

Application of zeolitic material synthesised from fly ash to the decontamination of waste water and flue gas[†]

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Abstract: Zeolitic material was synthesised from fly ash using two different conversion methodologies. The two conversion products obtained were: (a) impure zeolitic material obtained by direct conversion from different Spanish fly ashes, and (b) a high purity 4A–X zeolite blend synthesised from the silica extracts obtained from the Meirama fly ash (NW Spain). The zeolitic material was tested for potential application as an ion exchanger to decontaminate waters containing high concentrations of ammonium and heavy metals. Preliminary results show high cation uptake efficiencies (up to 4.7 meq g⁻¹) which allowed fast decontamination of different types of industrial or acidic mine waste waters. The CO₂, SO₂ and NH₃ sorption capacity of several zeolitic products was also determined and very promising results were obtained for the 4A–X blend. Sorption capacity values of up to 74, 297, and 111 mg g⁻¹ for CO₂, SO₂ and NH₃ respectively were obtained for the zeolitic material synthesised from silica extracts from fly ash and a high-aluminate waste water.

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Keywords: coal fly ash; zeolite synthesis; ion exchange; gas adsorption

INTRODUCTION

Zeolites have two major characteristics that make this crystalline material suitable for environmental applications: (a) high cation exchange capacity of some zeolites as a result of replacement of Si(IV) by Al(III) in the SiO₄ tetrahedral basic unit of the zeolite structure; and (b) microporous structure, with channels usually in the range of 1–10 Å, which makes them very useful molecular sieves.

Zeolites may be obtained from both natural deposits and laboratory synthesis. In the latter case, the possibility of obtaining high purity 'tailor-made' zeolites makes them a more interesting material for use as an ion exchanger or a gas adsorbent.

Synthetic zeolites are obtained on an industrial scale from pure Si–Al solutions, combined with the appropriate cation (Na, K, Ca, Mg, Sr, Ba). Very interesting information on applications and synthesis parameters of zeolites may be found in the Breck's Handbook of Zeolites.¹ In the last decade intensive research has been focused on the use of other starting materials for

zeolite synthesis, such as coal fly ash. The high content of an easily degradable Si–Al glass matrix, similar to that in volcanic rocks from which most of natural zeolites originate, generally present in pulverised coal fly ashes makes this material a suitable starting material for zeolite synthesis.

The following processes are currently used for the synthesis of zeolites from fly ash: (a) direct conversion by simple alkaline activation of the fly ash with KOH or NaOH solutions;^{2–4} and (b) the extraction of silica from fly ash and the subsequent combination of the silica leachate with high aluminate solutions to produce pure zeolitic products.⁵ Zeolitic material with a high potential for environmental applications may be obtained by these two methods of synthesis. Intensive research has been carried out on two major topics in this field: (a) the application of zeolitic material as ion exchangers in the treatment of waste waters;^{6–8} and (b) the use of zeolites as molecular sieves for flue gas treatment and separation and recovery of gases.^{9,10}

This study shows the results on the application of

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

Contract/grant sponsor: European Union; contract/grant number: BRPR-CT98-0801

Contract/grant sponsor: Spanish CICYT; contract/grant number: AMB99-1147-CO2-O2

(Received 4 July 2001; accepted 7 December 2001)

zeolitic material synthesised from coal fly ash, both by direct conversion and the silica extraction methods, in the following fields: (a) the decontamination of acid mine waters heavily contaminated with metals, and ammonium-rich industrial waste water; and (b) the adsorption of gaseous pollutants such as CO₂, SO₂ and NH₃.

METHODOLOGY

Materials

Direct conversion products

NaP1-, Na-chabazite-, analcime-, sodalite-, F- and KM-rich products were obtained by direct alkaline conversion from the Teruel and Narcea fly ashes. The experimental synthesis conditions were obtained from prior studies¹¹ and are summarised in Table 1. The conversion experiments were carried out using 4g of fly ash in 4744 Parr digestion bombs with Teflon reactors. After the conversion, the zeolitic product was filtered, washed, dried and stored for subsequent experimentation. XRD analysis revealed a high content of zeolite in all the conversion products. The experimental conditions for the synthesis of an NaP1-rich product (65%) from Narcea fly ash were reproduced at a pilot plant scale¹² and 1 kg of this zeolitic product was used in the application tests.

Pure zeolite products synthesised from silica extracts obtained from fly ash

Pure zeolitic material was obtained from high silica solutions extracted from the Meirama fly ash produced in north-western Spain. The SiO₂ extraction tests were developed using 1 kg of the Meirama fly ash and 3 dm³ of the extractant solution (2 mol dm⁻³ NaOH) in a 5 dm³ Bachiller autoclave, with continuous stirring, at 90 °C for 6 h. The resulting solution containing 14.6 g Si dm⁻³ was filtered and combined with a waste water from an Al-anodising plant containing 57.6 g dm⁻³ Al and 14.9 g dm⁻³ NaOH to obtain a pure zeolite product using the synthetic conditions for zeolite 4A optimised by Sáez.¹³ The two starting solutions were combined to provide Na₂O/SiO₂, H₂O/Na₂O and SiO₂/Al₂O₃ molar ratios of 1.3, 38.9 and 2.1, respectively. The synthesis procedure was completed with a 1 h gelling stage at 80 °C with stirring, a 22 h aging stage at room temperature, and a final 10 h crystallisation stage at 80 °C. XRD analysis showed that the synthesis product consisted of a pure 4A-X (60:40%) blend.

Cation uptake from polluted waters

Cation exchange capacities (CEC) were determined for all the above zeolitic products using ammonium solutions following the International Soil Reference and Information Centre methodology.¹⁴

Two sets of experiments were set up to evaluate the potential application of the NaP1-rich material (hence for NaP1) and the 4A-X blend (hence for 4A) as cation exchangers for waste water decontamination. These products were selected for the decontamination experiments because of their higher CEC values compared with the other products obtained.

For the uptake of heavy metals from polluted waters, a water sample containing high levels of heavy metals was collected from the Tinto River in the vicinity of Niebla village. This acidic (2.5 pH) and Fe-/S-rich water is highly polluted with heavy metals as a consequence of the intensive leaching of sulfide wastes and the widespread mining works in the Rio Tinto Pyrite Belt. Decontamination experiments were performed by mixing 500 cm³ aliquots with the NaP1 and the 4A products with continuous stirring at room temperature for 30 min in PVC containers. Both zeolitic products were dosed in the range 5–30 g dm⁻³.

For the uptake of NH₄⁺ a high-NH₄⁺ water from Clariant Products SA, a black-dye manufacturer, was sampled to develop decontamination experiments using the NaP1 product. This wastewater is an extreme case because its very high sodium concentration will have a negative effect on the NH₄⁺ capacity of the zeolite product due to ion competition. Preliminary tests using 20–62 g dm⁻³ doses were developed to extract NH₄⁺ from synthetic solutions with different Na⁺ concentrations (30–30000 mg dm⁻³ NaCl–Na₂SO₄) to study the effect of the NH₄⁺/Na⁺ ratio. Optimal conditions were used to extract ammonium from the bulk Clariant waste water (1635 mg NH₄⁺ dm⁻³, 5 g NaCl dm⁻³, 50 g Na₂SO₄ dm⁻³ and 150 g Na₂S₂O₃ dm⁻³) and Clariant effluent waters (1596 mg NH₄⁺ dm⁻³, 1.5 g NaCl dm⁻³, 1.5 g Na₂SO₄ dm⁻³, and 5 g Na₂S₂O₃ dm⁻³).

The contents of major and trace elements were determined in the original water samples and each of the decontaminated solutions from the different tests by ICP-AES and ICP-MS. Levels of ammonium were determined when required by FIA-colorimetry methods.

Adsorption of CO₂, SO₂ and NH₃

The CO₂, SO₂ and NH₃ adsorption capacities of the

Table 1. Experimental conditions and zeolitic material synthesised from the Teruel and Narcea fly ashes by direct conversion for subsequent wastewater and flue gas decontamination tests

Main zeolite	Power plant	Synthesis conditions
Na-chabazite	Narcea	NaOH, 5 mol dm ⁻³ , 150 °C, 8h, 2 cm ³ g ⁻¹ fly ash, no stirring
NaP1	Narcea	NaOH, 3 mol dm ⁻³ , 125 °C, 9h, 2 cm ³ g ⁻¹ fly ash, stirring
Analcime	Narcea	NaOH, 1 mol dm ⁻³ , 200 °C, 24h, 18 cm ³ g ⁻¹ fly ash, stirring
Sodalite	Teruel	NaOH, 3 mol dm ⁻³ , 150 °C, 24h, 18 cm ³ g ⁻¹ fly ash, stirring
KM	Narcea	KOH, 1 mol dm ⁻³ , 200 °C, 48h, 18 cm ³ g ⁻¹ fly ash, stirring
Linde F	Teruel	KOH, 3 mol dm ⁻³ , 150 °C, 24h, 18 cm ³ g ⁻¹ fly ash, stirring

zeolitic materials were determined using thermogravimetric analysis and equipment for gas sorption analysis with direct detection of desorbed gases. Both methodologies were based on a sorption chamber with a flow ranging from 30 to 60 cm³ min⁻¹ of gas mixture through a sample holder. In the case of the gas sorption analysis, the gas compositions (%v active gas in a He mixture) and adsorption temperatures were 30% CO₂ at -78 °C, 1% SO₂ at -10 °C and 10% NH₃ at -23 °C. Under these conditions, only physical sorption is expected for each gas phase. A 400 mg sample of the zeolite was placed in a glass reactor and activated at 200 °C before the adsorption runs to remove water molecules from the zeolite. After saturation, the samples were purged at temperatures from 20 to 80 °C and the desorbed gas was measured by thermal conductivity. In the case of the thermogravimetric determination of the sorption capacity of SO₂ and NH₃, the gas compositions tested were 0.3 %v for SO₂ and NH₃ in a N₂ flow. The sorption tests were carried out with 10 mg of each zeolitic material, at 25 °C for 2 h, after activation at 400 °C. After the sorption experiments, the samples were heated to 150 °C to determine the chemical and physical sorption capacities as well as the regeneration potential. The different activation temperatures (200 and 400 °C) and sorption conditions used in the two methodologies were selected to study the interference of water molecules on the sorption capacity of the different gases, and the influence of temperature on the sorption capacity.

RESULTS AND DISCUSSION

The original Meirama, Narcea and Teruel fly ashes showed a very low CEC (<0.05 meq g⁻¹, Table 2). However, the synthesised zeolitic products gave very high CEC, specially the 4A-X blend synthesised from the silica extracts (4.7 meq g⁻¹, Table 2). The CEC of the direct conversion products ranged from relatively high values obtained for NaPl, Na-chabazite, KM and linde F (2.7, 2.1, 1.9 and 1.9 meq g⁻¹, respectively) down to the low CEC of analcime and sodalite (0.6 and 0.3 meq g⁻¹). The high CEC values obtained for the pure 4A-X blend and many of the direct conversion products make these materials very inter-

Table 2. CEC (meq g⁻¹) determined for the zeolitic material and the original fly ash

Main zeolite	CEC
4A-X	4.7
NaPl	2.7
Na-chabazite	2.1
KM	1.9
Linde F	1.9
Analcime	0.6
Sodalite	0.3
Fly ash	<0.05

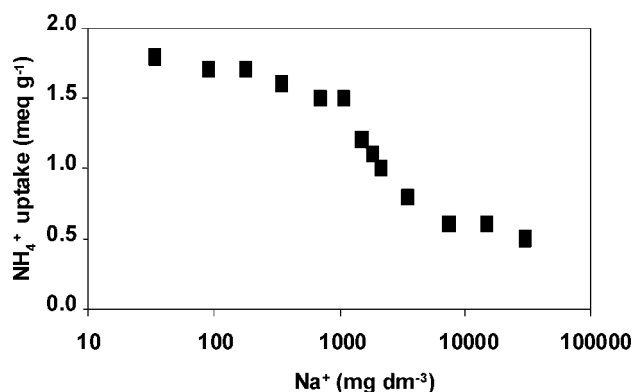


Figure 1. NH₄⁺ uptake capacity of the NaPl product obtained for solutions with different Na⁺ concentrations and a fixed 800 mg NH₄⁺ dm⁻³ content.

esting for industrial applications since natural commercial clinoptilolite and phillipsite³ usually have CEC values ranging from 1 to 2 meq g⁻¹. Since the highest CEC values were obtained for the 4A-X and NaPl products, these were selected for subsequent decontamination tests.

NH₄⁺ uptake from waste and effluent water from a black-dye factory

Although very high NH₄⁺ uptake values were obtained from the laboratory tests, the complex matrix of actual wastewaters may considerably reduce these maximum values due to ion competition with other major cations in the solution. To check the ammonium uptake capacity of the zeolitic materials from a complex wastewater matrix, high NH₄⁺ waste and effluent waters (around 1600 mg NH₄⁺ dm⁻³) from a black-dye factory (Clariant Products SA) were selected for study with the NaPl zeolite. These industrial waters are characterised by high levels of NH₄⁺ in a matrix with a very high Na⁺ ion concentration.

Prior to the decontamination tests, NH₄⁺ uptake experiments with high NaCl solutions showed that the NH₄⁺ uptake is kept >1.3 meq g⁻¹ if the Na⁺ content of the solutions is <1.1 g Na⁺ dm⁻³, but the uptake decreases drastically to 0.8–0.5 meq NH₄⁺ g⁻¹ in solutions containing 7.5–30 g Na⁺ dm⁻³ (Fig 1). The high Na⁺/NH₄⁺ ratio of the Clariant wastewater (1.6 g NH₄⁺ dm⁻³ in a 150 g Na₂SO₄ dm⁻³ and 100 g NaCl dm⁻³ matrix) was responsible for a drop in the NH₄⁺ uptake to 0.3–0.4 meq NH₄⁺ g⁻¹ (Table 3). However, the NH₄⁺ uptake capacity of NaPl using the effluent water, which contains a similar NH₄⁺ content in a

Table 3. NH₄⁺ uptake capacities of the NaPl product obtained for the Clariant waste and effluent waters

NaPl dose (g dm ⁻³)	Wastewater NH ₄ ⁺ uptake (mg g ⁻¹)	Effluent water NH ₄ ⁺ uptake (mg g ⁻¹)
20	9	19
40	7	17
62	6	16

water matrix with Na^+ concentrations reduced 30 times ($1.5 \text{ g NaCl dm}^{-3}$ and $5 \text{ g Na}_2\text{SO}_4 \text{ dm}^{-3}$), was maintained at $1.0 \text{ meq NH}_4^+ \text{ g}^{-1}$ for a NaP1 dose of 20 g dm^{-3} . Consequently, the NaP1 zeolite has a potential application for the removal of NH_4^+ from the Clariant effluent waters.

Heavy metal uptake from acid mine waters

The doses of the NaP1 and 4A-X zeolitic products tested for the uptake of heavy metals from the Tinto River water ranged from 5 to 30 g dm^{-3} . The original water contained very high Fe^{3+} and Al^{3+} contents (440 and 110 mg dm^{-3} , respectively). These trivalent cations have a higher affinity for the Na^+ exchange site of the zeolites with respect to most of the divalent heavy metals (Zn^{2+} , Cu^{2+} , Pb^{2+} , Cd^{2+}), and consequently high concentrations of these two cations may reduce the heavy metal uptake capacity of the zeolitic products.

The results obtained with the 4A-X zeolite (Table 4, Fig 2) showed that the zeolite dose needed to decontaminate the Tinto River water ranged from 10 to 25 g dm^{-3} depending on the quality standards required. Thus, with the 25 g dm^{-3} dose, the concen-

trations of major pollutants decreased by two orders of magnitude: to 1 mg dm^{-3} Al, and $<0.3 \text{ mg dm}^{-3}$ for Cu, Fe, Mn and Zn. Moreover, levels of Ba, Cd, Cr, Mo, Sb, U and V were reduced to $<1 \mu\text{g dm}^{-3}$. Finally, a drastic drop in the concentrations of As, Co and Ni to 4, 7 and $17 \mu\text{g dm}^{-3}$, respectively was also obtained (originally 955, 751 and $316 \mu\text{g dm}^{-3}$). Final Na^+ contents in the treated samples reached 1100 mg dm^{-3} because of the ion exchange of the heavy metals.

As a result of the lower CEC of the NaP1 product with respect to 4A-X, the maximum zeolite dose (30 g dm^{-3} , Table 4, Fig 2) was needed to obtain similar water quality standards to those obtained with a 15 g dm^{-3} dose of the 4A-X product. However, although the contents of leachable elements from residual fly ash particles (As, B, Cr, Mo, U and V) in the Tinto River water treated with 4A-X zeolite were, in most cases, lower than the original content in the polluted water sample. An exception was Cr in the case of the highest NaP1 zeolite doses, where the content of Cr reached $120 \mu\text{g dm}^{-3}$.

The addition of zeolite material caused the pH to increase in all the experiments. As the pH rises minerals may become supersaturated and could

Table 4. Concentrations of major and trace elements before and after the decontamination tests of a water sample from the River Tinto (doses refer to $\text{g zeolites dm}^{-3}$ water)

River Tinto Water	Zeolite dose (g dm^{-3})													
	NaP1							4A-X						
	0	5	7.5	10	15	20	30	5	7.5	10	15	20	25	30
	mg dm^{-3}													
pH	2.5	3.3	3.7	4.0	4.3	4.6	5.5	3.6	3.8	4.0	4.6	5.2	5.6	6.2
Al	112	152	119	77	14	2	2	115	75	40	4	4	1	1
B	0.4	0.4	0.4	0.5	0.6	0.7	0.8	0.2	0.3	2.8	0.3	0.3	0.3	0.3
Ca	94	158	162	154	156	147	122	62	46	28	8	3	1	0.4
Mg	103	106	107	104	105	105	91	84	79	68	42	25	11	6
Na	46	339	434	518	691	839	1027	542	748	872	1043	110	116	120
Cu	36	28	18	11	4.6	1	0.2	19	12	5.6	1.0	0.4	0.2	0.1
Fe	444	3.8	3.3	2.4	3.1	4.1	3.3	0.9	0.5	0.3	0.2	0.3	0.3	0.1
Mn	11	11	11	11	10	8	4	8	6	4	1	0.5	0.2	0.1
Zn	54	51	48	42	33	20	3	35	25	15	3	0.8	0.3	0.1
SO_4^{2-}	884	843	848	817	833	886	911	746	790	777	791	803	823	840
SiO_2	19	80	74	75	73	51	28	163	167	161	128	110	101	95
	$\mu\text{g dm}^{-3}$													
As	955	5	10	10	5	7	8	9	6	4	2	3	4	2
Cd	186	126	73	12	<0.1	<0.	<0.1	103	56	21	<0.1	<0.1	<0.1	<0.1
Co	751	784	804	788	720	627	236	603	475	360	113	34	7	3
Ni	316	349	353	360	342	320	188	217	185	169	92	40	17	11
Pb	240	<0.	<0.	<0.	<0.1	<0.	<0.1	10	4	1	<0.1	<0.1	<0.1	<0.1
Ba	14	10	4	3	<0.1	5	17	7	3	1	<0.1	<0.1	<0.1	<0.1
Cr	24	12	13	16	18	41	127	3	1	<0.	<0.1	<0.1	<0.1	<0.1
Mo	13	10	6	8	7	16	16	<0.	<0.	<0.	<0.1	<0.1	<0.1	<0.1
Sb	17	12	13	11	11	13	11	2	2	2	2	2	2	2
U	15	29	34	51	23	3	11	7	6	5	2	1	1	1
V	54	<0	<0	<0	<0.1	<0	<0.1	<0	<0	<0	<0.1	<0.1	<0.1	<0.1
	<i>Ion balance between Na^+ and cation uptake (meq g^{-1})</i>													
Na^+	2.5	2.3	2.0	1.9	1.7	1.4	4.3	4.1	3.6	2.9	2.3	1.9	1.7	
$\Sigma\text{cations}$	4.8	3.3	2.9	2.4	1.9	1.3	5.6	4.6	4.0	3.2	2.5	2.1	1.7	

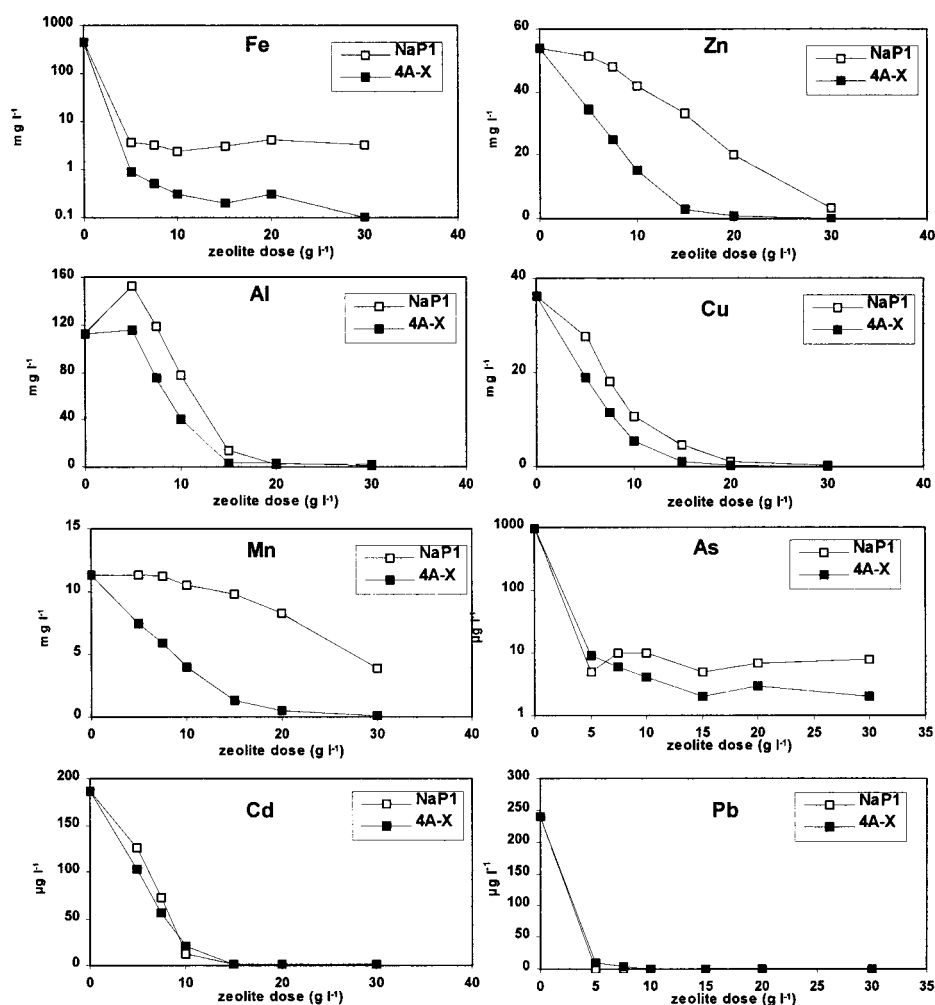


Figure 2. Plots of Fe, Al, Zn, Cu, Mn, As, Cd and Pb concentrations versus zeolite dose applied in the decontamination tests of the River Tinto water using 4A and NaP1 zeolite products.

precipitate as stable solid phases. It is important to distinguish whether the drop in metal content with increase of the zeolite dose is due to cation exchange with sodium or to solid precipitation. Firstly, the ion imbalance between the Na⁺ released and the total cation extracted from the solution (Table 4) suggests that in addition to cation exchange, precipitation processes occur, given the excess of cations with respect to exchanged Na⁺. Moreover, a significant decrease of Fe and Al at the beginning of the experiments suggests precipitation of an Fe–Al-containing solid. Common minerals known to precipitate from acid waters are amorphous Al(OH)₃ and Fe(OH)₃, gypsum, natrojarosite (NaFe₃(SO₄)₂(OH)₆), jurbanite (AlOHSO₄), and basaluminite (Al₄(OH)₁₀SO₄).

Interestingly, the content of leachable fly-ash bearing elements, such as V and As, was drastically reduced in the treated water from the Tinto River. Both As and V form anions within the range of pH of the experiments, and this drop of the concentrations cannot be attributed to cation exchange. Thus removal may be due to the precipitation of scorodite (FeAsO₄·H₂O) as the pH is increased by the zeolite addition. No equivalent phase is known for V but similar As–V behaviour was described in recent studies

to interpret the precipitation of both elements from high Ca fly ash leachates.¹¹

Although a rise in pH to precipitate the heavy metals from the Tinto River water may be more appropriate than cation exchange for decontamination purposes, the results demonstrate that acid mine waters can be treated with a fly ash-derived zeolite product to drastically reduce the heavy metal load. From the results of the water decontamination tests the following tentative order for the affinity of the different cations for the zeolite exchange sites can be proposed: Fe³⁺ > Al³⁺ ≥ Cu²⁺ ≥ Pb²⁺ ≥ Cd²⁺ = Tl⁺ > Zn²⁺ > Mn²⁺ > Ca²⁺ = Sr²⁺ > Mg²⁺. Precipitation of metal-bearing solid phases, in addition to the ion exchange process, enhances the efficiency of the decontamination tests.

Adsorption of CO₂, SO₂ and NH₃

The CO₂, SO₂ and NH₃ adsorption capacities and the CO₂ surface area at 273K (*S*_{CO₂}) determined for the zeolitic products are shown in Table 5. The pure blend of 4A–X zeolites has the highest adsorption capacity for all the gas molecules tested. This zeolitic product has adsorption capacities higher by one order of magnitude for all three gas molecules with respect to the zeolitic material synthesised from coal fly ash by

	CO ₂	SO ₂	NH ₃	S _{CO₂}		
Activation T (°C):	200	200	400	200	400	
Adsorption T (°C):	-78	-10	25	-23	25	
Concentration (ppmv):	300000	10000	3000	100000	1200	
	(mg g ⁻¹)	(mg g ⁻¹)	(mg g ⁻¹)	(m ² g ⁻¹)		
4A-X	74	22	297	111	72	693
Na-chabazite	30	9	99	8	38	135
NaP1	9	4	20	2	17	47
F	9	4	nd	2	nd	34
KM	5	2	33	5	20	32
Sodalite	5	4	nd	1	nd	27
Analcime	3	1	nd	1	nd	23

Table 5. CO₂, SO₂ and NH₃ adsorption capacities (mg g⁻¹) determined for the zeolitic products and S_{CO₂} (m² g⁻¹)

nd: not determined.

direct conversion. This is probably due to the wider channels of zeolite X and 4A (7 and 4 Å, respectively) with respect to the other zeolites that allow the gas molecules to reach the inner pores of the zeolite. Na-chabazite (or hirschelite) has the highest CO₂, SO₂ and NH₃ adsorption capacities for the direct conversion zeolites, but is still one order of magnitude lower than the 4A-X zeolite blend.

The results also showed a close correlation between S_{CO₂} and the gas uptake capacities. Thus, the blend of 4A-X zeolites exhibited S_{CO₂} values one order of magnitude higher than all the direct conversion products with the exception of Na-chabazite. Given the wider diameter of the channels of these two zeolites, it is possible that the internal surface of channels is being measured.

Under the working conditions used in the sorption tests at the lowest temperatures, the uptake of gas molecules is exclusively due to a physical sorption process. In all cases, the SO₂ uptake capacity was drastically improved (by an order of magnitude) when the sorption was carried out at 25 °C and the thermal activation was increased from 200 to 400 °C.

Figure 3 shows an example of the time of evolution of sorbed/desorbed H₂O and SO₂ under different

thermal treatments obtained in the sorption experiments at 25 °C. The results showed that about 74% of the sorption is the result of physical adsorption processes, as deduced from the large proportion of SO₂ desorbed below 150 °C. This is very important since it is clear that regeneration of the zeolitic material is possible.

It is important to note that the presence of water vapour in the flue gas may considerably reduce the gas uptake capacity of these zeolites in actual industrial applications. Consequently, the major potential applications of this zeolitic material for gas treatment may be in either water vapour uptake, or SO₂ or NH₃ sorption from low water-containing gaseous effluents.

It may be concluded from the point of view of flue gas cleaning that the most interesting materials are the 4A and X zeolites, followed by Na-chabazite. The two first zeolites may be obtained in significant amounts from silica extracts from fly ash, but not from direct conversion since their synthesis is strongly limited at temperatures < 100 °C. If this low temperature range is used in the direct conversion process, the low dissolution of the fly ash glass matrix accounts for the low synthetic yield. Although 4A and X zeolites have been obtained by direct conversion from fly ash, the

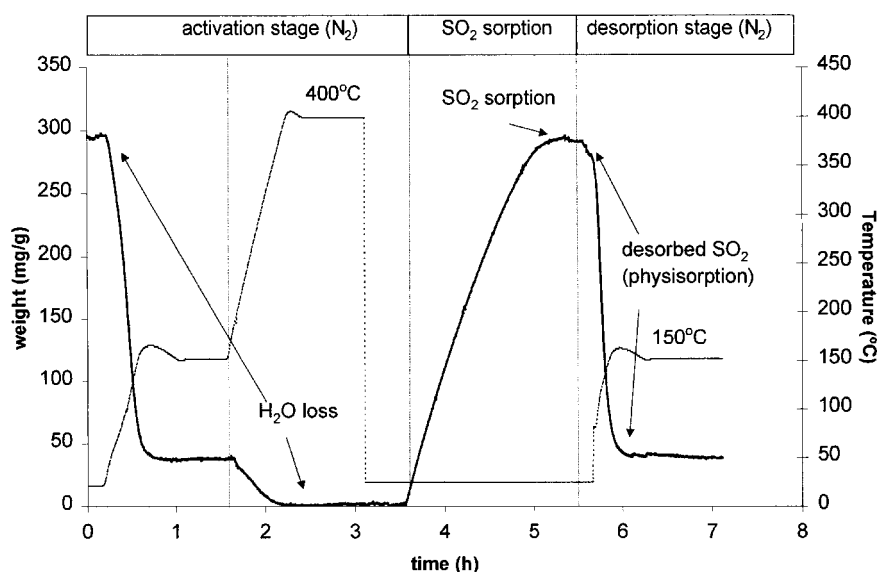


Figure 3. Thermogravimetric evolution of the SO₂ sorption experiment with the 4A-X blend obtained from the silica extracts from Meirama fly ash.

concentration of the zeolite in the end product is very low. In the direct conversion, higher temperatures are needed to dissolve, partially or totally, the Al-Si fly ash phases prior to the precipitation of neomorphic zeolites.

ACKNOWLEDGEMENTS

This study was supported by the BRITE-EURAM Program from the 4th Framework of R&D of the European Union (SILEX, BRPR-CT98-0801) and by the Spanish CICYT (AMB99-1147-C02-02). We would also like to express our gratitude to the power generation companies ENDESA and Unión FENOSA for supplying the fly ash samples.

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