Fly Ash Zeolitization Products Applied to Waste Water and Flue Gas Decontamination

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INTRODUCTION

In the last decades intensive research 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 volcanic rocks from which most of natural zeolites originated) present generally in pulverized coal fly ashes makes this material a suitable starting material for the synthesis of zeolites. The synthesis of zeolites from fly ash are mainly based on the following strategies: a) the direct activation of fly ash particles by means of KOH or NaOH solutions [1-3] and b) synthesis of pure zeolites from silica extracts obtained from fly ash[4]. These two methods allow to obtain zeolitic material with a high application potential as an ion exchanger in the treatment of waste waters[5-7]; or as molecular sieves for flue gas treatment, separation and recovery[8,9]. This study deals with the evaluation of the application of zeolitic material synthesized from coal fly ash (by both direct activation and the silica extraction methods) in the following fields: a) the decontamination of actual high heavy metal acid mine waters and ammonium-rich industrial waste water, and b) the adsorption of gaseous pollutants such as CO_2, SO_2 and NH_3.

METHODOLOGY

Materials

NaP1-, Na-chabazite-, analcime-, sodalie-, F- and KM-rich products where obtained by direct alkaline conversion from the Teruel and Narcea fly ashes. The experimental conditions were obtained from prior studies[10] and are summarized in Table 1. The conversion experiments were carried out using 4 g 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. The XRD analysis revealed a high content of zeolite in all the conversion products. The experimental conditions for the

synthesis of a NaP1-rich product (65 %) from Narcea fly ash were reproduced at a pilot plant scale (see Moreno et al., in this volume) and 1 kg of this zeolitic product was also used in the application tests.

Table 1. Experimental conditions and zeolitic material synthesized from the Teruel (TE) and Narcea (NA) fly ashes by direct conversion for subsequent waste water and flue gas decontamination tests.

MAIN ZEOLITE	FLY ASH	NaOH	KOH	T	t	W/FA	Stirring
Herschelite	NA	5 M	--	150ºC	8 h	2 ml g^{-1} fly ash	No
NaP1	NA	3 M	--	125ºC	9 h	2 ml g^{-1} fly ash	Yes
Analcime	NA	1 M	--	200ºC	24 h	18 ml g^{-1} fly ash	Yes
KM	NA	--	1 M	200ºC	48 h	18 ml g^{-1} fly ash	Yes
Sodalite	TE	3 M	--	150ºC	24 h	18 ml g^{-1} fly ash	Yes
Linde F	TE	--	3 M	150ºC	24 h	18 ml g^{-1} fly ash	Yes

Furthermore, pure zeolitic material was obtained from high silica solutions extracted from the Meirama fly ash produced in north-western Spain. The SiO_2 extraction tests were developed using 1 kg of the Meirama fly ash and 3 l of the extractant solution (2M NaOH) in a 5 l autoclave, with continuous stirring, under 90ºC and 6 h. The resulting 14.6 g Si l^{-1} extractant solution was filtered and combined with a waste water from an Al-anodizing plant (57.6 and 14.9 g l^{-1} of Al and NaOH, respectively) to obtain a pure zeolite product by applying the 4A synthesis conditions optimized by Sáez[11]. The two starting solution were combined to obtain Na_2O/SiO_2, H_2O/Na_2O and SiO_2/Al_2O_3 molar ratios of 1.3, 38.9 and 2.1, respectively. Subsequently, a 1 h gelification stage with stirring under 80 ºC, a 22 h aging stage at room temperature, and a final 10 h crystallization stage under 80 ºC completed the synthesis procedure. XRD analysis evidenced that the synthesis product is made up 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 methodology of the International Soil Reference and Information Centre[12]. Two sets of experimentation 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 due to the 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 Tinto River in the vicinity of Niebla village. This acidic (2.5 pH) and Fe- and S- rich water is highly polluted with heavy metals as a consequence of the intensive leaching of sulfide wastes and mining works widespread in the Rio Tinto Pyrite Belt. Decontamination experiments were performed by mixing 500 ml aliquots with the NaP1 and the 4A products with continuous stirring at room temperature during 30 minutes in PVC containers. Both zeolitic products were dosed from 5 to 30 g l^{-1}.

For the uptake of NH_4^+ from an actual industrial waste water, a high-NH_4^+ water from Clariant products S.A. (a black dye manufacturer) was sampled to develop decontamination experiments using the NaP1 product. This waste water is an extreme case because its very high sodium concentration have a negative effect on the NH_4^+ uptake capacity of the zeolite product due to ion competition. Preliminary tests using 20 to 62 g l^{-1} doses were developed to extract NH_4^+ from synthetic solution with different Na^+ concentrations (30 to 30000 mg l^{-1} NaCl-Na_2SO_4) to study the effect of the NH_4^+/ Na^+ rate. Optimal conditions were used to extract ammonium from the bulk Clariant's waste water (1635 mgNH_4^+ l^{-1}, 5 gNaCl l^{-1}, 50 gNa_2SO_4 l^{-1} and 150 g $Na_2S_2O_3$ l^{-1}) and the Clariant's effluent waters (1596 mg NH_4^+ l^{-1}, 1.5 gNaCl l^{-1}, 1.5 gNa_2SO_4 l^{-1}, and 5 g $Na_2S_2O_3$. l^{-1}).

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

Adsorption of CO_2, SO_2 and NH_3

CO_2, SO_2 and NH_3 adsorption capacities of the zeolitic materials were determined using thermo-gravimetrical analysis and an 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 ml 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 for every gas tested were 30% CO_2 under -78 ^{o}C, 1% SO_2 under –10 ^{o}C and 10% NH_3 under -23 ^{o}C. Under these conditions, only physical sorption is expected for each gas phase. 400 mg of sample was placed into a glass reactor and activated under 200 ^{o}C before the adsorption runs to extract water molecules from the zeolite . After saturation, samples were purged under temperatures from 20-80 ^{o}C and the gas desorbed was measured by thermal conductivity. In the case of the thermo-gravimetrical determination of the SO_2 and NH_3 sorption capacity, the gas compositions tested were 0.3 %v for SO_2 and NH_3 in a N_2 flow. The sorption tests were carried out with 10 mg of each zeolitic material, under 25 ^{o}C during 2 h, after 400 ^{o}C activation stage. After the sorption experiments, the samples were heated up to 150 ^{o}C to determine the chemical and physical sorption capacities as well as the regeneration potential. The different activation temperatures (200 and 400 ^{o}C) and sorption conditions used in the two methodologies were selected to study the interference of water molecules in the sorption capacity of the different gases, and the influence of temperature on the sorption capacity.

RESULTS AND DISCUSSION

The original Narcea and Teruel fly ashes showed a very low CEC (<0.05 meq g^{-1}, Table 2). However, the zeolitic products reached very high CEC, specially the 4A-X blend synthesized from the silica extracts (4.7 meq g^{-1}, Table 2). The CEC of the direct conversion products ranged from the relatively high values obtained for NaP1, 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}). These high CEC values obtained for the pure 4A-X blend and many of the direct conversion products make these materials very interesting from the point of view of industrial application since natural commercial clinoptilolite and phillipsite[3] have usually CEC ranging from 1 to 2 meq g^{-1}. Since the highest CEC values were obtained for 4A-X and NaP1 products, these were selected for subsequent decontamination tests.

NH$_4^+$ uptake from waste and effluent water from a black dye factory using NaP1 zeolite

Although very high NH$_4^+$ uptake values were obtained from the laboratory tests, the complex matrix of actual waste waters may reduce considerably these maximum values due to ion competition with other major cations. With the aim of checking the ammonium uptake capacity of the zeolitic material from a complex waste water matrix, actual high NH$_4^+$ waste and effluent waters (around 1600 mg NH$_4^+$ l^{-1} in both water samples) from a black dye factory (Clariant Products SA) were selected for the study of NH$_4^+$ uptake of the NaP1 zeolite. These industrial waters are characterized by high levels of NH$_4^+$ in a very high Na$^+$ matrix.

Table 2. CEC (meq g^{-1}) determined for the zeolitic material and the original fly ash.

4A-X	4.7	Na-chabazite	2.1	linde F	1.9	sodalite	0.3
NaP1	2.7	KM	1.9	analcime	0.6	Fly ash	<0.05

Prior to the decontamination tests, NH$_4^+$ uptake experiments using high NaCl solutions showed that the NH$_4^+$ uptake is kept >1.3 meq g^{-1} if Na$^+$ contents of the solutions are in the range of <1.1 g Na$^+$ l^{-1}, but the uptake values decrease drastically down to 0.8-0.5 meq NH$_4^+$ g^{-1} in solutions containing 7.5-30 g Na$^+$l^{-1} (Figure 1).
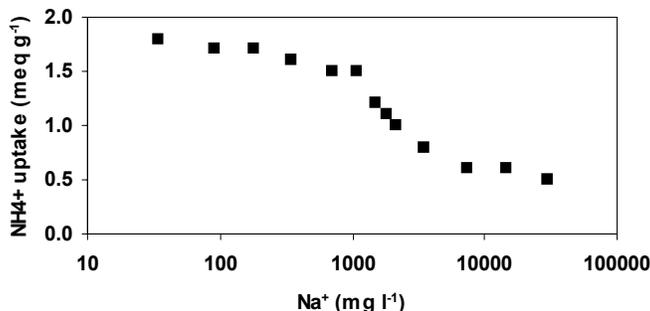

Figure 1. NH$_4^+$ uptake capacity of the NaP1 product obtained for solutions with different Na$^+$ concentrations and a fixed 800 mg NH$_4^+$ l^{-1} content.

The high Na$^+$ / NH$_4^+$ ratio of the Clariant's waste water (1.6 g NH$_4^+$ l^{-1} in a 150 g Na$_2$SO$_4$ l^{-1} and 100 g NaCl l^{-1} matrix) was responsible for the drop of the NH$_4^+$ uptake down to 0.3-0.4 meq NH$_4^+$ g^{-1} in the waste water (Table 3). However, the NH$_4^+$ uptake capacity of NaP1 using the effluent water, which contains similar NH$_4^+$ contents in a water matrix with Na$^+$ concentrations reduced 30 times (1.5 g NaCl l^{-1} and 5 g Na$_2$SO$_4$ l^{-1}), was kept

at 1.0 meq NH_4^+ g^{-1} for a NaP1 dose of 20 g l^{-1}. Consequently, the NaP1 zeolite has a potential application for the uptake of NH_4^+ from the Clariant's effluent waters.

Heavy metal uptake from acid mine waters using NaP1 and A4-X zeolite

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/l . The original water contained very high Fe^{3+} and Al^{3+} contents (440 and 110 mg l^{-1}, respectively). These trivalent cations have a higher affinity for the Na^+ exchange position 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 metals uptake capacity of the zeolitic products.

Table 3. NH_4^+ uptake capacities of the NaP1 product obtained for the Clariant's waste and effluent waters.

NaP1 dose (g l^{-1})	waste water NH_4^+ (mg g^{-1}) uptake	effluent water NH_4^+ (mg g^{-1}) uptake
20	9	19
40	7	17
62	6	16

The results obtained with the 4A-X zeolite (Table 4) showed that the zeolite dose needed to decontaminate the Tinto River water ranged from 10 to 25 g l^{-1} depending on the quality standards required. Thus, with a 25 g l^{-1} dose, the concentrations of major pollutants decreased by two orders of magnitude: down to 1 mg l^{-1} Al, and <0.3 mg l^{-1} for Cu, Fe, Mn and Zn. Levels of Ba, Cd, Cr, Mo, Sb, U and V were reduced to < 1 µg l^{-1}. Finally, a drastic drop of the concentrations of As, Co and Ni down to 4, 7 and 17 µg l^{-1}, respectively was also attained (originally 955, 751 and 316 µg l^{-1}).

As a result of the lower CEC of the NaP1 product with respect to 4A-X, the maximum zeolite dose (30 g l^{-1}, see Table 4) was needed to obtain similar water quality standards attained with a 15 g l^{-1} dose of the 4A-X product. However, although the contents of leachable elements from relict 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 contents in the polluted water sample, in the case of the highest NaP1 zeolite doses, the contents of Cr reached 120 µg l^{-1}.

The addition of zeolite material caused the pH to increase in all the experiments. As pH rises minerals may become supersaturated and could precipitate as stable solid phases. It is important to distinguish whether the drop in metal content with the 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) suggest that in addition of cation exchange, precipitation processes occurred, given the cation excess with respect to exchanged Na^+. Moreover, a significant decrease of the Fe and Al contents at the beginning of the experiments suggests the precipitation of a Fe-Al-containing solid.

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 g of zeolite per litre of water.

| | Dose (g l^{-1}) | | | | | | | | | | | | | |
| Tinto River | | NaP1 | | | | | | 4A-X | | | | | | |
Water	0	5	7.5	10	15	20	30	5	7.5	10	15	20	25	30
	mg l^{-1}													
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	1105	1162	1203
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
	µg l^{-1}													
As	955	5	10	10	5	7	8	9	6	4	2	3	4	2
Cd	186	126	73	12	<0.1	<0.1	<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	<0.1	<0.1	<0.1	<0.1	<0.1	<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	<0.1	<0.1	<0.1	<0.1	<0.1
Mo	13	10	6	8	7	16	16	<0.1	<0.1	<0.1	<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	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	ion balance between Na$^+$ and cation uptake (meq g^{-1})													
Na$^+$		2.5	2.3	2	1.9	1.7	1.4	4.3	4.1	3.6	2.9	2.3	1.9	1.7
Σcations		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

Interestingly, the content of leachable fly-ash bearing elements such as V and As contents, was drastically reduced in the treated water. Both, As and V for anions within the range of pH of the experiments, and the drop of concentrations cannot be attributed to cation exchange. The removal may be due to the co-precipitation of As-Fe-V.

The results demonstrate that acid mine waters may be treated with fly ash derived zeolite products for a drastic reduction of the heavy metal load. From the results of the water decontamination tests the following tentative order for the sorption potential: $Fe^{3+}>Al^{3+} \geq Cu^{2+} \geq Pb^{2+} \geq Cd^{2+}=Tl^{+} > Zn^{2+} > Mn^{2+}> Ca^{2+}= Sr^{2+} > Mg^{2+}$. Precipitation of metal-bearing solid phases, in addition to the ion exchange process, enhances the efficiency of the decontamination tests.

Adsorption of CO$_2$, SO$_2$ and NH$_3$

The CO$_2$, SO$_2$ and NH$_3$ adsorption capacities and the CO$_2$ surface area at 273K (S$_{CO2}$) determined for the zeolitic products are shown in Table 5. The results evidenced that 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 in one order of magnitude for all three gas molecules with respect to the zeolitic material synthesized from coal fly ash by 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 zeolite porosity. Na-Chabazite (or herschelite) has the highest CO_2, SO_2 and NH_3 adsorption capacities for the direct conversion zeolites, but still one order of magnitude lower than the 4A-X zeolite blend. The results evidenced also a close correlation between S_{CO2} and the gas uptake capacities. Thus, the blend 4A-X zeolites exhibited also S_{CO2} values one order of magnitude higher than all the direct conversion products with exception of herschelite. 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 SO_2 uptake capacity was drastically improved (by an order of magnitude) when the sorption was carried out under 25 °C and the thermal activation was increased from 200 to 400 °C.

Table 5. CO_2, SO_2 and NH_3 adsorption capacities (mg g^{-1}) determined for the zeolitic products and S_{CO2} (m^2 g^{-1}).

	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	
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	-	2	-	34
KM	5	2	33	5	20	32
Sodalite	5	4	-	1	-	27
Analcime	3	1	-	1	-	23

Table 6 shows an example of the time evolution of sorbed/desorbed H_2O and SO_2 under different thermal treatments obtained in the sorption experiments under 25 °C. The results evidenced that about 84 % of the sorption is carried out by physical adsorption processes, as deduced from the large proportion of SO_2 desorbed under 150 °C. This is very important since it is clear that the regeneration of the zeolitic material is possible. It is important to note that the presence of water vapor 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 both the water vapor uptake or the SO_2 or NH_3 sorption from low water gaseous effluents.

From the point of view of flue gas cleaning the most interesting zeolites are 4A and X zeolites, followed by herschelite. 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 by temperature (<100 ^{o}C). 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.

Table 6. Thermo-gravimetric evolution of the SO_2 sorption experiment performed with the 4A/X blend obtained from the silica extracts from Meirama fly ash

	H_2O desorption		SO_2 sorption	SO_2 desorption
	mg g^{-1}			
T	150°C	400°C	25°C	150°C
0.0-0.5 h	-252	--	--	--
0.5-3.0 h	--	-48		--
3.0-5.5 h	--	--	297	--
5.5-7.2 h	--	--	--	249

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