

Synthesis of high ion exchange zeolites from coal fly ash

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ABSTRACT

This study focuses on the synthesis at a pilot plant scale of zeolitic material obtained from the coal fly ashes of the Teruel and Narcea power plants in Spain. After the optimisation of the synthesis parameters at laboratory scale, the Teruel and Narcea fly ashes were selected as low and high glass fly ashes. The pilot plant scale experiments were carried out in a 10 m³ reactor of Clariant SA (Barcelona, Spain). The results allowed obtaining 1.1 and 2.2 tonnes of zeolitic material with 40 and 55% of NaP1 content, in two single batch experiments of 24 and 8 hours, for Teruel and Narcea fly ashes, respectively. The cation exchange capacities (CEC) of the final product reached 2.0 and 2.7 meq g⁻¹ for Teruel and Narcea zeolitic material, respectively, which are very close to the usual values reached by the high quality natural zeolitic products. Finally, with the aim of testing possible applications of the commercial NaP1-IQE and pilot plant NaP1-Narcea zeolitic products in water decontamination, efficiency for metal uptake from waste waters from electroplating baths was investigated.

KEYWORDS | Coal fly ash. Zeolite synthesis. Metal exchange. Electroplating baths. Waste waters. Pilot plant.

INTRODUCTION

A number of studies proposed different methods for synthesising zeolites from fly ash by hydrothermal alkaline conversion (Höller and Wrisching, 1985; Kato et al., 1986; Bergk et al., 1987; Mondragón et al., 1990; Larosa et al., 1992; Kolousek et al., 1993; Lin and His, 1995; Park and Choi, 1995; Singer and Bergkaut, 1995; Shih et al., 1995; Querol et al., 1995, 1997a, 2001; Park et al., 2000a, b; Rayalu et al., 2000, 2001). The classical alka-

line conversion uses open or closed systems with different activation solution/fly ash ratios. NaOH or KOH solutions, at atmospheric and water vapour pressures, from 80 to 200°C and for 3 to 48 h have been combined to synthesise up to 15 different zeolites from the same fly ash. The zeolite contents of the resulting material varied widely (20 to 65%), depending on the activation conditions. The method has been improved by introducing an alkaline fusion stage prior to the conventional synthesis (Shigemoto et al., 1992; Bergkaut and Singer, 1996;

Rayalu et al., 2000, 2001), by applying a dry conversion system (Park et al., 2000a, b) or by applying microwaves (Querol et al., 1997b) to reduce the reaction time down to 30 min. A two stage synthesis procedure (Hollman et al., 1999) enables the production of >90% pure zeolite material from high-Si fly ash extracts. Moreover, a zeolitic material with lower purity is also obtained from the residue resulting from this Si-extraction. All these different processes resulted in the synthesis of low-silica sodium and potassium zeolitic (NaP1, A, X, KM, chabazite, faujasite) material.

The potential industrial application of the zeolitic material obtained varies as a function of the prevalent zeolite type. Thus, zeolite X has a large pore size (7.3 Å) and a high CEC (5 meq g⁻¹), which make this zeolite an interesting molecular sieve and a high cation exchange material. However, the small pore size of hydroxysodalite (2.3 Å) accounts for the low potential application for both molecular sieving and ion exchange. Thus, simultaneously with the development of synthesis methods, intensive research has been carried out on the potential

application of the zeolites synthesised from fly ash. The high Al (III)/Si (IV) ratio of these zeolites accounts for the high CEC of some of them such as NaP1, 4A, X, KM, F, chabazite, herschelite, and faujasite. Owing to this high CEC, these zeolites have a high potential for application in water decontamination. In particular, the removal of heavy metals and ammonium from solutions was tested extensively (Park and Choi, 1995; Singer and Berggaut, 1995; Berggaut and Singer, 1996; Amrhein et al., 1996; Suyama et al., 1996; Patane et al., 1996; Querol et al., 1997a, 2001; Lin et al., 1998; Moreno et al., 2001a,b).

The synthesis of zeolites from 23 European coal fly ashes at laboratory scale and on the potential application of the zeolitic material was investigated in the framework of the SILEX project (supported by the 4th Framework of R&D of the European Union, BRPR-CT98-0801). The results of this research project allowed fixing the synthesis conditions using KOH and NaOH solutions with a solution/fly ash ratio from 1 to 20 mL g⁻¹. The Narcea, Compostilla, Soto de Ribera and Espiel fly ashes showed the highest synthesis yields (up to 75% of zeolite content)

TABLE 1 | Major chemical and physical characteristics of the Teruel and Narcea fly ashes.

	Teruel	Narcea		Teruel	Narcea
Major oxides (wt %)			Mineral composition (wt %)		
SiO ₂	48.3	55.2	Mullite	19.4	3.8
Al ₂ O ₃	23.9	23.3	Quartz	8.6	6.6
Fe ₂ O ₃	16.0	6.9	Anhydrite	1.5	0.2
CaO	5.4	4.0	Lime	0.7	0.4
MgO	1.0	2.5	Hematite	5.9	<0.3
Na ₂ O	0.2	0.7	Magnetite	1.3	1.5
K ₂ O	1.4	3.8	Feldspar	<1.0	0.2
P ₂ O ₅	0.2	0.3			
TiO ₂	0.8	0.9	Glass	62.7	85.6
SO ₃	0.8	0.4			
SiO ₂ /Al ₂ O ₃	2.0	2.4			
Trace elements (µg g⁻¹)			Physical characterisation		
As	79	98	Grain size (µm) P10%	4.6	3.0
B	342	98	Median	21.8	11.8
Ba	311	1047	P90%	75.7	50.3
Cr	107	177	True density (g cm ⁻³)	2.5	2.4
Cu	52	86	Apparent density (g cm ⁻³)	1.1	0.9
Li	256	220	Porosity (%)	58.2	63.4
Mo	15	6	BETSA (m ² g ⁻¹)	1.9	1.7
Pb	65	90			
Sr	523	235			
U	20	9			
V	206	173			
Zn	174	171			

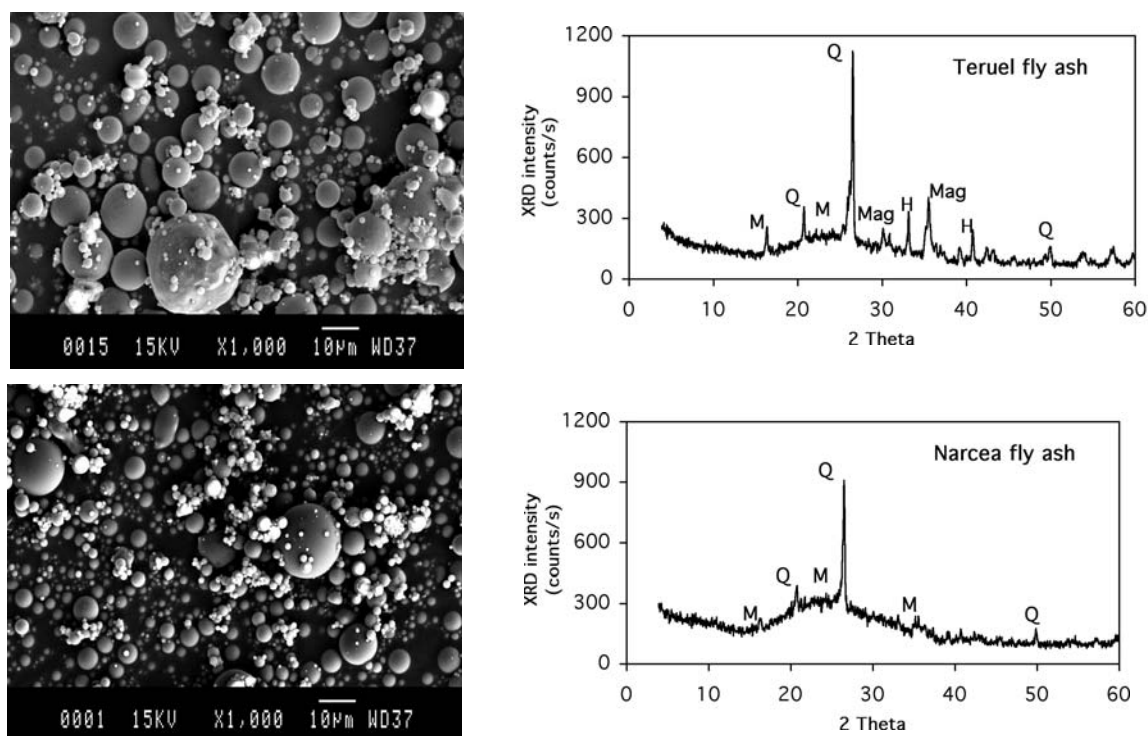


FIGURE 1 | SEM micro-photograph (left) and XRD pattern (right) of the original Teruel (up) and Narcea (down) fly ashes, where Q means quartz; M, mullite; Mag, magnetite and H, hematite.

probably due to the very high glass content (>80% wt), whereas the Meirama, Escucha, Los Barrios, La Robla and Teruel fly ashes showed lower synthesis yields, due to the higher content of less soluble crystalline phases.

The present study summarises the results on the zeolite synthesis from fly ash at a pilot plant scale using the Teruel (low glass) and Narcea (high glass) fly ashes (Table 1 and Fig. 1). Subsequently, with the aim of testing possible applications of the commercial NaP1-IQE and pilot plant NaP1-Narcea zeolitic products in water decontamination, the efficiency for metal uptake from waste waters from electroplating baths was investigated.

MATERIALS AND METHODS

The Teruel and Narcea fly ashes were selected to reproduce the laboratory tests at a pilot plant scale to experiment with high- and low-glass fly ashes (see major characteristics of these fly ashes in Table 1). The synthesis conditions were selected from prior studies (Querol et al., 1997a; Moreno et al., 2001a, b) to obtain high NaP1 ($\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$) products using a relatively low NaOH solution/fly ash ratio (2 L Kg^{-1}). These were 2M NaOH solution, 150°C and 24h for the low-glass Teruel fly ash, and 3M NaOH solution, 125°C and 8h for the high-glass Narcea fly ash. The lower the glass content the

longer the time needed for alkaline activation. The experiments were carried out in a 10 m^3 R-410-A reactor made of 304 stainless steel, details on the pilot plant design were supplied elsewhere (Querol et al., 2001a), but previously the synthesis parameters were tested at laboratory scale in an autoclave reactor (5 L BACHILLER) with temperature and pressure controls.

Semi-quantitative X-ray diffraction (XRD) powder analysis of the original fly ashes was obtained by the Internal Reference Method, using fluorite as an internal standard. The zeolitic material obtained from the different experiments was filtered and washed with distilled MilliQ water, dried at room temperature and analysed by means of XRD with Cu K α radiation. A semiquantitative estimation of the zeolite contents was obtained for by comparing their cation exchange capacity (CEC) with the CEC value of a pure NaP1 commercial product (produced by Industrias Químicas del Ebro, IQE). The CEC of the zeolitic materials was obtained using ammonium solutions following the methodology of the International Soil Reference and Information Centre (ISRIC, 1995). Levels of ammonium in solutions were measured using FIA-colorimetry methods. With the aim of testing possible applications of the commercial NaP1-IQE and pilot plant NaP1-Narcea zeolitic products in water decontamination, the efficiency for metal uptake from waste waters from electroplating baths was investigated. To this end samples

of waste water effluents of an electroplating plant were obtained. The sample was obtained from the collection tank where all the effluents are stored waiting for treatment. The sample was characterised by high concentrations of Fe (613 mg L⁻¹), Ca (171), K (240), Zn (272), Na (1023), Cr (7), Mn (5), Sr (3), Ni (0.7), Cu (0.7) and Ti (0.5).

Cation uptake tests were carried out in batch experiments, using PVC bottles, at room temperature and mechanical shaking, using aliquots of 50 mL of each water sample and zeolite powder doses from 0 to 45 g L⁻¹.

Major and trace element contents in the treated and untreated water samples were determined by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

RESULTS

Synthesis and characterization of the products

Table 2 summarises the results obtained from the synthesis of zeolitic material at laboratory scale with one kg sample size, in the autoclave reactor, from Narcea and Teruel fly ashes. This table shows that herchelite (Na-Chabazite) and NaP1 may be obtained for two fly ashes studied with high synthesis yields. Subsequently, two runs of 1.1 and 2.2 tonnes were carried out with the Teruel and the Narcea fly ashes (Fig. 2), respectively in the pilot plant scale. The experimental conditions are summarised in Table 3.

The XRD patterns and SEM micro-photograph of the Teruel and Narcea original fly ashes show that hematite and magnetite are only present in XRD detectable levels

in Teruel fly ash (Fig. 1). The high quartz and mullite contents of the Teruel fly ash (Table 1) accounted for the longer conversion time need (24 h) to reach acceptable synthesis yields. In contrast, as explained below, the high content of soluble glass (86%, see Table 1) of the Narcea fly ash accounted for the high synthesis yield reached in only 8 h in a laboratory scale.

The pilot plant scale experiments highly reproduced the results from the laboratory scale. The main difference found was that trace levels of analcime detected in the pilot plant product obtained from the Teruel fly ash. This phase was not determined in the Narcea fly ash, neither in the laboratory or the pilot plant scale experiments. This difference was appreciated previously in the laboratory scale (Table 2). Figure 3 shows the XRD patterns and SEM microphotographs of the zeolitic products obtained from Teruel and Narcea fly ashes. Table 4 shows the results on the quality evaluation (determined by CEC) of the different products obtained for laboratory to pilot plant scale experiments. The purity of the zeolitic products was evaluated by comparing the CEC values obtained of these products with the CEC value of commercial zeolite (NaP1-IQE). The CEC values obtained using the conventional methodology after ISRIC (1995) were estimated in: 5.0 meq g⁻¹ for commercial NaP1-IQE zeolite, 2.7 meq g⁻¹ and 2.0 meq g⁻¹ for synthesised NaP1-Narcea and NaP1-Teruel zeolitic material, respectively. The comparison of CEC values between commercial and synthetic zeolites indicated that the zeolite content in the fly ash derived material was close to 55 and 40%wt, respectively. The CEC values obtained are very close or even higher than those obtained for natural clinoptilolite-rich products (2.2 meq g⁻¹, Breck, 1974).

The conversion methodology used requires a minimum water consumption of 3 L of water per 1 kg of fly

TABLE 2 | Direct conversion experiments using the Teruel and Narcea fly ashes with stirring varying conditions with NaOH solutions and extractant solution / fly ash ratio of 2 L kg⁻¹ using a 1 kg sample size in a 5 L autoclave reactor. Values are XRD normalised intensities (counts/second) of major reflections of crystalline phases in the solid residue.

	T (°C)	t (h)	Quartz	Mullite	NaP1	Herchelite	Analcime	Sodalite	Cancrinite
Teruel									
2 M	150	8	5	27	155	<1	<1	<1	<1
2 M	150	12	<1	4	97	<1	18	7	<1
2 M	150	24	<1	5	92	<1	10	10	7
2 M	125	24	<1	<1	214	<1	<1	<1	<1
Narcea									
5 M	150	8	<1	<1	<1	<1	155	<1	36
3 M	150	8	<1	<1	114	<1	199	<1	<1
3 M	125	8	<1	<1	259	<1	<1	<1	<1

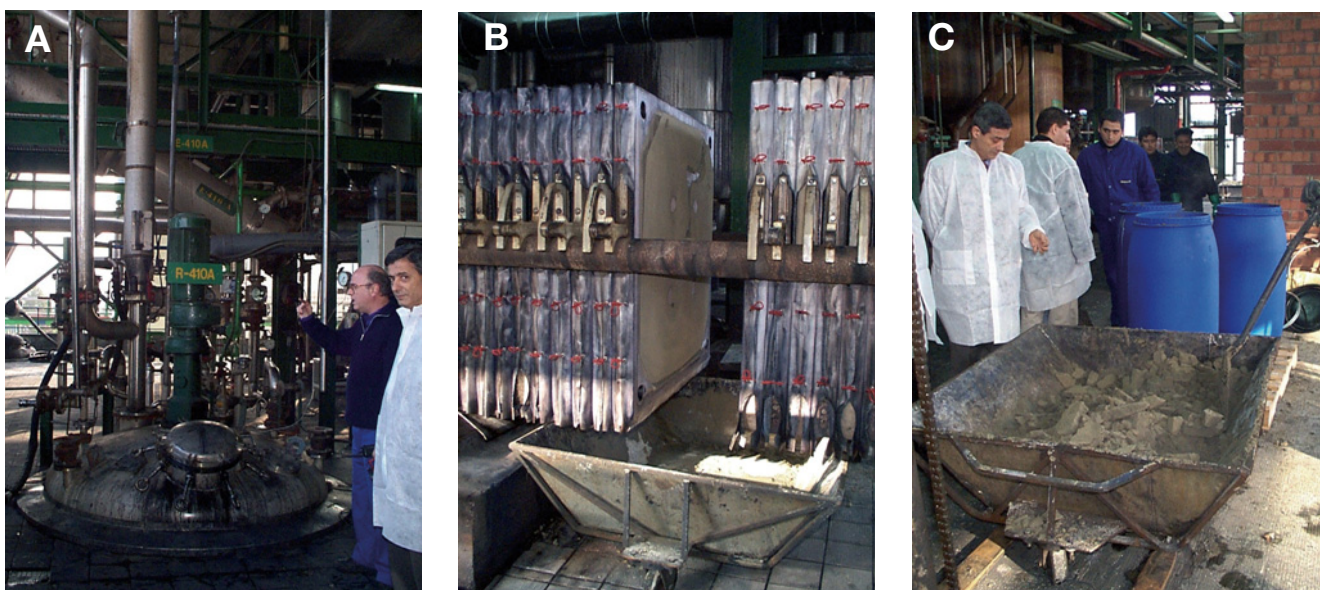


FIGURE 2 | A) Top of the R-410, 10 m³ reactor used for the synthesis of NaP1 zeolite from fly ashes at a pilot plant scale. B) pneumatic press filters used for washing and drying of the NaP1 zeolite from fly ashes at pilot plant experiment. C) packing of 2.7 tonnes of NaP1-rich product synthesised from the Narcea fly ash.

ash for the activation (2 L) and washing (1 L) processes. The water consumption could be diminished by optimising the stoichiometry of the reaction in order to avoid the washing process. The waste solutions resulting from the synthesis experiments are very alkaline (13.0 and 12.7 pH) and contain relatively high concentrations of leachable elements such as S (500-1500 mg L⁻¹), B (20-100 mg L⁻¹), V (50 mg L⁻¹), As (15 mg L⁻¹), Mo (2-6 mg L⁻¹) which have to be taken into account for the water treatment needed to recycle the activation solution in the potential industrial application of the process.

The leachable residual fly ash products still present in the zeolitic material have to be taken into account when this product is used for the cation uptake from polluted waters. Leaching tests of the NaP1-Narcea product using distilled water (30 g L⁻¹) showed that the leachable ele-

ments of the zeolitic product are ($\mu\text{g L}^{-1}$): S (6400), Ca (720), B and V (450), Al (300), Cr (210), As (72), Mo (36) and Cd (12).

Another limiting factor for the use of this material is that the zeolitic products may be soluble under extremely acidic environments such as acid mine waters. However, in these cases, the alkalinity of the product may neutralize acidic solutions with the consequent preservation of the zeolitic material and the precipitation of a large proportion of the heavy metal load (Moreno et al., 2001a, b).

Application tests

The metal uptake efficiency from the electroplating bath waste water was tested for the commercial NaP1-IQE and pilot plant NaP1-Narcea zeolitic products. Table

TABLE 3 | Experimental parameters used for the pilot plant zeolite synthesis using the Teruel and Narcea fly ashes.

Reactor:	R-410-A, 10m ³ stainless steel 304	Pressure	water vapour pressure
Teruel FA	1100 kg	Cooling:	2 h
Narcea FA	2200 kg	Filtration:	55 pneumatic press filters, 90 °C, 1 h
water / fly ash:	2 L kg ⁻¹	Washing:	85 °C, 40 min
time	24 h (Teruel) 8 h (Narcea)	Products	
T	150°C (Teruel) 125°C (Narcea)	Moisture	48 %
Concentration	2 M NaOH (Teruel) 3 M NaOH (Narcea)	Zeolite content	Teruel, 40%wt Narcea, 55%wt

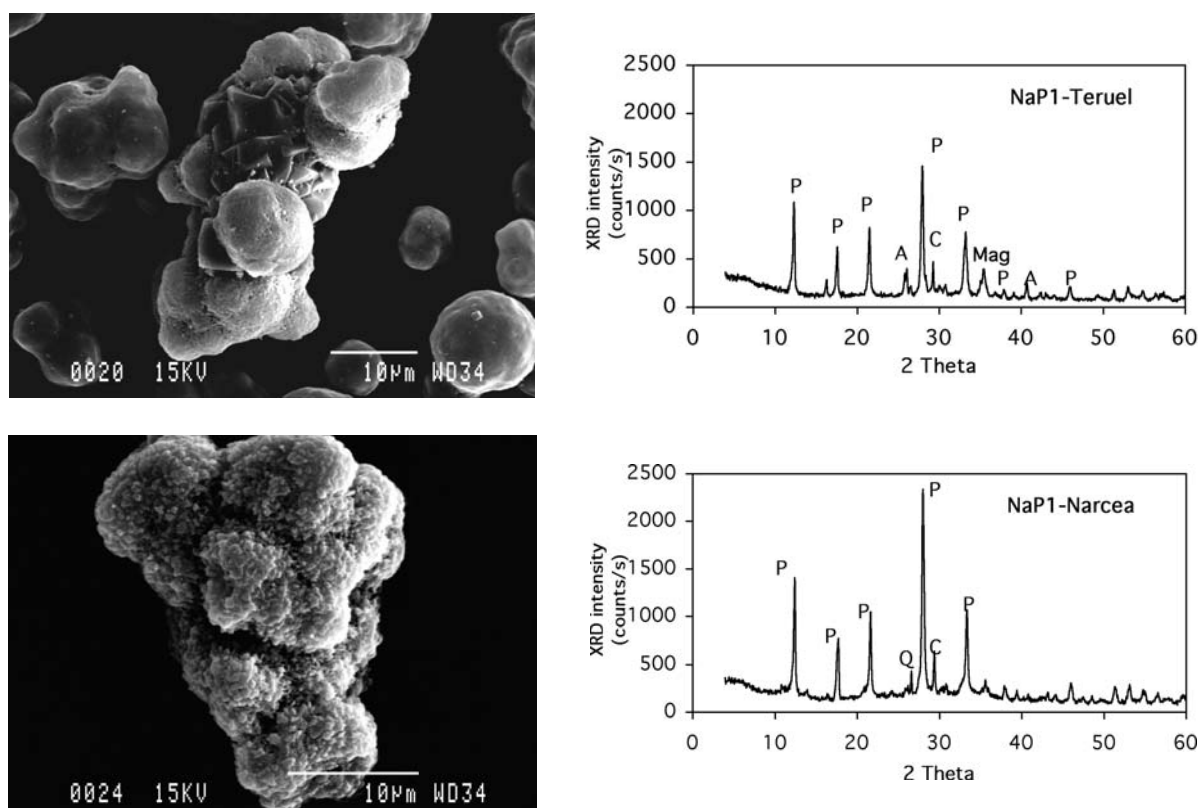


FIGURE 3 | SEM micro-photograph (left) and XRD pattern (right) of the NaP1 zeolitic product from Teruel (up) and Narcea (down) fly ashes. Q: quartz; Mag: magnetite; P: NaP1 zeolite; A: analcime; and C: calcite.

5 summarises the chemical analyses of the initial electroplating water and those of the residual solutions after applying different doses of zeolites. All the analyses show positive ionic unbalance probably due to the presence of Cl which was not analyzed. Moreover, Al was always below ICP-AES detection limit (2 mg L^{-1}). As shown in Table 5 the levels of most major (Zn, Cr, Mn, Sr and Fe)

TABLE 4 | Cation exchange capacity (CEC, in meq g^{-1}) of zeolitic material synthesized from fly ashes (using the ISRIC method). CEC for Spanish fly ashes and natural commercial zeolitic products are reported for comparison.

ZEOLITIC PRODUCT	CEC	zeolite content
	meq g^{-1}	%
Teruel and Narcea fly ash	<0.05	<0.1
NaP1 synthetic commercial	5.0	100
Clinoptilolite natural commercial	1.5-2.0	30-40
NaP1-Te lab. scale (4 g)	2.3	45
NaP1-Te intermediate scale (1 kg)	2.3	45
Pilot plant NaP1-Teruel	2.0	40
NaP1-Na lab. scale (4 g)	3.1	62
NaP1-Na intermediate scale (1 kg)	3.1	62
Pilot plant NaP1-Narcea	2.7	55

and trace (As, Ba, Cd, Co, Ni, Pb, Cu, Sn and V) metals were drastically reduced by applying different doses of the synthetic products. Thus, a dosage of 25 or 30 g L^{-1} of commercial NaP1-IQE, or the Narcea-NaP1 products, reduced the metal content from 613 , 272 , 8 and 5 mg L^{-1} of Fe, Zn, Cr and Mn down to 15 , 3 , <0.1 and 0.2 mg L^{-1} (IQE) and to <1 , 10 , <0.1 and 1.6 mg L^{-1} (Narcea). For other minor and trace elements the following significant reduction of their contents was also attained: Cu from 673 to $<60 \text{ } \mu\text{g L}^{-1}$, As from 32 to $<5 \text{ } \mu\text{g L}^{-1}$, Ba from 73 to $<1 \text{ } \mu\text{g L}^{-1}$, Cd from 14 to $1 \text{ } \mu\text{g L}^{-1}$, Co from 38 to $1 \text{ } \mu\text{g L}^{-1}$, Ni from 691 to $<40 \text{ } \mu\text{g L}^{-1}$, Pb from 48 to $1 \text{ } \mu\text{g L}^{-1}$, Sn from 27 to $1 \text{ } \mu\text{g L}^{-1}$ and V from 86 to $32 \text{ } \mu\text{g L}^{-1}$. Other elements such as Sr and Mo reduced from 3368 to $23 \text{ } \mu\text{g L}^{-1}$ and from 38 to $6 \text{ } \mu\text{g L}^{-1}$, respectively with 25 g L^{-1} of NaP1-IQE, whereas NaP1-NA only reduced the content to around $2000 \text{ } \mu\text{g Sr L}^{-1}$, or even slightly increased the content up to $40 \text{ } \mu\text{g Mo L}^{-1}$, using the dose of 30 g L^{-1} , as a consequence of the leaching of fly ash relict particles.

In order to discuss the feasibility of metal removal due to mineral precipitation as pH increases during zeolite dosing, the saturation index of the solution with respect to the solids that may precipitate from the main solutes was calculated using the code PHREEQC (Parkhurst and

TABLE 5 | Concentrations of major and trace elements in original and treated electroplating waste waters. The field expressed as meq g⁻¹ shows the ion balance between Na⁺ and the addition of the uptake cations. Saturation index (S.I.) of the solutions with respect to some common solids calculated with PHREEQC (Parkhurst and Appelo, 2002) and the MINTeq thermodynamic database (Allison et al., 1991)

		Original Solution	NaP1-IQE				NaP1-NA			
g l ⁻¹		0	18	20	25	30	25	30	36	45
pH		2.0	3.8	4.3	5.0	7.5	4.8	6.7	8.3	8.7
mg L⁻¹	B	7.6	7.2	7.1	7.0	7.1	7.4	7.3	6.9	6.3
	Ca	171.4	23.4	15.7	6.9	4.6	179.0	160.9	136.5	100.1
	Fe	613.4	54.7	37.2	14.9	12.0	1.0	0.5	0.6	0.5
	K	240.0	134.6	122.9	108.9	105.2	225.4	237.4	245.8	259.4
	Mg	32.6	18.6	13.1	5.9	4.2	34.7	33.4	32.2	26.9
	Mn	5.3	0.9	0.6	0.2	0.1	3.0	1.6	0.6	0.1
	Zn	272.2	13.4	9.0	3.1	1.8	34.9	10.9	2.1	0.3
	Na	1023.4	2351.0	2394.0	2480.0	2536.0	2242.0	2420.0	2560.0	2750.0
	SO₄	4206	4302.6	4310.4	4332	4354.2	4324.2	4372.8	4409.4	4428
meq g⁻¹	ΔNa⁺		3.2	2.9	2.5	2.2	2.1	2.0	1.8	1.7
	Δcations		2.8	2.5	2.2	1.9	1.6	1.4	1.2	1.0
μg L⁻¹	As	32	4	5	4	5	4	6	7	23
	Ba	73	1	1	0	1	19	18	16	13
	Cd	14	1	0	1	1	2	1	1	1
	Co	38	4	3	1	1	15	8	3	1
	Cr	7692	11	9	8	8	4	5	11	28
	Cu	673	50	53	58	70	107	96	99	96
	Ga	8	1	1	1	2	2	2	2	2
	Li	35	65	71	77	81	749	787	705	628
	Mo	38	1	3	6	8	14	43	100	180
	Ni	691	169	99	39	33	170	96	44	13
	Pb	48	2	1	1	1	1	1	1	1
	Sb	9	1	1	1	1	2	3	5	11
	Se	35	22	11	7	18	36	44	42	37
	Sn	27	1	1	1	<0.5	<0.5	<0.5	<0.5	<0.5
	Sr	3368	86	59	23	19	2409	2115	1842	1236
	Ti	476	289	287	293	334	409	408	425	439
V	86	51	43	32	30	4	5	13	33	
S.I.	Calcite		-9.4	-8.7	-7.7	-2.8	-6.5	-2.9	0.2	0.9
	Gypsum		-1.0	-1.1	-1.5	-1.7	-0.1	-0.2	-0.2	-0.4
	Ferrihydrite		0.9	1.6	2.1	4.4	0.7	2.3	3.1	2.8
	Goethite		5.2	5.9	6.3	8.6	5.0	6.6	7.4	7.0
	Schwertmannite		18.7	22.7	23.7	33.0	13.3	19.4	20.3	16.0
	Hydrozincite		-36.5	-33.3	-28.6	-4.8	-25.3	-8.8	2.6	-1.5
	Zn(OH)₂ (α)		-9.1	-8.5	-7.6	-2.8	-6.7	-3.6	-1.3	-2.1
	Cr(OH)₃(α)		-10.8	-11.4	-12.1	-16.1	-12.2	-14.7	-17.5	-17.9
	Malachite		-15.2	-13.1	-10.3	-1.4	-10.5	-3.1	-0.9	-0.9
	Calcalthite		-6.2	-6.2	-6.1	-6.7	-5.8	-5.9	-8.0	-8.8
	Cu(OH)₂		-8.1	-7.1	-5.6	-1.2	-5.7	-2.0	-0.9	-0.9
	NiCO₃		-13.6	-12.8	-11.8	-7.0	-11.5	-8.0	-6.3	-6.9
	Ni(OH)₂		-9.2	-8.4	7.4	-2.6	-7.2	-3.6	-1.9	-2.5
	Celestite		-1.9	-2.1	-2.5	-2.6	-5	-0.6	-0.6	-0.8
Strontianite		-11.2	-10.5	-9.5	-4.6	-7.7	-4.1	-1.0	-0.3	

Appelo, 2002) and the MINTEQ thermodynamic database (Allison et al., 1991). The solutions were assumed in equilibrium with the atmospheric O₂ and CO₂. As shown in Table 5, for practically all zeolite doses, only Fe oxyhydroxides (assuming that all the analyzed Fe is Fe(III)) are supersaturated. The rest of cations uptaken from the solution (Ca, Zn, Cr, Cu, Ni, Sr) are not expected to precipitate as common solids (carbonates, sulfates, hydroxides) since the solutions are subsaturated with respect to them. Moreover, Table 5 also shows that the cations uptaken and the Na⁺ released to the solution during zeolite dosing show a fairly consistent ionic balance. The slightly higher Na⁺ concentration may be due to several reasons, such as H⁺ exchange and zeolite dissolution, not included in the calculations.

Therefore, although it is probable that most of trivalent cations reduced the concentrations as a consequence of precipitation processes, the ion balance between the uptaken cations and the Na⁺ suggests that cation exchange is the dominant process accounting for the uptake of a large proportion of metals.

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