

# POTENTIAL ENVIRONMENTAL APPLICATIONS OF PURE ZEOLITIC MATERIAL SYNTHESIZED FROM FLY ASH

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**ABSTRACT:** A pure 4A/X (60/40) zeolite product was synthesized from silica extracts of the Meirama fly ash in northwestern Spain. A high cation-exchange capacity (4.7 meq/g) was obtained for the zeolitic material. The potential application of this coal fly ash conversion product for decontamination of high heavy metal waters was evaluated using three high heavy metal waters from acid mine drainage around the pyrite Huelva belt. The results were compared with those obtained with an equivalent pure commercial synthetic zeolite. A considerable reduction in the heavy metal content was attained (Zn from 174 to <0.1 mg/L, Cu from 36 to 0.1 mg/L, Fe from 444 to 0.8 mg/L, Mn from 74 to <0.1 mg/L, Pb from 1.5 to <0.1 mg/L, and Cd from 0.4 to <0.1 mg/L), even in high Ca and Fe waters using zeolite doses from 5 to 30 mg/L. Both precipitation and cation-exchange processes accounted for the reduction in the pollutant concentration in the treated waters. Leachable hazardous elements from coal fly ash, such as Mo, B, As, V, and Cr, were not fixed in the synthesis of pure zeolites from the silica extracts. Consequently, they did not restrict the potential applications of this material as an ion exchanger, unlike the zeolitic material obtained from fly ash by direct alkaline conversion.

## INTRODUCTION

A number of hydrothermal activation methods have been proposed to synthesize different zeolites from fly ash using alkaline solutions (mainly NaOH and KOH solutions). The traditional conversion methods differ in the molarity of the alkaline reagents, activation-solution/fly-ash ratio, temperature (80°–200°C), reaction time (3–48 h), and pressure, depending on the type of zeolite desired. Details of the different activation methods proposed are reported by Höller and Wirshing (1985), Kato et al. (1986), Bergk et al. (1987), Mondragón et al. (1990), Larosa et al. (1992), Shigemoto et al. (1992); Kolousek et al. (1993), Catalfamo et al. (1993), Singer and Berggaut (1995), Berggaut and Singer (1996), Lin and Hsi 1995, Park and Choi (1995), Querol et al. (1995, 1997b, 1999, 2001a), Shih et al. (1995), and Inoue et al. (1995). Up to 15 different types of zeolite have been produced from one type of fly ash by varying the synthesis conditions. The zeolite content in the conversion product varies (20–65%) as a function of the fly ash properties and the conditions selected (Querol et al. 1999, 2001a). Because of the incomplete conversion, the zeolitic product also contains a non-reactive fly ash fraction made up of nonactivated aluminum-silicate phases and other components such as magnetite, hematite, calcite, and lime. Shigemoto et al. (1992) and Berggaut and Singer (1996) have improved the traditional conversion process by introducing an alkaline fusion stage prior to the conventional zeolite synthesis. This alteration resulted in an increased conversion rate and

in the synthesis of very interesting types of zeolite. The conversion time has been further reduced (down to minutes) by using microwave synthesis (Querol et al. 1997a). However, further studies are needed to optimize the reduction of production costs to make this process feasible.

In all these methodologies the resulting zeolitic products contain a nonconverted part of fly ash. Owing to the partial conversion of fly ash, the cation-exchange capacity of these zeolites is much lower (30–65%) than that of the pure ones. Moreover, the residual fly ash fraction may contain relatively high levels of leachable B, Mo, As, V, Cr, and Se, which may invalidate the utilization of this zeolitic material in wastewater purification processes. These were the two main reasons for research into the production of pure zeolites from fly ashes undertaken by Hollman et al. (1999). They developed a two-step procedure consisting of an initial Si-extraction from fly ash by using a light alkaline treatment of fly ash followed by a synthesis of pure zeolites by adding an Al-bearing residue solution obtained from the Al-anodizing industry. The solid residue that remains after the Si-extraction can also be converted into a zeolitic product by using the traditional conversion method. The cation-exchange capacity of this residual product is much lower than that of the pure zeolites.

In all the aforementioned processes, zeolites such as NaP1, A, X, KM, F, hydroxy-sodalite, hydroxy-cancrinite, nepheline, analcime, chabazite, herschelite, tobermorite, and faujasite are synthesized. The potential use of fly-ash-derived zeolites with a high cation-exchange capacity (up to 5 meq/g) in the purification of wastewater has been evaluated by a number of research groups. To date, the removal of heavy metals and ammonium from wastewater has been tested extensively (Catalfamo et al. 1993; Kolousek et al. 1993; Lin and His 1995; Park and Choi 1995; Singer and Berggaut 1995; Amrhein et al. 1996; Berggaut and Singer 1996; Patane et al. 1996a,b; Suyama et al. 1996; Querol et al. 1997a, 2001a; Lin et al. 1998). The possibility of using these zeolites as molecular sieves in gas purification technology has also been investigated in a few studies (Querol et al. 1999; Srinivasan and Grutzeck 1999). As regards water purification, most studies evaluated the potential use of zeolites for the retention of selected water pollutants employing exclusively monocationic synthetic solutions. From the studies carried out, it is clear that there is considerable competition between cations in a solution in order to occupy exchangeable places in zeolites (Querol et al. 1999), and consequently, the matrix composition plays an

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important role in the pollutant uptake efficiency of a given zeolite. Thus, high  $\text{Fe}^{3+}$  or  $\text{Ca}^{2+}$  or solutions in urban and acidic wastewaters may considerably reduce the uptake of ammonium or heavy metals. Moreover, the number of molecules present in the solution plays a very important role in this case.

This study focuses on the potential application of pure zeolitic material obtained in a two-step conversion process from pure Si extracts obtained from coal fly ash. The application of the zeolitic material in the purification of acidic mine waters from the Tinto River and wells polluted by the Aznalcóllar toxic spill (both in southwestern Spain) is investigated at a laboratory scale. These waters were  $\text{CaSO}_4$ -rich with high metal contents (Fe, Al, Zn, Mn, Cu, Pb, and Cd). Both calcium and metal ions were expected to compete for the exchange sites in the zeolites. Decontamination tests were devised for the extraction of pollutants by using 4A zeolitic material obtained from fly ash and a commercial 4A zeolite.

## EXPERIMENTAL

### Materials

Zeolitic material was obtained from the silica extraction from the fly ash produced at the Meirama power plant in north-western Spain. The major chemical, mineral, and physical characteristics of the Meirama fly ash are summarized in Table 1. The Meirama fly ash was selected because of its high  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio (2.8 by weight) and its high cristobalite content, which is useful to obtain  $\text{SiO}_2$ -rich solutions to synthesize pure zeolite (Querol and Moreno 1999).

$\text{SiO}_2$  extraction tests were performed in 60-mL teflon reactors with an alkaline-solution/fly-ash ratio of 3L/kg and continuous stirring. Table 2 summarizes the different experimental conditions tested for the silica extraction, based on the methodology devised by Hollman et al. (1999). After optimization of the extraction parameters, selected conditions (2M NaOH,

**TABLE 1.** Major Chemical, Mineralogical, and Physical Characteristics of Meirama Fly Ash (Loss on Ignition, BETSA, surface area)

Major oxides and trace element contents				Mineral composition	
	% wt		mg/kg		% wt
$\text{SiO}_2$	49.2	As	94	Mullite	19.6
$\text{Al}_2\text{O}_3$	17.6	B	158	Quartz	6.9
$\text{Fe}_2\text{O}_3$	10.4	Ba	1601	Cristobalite	4.5
CaO	11.8	Be	4	Anhydrite	2.6
MgO	2.0	Cd	1	Hematite	2.5
$\text{Na}_2\text{O}$	0.4	Co	20	Feldspar	0.7
$\text{K}_2\text{O}$	0.4	Cr	47	Glass	62.5
$\text{P}_2\text{O}_5$	0.2	Cu	44		
$\text{TiO}_2$	0.5	Ge	3		
MnO	0.1	Li	37		
$\text{SO}_3$	2.2	Mo	5	<b>Physical characterization</b>	
N	0.03	Ni	49	True density ( $\text{g}\cdot\text{cm}^{-3}$ )	2.4
C	0.7	Pb	40	Apparent density ( $\text{g}\cdot\text{cm}^{-3}$ )	0.7
Moist	2.4	Rb	26	Porosity (%)	71.6
LOI	5.2	Se	7	BETSA ( $\text{m}^2\cdot\text{g}^{-1}$ )	12.4
$\text{SiO}_2/\text{Al}_2\text{O}_3$	2.8	Sr	757	Grain size distribution ( $\mu\text{m}$ )	
		Th	20	Percentile 10	8.9
		U	6	Median	40.5
		V	154	Percentile 90	248
		Zn	112		

**TABLE 2.** Experimental Conditions Used for Silica Extraction from Meirama Fly Ash and Mineral Composition of Residue Compared with Original Fly Ash

Test number	Leaching Conditions	Extraction		Solid Residue (% by weight)								
		Solution/fly ash (L/kg)	Na used (%)	Yields	Glass	Q	C	Mu	AN	TOB	NaP1	
Original fly ash	—	—	—	—	—	63	7	3	20	—	—	—
1 (NaOH 2 M/90°C/6 h)	No	3.0	0.0	36.6	2.4	55	6	<1	20	<1	<1	3
2 (1st steep) (NaOH 2 M/90°C/6 h)	Yes	3.0	26.7	120.0	0.1	21	7	<1	19	<1	<1	38
2 (2nd steep) (NaOH 2 M/90°C/6 h)	Yes	3.0	19.8	50.1	0.1	21	6	<1	19	<1	<1	52
2 (3rd steep) (NaOH 2 M/90°C/6 h)	Yes	3.0	3.5	8.9	0.7	21	5	<1	19	<1	<1	53
3 (NaOH 2 M/90°C/9 h)	Yes	3.0	46.4	84.0	0.1	23	7	<1	20	<1	<1	45
4 (NaOH 2 M/200°C/24 h)	No	2.0	87.7	3.3	<0.1	17	<1	<1	<1	49	<1	22
5 (NaOH 1 M/90°C/6 h)	No	6.0	3.4	24.3	2.8	60	7	<1	20	<1	<1	<1
6 (NaOH 1 M/90°C/6 h)	Yes	3.0	45.3	50.9	0.1	49	7	<1	20	<1	<1	18
7 (NaOH 1 M/150°C/24 h)	No	18.0	24.7	68.6	2.9	18	<1	<1	<1	<1	5	66
8 (NaOH 0.5 M/90°C/6 h)	No	11.9	7.5	25.7	1.4	55	7	<1	19	<1	<1	<1

Note: Glass = aluminium-silicate glass; Q = quartz; C = cristobalite, Mu = mullite, AN = analcime, TOB = tobermorite, NaP1 = zeolite.

**TABLE 3.** Experimental Conditions Used for Synthesis of 4A-X Zeolite from High Silica and Alumina Solutions by Sáez (1999)

Parameter	Stirring	Time (h)	T (°C)	PFA Reactor
Gelification	Yes	1	80	Closed
Aging	No	22	25	Open
Crystallization	No	10	80	Closed

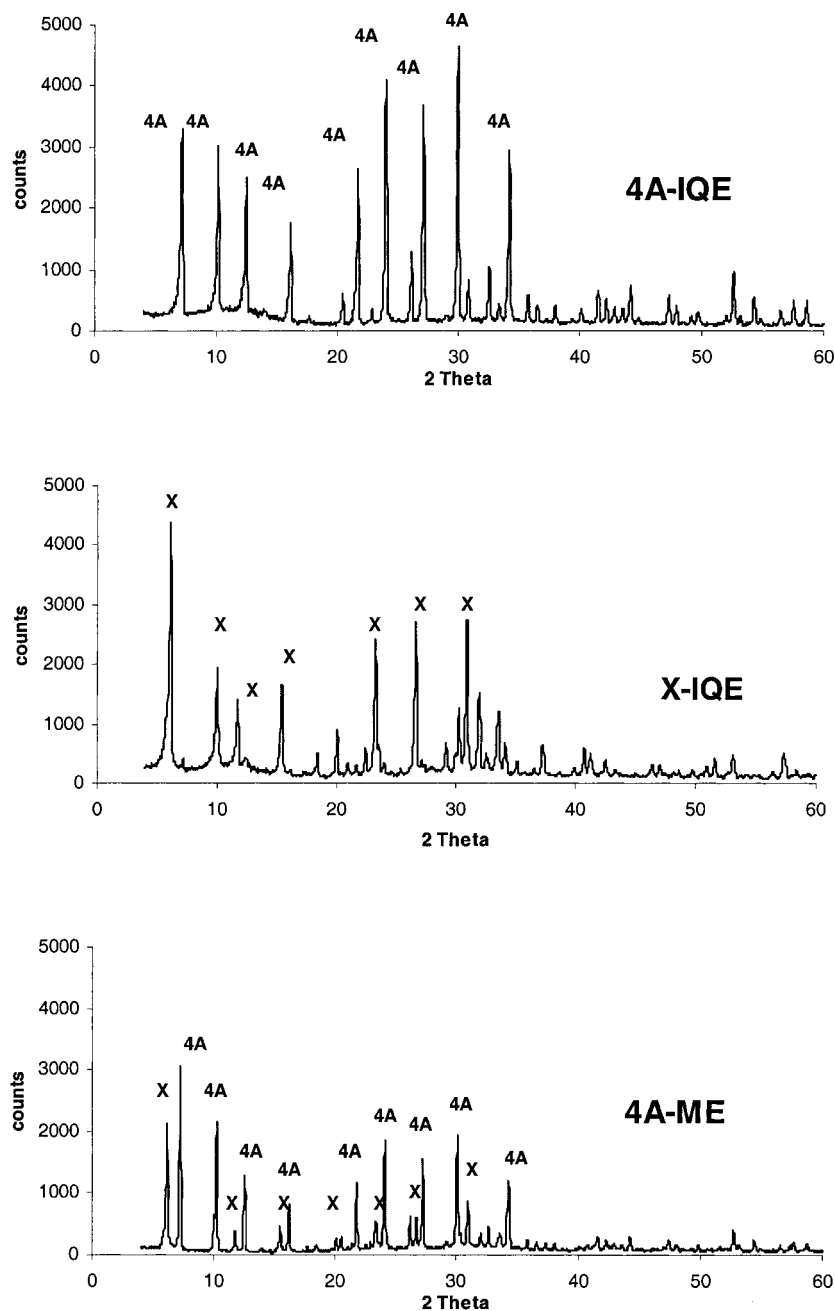
Note: Molar ratios— $\text{Na}_2\text{O}/\text{SiO}_2 = 1.3$ ,  $\text{H}_2\text{O}/\text{Na}_2\text{O} = 38.9$ ,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 2.1$ .

90°C, 6 h, and continuous stirring) were reproduced on a larger scale by using 1 kg of the Meirama fly ash and 3 L of the extractant solution in a 5 L Bachiller autoclave with temperature and pressure control. The resulting 14.6 g Si/L extraction solution was filtered and stored at 4°C for subsequent zeolite synthesis. Wastewater from an Al anodizing plant, containing 57.6 and 14.9 g/L of Al and NaOH, respectively, was combined with the high-Si solution, obtained from the Meirama fly ash,

in an attempt to obtain a pure zeolite product by applying the 4A synthesis conditions optimized by Sáez (1999) (Table 3).

In addition to the synthesized zeolites, three commercial zeolite types (4A, X, and NaP1) were supplied by Industrias Químicas del Ebro SA (IQE) for decontamination tests. Fig. 1 shows the X-ray diffraction patterns of all these zeolite products.

Water samples containing high levels of heavy metals were collected from two irrigation wells from the Guadimar valley, southwestern Spain. These two wells were flooded with pyrite sludge and acidic water during the Aznalcóllar spill (Manzano et al. 1999), which occurred on March 25, 1998. The water from the two wells was acidic (2.6 and 3.7 pH), with contents of calcium and sulfate, and different degrees of heavy metal pollution. Water in well No. 70 was highly polluted and for decontamination purposes an increase in the pH (to induce the precipitation of heavy metals) was more appropriate than an ion-exchange treatment. However, water in well No. 71 could be directly decontaminated by a cation-exchange treatment.



**FIG. 1.** X-Ray Diffraction Patterns of Commercial Zeolites (4A-IQE and X-IQE) and 4A Zeolite Synthesized from Meirama Fly Ash (4A-ME)

**TABLE 4.** Ionic Competition Tests Using Synthetic Solutions with 200 mg/L of Cu<sup>2+</sup> and Zn<sup>2+</sup> for Each Zeolite Type

Parameter	Zeolite dose (g/L)	Cu <sup>2+</sup> (200 mg/L)					Zn <sup>2+</sup> (200 mg/L)				
		Concentration (mg/L)			Ion Exchange (meq/g)		Concentration (mg/L)			Ion Exchange (meq/g)	
		Ca	Cu	Na	Ca + Cu	Na	Ca	Zn	Na	Ca + Zn	Na
<b>4A-IQE</b>											
500 mg/L Ca	0	492	207	0	—	—	510	208	0	—	—
500 mg/L Ca	5	145	0	545	4.8	4.8	120	1	591	5.0	5.0
500 mg/L Ca	10	5	0	715	3.1	3.1	3	0	747	3.1	3.1
1,000 mg/L Ca	0	984	209	0	—	—	1,046	201	0	—	—
1,000 mg/L Ca	5	598	0	577	5.3	5.1	583	2	620	5.7	5.3
1,000 mg/L Ca	10	205	0	1,026	4.5	4.4	195	0	1,112	4.7	4.7
<b>NaP1-IQE</b>											
500 mg/L Ca	0	492	207	0	—	—	510	208	0	—	—
500 mg/L Ca	5	164	4	504	4.6	4.4	134	32	547	5.0	4.9
500 mg/L Ca	10	2	0	707	3.1	3.1	2	0	721	3.2	3.1
1,000 mg/L Ca	0	984	209	0	—	—	1,046	201	0	—	—
1,000 mg/L Ca	5	610	16	519	4.9	4.5	571	68	579	5.4	4.9
1,000 mg/L Ca	10	217	1	1,002	4.5	4.4	168	10	1,070	4.8	4.5
<b>X-IQE</b>											
500 mg/L Ca	0	492	207	0	—	—	510	208	0	—	—
500 mg/L Ca	5	240	11	409	3.8	3.6	192	31	449	4.2	3.8
500 mg/L Ca	10	13	0	681	2.9	2.9	16	2	672	3.2	3.0
1,000 mg/L Ca	0	984	209	0	—	—	1,046	201	0	—	—
1,000 mg/L Ca	5	701	26	444	3.9	3.8	660	59	484	4.7	4.2
1,000 mg/L Ca	10	353	4	835	3.5	3.4	357	19	862	4.1	3.8

Moreover, water from the river Tinto was sampled in the vicinity of Niebla. The water from the Tinto River was also acidic (pH 2.5) and contained high levels of iron, aluminum, and other heavy metals as a consequence of the intensive leaching of sulfide wastes and mining works, which are widespread in the Tinto River Pyrite Belt.

#### Determination of Cation-Exchange Values and Decontamination Tests

Cation-exchange capacity values were obtained using ammonium solutions, following the methodology of the International Soil Reference and Information Center (ISRIC) (1995). Similar tests were carried out using distilled water to determine the leachable Na<sup>+</sup> levels from the zeolitic products, which could be erroneously attributed to ionic exchange processes.

Preliminary tests of ionic competition of a major element (Ca<sup>2+</sup>) with respect to Cu<sup>2+</sup> and Zn<sup>2+</sup> were performed by adding different zeolite doses to synthetic solutions, prepared with deionized water, containing 200 mg/L of a heavy metal, and varying the Ca<sup>2+</sup> concentrations from 200 to 1,000 mg/L (Table 4). The zeolites used in these tests were the commercial NaP1, 4A, and X. Aliquots of 100 mL of each solution were mixed with continuous stirring at room temperature for 30 min in PVC containers with zeolites, using doses of 5, 10, 20, and 30 g/L. The results demonstrate that Zn<sup>2+</sup> and Cu<sup>2+</sup> have a higher affinity with the zeolite types investigated than Ca<sup>2+</sup>. Thus, solutions containing 200 mg/L of these heavy metals, and up to 1,000 mg/L of Ca<sup>2+</sup> treated with all the zeolites investigated, reduced the metal content to <0.5 mg/L with up to 550 mg/L of Ca<sup>2+</sup> remaining in the solution (Table 4). Given that the highest heavy metal affinity was obtained for the 4A zeolite, the NaP1 and X zeolites were not used in the subsequent experiments.

Finally, decontamination tests were carried out with the polluted water samples and different doses of the 4A zeolites (commercial and synthesized from fly ash). Aliquots of 500 mL of each water sample were mixed with zeolite powder following the same procedure as the ionic competition tests, with doses from 5 to 40 g/L. Tests were reproduced by duplicate under room temperature, continuous stirring, and 30 min of reaction. At the end of each experiment, the mixture was filtered and the pH values of the treated waters were mea-

sured prior to the subsequent analysis of the content of major and trace elements. The same procedure was applied for control samples of the original water samples (zeolite dose = 0) in the four batches of experiments. Table 5 shows the mean relative standard deviation for the analysis of the major and trace elements determined in the control samples. Most of the elements showed <10% standard deviation, only determinations of B, Cr, Mo, Sb, and V showed <18% relative standard deviation, especially in samples where the contents of these elements were very low (<0.5 mg/L).

#### Analysis

Major and trace element contents in fly ash were determined by inductively coupled plasma atomic emission spectrometry

**TABLE 5.** Relative Standard Deviations (Percent of Original Water Samples) Obtained for Major and Trace Element Determinations in Control Samples of Four Batches of Decontamination Experiments

Sample	Relative Standard Deviation (%)		
	No. 70	No. 71	Tinto
Al	3.3	3.0	2.4
B	15.9	5.9	9.9
Ca	4.9	5.5	3.1
K	3.4	2.4	4.2
Mg	2.5	2.8	2.1
Na	5.9	4.6	1.7
Cu	4.3	6.4	2.3
Fe	9.2	4.6	4.2
Mn	4.9	4.9	2.8
Zn	5.0	3.5	1.7
S	2.2	2.5	2.3
Si	3.9	2.8	4.6
As	10.3	7.4	5.9
Cd	4.8	5.1	0.5
Co	9.1	6.4	2.9
Ni	6.6	5.4	6.4
Pb	1.8	8.2	7.7
Tl	5.0	9.5	8.6
Cr	14.2	2.3	13.7
Mo	11.5	12.0	8.9
Sb	17.2	16.8	17.8
U	1.4	6.1	14.8
V	11.6	2.2	16.2

(ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) following the procedures described by Querol et al. (2001b). The levels of ammonium were assessed by using flow induction analysis (FIA)-colorimetry methods. These two analytical tools were also employed for the determination of major and trace elements in the water samples and the different solutions resulting from the cation-exchange capacity and decontamination tests. The analytical conditions used allowed one to reach detection limits close to 0.1 mg/L for major and trace elements determined by ICP-AES and close to 0.1 µg/L for the trace elements (As, Cd, Co, Cr, Mo, Ni, Pb, Sr, Tl, U, and V) determined by ICP-MS. The analytical work focused attention on a wide range of elements to control the following objectives:

- To assess the efficiency of the decontamination tests for major and trace cations
- To carry out ionic balances for the determination of exchange values (moreover, the ionic balance between the exchanged Na<sup>+</sup> and the major and trace cations in the decontamination tests was carried out to deduce if exchange or precipitation processes occurred after the zeolite addition)
- To evaluate possible leaching of pollutants from the fly-ash-derived zeolites when high zeolite doses were used in the decontamination tests

Mineral analyses of fly ash and zeolite samples were performed by X-ray diffraction analysis. Semiquantitative data on the fly ash composition were obtained by the internal reference method, using fluorite as an internal standard, whereas the zeolite content was estimated after comparing the cation-exchange capacity values of the samples with those of the pure commercial 4A zeolite.

## RESULTS AND DISCUSSION

### Zeolite Synthesis

The results from the optimization of SiO<sub>2</sub> extraction from the Meirama fly ash (Table 2) showed that a single extraction using a solution/fly-ash ratio of 3L/kg, 90°C, and 6 h and a concentration of the extractant of 2M NaOH yielded a relatively high silica extraction (120 g SiO<sub>2</sub>/kg fly ash). Using this relatively light alkaline attack, Si-bearing phases may be dissolved from fly ash components without zeolite precipitation. As shown in Table 2, if higher temperature or extraction time are used, the Si extraction yield is reduced as a consequence of the trapping of dissolved Si by the precipitation of zeolitic phases such as NaPl, analcime, or tobermite. The results evidenced that a high Si content in the glass matrix in the Meirama fly ash, coupled with the presence of highly soluble opaline phases (cristobalite) account for the high Si extraction yields obtained with the Meirama fly ash. Table 2 shows that

**TABLE 6.** Concentrations of Major and Trace Elements before (Zeolite Dose = 0) and after Decontamination Tests of Water Sample from Well No. 70 in Aznalc llar Area (Doses Refer to Grams of Zeolite per Liter of Water)

Sample #70	4A-IQE					4A-ME						
	0	10	20	30	40	5	7.5	10	15	20	25	30
<b>Zeolite dose g/L</b>												
<b>pH</b>	2.6	6.5	7.8	8.5	8.8	4	4.4	5	5.8	6.3	6.6	7.1
<b>mg/L</b>												
<b>Al</b>	70	0.1	0.5	1.2	3.8	16	7	3	1	2	2	3
<b>B</b>	0.4	0.4	0.3	0.3	0.3	1.5	0.2	0.2	0.2	0.2	0.3	0.3
<b>Ca</b>	541	141	21	4	0.3	420	335	256	118	51	29	18
<b>K</b>	5	5	3	2	2	8	7	8	9	8	9	9
<b>Mg</b>	260	215	52	6	0.8	235	216	200	163	116	87	59
<b>Na</b>	54	994	1414	1544	1602	553	732	874	1133	1224	1410	1475
<b>Cu</b>	3	<0.1	<0.1	<0.1	<0.1	0.8	0.4	0.3	0.8	<0.1	0.2	<0.1
<b>Fe</b>	11	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
<b>Mn</b>	74	18	1.7	0.2	<0.1	59	48	38	17	7	3	2
<b>Zn</b>	174	2.9	<0.1	<0.1	<0.1	89	57	33	7	3	1	1
<b>SO<sub>4</sub><sup>2-</sup></b>	1130	1163	1155	1163	1165	1112	1113	1109	1112	1054	1135	1133
<b>Si</b>	50	13	3	1.6	1.5	85	77	75	64	45	42	37
<b>µg/L</b>												
<b>As</b>	7	1	5	1	<0.1	4	2	3	3	2	2	1
<b>Cd</b>	398	<0.1	<0.1	<0.1	<0.1	38	18	9	<0.1	<0.1	<0.1	<0.1
<b>Co</b>	670	89	2	<0.1	<0.1	472	410	333	156	63	23	11
<b>Ni</b>	443	286	9	<0.1	<0.1	308	297	241	139	74	40	106
<b>Pb</b>	1516	<0.1	<0.1	<0.1	<0.1	2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
<b>Tl</b>	46	1	1	<0.1	<0.1	4	4	3	2	2	1	1
<b>Cr</b>	6	4	4	6	7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
<b>Mo</b>	5	6	11	7	6	0	0	1	1	<0.1	1	1
<b>Sb</b>	10	9	9	10	9	3	2	2	3	3	3	3
<b>U</b>	10	1	1	<0.1	2	6	5	4	2	1	1	1
<b>V</b>	6	8	6	5	3	2	2	3	2	2	3	2
<b>ion balance between Na<sup>+</sup> and cation uptake (meq/g)</b>												
<b>Na<sup>+</sup></b>		4.0	2.9	2.1	1.7	4.3	3.9	3.5	3.1	2.5	2.3	2.0
<b>Σcations</b>		4.0	2.9	2.1	1.6	4.2	3.9	3.6	3.2	2.8	2.4	2.1

quartz and mullite are not dissolved from the fly ash in the alkaline attack. The Si extraction is favored by a high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio of the glass matrix, because a simultaneous dissolution of Al and Si will result in the fast precipitation of zeolite material with the consequent trapping of dissolved silica molecules. In addition to the above chemical and mineralogical patterns, the high SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio (2.8) and BET surface area (12.4 m<sup>2</sup>/g) probably account for the high Si extraction yields obtained from the Meirama fly ash. The relatively low contents of hazardous trace elements and soluble phases of this fly ash are also important factors for the Si leaching. Thus, leachates from zeolitic products obtained from the Si extracts of the Meirama fly ash exhibit <0.1 µg/L of As, V, Cr, and other hazardous elements, even using high zeolite doses (up to 40 g/L).

A zeolite-rich material was synthesized from the SiO<sub>2</sub> extract of 1 kg of fly ash using a solution/fly-ash ratio of 3 L/kg, 90°C, and 6 h and a concentration of the extractant of 2 M NaOH. This extract was combined, under the conditions summarized in Table 3, with wastewater from an Al-anodizing industry, resulting in the synthesis of 360 g of a blend of 4A and X zeolite (afterwards named 4A-ME) in a proportion of 60/40 (Fig. 1).

The highest cation-exchange capacity values were obtained for the 4A-IQE zeolite (5.4 meq/g), followed by the NaPI-IQE (5.0 meq/g), 4A-ME (4.7 meq/g), and X-IQE (4.3 meq/g). The comparison of the cation-exchange capacity values of the

commercial 4A-IQE and X-IQE with the synthesized 4A-ME (4A and X zeolites in a ratio 60/40) indicates that the zeolite content in the fly-ash-derived material is close to 95% by weight. These final cation-exchange capacity values were calculated by subtracting 0.5 and 0.4 meq/g from the cation-exchange capacity values obtained for the 4A zeolites, given that the water leaching experiments revealed these fractions of soluble Na from the zeolite material.

### Decontamination Test

The doses of the zeolite material needed for the decontamination tests ranged from 5 to 40 g/L, depending on the concentration of pollutants and on the 4A type. The results showed that the appropriate zeolite dose for the complete decontamination of the No. 70 water sample was 20–30 g/L. Using the first dose and the 4A-IQE zeolite, the concentrations of pollutants were reduced from 174 to <0.1 mg Zn/L, from 74 to 1.7 mg Mn/L, and from 400 to <0.1 µg Cd/L (Table 6). The final pH values of the treated solutions reached 8.5 and 7.1, with the largest zeolite dose using the 4A-IQE and 4A-ME, respectively. A considerable reduction in the treated water was obtained for Pb, Tl, and U (<1 µg/L) and for Cu and Ni (<100 µg/L). The 4A-IQE doses of 10 g/L were sufficient to reduce the concentrations to 2.9 mg Zn/L, 0.1 mg Al/L, <0.1 mg/L Fe and Cu, <1.0 µg/L Tl and As, and <0.1 µg Pb/L, whereas the Co and Ni were still present in significant concentrations

**TABLE 7.** Concentrations of Major and Trace Elements before (Zeolite Dose = 0) and after Decontamination Tests of Water Sample from Well No. 71 in Aznalc6llar Area (Doses Refer to Grams of Zeolite per Liter of Water)

Sample #71 Zeolite dose g/L	4A-IQE						4A-ME						
	0	5	10	20	30	40	5	7.5	10	15	20	25	30
pH	3.7	8.1	9	9.6	9.9	10.1	6.1	6.5	6.9	7.2	7.4	7.5	7.6
<b>mg/L</b>													
Al	10	1.2	3	9.4	13.8	16.2	1	3	2	2	3	4	4
B	0.1	0.1	0.2	0.2	0.3	0.3	1.7	0.1	0.2	0.2	0.2	0.2	0.2
Ca	297	12.9	0.3	<0.1	<0.1	<0.1	60	21	8	2	1	1	0.4
K	15	6.6	2.1	2	1.6	2.4	10	7	6	5	5	4	4
Mg	37	11.7	0.1	<0.1	<0.1	<0.1	20	11	6	1.1	0.4	0.5	0.2
Na	28	461	529	585	632	674	434	508	548	566	544	579	541
Cu	0.7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fe	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
Mn	7.4	0.1	<0.1	<0.1	<0.1	<0.1	1.3	0.4	0.5	<0.1	<0.1	<0.1	<0.1
Zn	16	0.2	0.5	0.7	0.2	<0.1	0.6	0.2	0.3	0.1	<0.1	0.1	0.1
SO <sub>4</sub> <sup>2-</sup>	365	369	374	373	375	374	360	362	369	361	344	361	330
Si	21	12	9	10	11	10	19	19	15	12	11	11	10
<b>µg/L</b>													
As	5	<0.1	1	2	3	3	1	2	2	4	5	6	11
Cd	46	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Co	69	<0.1	<0.1	<0.1	<0.1	<0.1	14	3	<0.1	<0.1	<0.1	<0.1	<0.1
Ni	50	1	<0.1	<0.1	<0.1	<0.1	29	8	4	3	5	6	3
Pb	1306	1	2	2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Tl	21	<0.1	<0.1	<0.1	<0.1	<0.1	1	1	<0.1	1	1	1	1
Cr	2	2	3	3	5	6	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Mo	3	3	3	3	3	4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sb	7	6	6	6	6	6	3	3	4	3	3	3	4
U	2	<0.1	1	1	2	4	<0.1	1	1	1	1	1	2
V	2	2	2	2	3	4	1	2	4	9	8	11	20
<b>ion balance between Na<sup>+</sup> and cation uptake (meq/g)</b>													
Na <sup>+</sup>		3.8	2.2	1.2	0.9	0.7	3.5	2.7	2.2	1.5	1.1	1.0	0.7
Σcations		3.6	2.0	0.9	0.6	0.5	3.3	2.6	2.1	1.4	1.1	0.8	0.7

(90 and 290 µg/L, respectively). The ion-exchange selectivity for the heavy metals is the result of the ionic competition between the major and trace cations to replace Na<sup>+</sup> in 4A. On the basis of a qualitative evaluation of the results, the following degrees of affinity with the cations studied is inferred: Fe<sup>3+</sup> = Al<sup>3+</sup> ≥ Cu<sup>2+</sup> ≥ Pb<sup>2+</sup> ≥ Cd<sup>2+</sup> = Tl<sup>+</sup> > Zn<sup>2+</sup> > Mn<sup>2+</sup> > Ca<sup>2+</sup> = Sr<sup>2+</sup> > Mg<sup>2+</sup>. The precipitation of metal-bearing solid phases could enhance the efficiency of the decontamination tests and may also influence this selectivity series.

These metals could be extracted efficiently from high-Ca-bearing solutions using the zeolite material, but owing to the ionic exchange, the content of Na<sup>+</sup> of the treated water increased to 900–1,600 mg/L, depending on the zeolite dose. However, the concentration of B, Cr, V, Mo, and As in waters treated with 4A-ME did not increase because of leaching from the relict fly ash particles, as occurs with the classic conversion products.

Similar results were obtained with the experiments carried out with the No. 71 well sample (Table 7). In this case, the lower content of pollutants accounted for the lower zeolite doses needed to extract the heavy metals. Thus, doses of 7.5 and 5 g/L of 4A-ME and 4A-IQE, respectively, allowed one to attain acceptable water quality levels after the treatment

(Table 7). In these experiments the pH reached 7.6 and 10 for the highest zeolite doses with 4A-ME and 4A-IQE, respectively. The high pH obtained with commercial zeolite accounted for the higher Al content of the effluents of the 4A-IQE treatment (up to 16 mg/L) when compared with 4A-ME (4 mg/L). It should be pointed out that this is the only experiment where Al contents showed a progressive increase in the course of the decontamination tests.

The results of the treatment of the river Tinto water (Table 8) were different owing to the very high Fe and Al contents (440 and 110 mg/L, respectively). Although Fe<sup>3+</sup> and Al<sup>3+</sup> exchanges cannot be excluded, a major precipitation process accounts for the uptake of these elements as deduced from the ion imbalance (Table 8) and the pH values reached. The very high Fe and Al contents may reduce the ion-exchange sites available for other heavy metals because these trivalent cations have a higher affinity with the Na<sup>+</sup> exchange in the zeolites. Table 8 shows a sharp decrease in the Fe<sup>3+</sup>, Al<sup>3+</sup>, and Pb<sup>2+</sup> concentrations in the initial stages of the decontamination tests, which could be attributed to both precipitation processes and preferential ion exchange. The results showed that the affinity of Fe<sup>3+</sup> ions with the exchange positions or the precipitation of solid phases appeared to be faster than Al<sup>3+</sup> with all

**TABLE 8.** Concentrations of Major and Trace Elements before (Zeolite Dose = 0) and after Decontamination Tests of Water Sample from River Tinto at Niebla (Doses Refer to Grams of Zeolite per Liter of Water)

<i>Tinto River</i>	<i>4A-IQE</i>							<i>4A-ME</i>							
	<i>Zeolite dose g/L</i>	0	1	2.5	5	7.5	10	15	5	7.5	10	15	20	25	30
<b>pH</b>		2.5	3.4	3.8	4.2	5.2	5.6	6.1	3.6	3.8	4	4.6	5.2	5.6	6.2
<b>mg/L</b>															
<b>Al</b>		112	254	137	8	0.8	1.4	1.5	115	75	40	4	4	1	1
<b>B</b>		0.4	0.2	0.1	0.2	0.2	0.2	0.3	0.2	0.3	2.8	0.3	0.3	0.3	0.3
<b>Ca</b>		94	97	94	85	51	8	1	62	46	28	8	3	1	0.4
<b>Mg</b>		103	107	105	105	98	78	21	84	79	68	42	25	11	6
<b>Na</b>		46	192	398	766	958	1056	1220	542	748	872	1043	1105	1162	1203
<b>Cu</b>		36	36	33	20	1.6	0.2	0.1	19	12	6	1	0.4	0.2	0.1
<b>Fe</b>		444	3.7	0.6	0.2	1.5	1.6	0.8	0.9	0.5	0.3	0.2	0.9	0.3	0.1
<b>Mn</b>		11	12	12	11	8	1	0.1	8	6	4	1.3	0.5	0.2	0.1
<b>Zn</b>		54	55	54	50	12	0.5	0.1	35	25	15	3	0.8	0.3	0.1
<b>SO<sub>4</sub><sup>2-</sup></b>		884	840	759	803	859	882	910	746	790	777	791	803	823	840
<b>Si</b>		19	156	205	143	54	33	29	163	167	161	128	110	101	95
<b>µg/L</b>															
<b>As</b>		955	1	<0.1	<0.1	4	7	3	9	6	4	2	3	4	2
<b>Cd</b>		186	200	187	147	<0.1	<0.1	<0.1	103	56	21	<0.1	<0.1	<0.1	<0.1
<b>Co</b>		751	765	765	755	586	49	2	603	475	360	113	34	7	3
<b>Ni</b>		316	324	327	328	311	224	65	217	185	169	92	40	17	11
<b>Pb</b>		240	97	37	1	<0.1	<0.1	<0.1	10	4	1	<0.1	<0.1	<0.1	<0.1
<b>Tl</b>		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	2	2	1	<0.1	1	1	1
<b>Cr</b>		24	<0.1	<0.1	<0.1	3	2	<0.1	3	1	<0.1	<0.1	<0.1	<0.1	<0.1
<b>Mo</b>		13	5	5	6	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1	<0.1
<b>Sb</b>		17	10	9	9	<0.1	<0.1	<0.1	2	2	2	2	2	2	2
<b>U</b>		15	15	17	9	<0.1	<0.1	<0.1	7	6	5	2	1	1	1
<b>V</b>		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
<b>ion balance between Na<sup>+</sup> and cation uptake (meq/g)</b>															
<b>Na<sup>+</sup></b>		6.4	6.2	6.1	5.3	4.4	3.4		4.3	4.0	3.6	2.9	2.3	1.9	1.7
<b>Σcations</b>		23.4	9.7	7.1	5.5	4.5	3.4		5.1	4.3	3.8	3.1	2.4	2.0	1.7
<b>Saturation index</b>															
<b>Fe (OH)<sub>3</sub> (a)</b>		-1.0	-0.8	-0.7	1.3	1.7	1.9		-1.2	-1.1	-0.9	-0.2	1.0	0.9	1.1
<b>Jarosite-Na</b>		0.2	-0.3	-0.6	2.7	2.8	1.9		-0.5	-0.5	-0.4	0.0	2.0	0.7	-0.9
<b>Scorodite</b>		-1.7	-3.0	-3.3	-0.7	-0.4	-1.2		-1.2	-1.4	-1.6	-1.9	-1.0	-1.4	-2.4

the zeolite types used. The experiments showed that the zeolite doses needed to decontaminate the Tinto water were 20 and 10 g/L for 4A-ME and 4A-IQE, respectively. Final Na<sup>+</sup> contents in the treated samples reached 1,100 mg/L.

The ion balance between the released Na<sup>+</sup> and the total cation extracted from solution No. 70 and 71 (Tables 6 and 7) indicates that cation exchange is the dominant process for metal uptake. However, it seems likely that the precipitation of Fe-hydroxides or sulphates mainly accounts for the abatement of Fe and Al contents in the case of the Tinto River water, as evidenced by the excess of the extracted cation load with respect to the exchanged Na<sup>+</sup> (Table 8). This is also deduced from the severe cation decrease at the start of the experiments for some elements such as Fe<sup>3+</sup>, Al<sup>3+</sup>, and Pb<sup>2+</sup> usually contained in Na-Jarosite [NaFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>]. The precipitation of this phase due to the raised pH under high Fe environments was also evident for As. Thus, the zeolite addition results in a drastic decrease in As and V contents (from 955 to 3 μg As/L and from 55 to <0.1 μg V/L) in the treated waters. Given that both As and V form anions within the range of the pH levels reached, ion uptake cannot be attributed to cation exchange. Arsenic may replace S in the jarosite structure (Dzombak and Morel 1990). The precipitation of this phase probably accounts for the sharp decrease in Fe, Al, Pb, and As in the initial stages of the experiments. The main decrease/increase in Fe and Al coincides with the values of the saturation index (Table 8), suggesting precipitation or equilibrium. A negative saturation index obtained with the geochemical code PHREEQC (Parkhurst 1995) indicates that the solution is subsaturated and that the solid tends to dissolve, whereas a positive value indicates precipitation and a value close to 0 suggests that the solution is in equilibrium with the solid. A similar precipitation process may account for the decrease of the V contents, which has been detected simultaneously with the As precipitation in alkaline fly ash leachates (Querol et al. 2001b).

## Conclusions

The results of this study allowed the synthesis of 360 g of pure zeolite from 1,000 g of the Meirama fly ash and a sodium aluminate wastewater. This zeolitic material was made up of a 4A and X zeolite blend (60/40) with a high cation-exchange capacity (4.7 meq/g).

The decontamination experiments showed that the optimal zeolite doses for the extraction of heavy metals from the polluted water range between 5 and 40 g/L, depending on the water matrix patterns (mainly, Ca<sup>2+</sup> and Mg<sup>2+</sup> or Fe<sup>3+</sup> contents) and the zeolite type. The high zeolite doses needed for the decontamination of water in well No. 70 and the river Tinto water are due to the high levels of pollution. A rise in the pH to precipitate heavy metals may be more appropriate than the cation-exchange treatment for these waters. By contrast, water in well No. 71 can be efficiently decontaminated by a direct cation-exchange treatment using low zeolite doses. The cation-exchange decontamination could be useful in cases, such as extraction wells, where it could be performed with no solid waste at the bottom of the well.

Based on the results of the water decontamination tests, a tentative order for the affinity of the different ion with the zeolite exchange sites can be deduced: Fe<sup>3+</sup> ≥ Al<sup>3+</sup> ≥ Cu<sup>2+</sup> ≥ Pb<sup>2+</sup> ≥ Cd<sup>2+</sup> = Tl<sup>+</sup> > Zn<sup>2+</sup> > Mn<sup>2+</sup> > Ca<sup>2+</sup> = Sr<sup>2+</sup> > Mg<sup>2+</sup>. These results demonstrate that 4A zeolite has a higher affinity with metal ions than with Ca<sup>2+</sup> and Mg<sup>2+</sup>. Thus, solutions containing up to 600 mg/L of these heavy metals and up to 800 mg/L of Ca can be treated with 4A zeolite to reduce the metal content to <0.5 mg/L, with relatively high levels of Ca remaining in the solution (see the river Tinto results, Table 8).

The precipitation of metal-bearing solid phases could en-

hance the efficiency of the decontamination tests. Although cation exchange is the main process, the quantification of the metal uptake owing to precipitation remains to be clarified. Further experiments involving individual ions are needed to confirm the extent of the exchange process and to determine the cation-Na<sup>+</sup> exchange coefficients required for quantitative modeling. Experiments addressing this point are currently in progress.

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