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SYNTHESIS OF ALUMINA BASED ON INDUSTRIAL WASTE MATERIAL

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ABSTRACT
A hazardous waste generated in slag milling process by the aluminium industry was used as a raw material for the synthesis of alumina, α-Al_2O_3. This waste is considered as hazardous material in the European legislation due to the release of toxic gases (hydrogen, ammonia, methane and hydrogen sulphide) in the presence of water. The process developed in this work allows to obtaining 1 ton of alumina from 4 tons of hazardous waste and generates an inert solid residue consisting principally of spinel, corundum and quartz with possible uses in cements or glass industry. This process consisted of two steps: in the first one, nearly 90% of aluminium present in the waste is recovered as a nanocrystalline boehmite, γ-AlOOH by hydrothermal treatment of the waste. In the second step, the alumina is obtained by calcination of the boehmite at 1400ºC in air. The chemical composition of the alumina obtained consisted of 95% Al_2O_3, 3.3% Fe_2O_3, 0.8% SiO_2 and other minor oxides to balance.

Keywords: alumina; boehmite; hazardous waste; aluminium industry;

INTRODUCTION
Sustainable development strategies of industrialized countries include the adoption of environmentally-friendly measures that affect production processes and efficient uses of the resource, as well as the generation and management of waste. Whether in the last decades environmental policies were aimed fundamentally to eliminate or reduce waste generation, nowadays they seek to save natural resources through the secondary resources management. This last strategy is promoted by the recent Directive of the European Parliament and of the Council on Waste (European Directive 2008/98/EC) [1]. Thus a number of researches have been focused on the use of waste for different applications and uses [2, 3].
Polymorphic aluminium oxides with the chemical formula Al_2O_3, and commonly referred with the generic name of alumina, are extensively used in numerous industrial applications (ceramics, abrasive materials, absorbents, catalysts, biomaterials, composites, pigments, etc). Commercial alumina is obtained from bauxite ore in a process which generated one of the major residues produced from the aluminium industry, the red mud. Two tons of bauxite are necessary to produce 1 ton of alumina. Also for specific purposes, alumina is obtained by thermal treatment of precursors, which are generally produced by precipitation of aluminium oxy-hydroxides from solution of reagent grade aluminium salts [4-6].
In this work, a hazardous waste obtained by the tertiary aluminium industry in the milling slag process was used as aluminous raw material for the synthesis of alumina. From a mineralogical point of view, this waste consisted principally of corundum, spinel, metallic aluminium, quartz, aluminium nitride, calcite, iron oxide, aluminium sulphide and other minor oxides and salts; the total aluminium content ranges from 25 to 40%. The waste is a heterogeneous material from the physical-chemical point of view because it is strongly dependant on the type and quality of the processed scrap, the classification and trapping methods used, etc. It is defined as H12 and considered as hazardous in the European legislation due to the release of toxic gases (hydrogen, ammonia, hydrogen sulphide, etc) in the presence of water, according to the next reactions [7]:

$2Al + 3H_2O\ (l) \rightarrow 3H_2\ (g) + Al_2O_3$ $\Delta G_0^{25ºC} = -208.0kcal$ (1)

$2AlN + 3H_2O\ (l) \rightarrow 2NH_3\ (g) + Al_2O_3$ $\Delta G_0^{25ºC} = -78.7kcal$ (2)

$Al_4C_3 + 6H_2O\ (l) \rightarrow 3CH_4\ (g) + 2Al_2O_3$ $\Delta G_0^{25ºC} = -405.7kcal$ (3)

$Al_2S_3 + 3H_2O\ (l) \rightarrow 3H_2S\ (g) + Al_2O_3$ $\Delta G_0^{25ºC} = -61.4kcal$ (4)

The waste was subjected to a hydrothermal treatment to produce the alumina precursor, boehmite, (γ-AlOOH), as describe by Gonzalo-Delgado et al. [8]. Boehmite was calcined at different temperatures to produce α-Al_2O_3. The thermal transformation of boehmite into alumina was followed by simultaneous thermogravimetric/differential thermal analysis (TG/DTA). Both boehmite and corundum were characterized by XRD, XRF and SEM/TEM. The aim of this study is the transformation of a waste into an added-value material in an attempt to achieve the definition of "end-of-waste" for this waste as defined in the European Directive on Waste [1].

EXPERIMENTAL

Materials and Methods

The waste product used in this work is a very fine grey coloured powder, with a characteristic odour derived from its aluminium nitride, carbide and sulphide contents. It comes from the fine suction system used in the slag milling operation and was supplied by a tertiary aluminium industry (Recuperaciones y Reciclajes Roman S.L. Fuenlabrada, Madrid, Spain). The major mineralogical composition of the waste is as follows: 31.2% Alº, 20.0% Al_2O_3 (corundum), 15.0% $MgAl_2O_4$ (spinel), 8.4% AlN, 8.0% SiO_2 (quartz), 8.2% $CaCO_3$ (calcite), 1.8% Fe_2O_3 (hematite), 1.5% TiO_2, 1.5% chloride (Na/K), 0.7 % Al_2S_3 and other minor metal oxides. From the contents of metallic aluminium, and aluminium nitride and sulphide the calculated emission of H_2, NH_3 and H_2S, per ton of waste are 388.3, 45.9 and 3.1Nm^3, respectively [8].
The procedure employed to produce alumina from the waste is shown in the Fig. 1.

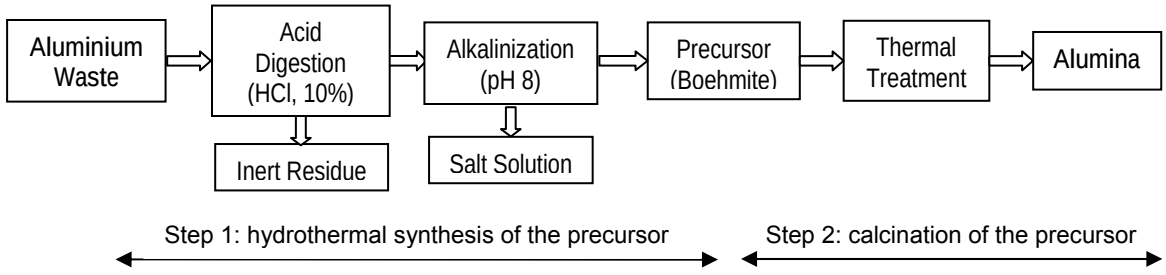

Fig.1. Scheme of the experimental procedure to obtain alumina from the aluminium waste.

The process to synthesis alumina from the aluminium waste consisted of two steps: in the first one, the precursor (nanocrystalline boehmite, γ-AlOOH) was obtained by hydrothermal treatment of the waste. In the second step, the alumina was obtained by calcination of that boehmite at 1400ºC in air for 7h.
In order to obtain the precursor boehmite, 50g of the waste were heat treated and vigorously stirred with 50mL of a solution of HCl (10% v/v) to dissolve the aluminium compounds during 150 min. The Al^{3+} solution obtained, with a pH lower than 2 was separated from the solid residue by filtration in a pressure system (Millipore YT30 142 HW with 0.2µm Isopore membrane filters). Then the acid solution was subjected to alkalinization up to pH 8 by dropwise adding a 1N NaOH solution. The precursor is obtained as a gel which was separated by centrifugation, washed with distilled water, dried at 150ºC and then it was crushed in a mortar to get a fine powder.

Characterization techniques

The chemical composition of the samples was determined by X-ray fluorescence (XRF, PANalytical AXIOS wavelength-dispersive X-ray spectrometer) on compacted specimen of 37mm diameter. X-ray diffraction (XRD) measurements for identification of crystalline phases were carried out in a Bruker D8 advance diffractometer equipped with $Cu_{K\alpha}$ tube. The morphological characterization of the samples was performed by Field Emission Gun Scanning Electron Microscopy (FEG-SEM, JEOL JSM-6500F). For those observations, the powdered sample was embedded in a polymeric resin and sputter coated with graphite to make the sample conductive. A Transmission electron microscopy (JEOL FEM-2100) was also used for the characterization of calcined samples.

The thermal transformation of boehmite into alumina was followed by simultaneous thermogravimetry/differential thermal analysis (TG/DTA) in a SETARAM DTA-TG Setsys Evolution 500 at a heating rate of 20 ºC min^{-1}, in air up to 1400 ºC. Alumina crucibles with 20 mg samples were used. The thermal treatment of the precursor was carried out in a high alumina refractory crucible using an electrical muffle furnace (Thermoconcept HT0417)

RESULTS AND DISCUSION

The XRD pattern of the aluminium waste is shown in Fig. 2a. The crystalline phases identified by comparison with the powder diffraction data (JCPDS files) are metallic aluminium (1), corundum (2), silica (3), aluminium nitride (4), calcium carbonate (5) and spinel (6). Besides, a certain amount of amorphous phases is inferred from the background. Compared with the XRD analysis report by Gonzalo-Delgado et al. [8], some minor differences were found, which can be attributed to the heterogeneity of the waste. As shown in Fig. 2b, the XRD pattern of the precursor obtained by the hydrothermal treatment of the waste consists of six broad boehmite diffraction peaks, indicating a very small grain and low crystallinity. In this figure, reflections were indexed according to JCPDS file 1-088-2112.

The chemical analysis of the precursor boehmite obtained by XRF and expressed as oxides wt%, is shown in Table 1. The balanced water was 31.8%. The amount of chloride in the sample comes from the first stage in the synthesis process. Taking into account the aluminium content in the waste, the 90% was recovered as boehmite of relatively high purity.

Table 1. XRF results of precursor boehmite and alumina (w/w, %).

Compound	Boehmite [%]	Alumina [%]
Al_2O_3	61.53	94.91
Fe_2O_3	2.05	3.31
SiO_2	0.64	0.94
ZnO	0.33	0.38
CuO	0.11	0.09
Cr_2O_3	0.09	0.07
PbO	0.03	0.07
Cl	3.20	----

Fig. 3a shows FEG-SEM micrographs of precursor boehmite which consists of small sized (below 100 nm) smooth round particles with certain level of agglomeration. The grain size and the low agglomeration level indicate a low degree of crystallinity, as observed in XRD pattern (Fig. 2b).

TG/DTA studies (figure no showed in this work) revealed that the dehydration of boehmite to transform into aluminium oxides takes place through a several overlapped endothermic reactions characterized by a continuous mass loss up to 1028ºC. The total mass loss of 30.30% obtained by TG fit well with the value obtained by XRF analysis and lets establish the stoichiometry $AlOOH{\cdot}nH_2O$, (n~0.8) [8]. The transformation of metastable alumina into corundum was observed by an exothermic peak in the temperature range between 1062-1204ºC.

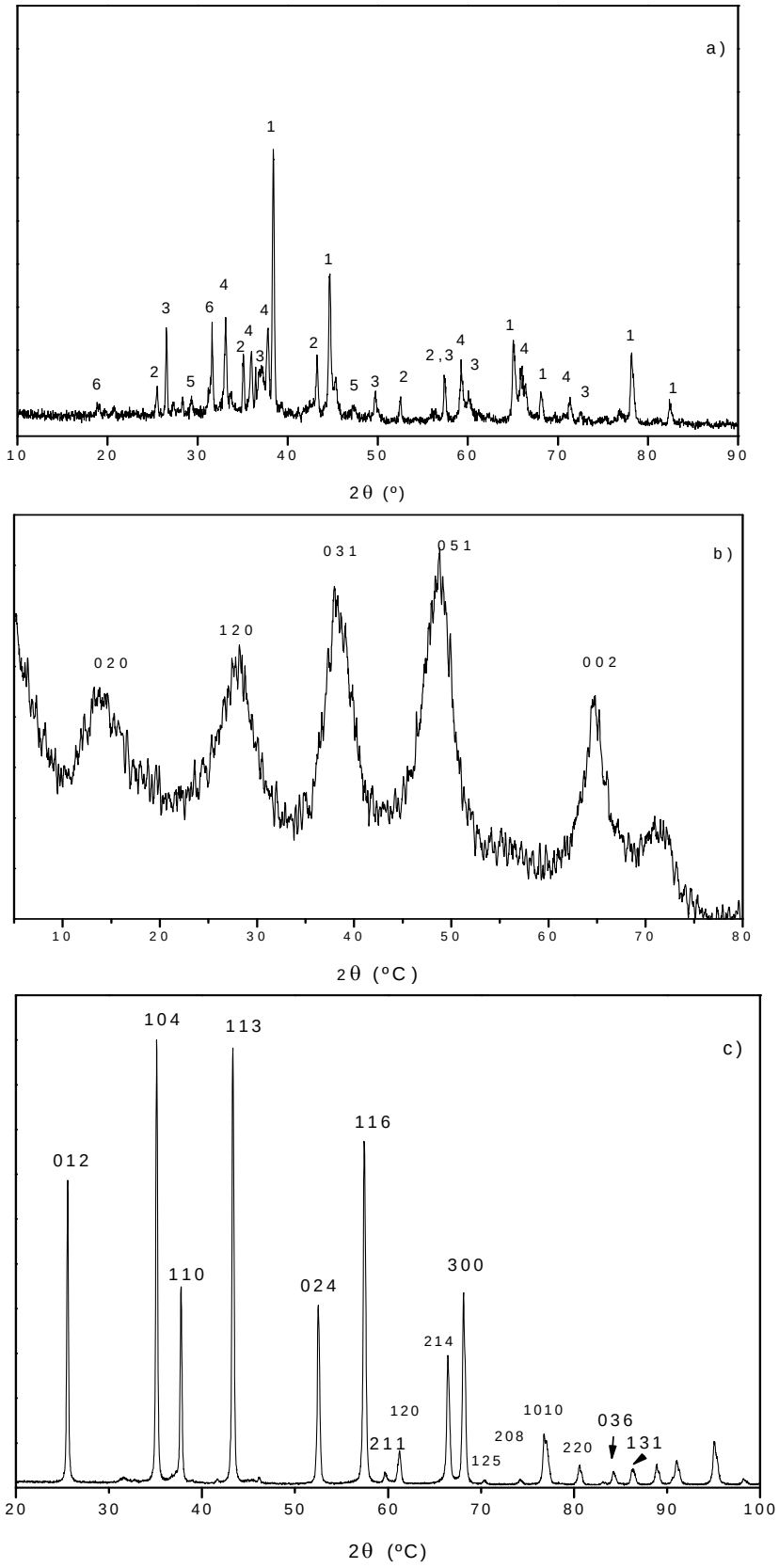

Fig. 2. XRD patterns of: a) aluminium waste (1: Al, 2: Al_2O_3, 3: SiO_2, 4: AlN, 5: $CaCO_3$, 6: $MgAl_2O_4$); b) boehmite obtained by hydrothermal treatment; c) α-Al_2O_3 (corundum) obtained by calcinations at 1400ºC, 7h.

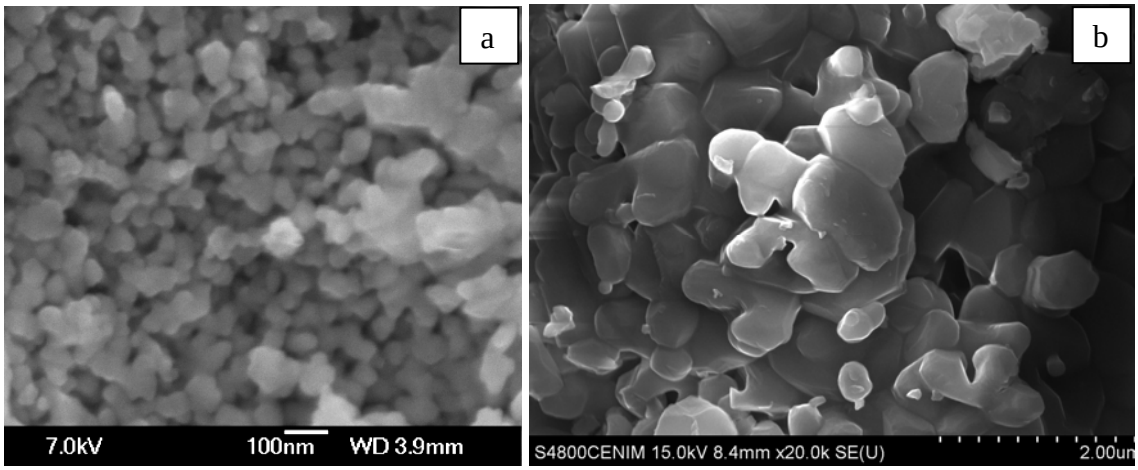

Fig. 3. Scanning electron micrograph of a) the precursor boehmite obtained by hydrothermal treatment of the waste and b) α-Al_2O_3 (corundum) obtained by calcinations of boehmite at 1400ºC, 7h.

Figure 2c shows the XRD pattern of sample obtained by heating the precursor boehmite at 1400ºC for 7h in air. This pattern corresponds to a highly crystalline material with narrow and well-defined diffraction peaks, which are assignable to the hkl reflections included in the JCPDS file 1-089-7717 of α-Al_2O_3 (corundum). The chemical composition of the alumina is collected in Table 1 and it corresponds to 95% purity alumina. Chloride was not detected. *α*-alumina exhibits the morphology of coalesced round plates, some of them with a certain tendency to present a hexagonal shape as shown in Fig. 3b. The crystals are pseudomorphs from the boehmite precursor, in agreement to Souza et al. [9] who indicated the particle shape of the α-Al_2O_3 varies with the nature of the precursor. Therefore, the formation of corundum takes place through a topotactic reaction of boehmite dehydration [10].
Fig. 4a shows a low magnification TEM image of an aggregate of small particles of corundum, and Fig. 4b shows a high magnification of a zone of the aggregate, in which the acquisition of the high resolution image let observe crystallographic planes. EDAX microanalysis of Fig. 4c confirmed the composition of the particle fit well to the chemical analysis of the sample by XRF.

CONCLUSION

This study shows the possibility to recover a hazardous waste as a secondary raw material for other industries, in an attempt to contribute to the reduction of natural resources. The process developed in this work allows to obtaining 1 ton of nanometric sized corundum particles with an aluminium oxide content of 95% from 4 tons of hazardous waste. The morphological and crystallographic characteristic of this alumina (α-Al_2O_3) would allow its use for the ceramic industry. In this process is also generated an inert solid residue consisting principally of spinel, corundum and quartz with possible uses in cements or glass industry.

Acknowledgments

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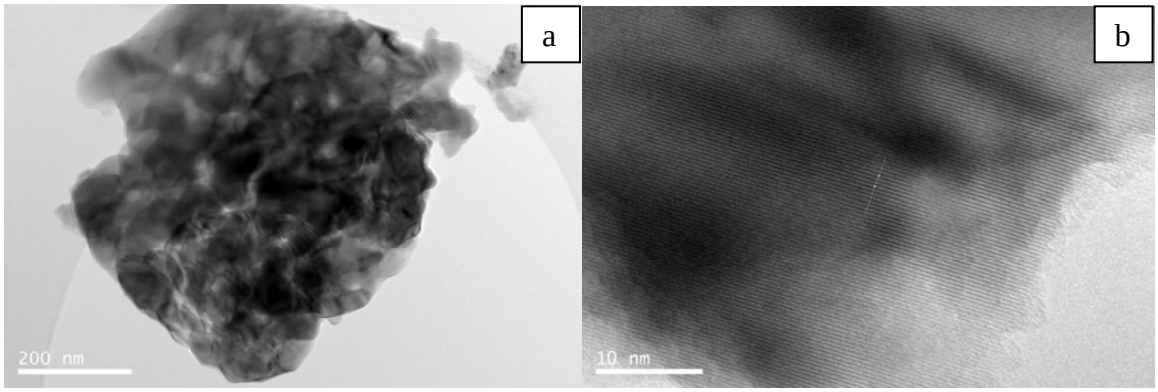

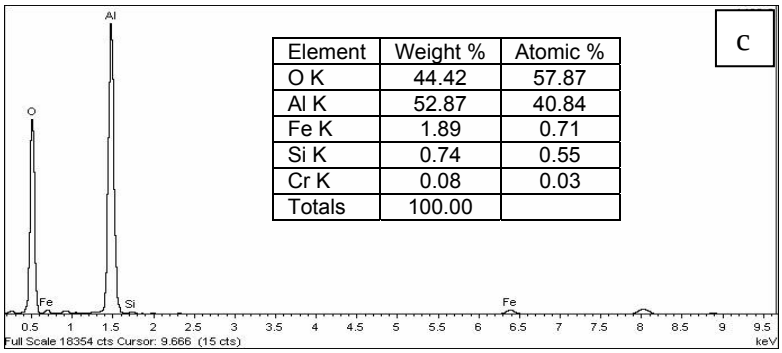

Element	Weight %	Atomic %
O K	44.42	57.87
Al K	52.87	40.84
Fe K	1.89	0.71
Si K	0.74	0.55
Cr K	0.08	0.03
Totals	100.00	

Fig. 4. Transmission electron microscopy of α-Al_2O_3 (corundum): a) low resolution image, b) high resolution of a selected area, and c) EDAX microanalysis.

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