175 °C. 10 h. 2.8 M NaOH. 2 $dm^3\,kg^{-1}$	28	0.2	266	136	82	294	136	60	77
Pre-treated 1100 °C +90 °C. 6 h 2 M NaOH. 3 $dm^3\,kg^{-1}$	132	<0.1	54	28	17	186	28	38	16
Pre-treated 750 °C +90 °C. 6 h 2 M NaOH. 3 $dm^3\,kg^{-1}$	112	<0.1	167	85	52	279	85	57	48
Pre-treated 550 °C +90 °C. 6 h 2 M NaOH. 3 $dm^3\,kg^{-1}$	110	0.2	185	94	57	295	94	60	54
Pre-treated 200 °C +90 °C. 6 h 2 M NaOH. 3 $dm^3\,kg^{-1}$	109	0.1	170	90	60	279	90	57	51
90 °C. 0.5 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	66	1.5	102	52	32	168	53	34	30
90 °C. 1 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	74	1.0	96	49	30	170	50	35	28
90 °C. 2 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	83	0.4	138	70	43	221	71	45	40
90 °C. 3 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	99	0.2	180	92	56	279	92	57	52
90 °C. 4 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	109	0.2	204	104	63	313	104	64	59
90 °C. 5 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	104	0.1	228	116	71	332	116	68	66
90 °C. 6 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	98	0.1	234	119	73	332	119	68	68
90 °C. 7 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	94	0.1	240	122	74	334	122	68	70
90 °C. 8 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	91	0.1	240	122	74	331	122	67	70
90 °C. 9 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	84	0.1	246	125	76	330	126	67	71
90 °C. 24 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	41	0.1	306	156	95	347	156	71	89
50 °C. 6 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	39	2.1	81	41	25	120	43	24	25
70 °C. 6 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	59	1.9	101	52	31	160	53	33	30
90 °C. 6 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	111	<0.1	160	82	50	280	82	55	46
120 °C. 6 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	125	<0.2	156	79	48	281	80	57	45
Puertollano fly ash									
Two extractions 90 °C. 6 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	162	31	238	89	80	400	120	68	43
90 °C. 6 h. 1 M NaOH. 3 $dm^3\,kg^{-1}$	24	1.0	96	49	30	120	50	21	18
90 °C. 9 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	105	0.2	246	125	76	351	126	60	46
125 °C. 8 h. 3 M NaOH. 2 $dm^3\,kg^{-1}$	44	2.0	118	60	37	162	62	28	23
Pre-treated 1100 °C +90 °C. 6 h 2 M NaOH. 3 $dm^3\,kg^{-1}$	207	<0.1	130	70	40	330	70	57	25
Pre-treated 750 °C +90 °C. 6 h 2 M NaOH. 3 $dm^3\,kg^{-1}$	180	<0.1	120	60	40	300	60	51	23
Pre-treated 550 °C +90 °C. 6 h 2 M NaOH. 3 $dm^3\,kg^{-1}$	140	0.3	130	70	40	270	70	46	25
Pre-treated 200 °C +90 °C. 6 h 2 M NaOH. 3 $dm^3\,kg^{-1}$	140	0.2	330	170	100	460	170	79	61
90 °C. 3 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	100	1.6	130	70	40	230	70	39	25
90 °C. 4 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	110	1.6	140	70	40	250	70	43	26
90 °C. 5 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	120	1.5	140	70	40	270	70	45	27
90 °C. 6 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	130	1.5	160	80	50	290	80	49	30
90 °C. 7 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	130	1.0	170	90	50	310	90	52	33
90 °C. 8 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	130	0.4	190	100	60	330	100	56	36
90 °C. 9 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	140	0.3	220	110	70	360	110	61	40
90 °C. 10 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	140	0.1	230	120	70	380	120	64	44
90 °C. 24 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	150	<0.1	270	140	80	420	140	72	50
70 °C. 6 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	90	2.9	30	20	10	130	20	22	7
90 °C. 6 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	120	3.0	180	90	60	310	100	52	35
120 °C. 6 h. 2 M NaOH. 3 $dm^3\,kg^{-1}$	190	0.1	240	120	80	440	120	74	45

which inhibits the possibility of synthesising 4A, X and other high CEC zeolites from the silica extracts.

Due to the large amount of experimental data obtained, only the results of two selected fly ashes (Meirama and Puertollano) are given in Table 3 to show the mass balance of SiO_2 and Al_2O_3 obtained under all the extraction conditions mentioned.

Synthesis of pure zeolites

The optimisation of the experimental conditions by Sáez[11] allowed synthesis of a 1:1 mixture of pure 4A and X zeolites (Fig 1) from the Si extracts of the Meirama fly ash. Different $SiO_2/Al_2O_3/NaOH$ ratios were tested by combining the Si extract with the Al-etching bath solution and additional NaOH. The high CEC obtained ($4.7\,meq\,g^{-1}$) indicates the high purity (97%) of the zeolitic product.

The optimisation of commercial recipes from zeolite producers (IQE procedure), using the Si extract and the Al-etching bath solution as starting materials, was rather unsuccessful. The low concentration of silica in the leachate compared with that in the sodium silicate solution used in industrial processes resulted in failure to obtain any zeolite apart from hydroxy-sodalite. Although high purity was obtained (Fig 1), this mineral has a low industrial interest due to the low effective CEC in potential application.

CONCLUSIONS

The correlation of the silica extraction yields with the results of the characterisation studies allowed identification of the following decisive factors favouring the silica extraction process:

- A high bulk silica content.
- High silica and a low alumina contents of the glass matrix. This will account for the extraction of silica without zeolite precipitation. When Al-bearing phases are dissolved the precipitation of zeolites occurs immediately with the subsequent capture of silica in the solid residue.
- The presence of opaline phases in the original fly ash also favours a high silica/alumina rate in the extraction leachates.

The Meirama, Montfalcone, Neutral and Puertollano fly ashes fulfil most of these conditions. Consequently, these fly ashes are suitable for silica extraction experiments. The Puertollano fly ash shows the highest silica extraction in a single step (6 h), 190 g $SiO_2\,kg^{-1}$ extraction yield. Moreover, the solid residue arising from the process contains around 40% of NaPl zeolite ($2.0\,meq\,g^{-1}$ of CEC).

Faster silica extraction is obtained with the Meirama fly ash (100 g $SiO_2\,kg^{-1}$ in 3 h) due to the presence of soluble opaline phases, but the extraction rate does not improve with time, and may even decrease, due to the low solubility of the other silica-bearing phases.

Thermal pre-heating at 1100 °C to devitrify the glass matrix prior to extraction allowed the extraction yields to be improved. Thus, values from 90 to 207 g SiO_2 kg^{-1} were obtained from the treated fly ashes in a single extraction stage.

The optimisation of the experimental conditions allowed the synthesis of a mixture of pure 4A and X zeolites from the Si extracts of the Meirama fly ash. The high CEC obtained ($4.7\,meq\,g^{-1}$) indicates the high purity (97%) of the zeolitic product.

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