One-step synthesis of NaP1, SOD and ANA from a hazardous aluminum solid waste

Ruth Sánchez-Hernández, Aurora López-Delgado*, Isabel Padilla, Roberto Galindo, Sol López-Andrés

a National Centre for Metallurgical Research, CSIC, Avda. Gregorio del Amo 8, Madrid, 28040, Spain

b Department of Crystallography and Mineralogy, Faculty of Geology, University Complutense of Madrid, C/ José Antonio Novais s/n, Madrid, 28040, Spain

*Corresponding author: Tel.:+34915538900
Email: alopezdelgado@cenim.csic.es
Abstract

NaP1, SOD, and ANA zeolites were synthesized from a hazardous aluminum waste as main aluminosilicate source by a one-step hydrothermal synthesis. This allowed the total transformation of the waste and no other solid residues were produced. The conversion of the waste into zeolites led to yields of ~2.5 kg of zeolite per kg of waste. Experimental parameters such as stirring, time, temperature, and concentration of alkalizing agent (NaOH solution) were studied to determine the best synthesis conditions. Samples were characterized by different techniques such as XRD, SEM-EDS, FTIR, TG-DTA; textural properties such as BET specific surface area, zeta potential, granulometry and cation-exchange capacity (CEC) were also determined. Temperature and alkali concentration were the parameters with strongest influence in the formation of the different zeolites. Thus, the optimal conditions to obtain NaP1 and ANA were 1 M NaOH solution for 6 h at 120 and 200 ºC, respectively, while SOD was prepared at 120 ºC for 6 h, using a very much higher alkali concentration (5 M). These zeolites exhibited similar characteristics to those obtained from conventional chemical reagents. Besides, the mother liquor from the synthesis of NaP1 was recycled twice in order to reduce water and alkalizing agent consumption. In this case, the only crystalline phase obtained was NaP1 showing morphological, textural and crystalline characteristics very similar to those of NaP1 prepared from fresh solutions. The results show that the aluminum waste can be transformed into different types of zeolites, considered as value-added materials, with promising adsorption properties.

Keywords: NaP1, sodalite and analcime; Hazardous waste; One-step hydrothermal synthesis; Mother liquor recycling; High-CEC zeolite
1. Introduction

Zeolites are crystalline aluminosilicates with structures based on a three-dimensional network of AlO$_4$ and SiO$_4$ tetrahedra that are linked to each other through the sharing of their oxygen atoms. Zeolites share the common feature of regular and uniform porous structures forming voids as channels, cages or cavities. Many of their unique properties are explained by the presence of these voids that allow the sorption and diffusion of ions and molecules. The substitution of Si (IV) by Al (III) in the tetrahedra induces negative charges in the structure that are compensated by extra-framework cations such as Na$^+$, K$^+$ and Ca$^{2+}$ [1, 2]. Zeolites have been intensively studied and widely used in catalysis, gas separation, water purification, membranes and many other industrial applications [3-7].

Zeolites can be found in nature or synthesized from a great variety of Si and Al sources. In the last decades, the use of waste materials like low-cost precursors for the preparation of zeolites has been increasing, driven by the need to minimize the waste disposal into landfills and to address associated environmental impacts. Among such precursors, coal and incineration fly ash, rice husk ash, natural clinker, etc. have been widely used for the synthesis of different zeolitic materials such as zeolites NaA, NaX, NaP1, sodalite, cancrinite, analcime, linde F, etc. [8-15]. Zeolites such as NaP1, analcime (ANA) and sodalite (SOD) are of interest due to their ion-exchange and sorption properties [16]. NaP1 zeolite is characterized by the gismondine-type structure with two types of channel size and by its high cation exchange capacity with potential applications in water remediation [2]. Zeolite ANA, which structure is made up of irregular channels formed by highly distorted eight-rings and small
pore entrances, can be used in heterogeneous catalysis and selective adsorption [17]. NaP1 is hydrothermally obtained at 90-120 °C, while at higher temperature ANA is the most stable phase. The cubic framework of SOD is based on regular truncated octahedral cages (β-cages) with small pore openings and characterized by its high stability in basic solution [2]. SOD is considered a promising candidate as membrane for the separation of small molecules, such as He and H₂, from gas or liquid streams.

Nowadays, both the conventional hydrothermal synthesis and other non-conventional methods, like microwave radiation and ultrasound energy, have been described in the literature for preparing a wide variety of zeolites. In general, these procedures involve a previous activation step by addition and simultaneously stirring of precursors and alkalizing agents (mainly, NaOH and KOH). Then, the conventional hydrothermal synthesis is carried out under autogenous pressure, at temperatures from 60 to 200 °C and for periods of time of several hours or days in order to improve the crystallinity. Long aging (about ≥ 1day), calcination or fusion (600-900 °C) and/or acid treatments (with HCl, H₂SO₄, etc.) can be necessary to improve the reactivity of certain types of wastes in order to be used as raw materials (rice hush, kaolin, electrolytic manganese residue, etc.) [2, 8, 11, 18-22]. For instance, Hollman et al. [23] carried out a two-step synthesis to obtain NaP1, NaX and NaA zeolites from fly ash. In a first step, an alkaline synthesis (90 °C for 6 h) was performed to obtain a fly ash residue and a high-Si filtrate. The Si/Al molar ratio of the high-Si filtrate was adjusted by adding an aluminate solution and then heated another 48 h at 90 °C to obtain pure zeolites from the residue as well as a new filtrate. In a second step, the fly ash residue obtained in the first synthesis of 6 h is mixed
with the new filtrate and heated again for 24 h at 90 °C to obtain high fly ash content zeolites. The results led to 50, 75 and 85 g of zeolites NaP1, NaX and NaA, respectively, per kg of fly ash. Atta et al. [11] synthesized trapezohedral analcime from a mixture of rice husk ash and metakaolin as silica and alumina sources, and sodium hydroxide solution (Na₂O/Al₂O₃=2.6). Before the synthesis, the rice husk and the kaolin were calcined at 800 and 900 °C, respectively, for 3 h. After calcination, the resulting metakaolin was dissolved in 4 M NaOH followed by refluxing at 90 °C. They carried out an aging step (3 days) followed by a hydrothermal process at 180 °C for 24 h. Bohra et al. [8] also reported the use of rice husk ash (obtained by calcination at 700 °C for 6 h), aluminum foil and a NaOH solution (Na₂O/Al₂O₃=2.1) to obtain zeolites NaA and NaP. Firstly, they carried out a stirring process of 15 h, followed by a hydrothermal heating at 100 °C of 15 h for NaA, and of 72 h for NaP. Król et al. [24] studied the effect of varying the temperature (30-90 °C) and the NaOH concentration (0.5-5 M) for different times (24-72 h) on the hydrothermal synthesis from a by-product of the expanded perlite production. Thus, they obtained as predominant phases hydroxy-sodalite and NaP1 (with traces of zeolite X) at 90 °C for 24 h with 5 and 3 M NaOH, respectively.

The recovery of metals from the metallurgical industry is one effective strategy in the waste management. It not only reduces the space requirement in landfills, but also preserves natural resources. Nowadays, aluminum is widely used in many sectors (transport, construction, packing, etc.) due to its well-known properties. This metal is obtained in the primary aluminum industry from bauxite, and the secondary industry from materials that have reached the end of their life (scraps). Both industries generate slags which are recycled for different
uses by the tertiary industry. This latter industry recovers residual aluminum present in the slag by different treatments which include the slag milling. The fine powdered solids produced from the milling process, which is highly composed of Al and Si, is considered as a hazardous waste according to the European Waste Catalogue, within the 10 03 21 group. Negative impacts of this waste come from its very fine grain size and heterogeneous composition with harmful substances (metallic aluminum, aluminum nitride, aluminum carbide, aluminum sulfide, heavy metals, etc.) leading to the release of toxic gases such as hydrogen, ammonia, methane and hydrogen sulfide in presence of water or humidity. In prior studies, we successfully developed the conversion of such waste into aluminas and Mg–Al hydrotalcites by extracting the soluble aluminum compounds via acid hydrolysis of the waste and posterior precipitation of the products by alkalining/aging processes [25-27]. However, in those processes only a small fraction of the total aluminum content in the waste was recovered, and a cake which included the non-soluble fractions of Al, Si and other compounds was remained as an inert solid waste. In the present work, the complete transformation of the waste into zeolites has been envisaged as a one of the best ways to recover this waste because value-added materials can be easily obtained and no solid residue is generated.

The objective of this work was to develop a simple one-step synthesis process to obtain, NaP1, sodalite and analcime, employing a hazardous aluminum waste as the main aluminosilicate source. Experimental synthesis parameters such as stirring, time, temperature, concentration of the alkalizing agent (NaOH solution) were investigated to determine the optimal conditions to obtain high quality zeolites. Products were well characterized by several techniques XRD,
SEM-EDS, FTIR and TG-DTA. Physical-chemical characterization was completed by the determination of the specific surface area, zeta potential, particle size distribution and cation-exchange capacity.

Furthermore, consecutive synthesis essays, in which the NaOH solution was totally substituted by the mother liquor (i.e. waste alkaline solution) obtained from the corresponding previous essay, were performed in order to study the possibility of its recycling to reduce the water and alkalizing agent consumption.

2. Experimental

2.1. Materials

The solid waste employed in this work came from the sleeve filter suction system of the aluminum slag milling process. One of the major problems to be faced when wastes are used as raw materials for any process is to solve the heterogeneity of samples. Thus, in order to get a representative sample of the waste, nine powdered samples from different Spanish industries were mixed and homogenized by successive quartering. The starting material, a very powdered solid, consisted mainly (> 50%) of particles less than 23 µm in diameter. The content of the main zeolite constituents (i.e. Al and Si) in the waste was Al$_2$O$_3$ 65.9 wt% and SiO$_2$ 5.3 wt% (see XRF results in Table 1), which yielded an Al$_2$O$_3$/SiO$_2$ ratio of ∼12.4 for the synthesis tests. These elements were identified in several crystalline phases (see XRD pattern in Fig. 1), namely, corundum (Al$_2$O$_3$), aluminum nitride (AlN), metallic aluminum (Al), quartz (SiO$_2$), spinel (MgAl$_2$O$_4$), together with metal chlorides such as halite (NaCl) and sylvite (KCl), which derived from inorganic compounds in the fluxes used to smelt the aluminum scrap. The high background of the XRD profile also
indicates the presence of non-well crystallized or amorphous phases in which metallic oxides such as iron oxide, among others, could be included. The waste was directly used without any previous treatment. Detailed information about the composition and physicochemical properties of this waste was published elsewhere [28].

For the synthesis of zeolites, the low SiO₂/Al₂O₃ molar ratio from the waste was increased by adding sodium silicate neuter solution (Na₂SiO₃, Panreac) up to 4. Sodium hydroxide solution, prepared by dissolving NaOH pellets (98% NaOH, Panreac) in distilled water at different concentrations (1-5 M), was used as alkalizing agent.

2.2. Methods

2.2.1. Direct synthesis of zeolites

The synthesis of zeolites was carried out by the conventional hydrothermal method, without a previous activation step, in the basic Na₂O-Al₂O₃-SiO₂-H₂O system and in absence of organic templates. Reactants, the solid waste (10 g), Na₂SiO₃ solution (to balance the Si/Al ratio) and NaOH solution were added into a Teflon-lined autoclave (Parr, 1L volume). All the experiments were performed at a fixed Si/Al molar ratio of ~2.0 (taking into account the chemical composition of reactants), using a liquid/solid ratio of 25 mL/g, with continuous stirring and under a nitrogen inert atmosphere (to maintain the same pressure inside the reactor, 10 bar). Variable time, temperature and alkali concentration were tested. Thus, for a fixed temperature of 120 ℃, time was varied at 3, 6 and 24 h; for a fixed time of 6 h, temperature was varied at 80, 90, 100, 120 and 200 ℃. For those experiments a 1M NaOH solution was used. To study the effect of
alkaline concentration, time and temperature were fixed at 6 h and 120 ºC and different NaOH solutions (1, 3, 4 and 5 M) were used. As the formation and crystallization of zeolites is very sensitive to the stirring, one test was performed without stirring. After finishing experiments, solid products were separated by filtration under pressure (at 5 bar) on a GTTP Millipore filter of 0.22 µm, washed with distilled water up to pH 10-11 and dried in air at 80 ºC for 24 h. The filtrate obtained in the filtration step (mother liquor) was analyzed to determine the aluminum and silicon content, and the pH and conductivity values in order to reuse this highly alkaline solution in the recycling experiments.

2.2.2. Recycling of alkaline effluent (mother liquor)

In general, the synthesis of zeolites, both from the pure chemical reagents and waste sources, produces a solid cake (the zeolitic material) and mother liquor or alkaline effluent. This latter may be susceptible to recycle in order to reduce the water and NaOH consumptions and accordingly the environmental impact of the process. The recycling of this alkaline effluent produced in the synthesis of zeolites has been scarcely aimed in the literature [23, 29-32]. The mother liquor (ML) from the synthesis of zeolites is usually a strongly alkaline solution that contains valuable elements such as Si, Al and Na, which are the main constituents of Na-type zeolites. The concentration of such elements was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). In the experiments realized to study the recycling of the ML, the corresponding NaOH solution was not added. Instead of it, the same volume of such alkaline effluent was used to maintain the same liquid/solid ratio (25 mL/g) employed in the experiments of synthesis. Thus, the ML was recycled twice, and the zeolites were also characterized.
The scheme of the process employed to synthesize zeolites from the aluminum waste is shown in Fig. 2.

2.3. Characterization

Chemical composition of the waste was determined by X-ray fluorescence (XRF) using a pressed pellet of 10 g of the waste without additives in a wavelength dispersive X-ray fluorescence spectrometer (Bruker, S8 Tiger). Mineralogical composition of samples was determined by X-ray diffraction (XRD) with CuKα radiation, from 2° to 65° 2θ, at a scan rate of 0.02° 2θ and 0.07 s per step in a Bruker D8 Advance diffractometer. Semi-quantitative analysis of the samples was determined by the reference-intensity-ratio (RIR) method using XRD data and EVA software. Crystallite size (D_{hkl}) of the products were calculated according to the Scherrer equation: \( D_{hkl} = \frac{(0.9 \cdot \lambda)}{(FWHM \cdot \cos \theta)} \), where \( \lambda \) is the wavelength of X-ray beam (0.15418 nm), FWHM is the full width at half maximum (in rad) and \( \theta \) is the experimental Bragg diffraction angle (in rad). The loss of ignition (LOI) was calculated by heating at 1000 °C for 1 h in a Pt crucible. Morphology and elemental composition of the products were examined by scanning electron microscope (SEM), in a Hitachi S4800 microscope, equipped with an energy dispersive X-ray detector (EDS) supplied by Oxford (previously, the samples were coated with graphite by sputtering procedure). Fourier transform infrared (FTIR) spectra were recorded on KBr discs (Nicolet Nexus 670-870) in the range of 400-4000 cm\(^{-1}\).

Thermogravimetric analysis (TG) and differential thermal analysis (DTA) were carried out in a thermoanalyzer model SDT-Q600, TA Instruments. The samples were heated up to 1000 °C, at a heating rate of 10 °C/min, in a Pt
crucible and under a N\textsubscript{2} flow of 100 mL/min. Textural characterization of the samples was performed by determination of nitrogen adsorption/desorption isotherms at 77 K in an ASAP 2010 Micromeritics equipment. Before the measurements, the samples were outgassed at 60 °C in vacuum for 24 h. The BET specific surface area (S\textsubscript{BET}) was calculated by the BET method in the P/P\textsubscript{0} range of 0.004-0.3. The external area (S\textsubscript{EXT}), i.e. the area of those pores which are not micropores (mesopores, macropores, and exterior surface of the particle), was calculated by the t-plot method from the slope of the linear fit in the thickness range (t) of 0.35-0.5 nm according to the Harkins-Jura equation. The pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method in the adsorption branches. The particle size distribution (parameters d\textsubscript{10}, d\textsubscript{50} and d\textsubscript{90}) was measured by laser diffraction (Mastersizer 2000, Malvern) using aqueous suspensions of the samples (0.001 g/mL) sonicated in ultrasounds prior to the measurements. The polydispersity index (PI) was calculated according to Naranjo et al. [33]. Zeta potential (ZP) was determined by a laser doppler electrophoresis analyzer (ZetaSizer Nano, Malvern) using 0.005 g of sample in 100 mL of aqueous dispersion at 25 °C. The cation-exchange capacity (CEC) of the zeolites was determined by NH\textsubscript{4}\textsuperscript{+} ion exchange method with a 1M NH\textsubscript{4}Cl solution (pH ~7). The composition of the alkaline effluent from the synthesis was analyzed by an inductively coupled plasma optical emission spectrometer, ICP-OES (Spectro Arcos). The pH and conductivity values were simultaneously measured by a multimeter provides with the two corresponding electrodes (MM41, Crison).

3. **Results and discussion**

3.1. **Direct synthesis of zeolites**
The experimental conditions of the different tests performed to obtain zeolites from the aluminum waste are summarized in Table 2, along with the crystalline phase identified by XRD and the reaction yield expressed as mass of product per mass of waste. Most of experimental conditions tested were favorable for the formation of zeolitic phases due to the high solubility in alkaline medium of various aluminum compounds, especially metallic aluminum and aluminum nitride and the presence of dissolved silicon. The zeolitization process of the waste would involve similar steps described in the preparation of zeolites from fly ash, namely, dissolution of the Al and Si content of the waste, condensation of the Al and Si polymers on the surface of the waste particles, and nucleation and crystal growth of zeolites [34]. Taking into account that the initial Si/Al molar ratio was the same for all the experiments, the formation of different zeolitic phases will depend on the other experimental parameters such as time, temperature and concentration of the alkalizing agent. This was confirmed by XRD studies.

Fig. 3 shows the XRD patterns of the samples obtained at 120 °C and 1 M NaOH for 3, 6 and 24 h and with/without agitation. In all the samples, NaP1-type zeolite was identified (JCPDS 01-071-0962) as the only zeolite phase. Well-defined XRD profiles were obtained except for the sample S1 prepared without agitation, as a result of the incomplete dissolution of the Si and Al sources from the waste, especially quartz and corundum, during the synthesis. This means that agitation had a huge positive effect on the formation and development of zeolites from the aluminum waste. No shift of the 2θ values was observed in the XRD profiles for all the samples. Thus, the 301 basal reflection of NaP1 was centered at 28.09, 28.09, 28.08 and 28.06°, for S1, S2, S3 and
S4, respectively. The crystallinity of the samples increased as the reaction time increased, as can be seen from the sharpness of the peaks (Fig. 3): the most crystalline NaP1 was obtained for 24 h (S4).

In the case of the sample obtained at 3 h with agitation (S2), small peaks attributable to analcime (around 2%) were found, probably, due to a overshooting of the set temperature in the synthesis experiment.

The amount of zeolite NaP1 obtained (Table 2) was around 2.4-2.5 kg per kg of waste for the different periods of time tested (3, 6 and 24 h). For sample S1 (without stirring) a lower value was obtained probably due to the incomplete dissolution of the waste and accordingly the incomplete zeolitization process.

Due to a reaction time of 6 h was considered adequate to get a well-crystallized products, it was selected to perform the next experiments in order to study the influence of other experimental parameters (alkali concentration, temperature and mother liquor recycling).

XRD patterns of the samples prepared at 120 °C for 6 h with different NaOH concentrations (S3, S5, S6 and S7) are shown in Fig. 4. When the alkali concentration was increased, from 1 to 5 M, both the intensity of peaks and the crystallite size corresponding to NaP1 phase gradually decreased due to the formation of sodalite (SOD) phase at an alkali concentration higher than 1 M. Due to the coincidence of XRD patterns of hydroxy-sodalite (JCPDS 01-076-1639) and chloride-sodalite (JCPDS 01-086-1844), it was not possible to decide between both phases unambiguously. For the samples S5 and S6, as the NaOH concentration was increased from 3 to 4 M, the crystallite size of NaP1 slightly diminished, and the percentage of this phase varied from 43 to 30%,
respectively. The crystallite size of SOD did not vary significantly, and it was obtained as the only crystalline phase characterized by the 211 basal reflection centered at 24.43°, in sample S7, which corresponds to the highest NaOH concentration tested (5 M). In the case of the samples obtained with 3 and 4M NaOH concentration, no shift of the 2θ value of the diffraction maximum peak was observed. The interactions between the negatively charged aluminosilicates and cations in the synthesis gel are extremely important in determining the final zeolite structure. Thus, the Na⁺ ions play a significant part in the crystallization of Na-type zeolites as NaP1 [35]. Murayama et al. [35] studied the role of cations Na⁺ and K⁺ on the production of zeolite from coal fly ash with different alkali solutions and their combinations, confirming that the crystal structure of the products changes from zeolite P to hydroxy-sodalite, via co-crystallization. Chun-Feng et al. [36] also observed the transformation of zeolite A obtained from fly ash into hydroxy-sodalite by increasing the NaOH concentration. The authors established that it is attributable to an extinction effect of the small crystallites of zeolite A, instead of the reduction in crystallinity of this phase. In our case, the decrease of the crystallite size as the alkaline concentration increased supports this last statement. The amount of SOD obtained per kg of waste was 2.2 kg.

Fig. 5 shows the XRD patterns of the samples synthesized employing 1 M NaOH for 6 h at different temperatures from 80 to 200 °C. For samples S9, S10 and S3 obtained at 90, 100 and 120 °C, respectively, the diffraction peaks were attributable to zeolite NaP1, whose XRD profiles indicate the increase of the crystallite size and the crystallinity of the sample as temperature increases. The amount of zeolite NaP1 per kg of waste also increased with the temperature,
showing values higher than 2.0 kg at temperatures above 100 °C. For the essay performed at 200 °C, the XRD pattern (sample S11) indicated the formation of analcime (JCPDS 00-041-1478) as the only zeolite phase with a diffraction profile composed of well-defined and narrow peaks, which are characteristic of highly crystalline samples. Analcime (ANA) is usually obtained at high temperature for long reaction time [9, 11, 37]. Thus, Sandoval et al. [9] used natural clinker at 150 °C for 24 h; and Atta et al. [11] prepared ANA using rice husk and kaolin, previously activated, at 180 °C for 96 h. In our case, the ANA was obtained directly from the transformation of the aluminum waste in a very much short one-step process.

For the lowest temperature tested, 80 °C, (sample S8), the XRD profile (Fig. 5) corresponds to an amorphous material, and only three diffraction peaks of quartz are observed. It can be justified due to the lower dissolution of Si sources from the waste at low temperature.

The yield obtained for ANA was of 2.4 kg per kg of waste. As the other zeolites obtained, the reaction yield is very high, and all the waste is transformed into a zeolitic material by one-step process and without other previous treatments of the waste. When these zeolites are obtained from fly ash, a previous activation step is usually required, and generally, the yield is very much lower (85-250 g of zeolite per kg of fly ash.) [23, 38] than using the aluminum waste.

In order to perform the complete characterization of the obtained zeolites, samples S3, S7 and S11 which correspond to pure NaP1, SOD and ANA, were subjected to further studies.

Fig. 6 shows the SEM images of the three zeolites at different magnifications.
NaP1 zeolite (S3) exhibited a homogenous morphology composed of “cauliflower-like” primary aggregates of around 15-45 µm (Fig. 6a and 6b). These primary aggregates consist of smaller secondary aggregates with an average diameter of 4 µm, which are formed by cubic nanocrystals with well-defined edges and an anisotropic growth of crystals, as can be seen in the Fig. 6c. It is characteristic of the typical gismondine-type structure. [23, 29, 35].

The images corresponding to SOD (S7) showed a similar morphology to that previously reported in the literature [3, 39], characterized by highly densified agglomerates composed of “raspberry-like” balls (Fig. 6d and 6e) with an average diameter of 1.5 µm. It was observed that a certain number of these microballs consisted of hollow balls as that showed in Fig. 6e. At higher magnification (Fig. 6f), intergrowth of distorted hexagonal tabular crystals with edges that ranged around 40-350 nm were observed.

The morphology of ANA (S11) (Fig. 6g and 6h) consisted of agglomerates of spherical particles with particle size ranged between 4 and 8 µm. At high magnification (Fig. 6i), euhedral crystals can be observed, forming trapezohedra with highly faceted crystals and well defined edges, most of the crystals exhibit intergrowths. Although the morphology is very sensitive to the experimental conditions, a similar morphology was described for zeolites obtained from fly ash for different authors [11, 29, 40].

Fig. 7 collects the EDS spectra and the microchemical point analysis of the selected zones for S3, S7 and S11 samples.

EDS analyses showed that Na⁺ is the main exchange cation in the structure of the three zeolites. For NaP1 (S3), the average Si/Al ratio obtained as an
average of ten microchemical points analysis was of 1.85. Although this value is slightly higher than that corresponding to the stoichiometric value (~1.67) of NaP1, Na₆Al₆Si₁₀O₃₂·12H₂O, variable Si/Al ratios have been reported in the literature depending on the synthesis conditions of zeolites [41]. An average Na/Al ratio of 0.93 was obtained and, in general, other exchange cations were not observed, but scarcely, minor content of K⁺ cation was detected in the microchemical point analysis of several crystals with a K/Na ratio very low (0.02). It is according to the results previously found in the literature, where not only K⁺, but also Ca²⁺,Mg²⁺ and Fe²⁺ ions have been also detected in NaP1, sodalite and analcime zeolites from fly ash [29, 42].

For SOD (S7), the average Si/Al ratio was of 1.02 and the average Na/Al ratio of 0.74 (Fig. 7), similar values to the theoretical of both hydroxy-sodalite (Na₆Al₆Si₆O₂₄(OH)₂·2H₂O) and chloride-sodalite (Na₄Al₃Si₃O₁₂Cl). Chloride peaks were observed in most of the microchemical point analysis as can be seen in the EDS spectrum (Fig. 7). This seems to indicate the partial replacement of OH⁻ by Cl⁻ ions and accordingly the formation of chloride-sodalite.

In the case of ANA (S11), the average Si/Al ratio was of 1.73 (Fig. 7), which fits well with the theoretical value for the stoichiometry of ANA (NaAlSi₂O₆·H₂O). Only Na⁺ was detected as exchange cation to balance the ANA structure, with a Na/Al ratio of 0.90, which is in good agreement with that reported by [9].

FTIR spectra of the samples S3, S7 and S11 recorded from 400-1200 cm⁻¹ are plotted in Fig. 8.
All the spectra showed bands corresponding to aluminosilicate materials. Thus, it can be observed the very strong and broad band around 1000 cm\(^{-1}\) which is assigned to the asymmetric stretch of internal Si-O or Al-O tetrahedra [18]. For sample S3, the obtained FTIR spectrum is characteristic of NaP1: three bands centered at 743, 679 and 604 cm\(^{-1}\) attributable to the symmetric stretching vibrational mode of internal tetrahedron, and the band at 433 cm\(^{-1}\) assigned to tetrahedron bending mode, which fits well with the spectra reported by Huo et al. [41] for NaP1 obtained from pure reagents. This indicates the high purity of the zeolite obtained from the aluminum waste.

In the case of sample S7, it is remarkable the characteristic triplet of SOD, in the region of the “finger-print” (symmetric stretching mode), at 732, 704 and 669 cm\(^{-1}\) and the two bands corresponding to the octahedron bending modes at 461 and 433 cm\(^{-1}\) [43]. These results are in good agreement with the results reported by Król et al. [24] for sodalite hydrothermally synthesized from expanded perlite.

For sample S11, the spectrum fit well with those previously reported in the literature for ANA from other waste sources such as kaolin and rice husk, and quartz syenite [11, 44]. Thus, the ANA spectrum showed the asymmetric stretching modes of tetrahedron at 1014 cm\(^{-1}\), the bands corresponding to symmetric modes at 872, 700 and 591 cm\(^{-1}\), and finally, the bending mode at 448 cm\(^{-1}\).

The TG-DTA curves from 25 to 1000 °C of the three samples are plotted in Fig. 9. The total mass loss was 13.9 wt.% for sample S3. This value fit well with the LOI (13.3 wt.%), and it would correspond to the release of 10 water molecules.
Although the theoretical mass loss for the stoichiometry \( \text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O} \) is higher (around 16.5%), even lower values of mass loss (12 wt.%) were reported by Kazemian et al. [18] for NaP1 obtained from fly ash. The maximum water losing rate took place at 115 ºC, according to the endothermic peak in DTA curve. Nevertheless, the water release occurred in several steps, as shown for both TG and DTA curves.

For sample S7, the total mass loss occurred in three steps and was of 10.9 wt.%, quite similar to the LOI value (10.2 wt.%). The obtained results are corroborated with the mass loss of 10 % for hydroxy-sodalite synthesized from pure reagents by Günther et al. [45]. DTA curve indicated that water is lost in the first two steps: a first endothermic peak at 113 ºC with a shoulder at 198 ºC. Thus, it results in a mass loss of 9.5 wt.%, that is, the corresponding water content (5 molecules) in the structure of SOD. The last step of mass loss (around 1.5 wt. %) was associated to an exothermic peak at 825 ºC. This effect could be attributable to the release of chloride and accordingly to the collapse of the SOD structure. Some authors associate this exothermic peak with the thermal transformation of sodalite in nepheline or carnegieite (\( \text{NaAlSiO}_4 \)) [45, 46].

The profiles of both TG and DTA curves for sample S11 indicate that the water molecules were released at a lower rate than those corresponding to samples S3 and S7. This profile is characteristic of ANA composed of smooth faceted high size crystals, which provokes a retarded dehydration [37]. Thus for ANA obtained from the aluminum waste the dehydration occurred from room temperature up to 400 ºC, with an associated endothermic effect centered at 292 ºC. The mass loss of 7.9 wt.% (quite similar to the LOI value of 8.2 wt.%) fit
well with the theoretical value for the stoichiometry of NaAlSi$_2$O$_6$·H$_2$O. The exothermic effect observed in DTA curve at 925 ºC, without associated mass loss could be attributable to the collapse of the ANA framework [9].

From the results of the elemental composition obtained by EDS analysis and the zeolitic water content determined by TG analysis, the approximate formulae were calculated for the zeolites as: Na$_{5.6}$Al$_6$Si$_{11.1}$O$_{34}$·10H$_2$O for NaP1 (S3), Na$_{2.2}$Al$_3$Si$_{3.1}$Cl$_{0.2}$O$_{11.9}$·5H$_2$O for SOD (S7), and Na$_{0.9}$AlSi$_{1.7}$O$_{5.4}$·H$_2$O for ANA (S11).

Table 3 collected the textural characteristics of the three samples along with other physical-chemical properties such as the particle size distribution, the polydispersity index (PI), the zeta potential (ZP) and the cation-exchange capacity (CEC).

The nitrogen adsorption/desorption isotherms for samples S3, S7 and S11 (Fig. 10), exhibited type IV behavior, which is typical of mesoporous materials, where the hysteresis loop is associated with the occurrence of pore condensation (according to the IUPAC). The hysteresis loop for all the samples was H3-type (observed at relative pressure range of 0.45-0.99), which is typical of systems with a distribution of “bottle shape” pores [47, 48]. The external area ($S_{\text{EXT}}$), i.e. the area not involved with the filling of the micropores, was almost the same as that calculated by the BET method ($S_{\text{BET}}$), both shown in Table 3, indicating that the obtained zeolites are practically no microporous materials. The low microporosity of the samples can be caused by the low outgassing temperature (<100 ºC) used prior to adsorption measurements, which was not high enough to remove the zeolitic water and/or other species generated during the
synthesis, leading to the blockage of the pores. The NaP1 and SOD zeolites, whose crystallite sizes were smaller than ANA, exhibited higher BET specific surface areas.

Concerning the pore size distribution (dV/dD curves) found by the BJH method (Fig. 10), all the samples exhibited a mainly mesoporous distribution. The highest porosity found was for S3 and S7, where the pore size was around 2.6 nm and 8 nm, respectively, while S11 showed a broad pore size distribution in the range of 1.7-48 nm due to its smallest pore size.

The particle size distribution of the synthesized zeolites from 0.1 to 100 μm (Fig. 11), revealed for the sample S11 (ANA), a bimodal distribution with two maxima centered at 0.3 and 12 μm. While a quasi-unimodal population was observed for the sample S3 (NaP1) centered at 17 μm, and also for the sample S7 (SOD) with a maximum at 40 μm. This latter sample presented the narrowest size particle profile. This was caused by the increase of the alkalinity in the reaction medium, resulting in an increase of the rate of nucleation and polymerization between silicate and aluminate anions, and thus, in the narrowest particle size distribution [49].

All the samples presented negative values of ZP according to the kind of materials, aluminosilicates, which are based on a three-dimensional framework of AlO4 and SiO4 tetrahedra with a negatively charged surface [50]. The results indicate that more negative charges were available in S3 and S7 than in S11, and hence, the highest electrostatic attraction between the positive charges and the active sites of S3 and S7 could be expected. Therefore, the three zeolites can be used for adsorption of cations. The lowest ZP value corresponded to S7.
(SOD). The excess of NaOH used in the synthesis tends to cause aggregation, as seen by the highest particle diameter values obtained for the sample S7, resulting from the interaction between the Na\(^+\) ions and the negative charges of SOD framework. Thus, SOD showed the highest polidispersity index due to its aggregative behavior [33].

With regard to the CEC results, NaP1 (S3) zeolite yielded the major result (2.73 meq NH\(_4^+\)/g), which is according to the values found in the literature (0.72-3.7 meq/g) [2, 29, 42]. The low temperature and alkali concentration used in the hydrothermal synthesis led to high-CEC NaP1. Contrary, low-CEC zeolites such as ANA and SOD (S11 and S7) were obtained when using higher temperature and/or higher alkali concentration in the synthesis [2]. The high-CEC of NaP1 obtained from aluminum waste makes it susceptible to be used in the wastewater treatment as potential adsorbent of heavy metals.

3.2. Effect of the recycling of alkaline effluent on zeolites

Fig. 12 shows the XRD patterns of the samples S12 and S13 obtained at 120 \(^\circ\)C for 6 h with a similar ML volume to the 1M NaOH solution employed for the synthesis of S3. The results reveal the presence of NaP1 (JCPDS 01-071-0962) as the only zeolite phase. For both samples well-defined XRD profiles were obtained, with the 301 reflection centered at 28.07\(^\circ\); no shifts of the 2\(\theta\) values were observed. A diffraction profile of narrower peaks and with higher intensity was observed for S12, probably, due to the beneficial effect of the small quantities of NaP1 seeds present in the first ML. These crystal seeds favor the nucleation and crystal growth of the zeolite as found in the literature [29]. Whereas for S13, it was observed a profile of slightly lower intensity where the
peak centered at 33.3° was broader. This could be ascribed to the presence of potassium cations in the reaction medium. The successive recycling of ML leads to the enrichment in salts (sodium and potassium chlorides, etc.) from the waste precursor. This would involve a competition between sodium and potassium cations, whose larger size originates a broadening of the XRD profile. As the amount of Na⁺ cations from the second ML could be deficient compared to the required amount for the synthesis of high-crystalline NaP1 (sample S3), probably, it would be necessary to accurately adjust the amount of Na⁺ adding a small volume of fresh 1M NaOH to obtain the theoretical Na/Al ratio of the NaP1 framework. The amount of zeolite NaP1 obtained in the first recycling (S12) per kg of waste was 2.5 kg (Table 2), while a somewhat lower yield was obtained during the second recycling of ML (S13).

The results obtained by SEM reveal the characteristic structure of NaP1 for S12 and S13, both samples exhibited a homogenous morphology similar to the sample prepared without ML recycling (S3). As an example, Fig. 13 collects the SEM image, the EDS spectra and the microchemical point analysis of the selected zones for S13 obtained from the second recycling of ML.

EDS analyses showed that sodium is the main exchange cation in the structure of the zeolite, along with minor quantities of potassium detected in the microchemical point analysis of several crystals with a K/Na ratio low (0.03) but slightly higher than S3. For S13, the average Si/Al ratio obtained was of 2.08, slightly higher than the corresponding value of S3 (Si/Al = 1.85), while a similar average Na/Al ratio (~0.90) was obtained.
Fig. 14 depicts the nitrogen adsorption/desorption isotherms and the pore size distribution in the mesopore and low macropore size range for samples S12 and S13, both compared with S3 synthesized without ML recycling.

The adsorption isotherms of the two samples exhibited type IV behavior characteristic of mesoporous materials, giving rise to zeolites practically no microporous. The values of $S_{\text{BET}}$ (12-13 m$^2$/g) and $S_{\text{EXT}}$ (12-13 m$^2$/g) were very similar, although slightly lower than sample S3. Both samples exhibited an average pore diameter, which was similar to S3, around 2.6 nm.

Table 4 shows the chemical composition (expressed as $\mu$g/mL) of the first and second recycled mother liquor (ML1 and ML2) used for the synthesis of samples S12 and S13, respectively, as well as, their pH and conductivity. According to the ICP-OES analysis of ML1 and ML2, the main elements detected were Na, Si, K and Al. As such elements form the framework of zeolitic materials, therefore, the mother liquor would be a favorable medium to take into account in the synthesis of zeolites. Moreover, both the pH and conductivity of the ML1 and ML2 were very similar to the 1M NaOH solution (pH = 13.26 and CE = 175 mS/cm), thus confirming that the mother liquors can be used in the zeolite synthesis instead of the alkali solution. On the other hand, a significant decrease of the Na$^+$ ion content was observed in ML2. It would mean that for the next recycling, in order to adjust the required amount to compensate the Na$^+$ amount provided by the 1M NaOH solution a certain amount of fresh alkaline solution should be added.

4. Conclusions
Three different types of zeolites, NaP1, SOD and ANA can be synthesized using a hazardous aluminum waste as main aluminosilicate source via a simple and one-step hydrothermal process. The complete transformation of the hazardous waste in a zeolitic material was attained, and other solid residues were not generated in the process. The amount of zeolite obtained per kg of waste (around 2.5 kg) was very much higher than that corresponding to zeolites obtained from fly ash. The formation of the different types of zeolite can be designed by selecting temperature and alkali concentration, principally. Thus, the best synthesis conditions to obtain NaP1 and ANA were 1 M NaOH solution for 6 h at 120 and 200 ºC, respectively, while SOD was prepared at 120 ºC for 6 h and using the highest alkali concentration (5 M). NaP1 showed a “cauliflower-like” morphology and the highest CEC. SOD was characterized by a morphology composed of “raspberry-like” balls and showed the highest zeta potential due to its aggregative behavior. ANA exhibited trapezohedral morphology with highly faceted crystals. The three zeolites had good thermal stability. The results reveals that the aluminum waste can be transformed into different types of zeolites, considered as value-added materials, with promising adsorption properties.

The mother liquor from the synthesis of NaP1, was successfully recycled twice, and NaP1 was obtained as the only crystalline phase with, morphological textural and crystalline characteristics very similar to those of NaP1 prepared with fresh solutions. This means that a very significant reduction in the water and alkalizing agent consumption could be attained, which is a very important achievement for a future up-scaled.
Acknowledgements

The authors thank Recuperaciones y Reciclajes Román S.L. and Metalquex S.L. (Madrid and Zaragoza, Spain) for supplying the wastes. The authors also thank MINECO for its financial support (Project CTM2012-34449). R. Sánchez-Hernández thanks MINECO for the grant BES-2013-066269.
References


Table 1

Chemical composition of the aluminum waste representative sample. (wt. %).

<table>
<thead>
<tr>
<th></th>
<th>XRF</th>
<th>KM</th>
<th>AAS</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Al₂O₃</strong></td>
<td>65.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>SiO₂</strong></td>
<td>5.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>MgO</strong></td>
<td>4.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>TiO₂</strong></td>
<td>3.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>CaO</strong></td>
<td>3.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Na₂O</strong></td>
<td>3.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Fe₂O₃</strong></td>
<td>1.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>SO₃</strong></td>
<td>1.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cl⁻</strong></td>
<td>8.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Others</strong></td>
<td>0.94</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>AlN&lt;sup&gt;a&lt;/sup&gt;</strong></td>
<td>13.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Al&lt;sup&gt;b&lt;/sup&gt;</strong></td>
<td>12.84</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Determined by the Kjeldhal method (KM).<sup>b</sup> Determined by atomic absorption spectroscopy (AAS).
Table 2

Experimental conditions of the synthesis of zeolites from aluminum waste, phase of zeolite obtained and reaction yield.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[NaOH] (mol/L)</th>
<th>t (h)</th>
<th>T (°C)</th>
<th>Phase</th>
<th>Yield (zeolite kg/waste kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1(^a)</td>
<td>1</td>
<td>3</td>
<td>120</td>
<td>NaP1+ amorphous phase</td>
<td>2.25</td>
</tr>
<tr>
<td>S2</td>
<td>1</td>
<td>3</td>
<td>120</td>
<td>NaP1</td>
<td>2.46</td>
</tr>
<tr>
<td>S3</td>
<td>1</td>
<td>6</td>
<td>120</td>
<td>NaP1</td>
<td>2.47</td>
</tr>
<tr>
<td>S4</td>
<td>1</td>
<td>24</td>
<td>120</td>
<td>NaP1</td>
<td>2.35</td>
</tr>
<tr>
<td>S5</td>
<td>3</td>
<td>6</td>
<td>120</td>
<td>NaP1, SOD</td>
<td>2.15</td>
</tr>
<tr>
<td>S6</td>
<td>4</td>
<td>6</td>
<td>120</td>
<td>NaP1, SOD</td>
<td>2.13</td>
</tr>
<tr>
<td>S7</td>
<td>5</td>
<td>6</td>
<td>120</td>
<td>SOD</td>
<td>2.17</td>
</tr>
<tr>
<td>S8</td>
<td>1</td>
<td>6</td>
<td>80</td>
<td>Amorphous phase</td>
<td>1.80</td>
</tr>
<tr>
<td>S9</td>
<td>1</td>
<td>6</td>
<td>90</td>
<td>NaP1</td>
<td>1.86</td>
</tr>
<tr>
<td>S10</td>
<td>1</td>
<td>6</td>
<td>100</td>
<td>NaP1</td>
<td>2.24</td>
</tr>
<tr>
<td>S11</td>
<td>1</td>
<td>6</td>
<td>200</td>
<td>ANA</td>
<td>2.39</td>
</tr>
<tr>
<td>S12(^b)</td>
<td>-</td>
<td>6</td>
<td>120</td>
<td>NaP1</td>
<td>2.45</td>
</tr>
<tr>
<td>S13(^c)</td>
<td>-</td>
<td>6</td>
<td>120</td>
<td>NaP1</td>
<td>2.19</td>
</tr>
</tbody>
</table>

\(^a\) Experiment performed without continuous stirring.

\(^b\) First recycling of ML.

\(^c\) Second recycling of ML.
Table 3

Specific surface area ($S_{\text{BET}}$), external area ($S_{\text{EXT}}$), particle size distribution, polydispersity index (PI), zeta-potential (ZP) and cation-exchange capacity (CEC) of the zeolites synthesized from the hazardous waste.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>$S_{\text{EXT}}$ (m$^2$/g)</th>
<th>Particle diameter (µm)</th>
<th>PI</th>
<th>ZP (mV)</th>
<th>CEC (meq NH$_4^+$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$d_{10}$</td>
<td>$d_{50}$</td>
<td>$d_{90}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>NaP1</td>
<td>14.2</td>
<td>14.5</td>
<td>1.5</td>
<td>1.99</td>
<td>-55.9</td>
<td>2.73</td>
</tr>
<tr>
<td>S7</td>
<td>SOD</td>
<td>15.5</td>
<td>14.6</td>
<td>2.0</td>
<td>2.29</td>
<td>-65.9</td>
<td>0.71</td>
</tr>
<tr>
<td>S11</td>
<td>ANA</td>
<td>4.6</td>
<td>4.5</td>
<td>0.4</td>
<td>1.97</td>
<td>-29.5</td>
<td>0.57</td>
</tr>
</tbody>
</table>
### Table 4

Chemical composition (µg/mL) determined by ICP-OES, pH and conductivity (CE) of the mother liquors.

<table>
<thead>
<tr>
<th>Mother liquor</th>
<th>Na</th>
<th>K</th>
<th>Si</th>
<th>Al</th>
<th>Si/Al Molar ratio</th>
<th>pH</th>
<th>CE (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML1</td>
<td>17000</td>
<td>224</td>
<td>1048</td>
<td>65</td>
<td>15.5</td>
<td>12.98</td>
<td>136.7</td>
</tr>
<tr>
<td>ML2</td>
<td>13700</td>
<td>170</td>
<td>326</td>
<td>145</td>
<td>2.2</td>
<td>13.56</td>
<td>106.3</td>
</tr>
</tbody>
</table>
Fig. 1. XRD pattern of the aluminum waste representative sample (A = Al; C = Al₂O₃; Q = SiO₂; N = AlN; H = NaCl; K = KCl; E = MgAl₂O₄).
Fig. 2. Hydrothermal synthesis and mother liquor recycling process used for the synthesis of zeolites from a hazardous aluminum waste.
Fig. 3. XRD patterns of zeolite NaP1 synthesized from aluminum waste at 120 °C and with 1M NaOH, for 3 h without stirring (S1), and for 3 h (S2), 6 h (S3) and 24 h (S4) with stirring. P1 = NaP1 (JCPDS 01-071-0962) and A= Analcime (JCPDS 00-041-1478).
Fig. 4. XRD patterns of the samples synthesized from the aluminum waste at 120 °C for 6 h with alkali concentration of 1 M (S3), 3 M (S5), 4 M (S6) and 5 M (S7). P1 = NaP1 (JCPDS 01-071-0962) and S = hydroxy-sodalite (JCPDS 01-076-1639) and/or chloride-sodalite (JCPDS 01-086-1844).
Fig. 5. XRD patterns of the samples synthesized with 1M NaOH for 6h at 80°C (S8), 90°C (S9), 100°C (S10), 120°C (S3) and 200°C (S11). P1 = NaP1 (JCPDS 01-071-0962), A = analcime (JCPDS 00-041-1478) and Q = quartz (JCPDS 00-046-1045).
Fig. 6. SEM images at different magnifications of zeolites obtained from the aluminum waste: (a-c) NaP1, (d-f) SOD, and (g-i) ANA.
Fig. 7. EDS spectra and microchemical point analyses of the zeolites obtained from the aluminum waste: NaP1 (S3), SOD (S7), and ANA (S11).
Fig. 8. FTIR spectra of NaP1 (S3), SOD (S7) and ANA (S11) obtained from the aluminum waste.
Fig. 9. TG (in Relative weight % - - - dash line) – DTA (in °C/mg — solid line) for obtained samples: NaP1 (S3), SOD (S7) and ANA (S11).
Fig. 10. Nitrogen adsorption/desorption isotherms and distribution of pore diameter of zeolite NaP1 (S3), SOD (S7) and ANA (S11).
Fig. 11. Particle size distribution of the zeolites synthesized: NaP1 (S3), SOD (S7) and ANA (S11) from the hazardous waste.
Fig. 12. XRD patterns of zeolite NaP1 synthesized from alkaline effluent recycling at 120 °C and for 6 h. Sample S12: obtained after first recycling and S13: after second recycling of ML. P1 = NaP1 (JCPDS 01-071-0962).
**Fig. 13.** SEM image and EDS spectra and microchemical point analyses of the zeolite obtained from the second ML recycling: NaP1 (S13).
Fig. 14. Nitrogen adsorption/desorption isotherms and distribution of pore diameter of zeolite NaP1 synthesized without ML recycling (S3) and with ML recycling (S12 and S13).
Graphical Abstract