

Utilization of Zeolites Synthesized from Coal Fly Ash for the Purification of Acid Mine Waters

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Two pilot plant products containing 65 and 45% NaP1 zeolite were obtained from two Spanish coal fly ashes (Narcea and Teruel Power Station, respectively). The zeolitic product obtained showed a cation exchange capacity (CEC) of 2.7 and 2.0 mequiv/g, respectively. Decontamination tests of three acid mine waters from southwestern Spain were carried out using the zeolite derived from fly ash and commercial synthetic zeolite. The results demonstrate that the zeolitic material could be employed for heavy metal uptake in the water purification process. Doses of 5–30 g of zeolite/L have been applied according on the zeolite species and the heavy metal levels. Moreover, the application of zeolites increases the pH. This causes metal-bearing solid phases to precipitate and enhances the efficiency of the decontamination process.

Introduction

Höller and Wirsching (1) highlighted the compositional similarity of fly ash to volcanic material, the precursor of natural zeolites. Since this study, a number of hydrothermal activation methods have been proposed to synthesize different zeolites from fly ash. All the methodologies developed have been based on the dissolution of Al–Si-bearing fly ash phases with alkaline solutions (mainly NaOH and KOH solutions) and the subsequent precipitation of zeolitic material.

The classic alkaline conversion of fly ash employs the combination of different alkaline solution/fly ash ratios with alkali concentration, temperature, and reaction time to obtain different zeolite species (2–14). The use of water vapor pressure in closed reactors accelerates the process. Sodium or potassium hydroxide solutions with a different molarity, 80–200 °C and from 3 to 48 h, have been combined to synthesize up to 15 different zeolites from the same fly ash. The zeolite contents of the resulting material varied widely (20–50%), depending mainly on the activation solution/fly ash ratio and on the reaction time (15). Microwave synthesis

considerably reduced the reaction time down to the scale of minutes (16). Shigemoto and co-workers (4) and Berggaut and Singer (8) implemented the conventional methodology by introducing an alkaline fusion stage prior to the conventional zeolite synthesis. This implementation resulted in high synthesis yields and in the crystallization of very interesting zeolite species.

In conjunction with the development of synthesis methods, intensive research has been carried out to develop potential applications for the synthesized zeolites. Most of the studies on the use of fly ash derived zeolites in the field of water purification have been performed for selected pollutants by using synthetic solutions under laboratory conditions. In particular, the removal of heavy metals and ammonium from water was tested extensively (5–10, 14–19). These studies have shown that the matrix effect of the solution exerts considerable influence on the pollutant uptake. The possibility of the use of zeolites as molecular sieves in gas purification technology has also been investigated in a number of studies (14, 20).

Our study focused on the decontamination of actual acid mine waters using fly ash derived zeolites. These were Ca²⁺-SO₄²⁻ rich waters with high metal contents (Fe, Al, Zn, Mn, Cu, Pb). 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 from the water by using both a zeolitic product obtained from fly ash at pilot plant scale and a commercial synthetic zeolite.

Experimental Section

Materials. Two zeolitic materials were obtained from two fly ashes produced in Spain (Teruel and Narcea). The synthesis conditions to obtain NaP1-rich zeolitic material were selected from earlier laboratory studies (13–16).

The major chemical, mineral, and physical characteristics of the Teruel and Narcea fly ashes are summarized in Table 1. These fly ashes were selected because of their high NaP1 synthesis yields obtained in earlier studies (14, 21). Moreover, the Teruel fly ash was also selected to test the leaching of potential pollutants (B, Mo, and U).

Conventional synthesis procedures were used to obtain NaP1-rich products at pilot plant scale with a 10 m³ reactor from Clariant Productos SA in Barcelona. Details of the methodology have been reported elsewhere (15). The NaP1 synthesis conditions were optimized for the two fly ashes at laboratory scale using 125 mL Parr digestion reactors (14). The optimal synthesis conditions are summarized in Table 2. Two synthesis experiments were carried out using 1.1 and 2.2 tonnes of the Teruel and Narcea fly ashes, respectively.

In addition to the fly ash derived zeolites, three commercial synthetic zeolites species (4A, X, and NaP1) were supplied by Industrias Químicas del Ebro SA (IQE) for the decontamination tests.

Water samples containing high levels of heavy metals were collected from two irrigation wells in the Guadamar valley, SW Spain. These two wells had been flooded with pyrite sludge and acidic water during the Aznalcóllar spill (22) in 1998. The water from the two wells was acidic (2.6 and 3.7 pH), with high contents of calcium and sulfate, and varying levels of heavy metal pollution. Well #70 was highly polluted, and an alkaline treatment to precipitate heavy metals was probably more appropriate than the cation exchange treatment. By contrast, well #71 could be decontaminated by a cation exchange treatment. In addition, a water sample from the River Tinto in the vicinity of the village of Niebla was also

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TABLE 1. Major Chemical, Mineralogical, and Physical Characteristics of the Teruel and Narcea Fly Ashes

(%)	Major Oxide (%) and Trace Element Contents ($\mu\text{g/g}$)																																
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	TiO ₂	MnO	SO ₃	SiO ₂ /Al ₂ O ₃	As	B	Ba	Be	Cd	Co	Cr	Cu	Ge	Li	Mo	Ni	Pb	Rb	Se	Sn	Sr	Th	U	V	Zn
Narcea	55.2	23.3	6.9	4.0	2.5	0.7	3.8	0.3	0.9	0.1	0.4	2.4	98	98	1047	5	2	30	177	86	1	220	6	82	90	185	6	4	235	24	9	173	171
Teruel	48.3	23.9	16.0	5.4	1.0	0.2	1.4	0.2	0.8	0.0	0.8	2.0	79	342	311	12	1	25	107	52	6	256	15	85	65	90	3	8	523	21	20	206	174
		Mineral Composition (%)																															
		mullite	quartz	cristobalite	anhydrite	calcite	lime	hematite	magnetite	feldspar	ettringite	glass																					
Narcea		3.8	6.6	<0.3	0.2	<0.3	0.7	<0.3	1.5	0.2	<1.0	85.6																					
Teruel		19.4	8.6	<0.3	1.5	<0.3	<1.0	5.9	1.3	<1.0	<1.0	62.7																					
		Physical Characterization																															
		grain size distribution (μm)																															
		P10%	median	P90%	true density (g/cm^3)	apparent density (g/cm^3)	porosity (%)	BETSA (m^2/g)																									
Narcea		3.0	11.8	50.3	2.4	0.9	63.4	1.7																									
Teruel		4.6	21.8	75.7	2.5	1.1	58.2	1.9																									

TABLE 2. Experimental Conditions Used for the Synthesis of NaP1 Zeolite from the Teruel and Narcea Fly Ashes at Pilot Plant Scale

reactor	R-410-A, stainless steel 304, 10 m ³ , Clariant Productos S.A.
fly ash	Teruel: 1100 kg, Narcea: 2200 kg
osmotized H ₂ O	Teruel: 2200 kg, Narcea: 4400 kg
NaOH concn	Teruel: 2 Molar, Narcea: 3 Molar
T	Teruel: 150 °C, Narcea: 125 °C
t	Teruel: 24 h, Narcea: 8 h
pressure	3.55 kg/cm ²
cooling t	2 h
filtration	polypropylene press filters (F-406, 55 plates), 2 m ³ manual extraction membrane pneumatic pump (16 m ³ air/h), T, 90 °C, t, 1 h
washing	T, 85 °C, t, 40 min water washing and 12 h of air drainage
evacuation	manual with 400 kg containers
moisture	48% moisture content of the final product

collected. This water was also acidic (pH 2.5) and contained high levels of iron, aluminum, and some heavy metals as a consequence of the intensive leaching of sulfide wastes and mining works.

Determination of Cation Exchange Values and Decontamination Tests. The cation exchange capacity (CEC) of the zeolitic materials was obtained using ammonium solutions following the methodology of the International Soil Reference and Information Centre (23). Other tests were carried out using distilled water to determine leachable Na⁺ levels from the zeolitic products (which may be erroneously attributed to ionic exchange processes). The levels of extractable heavy metals from the relict fly ash particles were also evaluated.

Acid mine water presents a typically high Ca concentration. Preliminary tests of Ca-heavy metal preferential adsorption were carried out by adding different zeolite doses to synthetic solutions containing 6 mequiv/L of heavy metals and Ca²⁺ concentrations ranging from 10 to 50 mequiv/L. The zeolites used in these tests were the commercial NaP1, 4A, and X as well as the NaP1 zeolite synthesized from the Narcea fly ash. Aliquots of 100 mL of each solution were mixed, stirring continuously at room temperature for 30 min

in PVC containers with zeolites using doses of 5, 10, 20, and 30 g/L.

Finally, decontamination tests were performed using the polluted water samples and different doses of zeolites (commercial and synthesized from fly ash). Batch experiments were carried out at room temperature, with continuous stirring in PVC containers, using aliquots of 500 mL of each water sample and zeolite powder doses from 5 to 40 g/L. After 1 h, the mixtures were filtered, and pH values and concentrations were immediately measured. The zeolite species selected for these experiments were the commercial 4A zeolite, the NaP1 zeolites synthesized from the Teruel and Narcea fly ashes, and a mixture containing 80 wt % of Narcea-NaP1 and 20 wt % of the commercial 4A zeolite.

Analysis. Major and trace element contents were determined by ICP-AES and ICP-MS. Levels of ammonium in solutions resulting from the CEC determination were measured using FIA-colorimetry methods.

Mineral species of fly ash and zeolite samples were identified by X-ray diffraction. The quantitative proportion of the different species was also determined by XRD using the Internal Reference Method with fluorite as an internal standard. Asemiquantitative estimation of the zeolite content in a sample was also made by comparing its CEC value with that of the pure zeolite.

Results and Discussion

Optimization tests of conventional zeolite synthesis showed that the highest yield for the Teruel fly ash (NaP1-TE) was obtained under 150 °C, 2 M NaOH and 24 h, whereas that for the Narcea fly ash (NaP1-NA) was achieved under 125 °C, 3 M NaOH and 8 h. These differences, mainly concerning reaction time, are probably due to the lower stability of the Al-Si-bearing phases of the Narcea fly ash. Higher degradability allows faster dissolution of Al- and Si-bearing phases and subsequent precipitation of zeolites. The higher glass content (easily dissolved by alkaline solutions) and the lower mullite and quartz contents of the Narcea fly ash probably enhance this effect. The X-ray diffraction pattern of the zeolitic product showed a high content of NaP1 zeolite in both cases and traces of analcime in the case of the NaP1-TE (Figure 1). The XRD patterns of the pure commercial zeolites are also shown in this figure for comparison.

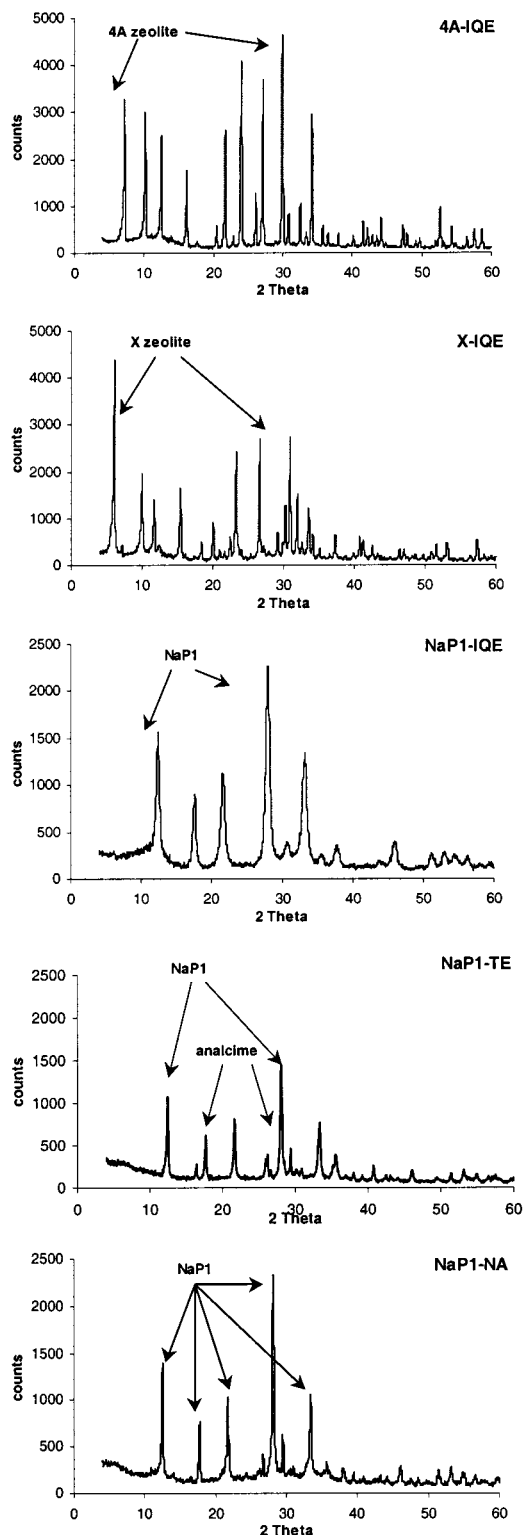


FIGURE 1. X-ray diffraction patterns (CuK α radiation) of commercial zeolites (4A-IQE, X-IQE, and NaP1-IQE) and the synthesized zeolitic material from fly ash (NaP1-TE and NaP1-NA).

The highest CEC values were measured for the 4A-IQE zeolite (5.4 mequiv/g), followed by the NaP1-IQE (5.0 mequiv/g), X-IQE (4.3 mequiv/g), NaP1-NA (2.7 mequiv/g), and NaP1-TE (2.0 mequiv/g). Comparison of the CEC values of the commercial NaP1-IQE with the synthesized NaP1-NA and NaP1-TE indicated that the zeolite content in the fly ash derived material was close to 65 and 45 wt %, respectively. The CEC values were calculated by subtracting 0.5 and 0.4

mequiv/g from the CEC values obtained for the NaP1-NA and 4A zeolites given that the water leaching experiments showed that these fractions of soluble Na were derived from the zeolitic material.

The DIN 38-414 leaching procedures (100 g/L of distilled water/fly ash ratio, room temperature, 24 h, without pH adjustment) applied to the NaP1-NA zeolite product showed that, under the pH levels reached (11.3 pH), the major leachable elements were as follows: Ca, As, B, Cr, V, and Mo. Using high zeolite doses (30 g/L), the treated solutions could attain up to 0.8 mg/L B, 0.2 mg/L Cr, 0.05 mg/L As, Mo, and V, and 0.03 mg/L U. In the case of NaP1-TE, low leachable concentrations were obtained for most of these elements (0.05 mg/L Mo and Cr, 0.03 mg/L V, and 0.01 mg/L As). However, the leachable U concentrations were relatively high (0.16 mg/L) as a result of the high U content of the Teruel fly ash (20 μ g/g). Owing to this high leachable U content and to its CEC value lower than those of the NaP1-NA, the NaP1-TE product was excluded from the subsequent water decontamination tests. It goes without saying that the extractable concentrations of some elements could increase if an acidic extractant is used. However, as described below, the leachable concentrations of As, V, Cr, and Mo resulting from the leaching tests resembled those obtained when acid mine waters were treated with this zeolitic product.

Preliminary tests on preferential adsorption demonstrated that Zn²⁺ and Cu²⁺ had a higher affinity than Ca²⁺ for the zeolite types investigated. Thus, solutions containing 6 mequiv/L of these heavy metals, and up to 50 mequiv/L of Ca²⁺, treated with all the zeolites studied reduced the metal content down to <0.01 mequiv/L, with up to 27.5 mequiv/L of Ca²⁺ remaining in the solution. Consequently, these heavy metals can be extracted from high-Ca solutions using the zeolitic material. The preliminary tests demonstrated that the optimal zeolite doses ranged between 10 and 30 g/L depending on the concentration of the major cations and zeolite species used. Zeolite X was not used in the following decontamination experiments given the lower exchange values of this product with respect to NaP1 and 4A zeolites.

Decontamination Experiments. The zeolite species selected for these experiments were NaP1-NA, 4A-IQE, and the zeolite blend of NaP1-NA/4A-IQE (80/20%). The working hypothesis is that the use of a product containing a high proportion of NaP1 zeolite with a fraction of alkaline fly ash particles could raise the pH and induce a favorable environment for ion exchange. In these types of zeolites the maximum exchange efficiency takes place under neutral to slightly alkaline conditions (9). However, the residual NaOH present in the commercial zeolite, even after intensive washing, induced an alkalinity higher than desired. A proportion of 20 wt % of the commercial zeolite was added to the NaP1-NA product to improve the efficiency of heavy metal uptake at low zeolite doses. Moreover, the replacement of a minor proportion of NaP1-NA by 4A-IQE decreased the As, Cr, Mo, U, and V leached from the exchange material.

The first experiments were carried out with the NaP1-NA product using doses of 10, 20, 30, and 40 g/L (Table 3). The results showed that a substantial reduction in the Zn, Cu, and Cd concentrations was obtained when doses from 10 to 30 g/L were added to the highly polluted sample from #70 well (Figure 2). Final pH values of these experiments reached 6.8 with the highest zeolite dose. The results shown in Table 3 and Figure 2 indicate that the appropriate zeolite dose for the decontamination of the #70 water sample is 30–40 g/L. Using the highest dose, the concentrations of pollutants were considerably reduced e.g. from 174 to 0.2 mg Zn/L, 74 to 6 mg Mn/L, and from 400 to <0.1 μ g Cd/L. An important reduction in the concentration of other metals such as Co, Ni, and Sr was also achieved in the experiments. Doses of 10 g/L were sufficient to reduce the concentrations down to

TABLE 3. Concentrations of Major and Trace Elements in the Water after the Decontamination Tests of a Sample from Well # 70 in the Anzcollar Area^a

sample #70 zeolite dose g/L	NaP1-NA				4A-IQE				NaP1-NA/4A-IQE (80/20)							
	10	20	30	40	10	20	30	40	5	7.5	10	12.5	15	20	25	
pH	2.6	5.4	6.1	6.5	6.8	6.5	7.8	8.5	8.8	5.1	5.7	6	6.2	6.4	6.5	7.1
	mg/L															
Al	70	0.1	<0.1	<0.1	0.1	0.1	0.5	1	4	0.7	0.2	0.1	0.2	0.1	0.1	0.1
B	0.4	0.5	0.7	0.8	0.9	0.4	0.3	0.3	0.3	0.2	0.2	0.3	0.3	0.3	0.4	0.5
Ca	541	393	253	149	84	141	21	4	0.3	502	426	375	325	266	184	124
K	5	47	65	75	95	5	3	2	28	32	38	40	42	50	53	
Mg	260	241	235	221	198	215	52	6	0.8	261	250	257	253	238	234	216
Na	54	488	786	970	1093	994	1414	1544	1602	409	540	681	755	812	984	1060
Cu	3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.5	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fe	11	<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	<0.1	<0.1
Mn	74	60	39	20	6	18	1.7	0.2	<0.1	71	61	56	52	40	27	15
Zn	174	81	15	2.7	0.2	2.9	<0.1	<0.1	<0.1	141	84	57	38	22	8	3
SO ₄ ²⁻	1130	1132	1126	1143	1149	1163	1155	1163	1165	1115	1093	1140	1134	1092	1127	1104
Si	50	25	22	21	19	13	3	1.6	1.5	43	28	27	25	22	19	17
	µg/L															
As	7	10	19	51	131	1	5	1	<0.1	6	4	4	5	6	8	18
Cd	398	59	11	2	<0.1	<0.1	<0.1	<0.1	<0.1	176	71	36	19	12	3	<0.1
Co	670	536	274	113	20	89	2	<0.1	<0.1	666	550	510	451	412	293	144
Ni	443	315	138	63	14	286	9	<0.1	<0.1	373	332	304	273	265	198	113
Pb	1516	<0.1	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	<0.1
Tl	46	2	<0.1	<0.1	<0.1	1	1	<0.1	<0.1	3	3	2	2	1	2	2
Cr	6	84	168	275	377	4	4	6	7	38	53	74	80	92	120	145
Mo	5	18	36	53	71	6	11	7	6	5	9	11	18	20	29	36
Sb	10	12	19	22	28	9	9	10	9	5	6	6	5	6	6	7
U	10	23	50	31	33	1	1	<0.1	2	5	3	3	4	6	8	14
V	6	14	31	43	70	8	6	5	3	4	5	8	9	13	18	24
	Ion Balance between Na⁺ and Cation Uptake (mequiv/g)															
Na ⁺		1.9	1.6	1.3	1.1	4.0	2.9	2.1	1.7	2.9	2.7	2.6	2.4	2.2	2.0	1.7
∑cations		2.0	1.6	1.3	1.1	4.0	2.9	2.1	1.6	2.8	2.8	2.4	2.2	2.2	1.9	1.7

^a The doses refer to the amount of zeolitic material added to the water.

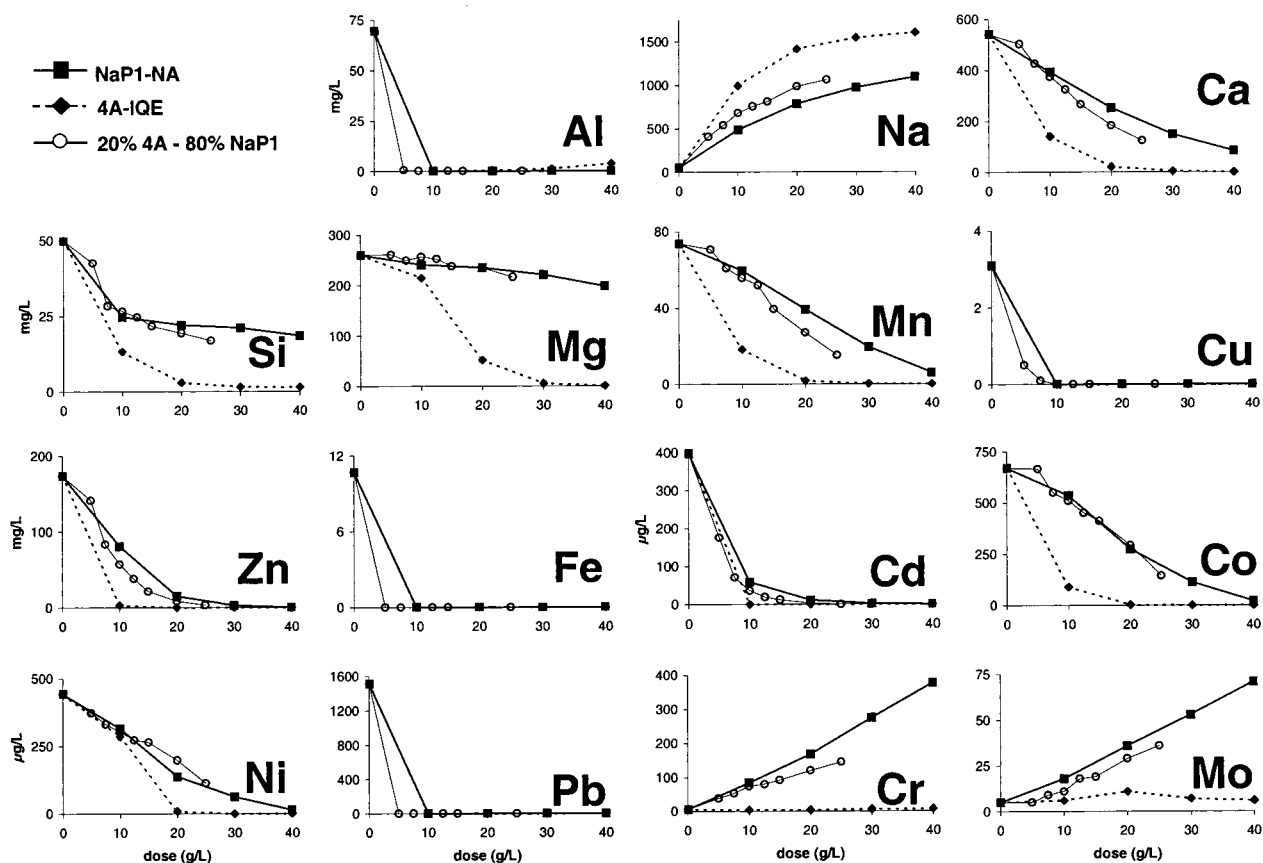


FIGURE 2. Reduction in the concentrations of selected elements (mg/L or µg/L, as indicated) in sample #70 after treatment with zeolitic material (dose in g/L).

TABLE 4. Concentrations of Major and Trace Elements in the Water after the Decontamination Tests of a Sample from Well # 71 in the Analcoliar Area^a

sample #71 zeolite dose g/L	NaP1-NA				4A-IQE					NaP1-NA/4A-IQE (80/20)			
	10	20	30	40	5	10	20	30	40	5	7.5		
pH	3.7	8.0	8.8	9.1	9.4	8.1	9.0	9.6	9.9	10.1	7.4	8.0	
						mg/L							
Al	10	0.1	0.6	0.8	0.3	1	3	9	14	16	0.1	0.2	
B	0.1	0.3	0.4	0.5	0.6	0.1	0.2	0.2	0.3	0.3	0.2	0.2	
Ca	297	50	11	4	1.8	12.9	0.3	<0.1	<0.1	<0.1	134	66	
K	15	40	41	43	51.1	6.6	2.1	2	1.6	2.4	29	29	
Mg	37	24	6	1.3	0.3	11.7	0.1	<0.1	<0.1	<0.1	34	30	
Na	28	397	491	535	578	461	529	585	632	674	315	413	
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	
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	
Mn	7.4	0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1	<0.1	<0.1	2.4	0.6	
Zn	16	0.4	0.2	0.2	<0.1	0.2	0.5	0.7	0.2	<0.1	0.3	0.1	
SO ₄ ²⁻	365	367	369	372	374	369	374	373	375	374	358	363	
Si	21	20	25	35	48	12	9	10	11	10	17	14	
						µg/L							
As	5	159	425	719	1011	<0.1	1	2	3	3	19	52	
Cd	46	<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	<0.1	<0.1	<0.1	<0.1	16	3	
Ni	50	<0.1	<0.1	<0.1	<0.1	1	<0.1	<0.1	<0.1	<0.1	26	13	
Pb	1306	<0.1	3	8	2	1	2	2	<0.1	<0.1	<0.1	<0.1	
Tl	21	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1	1	
Cr	2	84	167	252	323	2	3	3	5	6	29	42	
Mo	3	18	34	53	67	3	3	3	3	4	8	11	
Sb	7	11	18	24	31	6	6	6	6	6	4	5	
U	2	3	1	1	1	<0.1	1	1	2	4	3	3	
V	2	102	277	447	603	2	2	2	3	4	26	46	
						Ion Balance between Na ⁺ and Cation Uptake (mequiv/g)							
Na ⁺		1.6	1.0	0.7	0.6	3.8	2.2	1.2	0.9	0.7	2.4	2.3	
Σcations		1.5	0.9	0.6	0.5	3.6	2.0	0.9	0.6	0.5	2.3	2.2	

^a The doses refer to the amount of zeolitic material added to the water.

0.1 mg Al/L, <0.1 mg/L Fe and Cu, and <0.1 µg Pb/L, whereas the remaining heavy metals continued to be present in significant levels. The following affinity for the cations studied, Fe³⁺ = Al³⁺ ≥ Cu²⁺ ≥ Pb²⁺ ≥ Cd²⁺ = Tl⁺ > Zn²⁺ > Mn²⁺ > Ca²⁺ = Sr²⁺ > Mg²⁺, was inferred from a qualitative evaluation of the results. However, precipitation of solid phases (which could enhance the efficiency of the metal uptake, as discussed below) may also contribute decisively to this affinity ordering.

Therefore, these metals may be extracted efficiently from high-Ca-bearing solutions using the zeolitic material, but owing to the ionic exchange, the content of Na⁺ of the treated water increased from 54 to 489–1100 mg/L, depending on the zeolite dose. Moreover, concentrations of Cr, V, Mo and As rose due to the leaching of the fly ash particles in the zeolitic material. Nevertheless, the levels of these elements remained below 0.4, 0.07, 0.07, and 0.1 mg/L, respectively, for the 40 g/L dose. An increase in the concentration of Sb and U was also observed, but levels were relatively low.

The experiments performed with the 4A-IQE (Table 3 and Figure 2) also showed high extraction efficiencies for heavy metals even for low zeolite doses. Thus, the same decontamination results obtained for the NaP1-NA 40 g/L dose were obtained with 20 g/L of the 4A-IQE zeolite with levels of Na⁺ in the treated waters reaching 1414 mg/L. In these cases, the Cr, V, As, Mo, and U contents did not increase, supporting the view that these elements were due to the leaching of the Narcea fly ash particles.

Similar results were obtained in experiments carried out with the #71 sample (Table 4 and Figure 3). In this case, the lower content of heavy metals accounted for the lower zeolite doses needed. Thus, doses of 10 and 5 g/L of NaP1-NA and 4A zeolitic products, respectively, allowed the water to reach acceptable quality levels after the treatment (Table 4). The

content of some fly ash-derived elements was relatively high, even for the low zeolite dose used. Concentrations of As, Cr, and V reached 0.16, 0.08, and 0.10 mg/L, whereas concentrations of Mo and U remained at 18 and 3 µg/L, respectively. This different behavior is due to the alkalinity reached (pH 8) which favored selective leaching of the first group of elements. As will be shown below, this problem was solved by using a zeolite blend. In the case of the #71 sample, there were no major differences in the water quality obtained with 10 g/L of 4A and NaP1-NA zeolitic products. The increase of the pure 4A zeolite dose raised the pH from 8 to 10. Simultaneously, the Al contents increased probably as a consequence of the dissolution of a small fraction of the zeolitic material at pH 10. This was not observed with the NaP1-NA treatment, even with the highest zeolite dose, probably due to the higher stability of NaP1 zeolite under alkaline media. However, the low 4A dose needed to decontaminate the #71 sample resulted in final Al contents below 1 mg/L.

The results of the treatment of the River Tinto water (Table 5 and Figure 4) were significantly different from those of the #70 and #71 samples. This was due to the very high Fe and Al contents of the Tinto water (444 and 112 mg/L, respectively). As noted above, Fe³⁺ and Al³⁺ have the highest affinity for the exchange positions in sodium zeolites, and, consequently, high concentrations of these two ions could reduce the ion exchange sites available for the remaining heavy metals. As shown by the sharp decrease in concentration, the affinity of Fe³⁺ ions for the exchange positions appeared to be higher than that of Al³⁺ for all the zeolite species used (Figure 4). However, precipitation of solid phases containing Al³⁺ and Fe³⁺ may also account for this sharp decrease of concentrations. The experiments showed that the zeolite

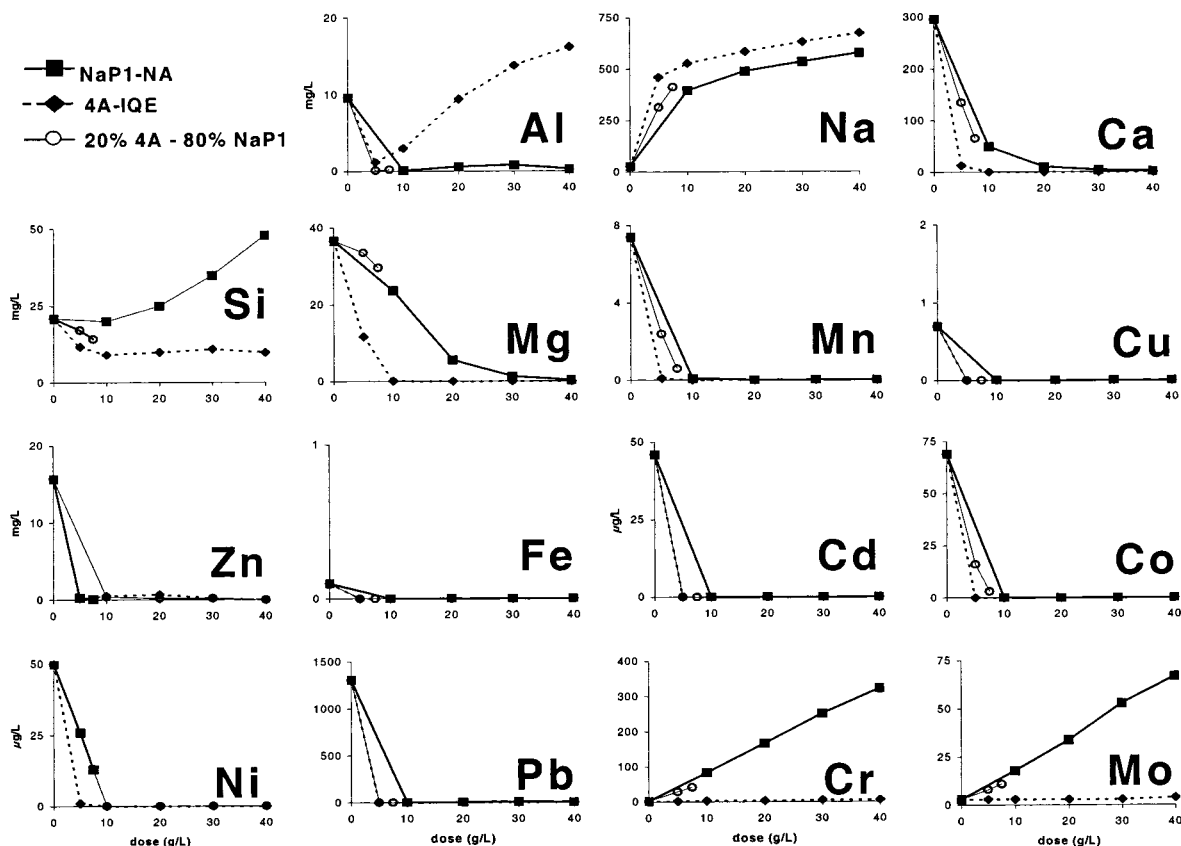


FIGURE 3. Reduction in the concentrations of selected elements (mg/L or $\mu\text{g/L}$, as indicated) in sample #71 after treatment with zeolitic material (dose in g/L).

doses needed to decontaminate the River Tinto water were 20 and 10 g/L for NaP1-NA and 4A, respectively. Contents of Co and Ni were only slightly reduced with the above NaP1 dose, but a significant decrease was obtained with the 4A product. Final Na^+ contents in the treated samples reached values of 800–1000 mg/L. In all these cases, the pH remained relatively low (4.6–6.0 pH for the adequate zeolite doses).

The addition of zeolite raised the pH in all the experiments. As the pH rises, the solutions become supersaturated for certain solid phases which could precipitate. It is important to determine whether the decrease in metal concentration is due to cation exchange or to solid precipitation. The ion balance between the released Na^+ and the total cation taken up from the solution in samples #70 and 71 (Tables 3 and 4) indicates that cation exchange is the dominant process taking place in these experiments. The sample from the River Tinto showed a significant imbalance and a sharp cation excess at the beginning of the experiments. Since this water contained a much higher amount of Fe, the ion imbalance suggests the precipitation of an Fe-containing solid. According to saturation indexes calculated with the geochemical code PHREEQC (24), Na-jarosite ($\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$), rather than amorphous $\text{Fe}(\text{OH})_3$, could account for the decrease in the Fe concentration at the initial zeolite doses applied to the River Tinto water (Table 5). A negative value of the saturation index indicates that the solution is subsaturated and that the solid tends to dissolve, whereas a positive value indicates a tendency to precipitate, and a value close to 0 suggests that the solution is in equilibrium with the solid.

Although the NaP1-NA zeolite dose was high, the concentration of leachable fly ash derived elements, especially V and As, was low in the treated water. Both As and V form anions within the pH range of the experiments, and their decrease cannot be attributed to cation exchange. The removal of As could not be due to the formation of scorodite

($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) because the saturation of the solution was not reached (Table 5). Arsenic removal from a solution has also been attributed to its sorption on the surfaces of amorphous iron hydroxide (25) and silicates (26) or to the replacement of S in the jarosite structure (25). The formation of the last solid could account for the simultaneous decrease in Fe, Pb, and As in the treated water since all these elements have been found in jarosite (27). No equivalent phase is known for V, but recent studies demonstrate that arseniates and vanadates precipitate simultaneously from fly ash leached under high Ca^{2+} alkaline conditions (28).

Decontamination tests were performed using a NaP1-NA/4A-IQE blend (80/20) to reduce zeolite doses. This minimized the impact of the leachable fly ash pollutants on water quality when high doses of fly ash derived zeolite were used. The application of the zeolite blend to the #70 sample did not lead to a significant reduction in dose with respect to NaP1-NA. Thus, the metal concentration resulting from the application of 25 g/L of the blend is comparable to that of 30 g/L (Table 3). A higher reduction in doses from 10 g/L for NaP1-NA to 5 g/L of blend was obtained for the decontamination of the #71 sample (Table 4). The application of the blend to the River Tinto water also resulted in a significant reduction in zeolite doses from the original 30 g/L of NaP1-NA down to 10–12.5 g/L (Table 5). The use of a 12.5 g/L dose reduced the content of the major pollutants to 1.8 mg/L of Al, 0.5 mg/L of Zn, 0.2 mg/L of Cu, and <0.1 mg/L for the remaining pollutants. As discussed above, the contents of leachable elements from the fly ash particles (As, B, Cr, V, and Mo) in the treated River Tinto water were in all cases lower than the original contents of the sample (Table 5). A drastic reduction in the content of these elements was also obtained in the treated water when applying the zeolite blend to the #71 water sample instead of only the NaP1-NA doses (Table 4).

TABLE 5. Concentrations of Major and Trace Elements in the Water after the Decantation Tests of a Sample from the River Tinto in the Village of Nebida^a

River Tinto zeolite dose g/L	NaPi-NA					4A-IOE					NaPi-NA/4A-IOE (80/20)									
	5	7.5	10	15	20	30	1	25	5	7.5	10	15	25	5	7.5	10	12.5	15	17.5	20
pH	2.5	3.3	3.7	4.0	4.3	4.6	5.5	3.4	3.8	4.2	5.2	5.6	6.1	3.9	4.1	4.9	5.5	5.7	5.9	6.4
Al	112	153	119	77	14	2	254	137	8	0.8	1.4	1.5	157	18	0.9	1.1	1.7	2.0	3.4	3.4
B	0.4	0.4	0.4	0.5	0.6	0.7	0.8	0.2	0.1	0.2	0.2	0.3	0.2	0.2	0.2	0.1	0.3	0.3	0.3	0.3
Ca	94	158	162	154	156	147	122	97	94	85	51	1	98	95	68	27	8	5	3	2
Mg	103	106	107	104	105	105	107	105	105	98	78	21	103	103	91	72	68	49	32	18
Na	46	339	434	518	691	839	1027	192	398	766	958	1056	354	654	789	812	1006	1153	1103	1209
Cu	36	28	18	11	5	1.1	0.2	36	33	20	1.6	0.2	31	20	3.2	0.4	0.2	0.1	0.1	0.1
Fe	444	3.8	3.3	2.4	3.1	4.1	3.3	3.7	0.6	0.2	1.5	0.8	0.8	0.8	2	1.6	1.5	1.2	2.2	2.9
Mn	11	11	11	11	10	8	4	12	11	11	8	1	11	11	9	3.2	0.7	0.3	0.2	0.1
Zn	54	51	48	42	33	20	3	55	54	50	12	0.5	53	50	25	2.5	0.4	0.2	0.2	0.1
SO ₄ ²⁻	884	843	848	817	833	886	911	840	759	803	859	882	910	782	761	673	833	911	838	889
Si	19	80	74	75	73	51	28	156	205	143	54	33	29	200	190	70	33	28	21	20
As	955	5	10	10	5	7	8	1	<0.1	<0.1	4	7	3	7	6	10	9	7	6	11
Cd	186	126	73	12	<0.1	<0.1	<0.1	200	187	147	<0.1	<0.1	<0.1	150	122	<0.1	<0.1	<0.1	<0.1	<0.1
Co	751	784	804	788	720	627	236	765	755	586	49	2	820	809	660	288	24	9	5	2
Ni	316	349	353	360	342	320	188	324	327	311	224	65	344	352	307	210	174	111	71	49
Pb	240	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	97	37	1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Tl	<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	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Cr	24	12	13	16	18	41	127	<0.1	<0.1	<0.1	3	2	-1	2	1	1	6	8	12	20
Mo	13	10	6	8	7	16	16	5	5	6	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sb	17	12	13	11	11	13	11	10	9	9	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
U	15	29	34	51	23	3	11	15	17	9	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
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	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Na ⁺	2.5	2.3	2.0	1.9	1.9	1.7	1.4	6.4	6.2	6.1	5.3	4.4	3.4	5.3	5.3	4.4	3.3	3.5	3.2	2.5
Σcations	4.8	3.2	2.9	2.4	1.9	1.9	1.4	23.4	9.7	7.1	5.5	4.5	3.4	9.5	7.0	5.2	4.4	3.6	3.2	2.5
Fe (OH) ₃ (a)	-1.4	-0.5	0.0	0.5	1.1	1.1	1.0	-1.0	-0.8	-0.7	1.3	1.7	1.9	-0.7	-0.3	1.1	1.6	1.8	1.9	2.7
jarosite-Na	-0.4	1.4	2.0	3.0	3.7	3.7	3.7	0.2	-0.3	-0.6	2.7	2.8	1.9	0.1	0.1	2.9	2.6	2.7	2.5	3.5
scorodite	-1.3	-0.5	-0.3	-0.4	0.0	0.0	0.0	-1.7	-3.0	-3.3	-0.7	-0.4	-1.2	-1.0	-1.0	-0.1	-0.3	-0.5	-0.7	-0.2

^a The doses refer to the amount of zeolitic material added to the water.

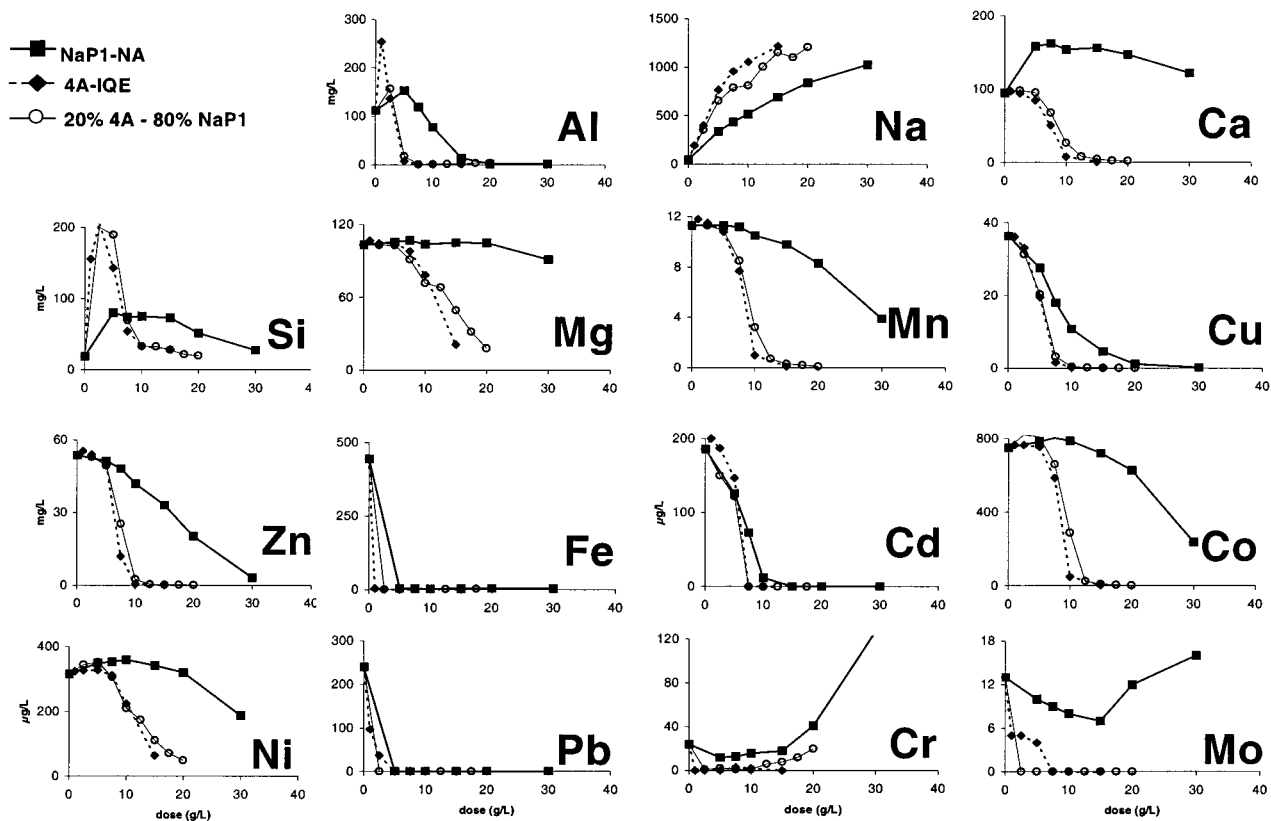


FIGURE 4. Reduction in the concentrations of selected elements (mg/L or $\mu\text{g/L}$, as indicated) in the River Tinto sample after treatment with zeolitic material (dose in g/L).

Well #70 and the River Tinto were highly polluted and a precipitation process could be more appropriate than the cation exchange treatment. By contrast, well #71 could be efficiently decontaminated by cation exchange treatment. The decontamination of acid mine discharges with zeolites yields a solid waste volume that is four times greater than that produced by the conventional treatment with lime. Thus, the total removal of the metal load in 1 L of the River Tinto water results in 4 cm^3 of the NaP1/4A blend, whereas the treatment with lime involves approximately 1 cm^3 of metal hydroxides and gypsum. The treatment with lime, however, demands constant care for an appropriate dose. Zeolites, in contrast, can be applied in excess without impairing the quality of the effluent water. This renders zeolites suitable for passive remediation systems of acid mine water. The high amount of solid waste generated requires the minimization of the metal load in the inflow. Therefore, zeolites are especially suitable for polishing effluents from other passive systems, such as reactive barriers and organic matter wetlands (29–31). Thus, 4 tonnes of the zeolite blend would allow the complete cleaning of a discharge of 1 L/s with 10 mg Zn/L during 1 year. Moreover, cation exchange decontamination may prove to be useful in cases where no solid waste is desired, e.g. zeolites could be suspended in a permeable bag inside an extraction well and then removed.

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