RECOVERY OF ALUMINIUM FROM A HAZARDOUS WASTE BY PRECIPITATION AS BOEHMITE

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Abstract

Boehmite was synthesized by a low temperature hydrothermal procedure, via sol-gel, from an aluminium hazardous waste (AHW). The method consisted of a first stage of acid digestion to solubilize the metal content, and a second stage of gel precipitation in alkaline medium. Several experiments were performed to study the effect of concentration, time and pH not only on the recovery of aluminium but on the purity of boehmite. A nanocrystalline boehmite was obtained as unique phase at pH8. At pH9 boehmite is obtained along with norstrandite. The complete characterization of samples was carried out by XRD, MEB, and TG/DTA. The procedure allows the recovery of 90% of the soluble aluminium content in the waste.

Keywords: Aluminium hazardous waste, boehmite, low temperature hydrothermal synthesis

INTRODUCTION

The boehmite is an aluminium oxy-hydroxide ($AlOOH{\cdot}nH_2O$) that has many applications in ceramic, composite, cement, cosmetic and paint [1-7]. Natural boehmite appears in bauxite ore along with gibbsite $Al(OH)_3$ and diaspore (AlOOH) [8]. The traditional method of synthesis of boehmite is the hydrothermal process from high purity inorganic aluminium salts [9,10].

AHW is fine powdery solid that proceeds from the milling and granulometric classification processes of slag [11]. AHW consists of Al_{metal}, corundum, spinel aluminium nitride, carbide and sulphide, quartz, calcite, iron oxide and other metal oxides, chlorides and other salts. It is considered as a hazardous waste because of its high chemical reactivity in the presence of environmental moisture [12,13]. Thus AHW emits CH_4, NH_3, H_2 and H_2S according to the following reactions [14,15].

$$2Al + 3H_2O\ (l) \rightarrow 3H_2\ (g) + Al_2O_3 \quad (1)$$
$$2AlN + 3H_2O\ (l) \rightarrow 2NH_3\ (g) + Al_2O_3 \quad (2)$$
$$Al_4C_3 + 6H_2O\ (l) \rightarrow 3CH_4\ (g) + 2\ Al_2O_3 \quad (3)$$
$$Al_2S_3 + 3H_2O\ (l) \rightarrow 3H_2S\ (g) + Al_2O_3 \quad (4)$$

The recent European Directive on waste, 2008/98/EC [13], seeks to reduce the use of natural resources by means of secondary resource management. Thus research should be directed towards the use of wastes as raw materials [16,17].

The purpose of this work is recovery the content of metallic Al of a hazardous waste as a value added material, boehmite. This means the transformation of a hazardous waste in a raw material for the synthesis of boehmite.

EXPERIMENTAL

The materials used are AHW provided by a tertiary aluminium industry, HCl 37% (Panreac) and NaOH pellets 98% (Panreac).

The chemical and mineralogical composition of AHW is strongly heterogeneous. So, a preliminary homogenization process by means of mixing and successively quartering was performed in order to obtain a representative sample.

The synthesis of boehmite was carried out by a two-stage low temperature hydrothermal method, via sol-gel [2-7,9,10,17-20]. In the first stage, a HCl solution was used to dissolve the acid-soluble aluminium compounds. Acid concentration, temperature and time of reaction were varied in order to study their effect on the aluminium recovery. In the second stage, alkaline sol-gel precipitations, up to pH 8 and 9, were performed by adding 1M NaOH solution. The gel obtained was washed, dried at 60ºC for 4 days and crushed in a mortar to obtain a fine powder.

The chemical analysis of samples was performed by atomic absorption spectrometry (AAS, Varian Mod Spectra AA-220 FS) and X-ray fluorescence (XRF) (Philips PW 1404 sequential wavelength dispersion unit). The mineralogical composition was determined by X-ray diffraction (XRD, Bruker D8 advance diffractometer) with CuKα radiation (scanning rate: 0.03º 2θ/s). The morphological characterization of samples was performed by scanning electron microscopy (SEM, Field emission Jeol JSM 6500F). For observation, the powdered sample was embedded in a polymeric resin and graphite-coated. Thermal analysis was performed by simultaneous TG/DTA (SETARAM DTA-TG Setsys Evolution 500) at a heating rate of 20 ºC min-1 in a He atmosphere up to 600ºC. Alumina crucibles with 20 mg samples were used. The skeletal density of boehmite was measured in a He displacement pycnometer (Micromeritics Accupyc Mod 1330).

RESULTS AND DISCUSSION

Characterization of the waste

From the chemical and mineralogical analysis of the AHW, the following major composition was obtained: 31.2% Al_{metal}, 20.0% Al_2O_3 (corundum), 15.0% $MgAl_2O_4$ (spinel), 8.4% AlN, 8.0%SiO2 (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 compounds (metal oxides).

Synthesis method

Figure 1 shows the percentage of aluminium recovery according to the experimental conditions of the acid digestion stage. The recovery of aluminium increases with the reaction time. For the same time, an increasing of the acid concentration yields a major aluminiun recovery. Thus a 90% of aluminiun can be recovered using a 10% HCl solution, with continuous stirring and heating for 3 hours.

Figure 2 shows the XRD pattern of gel obtained in the alkaline sol-gel precipitation. Pattern of gel obtained at pH8 shows five bad-defined peaks, centered at 12.9, 28.1, 38.6, 49.5, and 61.4 2θ degrees, which are characteristic of boehmite (AlOOH, JCPDS no. 03-0066). For gel obtained at pH9, two peaks centered at 18.4 and 20.7 2θ degrees, are observed along with the peaks of boehmite. Those peaks were assigned to nordstrandite ($Al(OH)_3$ JCPDS no. 18-0050).

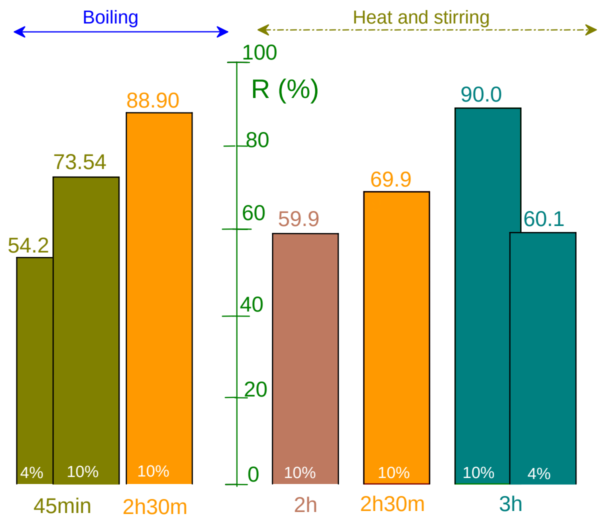

Figure 1. Percentage of aluminiun recovered at the different experimental conditions of the acid digestion

Gel characterization

The low crystallinity of samples is typical of products obtained by sol-gel method; the low solubility of the aluminium oxy-hydroxides causes a quick supersaturation in the medium and a massive precipitation (with low crystallinity rates) [21].

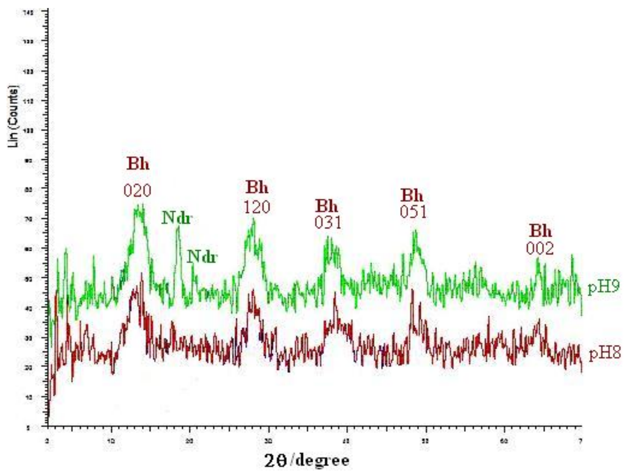

Figure 2. XRD pattern of gel obtained at pH8 (red) and pH9 (green)

Figure 3a shows a SEM micrograph, of sample obtained at pH8, in which boehmite appears as a homogeneous agglomerate of spherical particles of 10 nm average size with botroidal-laminar habit.

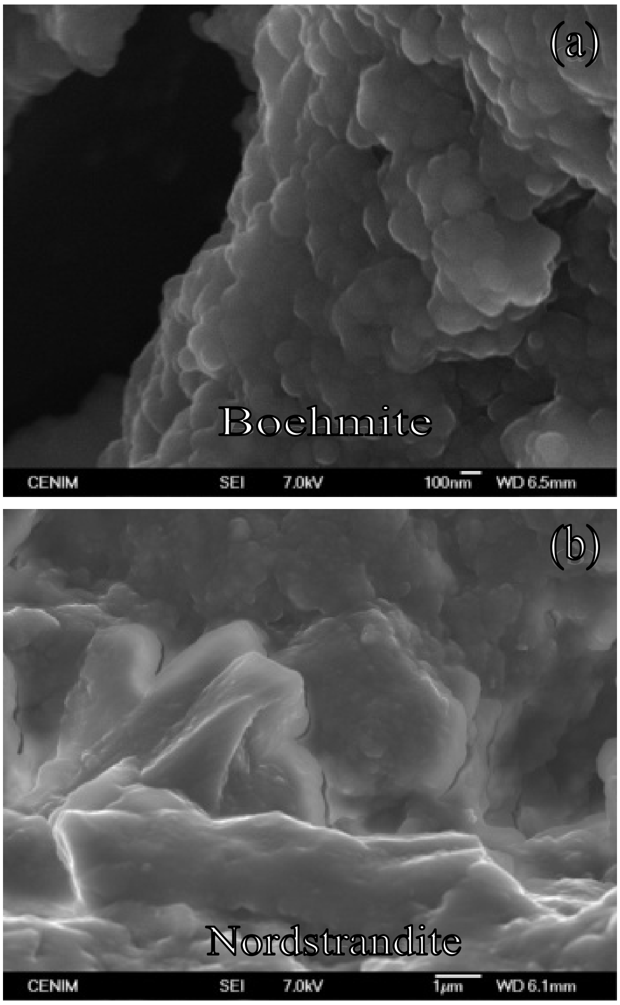

Figure 3. SEM micrograph of gel obtained at (a) pH8 and (b) pH9.

The pH9 gel exhibits the same botroidal-laminar habit (with the same homogeneous agglomerates) which corresponds to boehmite and several crystals with tabular habit (figure 3b). These last crystals would correspond to Nordstrandite, as identified by XRD.

The DTA and TG curves of pH8 and pH9 gel are shown in figure 4a and 4b respectively.

Three zones are distinguished in DTA curves. The first one, from room temperature up to 190ºC, is similar for both samples. A very broad endothermic peak is observed which corresponds to the dehydration process of gel. From 190 up to 340ºC a second endothermic effect is observed, but only in the curve corresponding to pH9 gel. The third effect, also endothermic, is observed in the temperature range between 340 and 450ºC. These two last effects correspond to the dehydroxilation processes of aluminium oxy-hydroxide [22-24].The different habits of the DTA curves is related to the different composition of samples (pH8, boehmite, and pH9, boehmite and nordstrandite). The TG curves show a continuous mass loss from room temperature to 600ºC, which is quite similar for both samples (25.8 and 26.3% w/w for pH9 and pH8, respectively). At that temperature, the mass loss observed is smaller than that corresponding to the complete dehydroxilation of boehmite to form alumina. This effect is reported by Alphonse et al. [24] as the conversion of boehmite into a transition alumina, which can be formulated as $Al_2O_{3-x/2}(OH)_x$.

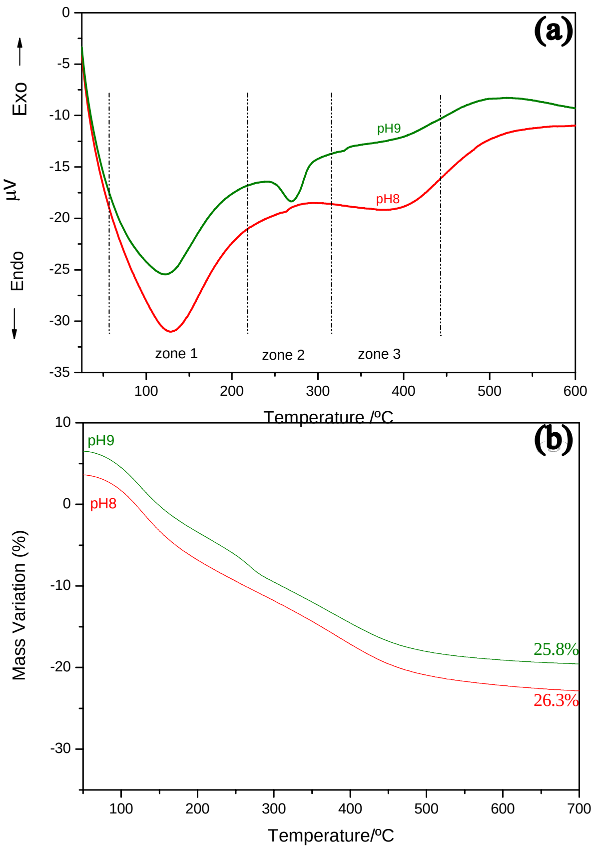

Figure 4. (a) DTA and (b) TG curves of gel obtained at pH 8 and 9.

The determination of density yielded values of 2.59 and 2.49 g/cm^3 for sample obtained at pH8 and pH9 respectively, which is closed to the theoretical values (2.3 g/cm^3) reported for synthetic boehmite [18].The content of Al_2O_3, determined by chemical analysis of pH8 gel is 72.02% w/w. This means that at this value of pH, the boehmite obtained has a 96% of purity. The balance corresponds to Fe_2O_3 and minor MgO. In the case of pH9 the purity value is lower because the Al_2O_3 content is 70.05% w/w.

CONCLUSIONS

Boehmite can be obtained from a aluminium hazardous waste by means of a hydrothermal process at low temperature, in two stages: an acid digestion and an alkaline sol-gel precipitation. The method developed in this work allows the recovery of the 90% of soluble aluminium content as an added value product, boehmite, with high grade of purity (96%).

REFERENCES

[1] Kim HJ, Lee HC, Rhee CH, Chung SH, Lee HC, Lee KH, Lee JS (2003) Alumina Nanotubes Containing Lithium of High Ion Mobility. *Journal of the American Chemical Society* 125, 13354-13355

[2] Okada K, Nagashima T, Kameshima Y, Yasumori A, Tsukada T (2002) Relationship between Formation Conditions, Properties, and Crystallite Size of Boehmite. *Journal of Colloid and Interface Science 253*, 308-314

[3] Liu Y, Ma D, Han X, Bao X, Frandsen W, Wang D, Su D (2008) Hydrothermal synthesis of microscale boehmite and gamma nanoleaves alumina. *Materials Letters* 62, 1297-1301

[4] Music S, Dragcevic D, Popovic S (1995) Formation of boehmite via precipitation from aqueous solutions. *Materials Letters* 24, 59-64

[5] Music S, Dragcevic D, Popovic S (1999) Hydrothermal crystallization of boehmite from freshly precipitated aluminium hydroxide. *Materials Letters* 40, 269-274

[6] Music S, Dragcevic D, Popovic S, Vdovic N (1998) Microstructural properties of boehmite formed under hydrothermal conditions. *Materials Science and Engineering B* 52, 145-153

[7] Raybaud P, Digne M, Iftimie R, Wellens W, Euzen P, Toulhoat H (2001) Morphology and Surface Properties of Boehmite (γ-AlOOH): A Density Functional Theory Study. *Journal of Catalysis* 201, 236-246

[8] Chang LLY (2002) Industrial Mineralogy: materials, processes and uses. Prentice Hall, New Jersey, USA, pp 472

[9] Mishra D, Anand S, Panda RK, Das RP (2000) Hydrothermal preparation and characterization of boehmites. *Mat. Letters* 42, 38-45

[10] Li Y, Liu J, Jia Z (2006) Fabrication of boehmite AlOOH nanofibers by a simple hydrothermal process. *Mat. Letters* 60, 3586-3590

[11] López-Delgado A, Tayibi H, López FA (2007) Treatments of aluminium dust: a hazardous residue from secondary aluminium industry. In: Mason LG (ed), Hazardous Materials Research. Nova Science Publishers, New York, USA, pp. 1-52

[12] US EPA, Definition of hazardous waste, Federal Register, 40 CFR, Part. 261.3 (1980)

[13] Directive 2008/98/EC of the European parliament and of the council on waste and repealing certain Directives; 2008

[14] López FA, Peña MC, López-Delgado A (2001) Hydrolysis and Heat Treatment of Aluminium Dust. *J. Air & Waste Manage. Assoc*. 51, 903-912

[15] López FA, Medina J, Gutiérrez A, Tayibi H, Peña C, López-Delgado A (2004) Treatment of aluminium dust by aqueous dissolution. *Revista De Metalurgia* 40, 389-394

[16] López-Delgado A, Tayibi H, Alguacil FJ, López FA (2008). A hazardous waste from secondary aluminium metallurgy as a new raw material for calcium aluminate glasses. *J. Hazardous Mat.* A65, 180-186

[17] Gonzalo-Delgado, L. 2008. Master Project. Universidad Complutense de Madrid, Spain. (http://hdl.handle.net/10261/6195)

[18] Bye GC, Robinson JG (1964) Crystallization processes in aluminium hydroxide gels. *Colloid & Polymer Science (Springer Berlin / Heidelberg)* 198, 53-60

[19]. Cesteros Y, Salagre P, Medina F, Sueiras JE (1999) Several Factors Affecting Faster Rates of Gibbsite Formation. *Chemistry of Materials* 11, 123-129

[20] Gevert BS, Ying Z (1999) Formation of Fibrillar Boehmite. *Journal of Porous Materials* 6, 63-67

[21] Tettenhorst R, Hofmann DA (1980) Crystal chemistry of boehmite. *Clays and Clay Minerals* 28, 373-380

[22] Tsukada T, Seqawa H, Yasumori A, Okada K (1999) Crystallinity of boehmite and its effect on the phase transition temperature of alumina. *Journal of Materials Chemistry* 9, 549-553

[23] Ram S, Singh TB, Srikant S (1998) Thermal desorption process of water in amorphous AlO(OH).αH2O fibres prepared by an electrochemical method. *Materials Transactions, JIM*, 39, 485-491

[24]Alphonse P, Courty M (2005) Structure and thermal behaviour of nanocrystalline boehmite. *Thermochimica Acta* 425, 75-89

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