

Industrial aluminum hazardous waste as a new raw material for zeolite synthesis

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Abstract

In Spain, the secondary aluminum industry is a mature activity which produces 35% of the total aluminum production. This industry generates slag (black dross) with a valuable content of aluminum which is recovered by dry milling processes in the aluminum tertiary industry. The powdered fine solid is trapped in the sleeve filter suction system of the aluminum slag milling process. This solid is considered as a hazardous waste within the 10 03 21 group in the European Waste Catalogue (EWC), because of the very fine grain size ($x_{50} < 50 \mu\text{m}$) and the presence of dangerous substances (metallic aluminum, AlN, heavy metals, etc.). The high aluminum nitride content, ranging between 2 and 24%, is remarkable and it releases ammonia gas in the presence of environmental humidity. The aim of this work was to evaluate the complete recovery of the fine powders coming from the sleeve filters in the aluminum tertiary industry, as a zeolite. Two types of zeolite, analcime and NaP were obtained by hydrothermal processes from the aluminum waste and silica as raw materials. Different compositions of wastes and parameters such as time and temperature were assayed to study their effects on the obtained zeolites. The materials were characterized by X-ray diffraction and scanning electron microscopy.

Keywords: aluminum hazardous waste, recycling, zeolite, analcime, NaP.

1 Introduction

Aluminum recycling is a large chain formed by several industries, which recovers this metal from wastes produced. Particularly, the secondary industry smelts waste such as scrap, slag, dross and skimming but generates the black



dross as an undesired by-product; a kind of aluminum slag with high content of molten salts. In Spain, this industry produces around 35% of the total aluminum production. According to basically economical aspects, the disposal into landfills is mostly the final destination of the black dross, as Tsakiridis *et al.* [1] described, but in many cases, dry milling processes are performed in order to recover the largest fraction of the remaining aluminum. These milling processes take place in other industries which are known as the aluminum tertiary industry.

Despite the benefits of milling, certain wastes are generated. Specifically, a fine powder is trapped into the sleeve filters of the suction systems. This solid is considered as a hazardous waste according to the European Waste Catalogue (EWC) within the 10 03 21 group and currently, is sent to landfill instead of recovered. The main features of this powder are the extremely fine grain size ($x_{50} < 50 \mu\text{m}$) and the presence of dangerous substances such as aluminum nitride (AlN), metallic aluminum, heavy metals, etc. In this sense, the high content of aluminum nitride is highly remarkable (ranging between 2 and 24% in weight) because this substance often interacts with the environmental humidity or water releasing ammonia gas in considerable quantities [2, 3]. The recent attempts performed to recover this waste are based on the production of viable added-value materials in order to overcome the economical barrier which prevents the implementation of conventional recovery processes [4].

Zeolites are an extensively studied group of aluminosilicates which are formed by three dimensional networks of AlO_4 and SiO_4 tetrahedra linked together by shared oxygen atoms [5]. The high microporosity present in these materials ("molecular sieve"), the number of documented methods to obtain them and the possibility to introduce variations on their compositions as well as morphologies [6] allow a huge number of applications in interesting fields such as catalysis, ion exchange, chemical separation, membranes, etc. Inside this group of porous materials, NaP and analcime are recognized by their excellent properties as ion exchangers. Both zeolites are formed in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. Thus, the gismondine-type structure is present for the NaP [7, 8] and analcime adopts different crystal symmetries as a function of the hydrothermal synthesis temperatures, being for instance orthorhombic at lowest temperatures and tetragonal or cubic depending on whether it rises [9].

Methods to obtain zeolites from unconventional sources and innovative techniques have been described in the literature. In particular, certain studies are based on the introduction of hazardous wastes as raw material in order to reduce their disposal into landfills. Examples such as the use of asbestos or fly ash from carbon combustion plants and municipal solid waste incinerators are remarkable [10, 11]. However, as far as we know, the use of aluminum hazardous waste from the tertiary industry has not been described.

Therefore, the aim of this work was to evaluate the complete recovery of the fine powders coming from the sleeve filters in the aluminum tertiary industry in order to obtain an added-value material as a zeolite. Thus, two types of zeolite, analcime and NaP were obtained by hydrothermal process from the aluminum waste and silica as raw materials. Different compositions and parameters such as

time and temperature were assayed to study their effect on the resulting zeolites. The materials were characterized by X-ray diffraction and scanning electron microscopy.

2 Experimental methods

Eleven different bulk samples (W1 to W11) of waste coming from the sleeve filter suction system of the aluminum slag milling process were provided by two tertiary industries in Madrid and Zaragoza (Spain). Wastes, which consisted of very fine and grey colored powders (with a characteristic odor due to the chemical composition), were divided into representative samples by a Laborette 27, a rotary cone sample divider (Fig. 1). Samples were characterized as follows: Particle size distribution was carried out using a Sympatec Helos 12LA and an ultrasonic dispersion of waste in isopropyl alcohol. The chemical composition was analyzed by X-ray fluorescence (XRF), employing a wavelength dispersive X-ray fluorescence spectrometer (Bruker, S8 Tiger). Measurements were acquired using fusion disks prepared with lithium tetraborate and lithium metaborate at 60k V and 170 mA. The main crystalline phases present in wastes were determined by X-ray diffraction (XRD) using a Bruker D8 Advance Diffractometer with $\text{CuK}\alpha$ radiation, from 5° to $85^\circ 2\theta$, at a scan rate of $0.02^\circ 2\theta$, 5s per step, 40 kV and 30 mA. The aluminum nitride content, one of the main components responsible for the waste hazardousness, along with metallic aluminum [2, 4], was analyzed by the Kjeldhal method using an automatic steam distilling unit UDK 130 A by Velp Scientifica, and subsequent titration with 1M HCl.

2.1 Zeolite synthesis

The synthesis of zeolite from the aluminum waste was carried out by a conventional hydrothermal method, employing a Teflon-lined autoclave (1 liter of capacity). Taking into account future large scale applications, a simple one-step zeolitification process without a previous alkalization/activation step was employed. In this sense, the raw materials selected for supplying the required amount of Al_2O_3 in the zeolite synthesis were waste. By this way, minor amounts of SiO_2 and Na^+ also were introduced. The SiO_2 and Na^+ balance was established by adding commercial silica and the activating aqueous solution, 0.5M NaOH (both reagents provided by Panreac, S.A) being the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ratio equal to 6/10 in all tests. The reactions took place in the autoclave for 3, 6 and 18 h. Temperature conditions ranged between 100 and 200°C and the autogeneous pressure was maintained at 10–12bar. When reaction time finished, products were filtered on a GTTP Millipore filter of $0.22\ \mu\text{m}$ and washed thrice with distilled water. Finally, they were dried in air at 80°C for 24 h. Solid products were characterized by XRD and scanning electron microscopy (SEM) using a Hitachi S4800 (15.0 kV, 14.8 mm).

3 Results and discussion

Table 1 presents the average chemical composition (main components) of the aluminum wastes with statistical values such as: mean value (\bar{x}) standard deviation (σ) minimum and maximum values (min, max) and mode obtained from the eleven samples analyzed. Minority components such as copper, lead, chromium, manganese, sulfide, etc., are included all together in the column denoted by “others”. As can be seen, a high deviation in the chemical composition appears, being product of the variable composition present in the raw slag. In other words, this fact is a direct consequence of the high heterogeneity present in all samples.

Table 1: Statistical values of waste chemical composition (main components) obtained by XRF (wt. %) and contents of aluminum nitride (AlN) calculated by Kjeldhal method (wt. %).

Compound	Al ₂ O ₃	MgO	Fe ₂ O ₃	TiO ₂	SiO ₂	CaO	K ₂ O	Na ₂ O	Cl	Others	AlN
\bar{x}	75	4.0	1.4	2.8	6.3	2.8	0.7	2.2	1.2	3.3	13.3
σ	8	1.2	1.0	2.3	4.7	1.1	0.7	2.7	1.2	1.3	5.4
min	53.38	1.32	0.35	0.40	2.56	1.64	0.23	0.00	0.01	0.97	1.40
max	80.96	6.76	3.44	8.30	17.79	5.97	2.98	10.46	3.49	5.69	23.60
mode	71	4.2	0.7	1.1	2.9	2.2	0.4	1.6	0.7	---	13.7

Concerning the granulometry, the wastes consisted of very fine size grain samples with x_{50} values smaller than 30 μm . The statistical values of particle size distribution determined for all samples are shown in Table 2. As a consequence of the intense process of milling performed to recovery these wastes, the high reduction in size generates powders with a high volatile component which is trapped in the sleeve filters and is also responsible for the waste hazardousness due to the high possibilities to cause severe health effects after prolonged exposure.

Table 2: Statistical values of particle size distribution of the aluminum solid wastes.

data	$x_{10} (\mu\text{m})$	$x_{50} (\mu\text{m})$	$x_{90} (\mu\text{m})$
\bar{x}	2.5	22.8	92.8
σ	1.7	11.8	39.9
min	0.9	5.1	40.4
max	7.1	47.4	164.0
mode	2.4	27.7	81.2

The particle size distribution, determined by laser diffraction, showed for the most of wastes a trimodal tendency. Several examples of the distribution density curves are collected in Figure 1 (samples W1, W2, W7, and W11). As it can be seen, the W11 sample showed a quite different curve with a multimodal profile. In this case was remarkable that peaks corresponding to small, medium and large sizes appeared within a small range of distribution density. Moreover, sample presented a maximum value of $164.0\ \mu\text{m}$ for x_{90} as can be appreciated in Table 2. This fact is related to the highest metallic aluminum content present in this sample as below mentioned, which forms spherical particles that are more hardly crushed in the milling process in comparison with the other oxidized phases and salts.

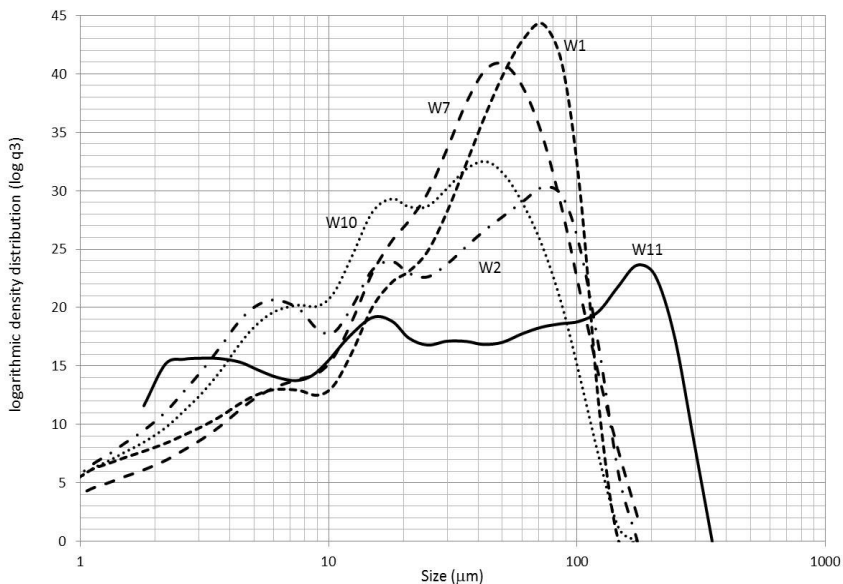


Figure 1: Particle size distribution curves of selected aluminum waste.

From a mineralogical point of view, wastes comprised a mixture of both amorphous and crystalline phases. The crystalline ones were mainly composed of not well defined peaks, with variable intensity, which were assigned to aluminum phases such as corundum, aluminum nitride, metallic aluminum and spinel, along with them, other phases as quartz, calcium carbonate and Na/K chloride were detected. As an example for the XRD patterns, two different wastes are shown in Figure 2. It is noticeable the high intensity of the peaks corresponding to the metallic aluminum for sample W11, which are located at 38.4 and 44.6° (2 θ) (see Figure 2b).

For the experiments of zeolite synthesis performed at 100°C , all formed products presented disordered amorphous phases which could not be identified by XRD. In the case of products obtained at 150°C , peaks appeared with very low

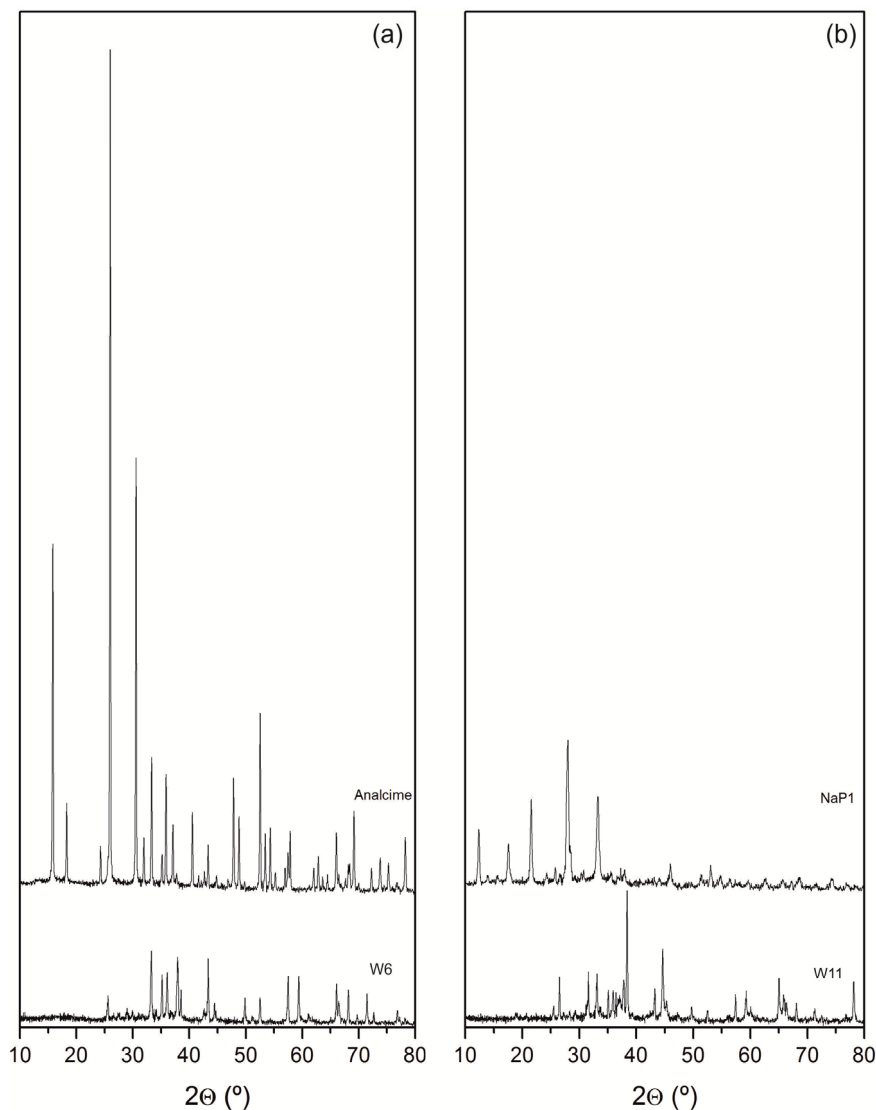


Figure 2: XRD patterns of waste samples (W6 and W11) and the zeolites: (a) analcime [JCPDS 00-041-1478]; (b) NaP1 [JCPDS 01-071-0962].

intensity, which were attributable to zeolitic materials. When essays were conducted at 200°C , all the products exhibited XRD patterns corresponding to defined crystalline phases of zeolite. These last findings were observed for essays conducted to a reaction time of 6 h. For the shortest time (3 h), XRD patterns consisted of amorphous phases, and for the longest time (18 h), differences were not found respect to the essays conducted to 6 h. Figure 2

shows the diffraction patterns of the zeolites corresponding to analcime and NaP which were prepared at same experimental conditions: 200°C, 6 h and 0.5 M NaOH solution, using two different wastes (W6 and W11). The XRD pattern of analcime, $\text{Na}(\text{Si}_2\text{AlO}_6) \cdot \text{H}_2\text{O}$, fitted well with the JCPDS reference (00-041-1478) and the NaP1 zeolite pattern, $3\text{Na}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2 \cdot 15\text{H}_2\text{O}$, with JCPDS 01-071-0962. In this figure, the axe for intensities was the same in all samples, in order to a better comparison of the different degree of crystallinity between wastes and zeolites.

As it can be seen, the pattern of analcime corresponds to a well crystallized sample with very high intensity and well defined peaks. On the contrary, the diffraction peaks corresponding to NaP1 present a lower intensity which indicates smaller crystallite size and lower crystallinity. All waste samples were tested in those experimental conditions. Analcime was obtained in all cases except when W11 was used. This finding can be associated with the above-mentioned characteristics present in this sample such as the more uniform distribution of grain size and also the highest content of metallic aluminum which favors the higher cumulative distribution at 90% (x_{90}). The hydrolysis rate for the different aluminum compounds (alumina, aluminum nitride, metallic aluminium, etc.) would be responsible on the different results. Thus, the kinetics of the hydrolysis suffers variations when higher amount of metallic aluminum is present, being much faster in comparison to the rest of aluminum compounds [12]. The faster kinetics favors the formation of NaP zeolite.

The macroscopic appearance of a waste sample used as synthesis precursor, the as-obtained wet zeolite after filtration and the dried zeolite are shown in Figure 3. The visual aspect for the wet product presented highly porous space between particles after filtering; this situation was coherent with the subsequent spongy and non-compacted texture in the case of the dry zeolite.

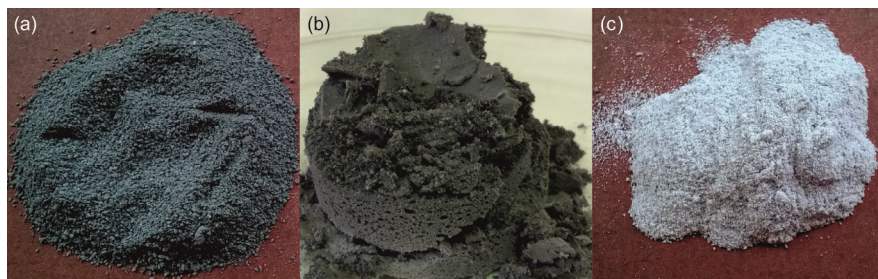


Figure 3: (a) Macroscopic appearance of an initial waste sample; (b) the as-obtained wet zeolite after filtering; (c) the corresponding dried zeolite.

The aluminum content in the remaining solution after filtration was analyzed by atomic absorption spectroscopy (AAS, (EspectrAA 220 FS, Varian Techtron, Australia Ply Ltd), being equal to 37 mg/l. This result indicated that 99.99% of the introduced aluminum from waste was transformed into zeolite.

The morphology of the analcime which exhibited trapezohedral crystals is shown in Figure 4. As can be seen at highest magnification, this zeolite-type presented well-formed pentagonal icositetrahedrons composed of 24 trapezohedral faces with clear crystal edges. Related to NaP1 zeolite (see Figure 5), SEM images showed agglomerates formed by tiny cubic crystallites. This fact was in agreement with the XRD results. In this sense, different morphologies for NaP1 have been obtained depending on the synthesis conditions which are documented in the literature [6, 8].

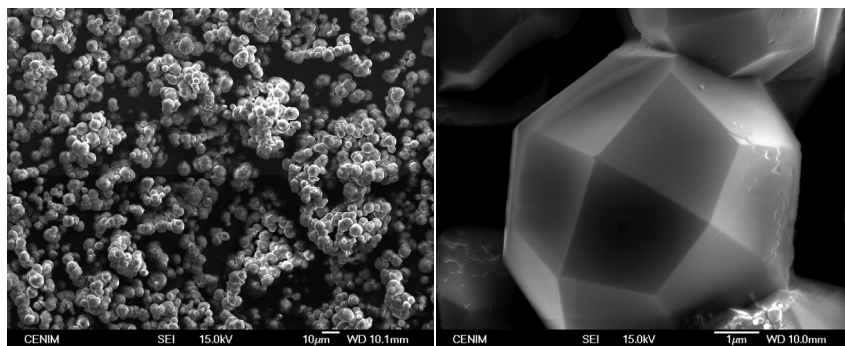


Figure 4: SEM images of analcime magnified at: (left) x500; (right) x13000.

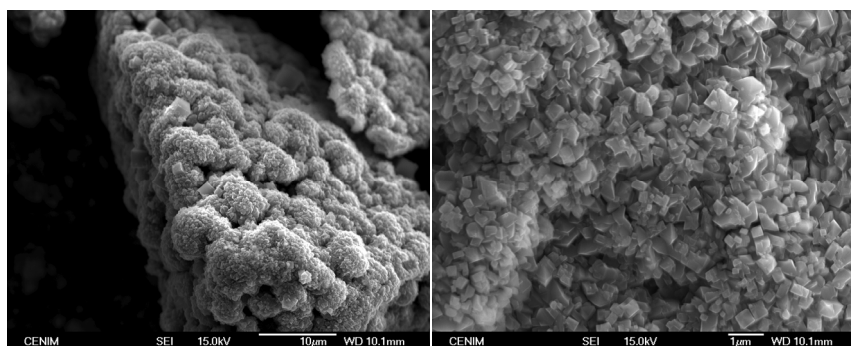


Figure 5: SEM images of NaP1 magnified at: (left) x2200; (right) x10000.

4 Conclusions

Samples of hazardous wastes from the aluminum tertiary industry were used as aluminum raw material for the preparation of zeolites. The synthesis method was based on a conventional alkaline hydrothermal process. A simple one-step zeolitification process was employed in order to decrease the process cost.

Two zeolite analcime and NaP were obtained depending on the temperature, time and waste composition. The higher granulometry and presence of highest metallic aluminum favored the NaP zeolite in comparison to analcime. This last exhibited a higher crystallinity than NaP.

The process allows the complete recovery of the industrial aluminium hazardous waste as a valuable material. Future research is going to be focused towards the application of the zeolites obtained.

Acknowledgements

Authors thank the MINECO (Spain) for financing the project CTM2012-34449 and the companies Recuperaciones y Reciclajes Roman S.L (Fuenlabrada, Madrid, Spain) and Metalquex, S.L. (Zaragoza, Spain) for supplying the wastes.

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