
Recycling of hazardous waste from tertiary aluminium industry in a value-added material

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Abstract

The recent European Directive on waste, 2008/98/EC seeks to reduce the exploitation of natural resources through the use of secondary resource management. Thus the main objective of this study was to explore how a waste could cease to be considered as waste and could be utilized for a specific purpose. In this way, a hazardous waste from the tertiary aluminium industry was studied for its use as a raw material in the synthesis of an added-value product, boehmite. This waste is classified as a hazardous residue, principally because in the presence of water or humidity, it releases toxic gases such as hydrogen, ammonia, methane and hydrogen sulfide. The low temperature hydrothermal method developed permits the recovery of 90% of the aluminium content in the residue in the form of a high purity (96%) AlOOH (boehmite). The method of synthesis consists of an initial HCl digestion followed by a gel precipitation. In the first stage a 10% HCl solution is used to yield a 12.63 g L⁻¹ Al³⁺ solution. In the second stage boehmite is precipitated in the form of a gel by increasing the pH of the acid Al³⁺ solution by adding 1 mol L⁻¹ NaOH solution. Several pH values were tested and boehmite was obtained as the only crystalline phase at pH 8. Boehmite was completely characterized by X-ray diffraction, Fourier transform infrared and scanning electron microscopy. A study of its thermal behaviour was also carried out by thermogravimetric/differential thermal analysis.

Keywords

Hazardous waste, tertiary aluminium industry, recycling, boehmite, hydrothermal process

Introduction

Aluminium is the most widely used non-ferrous metal. More than 60 million tons of this metal are consumed in packaging, cars, aircraft, buildings, machinery and thousands of other products. Primary aluminium is obtained from its main raw material, bauxite, by electrolytic reduction of alumina dissolved in a cryolite bath. Although few compounds of aluminium are classified as toxic according to Annex 1 of the European Economic Union Council (EEC) Directive 67/1548, the industry itself is considered to be one of the most polluting, and aluminium production has been classified as carcinogenic for humans by the International Agency for Research on Cancer (IARC 1987). When aluminium products reach their end of their useful life, they become scrap, and as a result, a new industry has grown up over the last few decades. This is the secondary industry, which

has developed the tools and technology to use this scrap as its raw material. Thus, secondary aluminium is obtained by processes involving the melting of aluminium scrap and other materials or by-products containing this metal, and the technologies used vary from one plant to another depending on the type of scrap, the oxide content, and the impurities, etc. According to the International Aluminium Institute (IAI 2010) in 2006, 16 million tonnes of total world production

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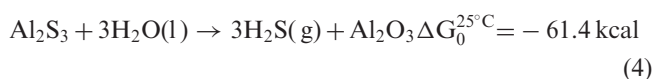
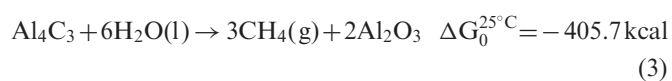
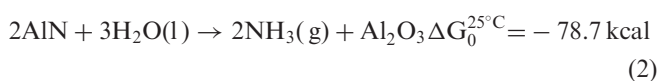
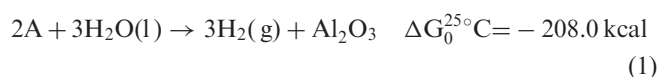
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of aluminium came from the secondary industry. In Europe, about 40% of aluminium demand is satisfied by recycled material. In Spain, secondary aluminium production (refiners) practically doubled in only 10 years, from 173 kt in 1997 to 345 kt in 2007 (OEА 2010).

As there is a market for the slag produced in the secondary industry, a tertiary industry has come into being, whose business is to obtain marketable products from slag milling. In this industry, slag is treated by milling, shredding and granulometric classification processes to yield different size fractions which are commercialized according to their aluminium content. The coarser the fraction, the higher is the aluminium content, and thus the more valuable the product. The finest fraction from the milling process constitutes the hazardous aluminium waste (HAW), which is kept in secure containers in special waste storage facilities. HAW is a very fine grey-coloured powdery solid with a characteristic odour (due to its aluminium nitride, carbide and sulfide contents). It also contains other aluminium compounds (metallic aluminium, corundum, spinel), quartz, calcite, iron oxide and other metal oxides, chlorides and salts. Its chemical composition varies depending on the process used to melt scrap (López et al., 2001, López-Delgado et al., 2007).

The United States Environmental Protection Agency (US EPA 1980) and the European Union (Council Directive 1994) classify this material as a hazardous residue, principally because of its poor chemical stability. European legislation defines the waste as H12 (Donatello et al., 2010), because in the presence of water or humidity, HAW releases toxic gases such as hydrogen, ammonia, methane and hydrogen sulfide, based on the following reactions (López-Delgado et al., 2007):



HAW has commonly been stockpiled in secure storage facilities in accordance with safety regulations 67/548/EC (79/831/EC) and Directive 99/31/EC (European Directive 1999). Processes developed for the treatment of HAW-related wastes have generally sought to render them inert, for example by very high temperature thermal treatment (Lindsay 1995) or by stabilization/solidification with cement or gypsum (López-Gómez & López-Delgado 2004, Shinzato & Hypolito 2005). Other procedures were

developed to obtain valuable products, using synthesis and crystallization methods (Lin & Lo 1998, López-Delgado et al., 2010). Vitriification has also been studied as a way of obtaining valuable glasses from waste similar to HAW, as an aluminium oxide source (López-Delgado et al., 2009). However, much more research needs to be done to find commercial uses for this waste, in accordance with the recent European Directive on waste, 2008/98/EC (European Directive 2008), which seeks to reduce the use of natural resources by means of secondary resource management. This Directive also includes a new status for waste, which is defined as ‘end-of-waste’. Several requirements have to be fulfilled by the waste in order for it to attain that status. These are: (1) the substance is commonly used for specific purposes, (2) markets exist for the substance, (3) the substance meets the technical requirements for the specific purposes and fulfils the existing legislation and standards applicable to products, and (4) the use of the substance will not lead to an overall adverse impact on the environment or human health. Recycling is therefore, acknowledged to be the best rational way of making use of resources that would otherwise end up being dumped and/or discarded.

Boehmite, an aluminium oxyhydroxyde described by the general formula $\text{AlOOH} \cdot n\text{H}_2\text{O}$, which crystallized within an orthorhombic system with a lamellar structure, is an important chemical used in many industries such as ceramics, composites, cement and derived-materials, paints and cosmetics. One of its most important applications is as a precursor of the major industrial catalysts supports: γ -alumina (Raybaud et al., 2001). Applications of boehmite depend mostly on its physic-structural properties, and these are very sensitive to the synthesis parameters (Okada et al., 2002). The hydrothermal process is a traditional method of boehmite synthesis in which inorganic aluminium salts of analytical grade (high purity) are commonly used as raw materials (Mishra et al., 2000, Li et al., 2006, Liu et al., 2008). This paper reports on the recycling of hazardous waste in an added value material. The purpose is then, to use hazardous waste as the raw material for the synthesis of boehmite. This means working towards the transformation of a waste into an “end-of-waste”, the new concept defined in the European Directive on waste, as mentioned above (European Directive 2008).

Experimental

Materials

A hazardous aluminium waste (HAW) sample was obtained from a slag milling installation of a tertiary aluminium company in Madrid (Spain). Slag is shredded in autogenous mills, and different size fractions were obtained. HAW is the powdery solid ($d_{90} < 100 \mu\text{m}$) which is captured by suction systems and treated in sieve filters.

From the point of view of the chemical and mineralogical composition, this waste is highly heterogeneous because it is

entirely dependent on the type of slag that is milled. So, a preliminary homogenization process was carried out. The as-received waste (25 kg) was homogenized in a mixer and then successively quartered to obtain a representative sample of 1 kg. This sample was then placed in an automatic sample divisor to obtain 100 g fractions. HCl 37% (Panreac) and NaOH pellets 98% (Panreac) were used as reactants.

Methods

A low temperature hydrothermal method was used to recycle HAW into an added-value material. The process consisted of two stages: the first one aimed at recovering the aluminium content of the HAW by dissolving it in an acid medium; and the second one, dealt with the value of the aluminium recovered in the first stage by means of its precipitation as boehmite. In the first stage (acid digestion) 50 g of HAW were digested in 500 mL of boiling HCl solution (120°C) in an open glass vessel to dissolve the acid-soluble aluminium compounds. Two HCl solutions of concentrations 4 and 10%, were used to study the effect on aluminium recovery. The reaction time varied from 15 up to 180 min and the Al^{3+} concentration in solution was determined by atomic absorption spectroscopy (AAS), at the different reaction times. The suspension obtained was centrifuged and the Al^{3+} solution was separated from the insoluble solid. This solid was characterized by chemical analysis and X-ray diffraction (XRD). The acidic Al^{3+} solution obtained at this stage was then subjected to the second stage (gel precipitation), in which a 1 mol L^{-1} NaOH solution was added dropwise to a magnetically stirred 100 mL of Al^{3+} solution until reaching pH values of 7, 8 and 9. This second stage was performed at room temperature and pressure. A gel started to precipitate from the first drop and was aged with continuous stirring for 24 h, after which it was separated by centrifugation and washed with deionized water until the total chloride was removed. The gel was dried at 60°C for 4 days and then crushed in a mortar to obtain a fine powder.

Analysis and characterization techniques

For the characterization of HAW, the next chemical analysis were performed: Al, Fe, Mg and Ca were determined in extracted acid solution, by AAS (Varian Spectra model AA-220FS). The AlN content was determined by analysing the nitrogen content, using the Kjendhal vapour distillation method (Velp Scientifica UDK 130). The SiO_2 was measured by a gravimetric method (ASTM E 34-88) and C and S were determined by oxygen combustion in an induction furnace (Leco model CS-244). Other elements such as Ti, Cu, Zn, Cr, etc., were determined by X-ray fluorescence (XRF; Philips, modelo PW-1480 dispersive energy spectrophotometer, anode Sc/Mo, in working conditions of 80 kV and 35 mA).

Table 1. Chemical composition of HAW

Element	Weight [%]
Al_{total}	47.45 ± 0.05
$\text{Al}_{\text{soluble}}$	36.87 ± 0.02
SiO_2	8.0 ± 0.5
C	1.06 ± 0.01
N	2.88 ± 0.02
S	0.14 ± 0.01
Cl	1.54 ± 0.06
F	0.59 ± 0.09
CaO	4.6 ± 0.2
MgO	4.2 ± 0.1
Fe_2O_3	1.8 ± 0.06
Na_2O	1.67 ± 0.06
TiO_2	1.53 ± 0.06
CuO	0.68 ± 0.03
K_2O	0.46 ± 0.03
ZnO	0.32 ± 0.02
PbO	0.12 ± 0.01
Cr_2O_3	0.11 ± 0.01

The crystalline phases of HAW, the insoluble solid obtained from the acid digestion and the boehmite samples were identified by XRD (Bruker D8 advance diffractometer, $\text{CuK}\alpha$ radiation). The morphological characterization of the samples was performed by scanning electron microscopy (SEM; Field emission Jeol JSM 6500 F). For observations, the powdered sample was embedded in a polymeric resin. A graphite coating was used to make the sample conductive.

The skeletal density of boehmite was measured in a He displacement pycnometer (Micromeritics Accupyc Mod 1330). The specific surface area (S_{BET}) was determined from the N_2 adsorption isotherms (Coulter Mod SA3100) at a relative pressure range of 0.04 to 0.2, after previously vacuum degassing the sample at 200°C. The characterization of boehmite was completed by Fourier transform infrared spectroscopy (FTIR, Nicolet Magna-IR 550). Spectra were recorded through a disc obtained by mixing the sample with CsI. Thermal analysis was performed by simultaneous thermogravimetry/differential thermal analysis (TG/DTA) (SETARAM DTA-TG Setsys Evolution 500) at a heating rate of $20^\circ\text{C min}^{-1}$, in a He atmosphere up to 1200°C. Alumina crucibles with 20 mg samples were used.

Results and discussion

Waste characterization

The chemical composition of the HAW is given in Table 1. The soluble aluminium content refers to all the aluminium compounds which dissolve in hydrochloric acid, for example, metallic aluminium, aluminium nitride, sulfide and different types of salts. The total aluminium content also refers to other compounds such as insoluble oxides. Figure 1 shows

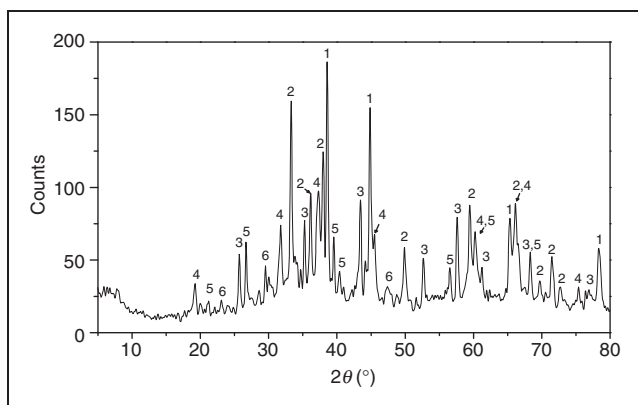


Fig. 1. XRD pattern of hazardous aluminium waste (HAW). 1: Al⁰, JCPDS 04-0787; 2: AlN, JCPDS 76-0565; 3: Al₂O₃, JCPDS 81-2266; 4: MgAl₂O₄, JCPDS 21-1152; 5: SiO₂, JCPDS 85-0865; 6: CaCO₃, JCPDS 85-1108.

Table 2. Mineralogical distribution and weight percentage of the major chemical elements present in HAW

Elements	Mineralogical phases	Weight (%)
Al	Al ⁰	31.2
	Corundum, Al ₂ O ₃	20.0
	Spinel, MgAl ₂ O ₄	15.0
	Aluminium Nitride, AlN	8.4
	Aluminium sulfide, Al ₂ S ₃	0.7
Si	Quartz, SiO ₂	8.0
Mg	Spinel, MgAl ₂ O ₄	15.0
Ca	Calcite, CaCO ₃	8.2
Fe	Hematite, Fe ₃ O ₄	1.8

the XRD pattern for HAW, identifying the principal crystal-line phases, such as metallic aluminium, spinel, corundum, aluminium nitride. From the chemical analysis and XRD study, the mineralogical distribution of the different major chemical elements constituting HAW is shown in Table 2, along with their composition expressed as wt.%. Figure 2 shows a SEM image of HAW in which the morphology of the different phases can be observed. Grains of metallic aluminium or alloyed aluminium of different size and shape can be observed along with grains of spinel; small particles of corundum are observed in disaggregation zones surrounding the metallic aluminium grains.

The hazardousness of HAW, as mentioned above, comes from the release of gases in the presence of water, according to Equations (1) to (4). From the contents of metallic aluminium, and aluminium nitride and sulfide (Table 2) the calculated emission of H₂, NH₃ and H₂S, per ton of HAW are 388.3, 45.9 and 3.1 Nm³, respectively.

Acid digestion stage

The total aluminium content of HAW is 47.5%, but only the part in the form of hydrochloric acid soluble compounds is

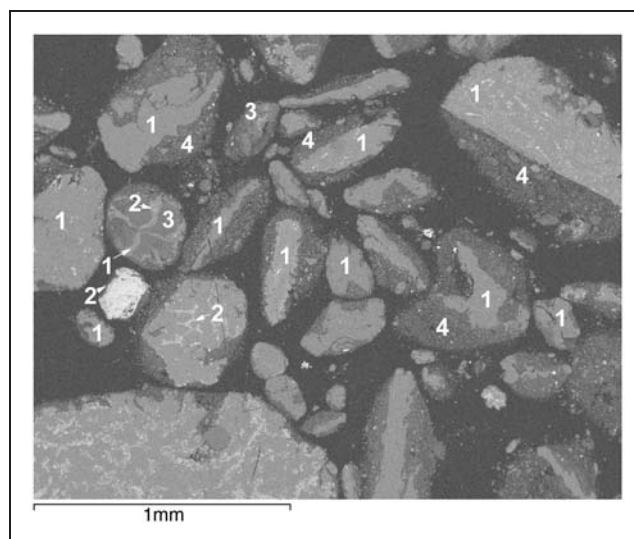


Fig. 2. SEM image of HAW. [1: Al⁰; 2: Al alloyed with Fe/Cu; 3: MgAl₂O₄; 4: Al₂O₃].

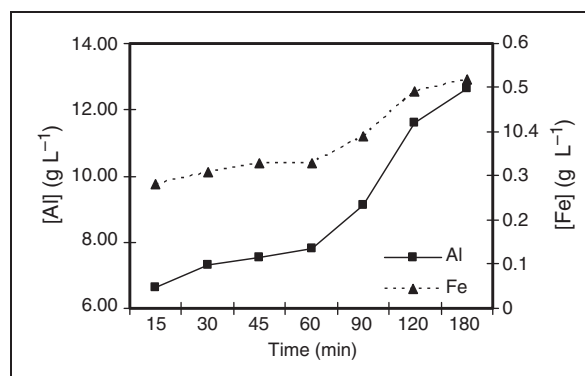


Fig. 3. Variation in [Al³⁺] and [Fe³⁺] in the acid solution obtained with 10% HCl.

recovered as an Al³⁺ solution in the HCl digestion stage. This value represents 78% of the total aluminium content and comes mainly from compounds such as Al⁰ and AlN and other soluble compounds. The recovery of aluminium increases with the reaction time. Thus when 10% HCl was used for a reaction time of 45 min, 73% of the aluminium was dissolved and for a time of 150 min, 90%. For the same time, an increase in the acid concentration yields a greater aluminium recovery. So, when digestion was carried out with 4% HCl the dissolved aluminium percentage was lower and for 45 min, only 54% of the aluminium was recovered. This indicates that the kinetics of aluminium dissolution from HAW with HCl is faster with an acid concentration of 10% than that of 4% acid. The variation in the Al³⁺ concentration in the acidic solution with time, using a 10% HCl, is shown in Figure 3. The [Al³⁺] concentration in the solution was 7.52 g L⁻¹ at a reaction time of 45 min, and the value increased up to 12.63 g L⁻¹, at 150 min.

The hydrochloric acid also partially dissolves iron oxide along with the aluminium compounds. The variation in the

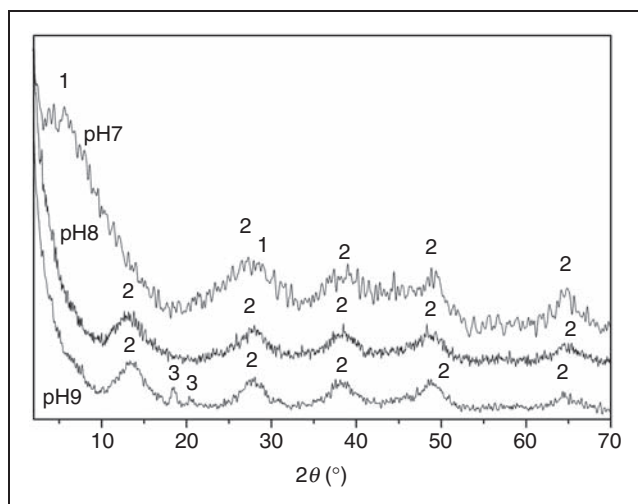


Fig. 4. XRD patterns of gel obtained at pH 7 (a), pH 8 (b) and pH 9 (c). (1: $\text{Al}(\text{OH})_{2.8}\text{Cl}_{0.2} \cdot 1.2\text{H}_2\text{O}$; 2: boehmite, AlOOH , JCPDS no. 03-0066; 3: Norstrandite, $\text{Al}(\text{OH})_3$, JCPDS n°18-0050).

Fe^{3+} concentration over time is also shown in Figure 3. The curves of both metals exhibit similar behaviour. Therefore it is very important to control the experimental conditions of acid digestion in order to achieve an aluminium solution with low iron content. Nevertheless, several procedures such as solvent extraction can be used to increase the purity of the Al^{3+} solution (Alguacil et al., 1987). In the present research, the Al^{3+} solution obtained directly from acid digestion was used for the next stage (gel precipitation), namely to obtain boehmite. On the other hand, the Al^{3+} solution obtained from the acid digestion of HAW may be used for many other purposes, in order to obtain added-value material, apart from boehmite.

The composition of the solution obtained in the acid digestion stage (HCl concentration: 10% and reaction time: 150 min) and subjected to gel precipitation was as follows: $[\text{Al}^{3+}]$ of 12.63 g L^{-1} and $[\text{Fe}^{3+}]$ of 0.49 g L^{-1} .

The solid residue generated in this stage is composed of the insoluble compounds of HAW. Its chemical analysis yielded: 69.50% Al_2O_3 , 20.19% SiO_2 , 4.00% MgO , 2.44% TiO_2 , 0.51% Fe_2O_3 , 0.64% CuO and 0.64% Cl^- . By XRD, only the crystalline phases such as corundum, spinel and quartz were identified. This solid may therefore be considered as an inert material which could be suitable for using, for example, in the cement industry.

Gel precipitation stage

Figure 4 shows the XRD patterns of the different gels obtained at pH 7, 8 and 9. The pattern of the pH 7 gel shows several poorly defined broad diffraction bands around 28, 39, 49 and 65° (2θ), but special attention must be paid to the band observed at a low angle, around 7–8° (2θ), which is common for lamellar structure compounds and seems to indicate the formation of a transitional phase prior

Table 3. XRD reflections of the pH 8 gel diffractogram

Reflections	2θ	d (Å)
020	12.934	6.839
120	28.097	3.173
031	38.674	2.326
051	49.505	1.839
002	64.121	1.451

to boehmite formation. Different authors (Okada et al., 2002, Ishikawa et al., 2006) have reported transitional phases in aluminium hydroxide formation with very similar diffraction patterns to the pH 7 gel, which are described as aluminium hydroxychloride. Chemical analysis of this gel suggests a stoichiometry of $\text{Al}(\text{OH})_{2.8}\text{Cl}_{0.2} \cdot 1.2\text{H}_2\text{O}$ for this phase.

The XRD pattern of pH 8 gel consists of five diffraction bands centred at 12.9, 28.1, 38.6, 49.5 and 64.1° (2θ) which fit well with the diffraction pattern corresponding to boehmite (AlOOH JCPDS no. 03-0066). The XRD pattern of pH 9 gel shows the same bands as the pH 8 gel and two others centred at 18.44 and 20.66 (2θ), indicating the presence of norstrandite ($\text{Al}(\text{OH})_3$ JCPDS n°18-0050) along with the boehmite. According to these results, the value of 8 seems to be the best pH to obtain boehmite from HAW, as the only crystalline phase. For their part, the products obtained at pH 7 and pH 9 may be suitable for obtaining alumina by thermal treatment, although this possibility is not studied in the present work. The percentage of aluminium recovered from the acidic solution, increased with the pH, from the value of 95% for pH 7 to 96.2% for pH 8. In the case of pH 9, this value (94.1%) is slightly lower than that of pH 8. Then, this last value of pH is the best for obtaining the highest recovery of aluminium.

Characterization of boehmite

The crystallographic parameters of boehmite were determined from the XRD pattern of gel pH 8. Table 3 shows the values of 2θ , d and hkl index. From reflection 020, which best characterizes boehmite, the following unit cell parameters were calculated: $a = 3.582 \text{ Å}$; $b = 13.678 \text{ Å}$; $c = 2.902 \text{ Å}$, in a face-centred rhombic symmetry and the space group Amam with Z (number of molecules per unit cell) of 4 (Tsukada et al., 1999, Okada et al., 2002, Liu et al., 2008). The crystallite size, calculated from Scherrer's equation (Music et al., 1999) is 4.7 nm and indicates that boehmite is a nanocrystalline sample. This low crystallinity is typical of products obtained by precipitation in aqueous media. The aluminium oxy-hydroxides have low solubility and this causes quick supersaturation and massive precipitation, which hinders the crystalline developed (Tsukada et al., 1999, Li et al., 2006).

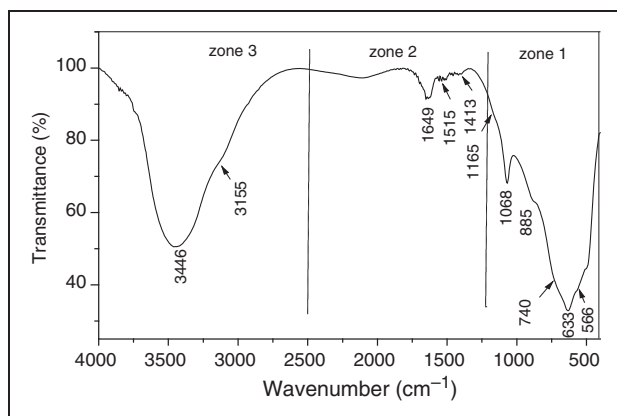


Fig. 5. FTIR spectrum of boehmite obtained from HAW.

From chemical analysis of gel pH 8, the stoichiometry of the boehmite can be formulated as $\text{AlOOH} \cdot 0.8\text{H}_2\text{O}$, with a purity grade of 96%. Iron oxide, probably in the form of FeOOH , and other minor compounds make up the rest of the composition.

The density of boehmite, determined in a helium pycnometer was 2.59 g cm^{-3} , which fits well with bibliographic values ranging between $2.3\text{--}3.03 \text{ g cm}^{-3}$ (Gevert & Ying 1999, Mishra et al., 2000). The S_{BET} of sample was $205.2 \text{ m}^2 \text{ g}^{-1}$, this value fits well with that reported by Okada et al., (2002) for the same crystallite size boehmite, obtained by a hydrothermal procedure using a pure aluminium nitrate solution as a starting material.

The FTIR spectrum of pH 8 gel is shown in Figure 5. Three different zones can be seen which correspond to the following wavenumber intervals: (1) $400\text{--}1200 \text{ cm}^{-1}$, (2) $1300\text{--}2500 \text{ cm}^{-1}$ and (3) $2800\text{--}4000 \text{ cm}^{-1}$. Zones 1 and 3 show the typical sample molecular vibrations and zone 2 provides information about the structural interconnection of the crystalline cell.

Zone 1: the band corresponding to bending of O–H (ν_3) appears at 1165 cm^{-1} as a shoulder of the very strong band at 1068 cm^{-1} , which corresponds to stretching vibration ν_2 $\text{Al}=\text{O}$. That weak vibration is characteristic of boehmite and its position is related to the crystallinity of the sample (Ram 2001). The vibration ν_4 $\text{Al}=\text{O}$ appears between 880 and 740 cm^{-1} and is also very sensitive to the crystallinity of the sample. At 630 cm^{-1} the band corresponding to bending in the plane of the angle $\text{HO}-\text{Al}=\text{O}$ (ν_5) is observed as a very broad, strong band.

Zone 2: In this area, three bands are observed at 1649 , 1515 and 1413 cm^{-1} . Their relative position and amplitude depend primarily on the degree of crystallinity of the sample and they are only observed in amorphous or nanocrystalline boehmite. Thus the first band is stronger than the others in nanocrystalline boehmite, and the second band is the strongest in amorphous samples (Ishikawa et al., 2006). The assignment of these bands is not clear because they cannot be assigned to overtones or combination bands. Ram (2002)

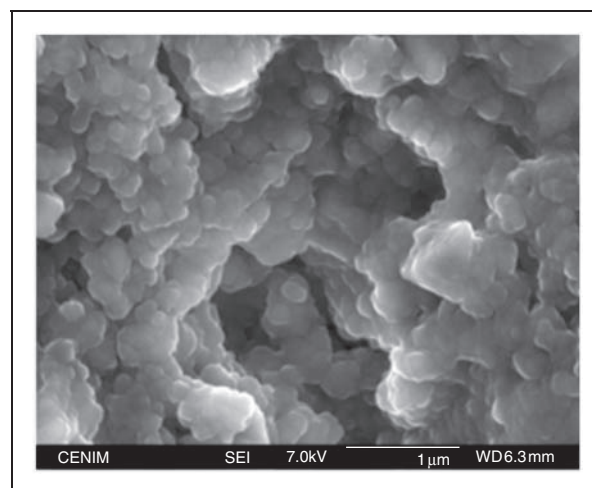


Fig. 6. SEM micrograph of boehmite obtained from HAW.

suggested that these bands are derived from the formation of amorphous superficial structures in nanocrystalline hydrated boehmite. This is the case of the boehmite obtained from HAW.

Zone 3: This area corresponds to stretching vibrations of O–H bonds. A very broad, strong band is observed at 3446 cm^{-1} with a shoulder at 3155 cm^{-1} . A difference of nearly 300 cm^{-1} between both bands is also found in the nanocrystalline structures.

Figure 6 shows the morphology of boehmite obtained at pH 8, revealing an agglomerate of very fine spherical particles of $7\text{--}15 \text{ nm}$ size. The grains are aggregates of amorphous particles which coalesce without any long distance order. Grains of crystalline appearance were not observed. This morphology agrees with the results of the physical and structural properties. Fine particle compounds are commonly used to obtain high densification ceramic products.

The TG and DTA curves of boehmite are shown in Figure 7. The DTA curve shows a first endothermic effect which appears as a very broad, strong band between 45 and 280°C with the maximum centered at 129°C . The mass loss associated with this effect is 15.3% and corresponds to a dehydration process of interlaminar water according to Equation (5):



The value of n calculated by mass loss is 0.60 , which is slightly lower than that obtained by chemical analysis and is consistent with the presence of a certain amount of absorbed water.

A second endothermic effect is observed between $281\text{--}548^\circ\text{C}$ with an associated mass loss of 14.0% . If all the water molecules had been lost at this stage in order to form aluminium oxide, a mass loss of 15% would have been attained. This means that the dehydration process is not

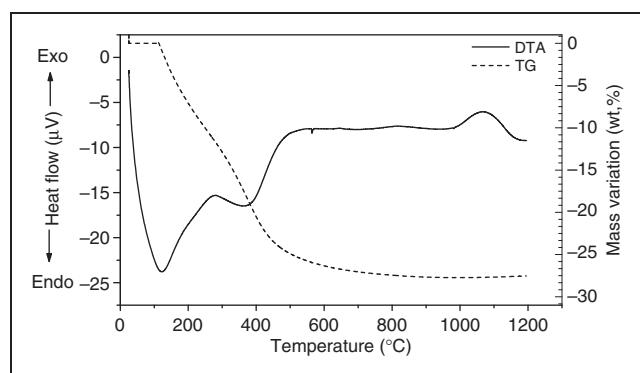
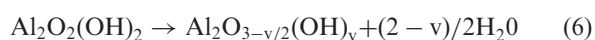


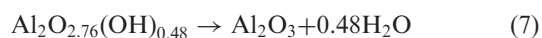
Fig. 7. DTA/TGA curves of boehmite obtained from HAW.

completed at this temperature and an intermediate phase can be formulated according to Equation (6).



This effect has been reported by Alphonse et al., (2005) as the conversion of boehmite into a transition alumina. The value of v was calculated from the mass loss as 0.48 and thus the intermediate phase can be formulated as $\text{Al}_2\text{O}_{2.76}(\text{OH})_{0.48}$.

A final exothermic peak is observed in the DTA curve at 1073°C, which is associated with a mass loss of 2.1%. This effect is attributable to the dehydration of the transition alumina to $\alpha\text{-Al}_2\text{O}_3$ according to Equation (7)



Then the boehmite obtained from the hazardous aluminium waste makes it possible to obtain $\alpha\text{-Al}_2\text{O}_3$ by thermal treatment at temperatures lower than 1100°C. Accordingly boehmite can be used as a precursor material for the synthesis of different aluminium oxides.

Conclusions

The results of this study show that a material such as hazardous aluminium waste, which has traditionally been considered as a residue, can effectively be recovered as a secondary source material for other industries. Thus, the method developed, a low temperature hydrothermal process, allows not only the recovery of 90% of the aluminium content in HAW, but also its recovery as an added value product, that is, a high purity boehmite (96%). The morphologic and crystallographic characteristics of the nanocrystalline boehmite (AlOOH) obtained make it a good candidate for use in the ceramics industry.

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References

- Alguacil FJ, Amer S and Luis A (1987) The application of Primene 81 R for the purification of concentrated aluminium sulphate solutions from leaching of clay minerals. *Hydrometallurgy* 18: 75–92.
- Alphonse P and Courty M (2005) Structure and thermal behaviour of nanocrystalline boehmite. *Thermochimica Acta* 425: 75–89.
- Council Directive of 12.12.1991 on Hazardous Waste 91/689/EEC, Council Directive 94/31/CE of 27.6.1994 amending Directive 91/689/EEC. 1994.
- Directive 2008/98/EC of the European Parliament and of the Council on Waste and Repealing Certain Directives, 2008.
- Donatello S, Tyrer M and Cheeseman CR (2010) EU landfill waste acceptance criteria and EU hazardous Waste Directive compliance testing of incinerated sewage sludge ash. *Waste Management* 30: 63–71.
- European Directive (1999) Council Storage Directive 99/31/CE on the landfill of waste.
- European Directive. Dangerous Substances Directive (67/548/EEC), later amending by Directive 79/831/EEC 'relating to the classification, packaging and labelling of dangerous substances'.
- Gevert BS and Ying Z (1999) Formation of fibrillar boehmite. *Journal of Porous Materials* 6: 63–67.
- IAI, (2010) International Aluminium Institute www.world-aluminium.org.
- IARC (1987) *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*. 89–91, Supplement 7.
- Ishikawa T, Matsumoto K, Kandori K and Nakayama T (2006) Synthesis of layered zinc hydroxide chlorides in the presence of Al (III). *Journal of Solid State Chemistry*. Vol 179: 1110–1118.
- Li Y, Liu J and Jia Z (2006) Fabrication of boehmite AlOOH nanofibers by a simple hydrothermal process. *Materials Letters*. Vol 60: 3586–3590.
- Lin SH and Lo MC (1998) Recovery of aluminum alum from waste anode-oxidizing solution. *Waste Management*. Vol 18: 281–286.
- Lindsay. R.D. (1995) Process for Treatment of Reactive Fines. US patent No. US5613996; 1995.
- Liu Y, Ma D, Han X, Bao X, Frandsen W, Wang D and Su D (2008) Hydrothermal synthesis of microscale boehmite and gamma nano-leaves alumina. *Materials Letters* 62: 1297–1301.
- López FA, Peña MC and López-Delgado A (2001) Hydrolysis and heat treatment of aluminium dust. *Journal of the Air & Waste Management Association* 51: 903–912.
- López-Delgado A, Tayibi H and López FA (2007) Treatments of aluminium dust: a hazardous residue from secondary aluminium industry. In: Mason LG (ed.) *Focus on Hazardous Materials Research*. Nova Publishers, 1–52.
- López-Delgado A, Tayibi H, Alguacil FJ and López FA (2009) A hazardous waste from secondary aluminium metallurgy as a new raw material for calcium aluminate glasses. *Journal of Hazardous Materials A65*: 180–186.
- López-Delgado A, López FA, Gonzalo-Delgado S, López-Andrés S and Alguacil FJ (2010) Study by DTA/TG of the formation of calcium aluminate obtained from an aluminium hazardous waste. *Journal of Thermal Analysis & Calorimetry* 99: 999–1004.
- López-Gómez, F.A. & López-Delgado, A. (2004) Procedimiento de estabilización/compactación de polvos de aluminio, Spanish patent No. ES2197797B1.
- Mishra D, Anand S, Panda RK and Das RP (2000) Hydrothermal preparation and characterization of boehmites. *Materials Letters* 42: 38–45.
- Music S, Dragcevic D and Popovic S (1999) Hydrothermal crystallization of boehmite from freshly precipitated aluminium hydroxide. *Materials Letters* 40: 269–274.
- OEA (2010) Organization of European Aluminium Refiners and Remelters www.oea-alurecycling.org. 2010.
- Okada K, Nagashima T, Kameshima Y, Yasumori A and Tsukada T (2002) Relationship between formation conditions, properties, and

- crystallite size of boehmite. *Journal of Colloid and Interface Science* 253: 308–314.
- Ram S (2001) Infrared spectral study of molecular vibrations in amorphous, nanocrystalline and $\text{AlO}(\text{OH}) \cdot \gamma\text{H}_2\text{O}$ bulk crystals. *Infrared Physics & Technology* 42: 547–560.
- Raybaud P, Digne M, Iftimie R, Wellens W, Euzen P and Toulhoat H (2001) Morphology and surface properties of boehmite: a density functional theory study. *Journal of Catalysis* 201: 236–246.
- Shinzato MC and Hypolito R (2005) Solid waste from aluminium recycling process: characterization and reuse of its economically valuable constituents. *Waste Management* 25: 37–46.
- Tsukada T, Seqawa H, Yasumori A and Okada K (1999) Crystallinity of boehmite and its effect on the phase transition temperature of alumina. *Journal of Materials Chemistry* 9: 549–553.
- US EPA (1980) Definition of hazardous waste, EPA/40 CFR/Part. 261.3, Federal Register.