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Production of added-value materials from a hazardous waste in the aluminium tertiary industry: Synergistic effect between hydrotalcites and glasses

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The powdered solids trapped in filter sleeves in the aluminium tertiary industry are currently disposed of in secure landfills as a result of environmental considerations. Their classification as a hazardous waste is due to their high aluminium content as metallic aluminium or in compounds such as aluminium nitride. These compounds can react with a very low moisture content to release toxic or hazardous gases such as hydrogen and ammonia. This paper presents a low-cost process for the full recovery of this hazardous waste in three steps leading to the production of two different added-value materials. In the first step, mild acid hydrolysis of the waste is carried out to obtain a concentrated aluminium solution and an inert cake. The following steps consist of hydrotalcite synthesis with the resulting solution, and the production of transparent glasses in the $CaO–Al_2O_3–SiO_2$ system with the cake. Characterisation of the products obtained indicates that the hydrotalcites can adsorb anionic pollutants (molybdates) in a simple way, while the glasses afford improved optical properties in comparison with those prepared by direct vitrification of the waste.

1. Introduction

Directive 2008/98/EC encourages hazardous waste recovery in a responsible and innovative manner instead of the traditional dilution to levels below legal thresholds. In this context, the slag milling process performed in the aluminium tertiary industry generates fine powders that are trapped in filter sleeves by air extraction systems. The European Waste Catalogue classifies these powders as a hazardous waste (code number 100321) and their treatment is currently based on disposal in secure landfills. Characterisation of the powders reveals a fine particle size and a complex, heterogeneous mixture of components such as corundum, spinel, aluminium nitride (10–25 wt%), metallic aluminium (7–30 wt%), quartz, calcite, iron oxide, other salts and minor metallic oxides [1]. The amount of residual aluminium in these phases is therefore still significant and potentially valuable.

The high metallic aluminium and aluminium nitride content in this waste promotes the release of toxic and hazardous by-products (hydrogen and ammonia) by simple reaction with a small amount of water (including air moisture) in inappropriate storage conditions [2]. The literature reports the use of aluminium waste for the synthesis of added-value materials, especially in the case of white and black dross, producing materials such as alumina and hydrotalcite [3,4]. However, very few papers reporting recovery processes evaluate the transformation of powdered hazardous waste from the aluminium tertiary industry into added-value materials. Examples include the preparation of concrete blocks by adding this waste to cement and sand after the hydrolysis reaction [5] and the synthesis of boehmite and corundum [6,7].

With regard to high added-value materials, hydrotalcite (a layered double hydroxide – LDH) is an anionic clay with intercalation properties that is well-known and valued for several applications such as catalysts, adsorbents, flame retardants, ion exchangers, drug releasers, anticorrosives, etc. [8–11]. This clay consists of positively charged brucite-type octahedral sheets alternating with interlayers containing anions [12]. Co-precipitation is probably the most reliable and reproducible technique for

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its preparation, often using conventional nitrate and chloride salts [13]. Several environmental uses involving the successful application of hydrotalcites have been reported in the literature, generally focused on the adsorption of pollutant gases such as NO_x, SO_2, CO_2, etc. [14–17] or the removal of organic dyes, toxic metals and anions present in wastewaters such as NO_3^-, Cr(VI), Mo(VI), As(V), Se(VI), Pb(II), etc. [18–23].

In relation with glasses, the CaO–Al_2O_3–SiO_2 ternary system presents a wide range of possibilities for the production of glassy materials. In general applications, such as glassware, window glass, ceramic glazes, *etc.*, the silica introduced in its composition is usually high, being a key factor influencing the resulting properties. Whether the aim is to achieve better transparency in the infrared region (combined with the visible) or a higher Young's modulus, the best option is to reduce the silica content in the glass composition (closest to the binary CaO–Al_2O_3). Calcium aluminate glasses have been motivated by their promising optical properties, such as ultralow optical losses, and wide optical transmission window extending to infrared wavelengths of approximately 5 μm [24]. In the literature, properties such as a high liquidus temperature and extremely fluid melt have been noted as a relevant advantage for the production of these glasses, in particular as windows in the infrared region. However, during cooling these glasses have shown undesirable high devitrification rates [25,26]. The technical solution adopted has consisted of the addition of a very small amount of silica to their composition in order to favour the glass's stability during the manufacturing process, since silica lowers the liquidus temperature (also the refractive index) and increases the viscosity of the melt [27]. As a negative aspect, the Young's modulus is considerably reduced. The presence of transition metals (in low concentrations) also modifies glass formation and affects its properties [28].

In this context, the aim of this work is to evaluate a new alternative methodology for the complete recovery of fine powders extracted from filter sleeves in the aluminium tertiary industry. This proposal is based on the production of added-value materials such as Mg–Al hydrotalcites, which have been tested for molybdate anion adsorption, and inorganic glasses in the CaO–Al_2O_3 system with a low silica content. The composition of these glasses includes large amounts of recovered aluminium, which facilitates the determination of possible defects in samples after moulding.

2. Experimental

2.1. The recovery procedure

2.1.1. Analysis of the waste composition

The powders were analysed by X-ray fluorescence (XRF) in order to determine the main chemical composition of the waste. The Kjeldahl method was used to calculate the aluminium nitride content, which can be directly correlated with the theoretical amount of ammonia that could be released by the waste. The total aluminium content soluble in the extremely strong HCl acid medium, such as metallic aluminium and aluminium nitride, was analysed by Atomic Absorption Spectroscopy (AAS). This value is useful to determine the theoretical amount of hydrogen that could be generated in the presence of water.

2.1.2. Pretreatment of the waste

The methodology consisted of dispersion of the hazardous waste (20 g) in a hydrochloric aqueous solution (200 ml, 1.2 mol/l) for 3 h at 80 °C, which favoured the following situations: nitride decomposition (a large part of the ammonia reacted with the acid and was trapped in the dispersion as ammonium); metal hydrolysis under controlled conditions (hydrogen was slowly released and separated from the ammonia gas), and; the solubility of other aluminium salts and transition metals. The dispersion was then filtered on a GTTP Millipore filter at 5 bar to obtain a concentrated aluminium solution and an inert solid cake (with magnesium aluminium spinel, corundum and other oxide compounds insoluble in the acid media) [6]. The solution was analysed by AAS in order to determine the Mg^{2+} and Al^{3+} contents and the solid cake was dried in air at 110 °C for 24 h.

The solution obtained was subsequently used as the aluminium precursor for the synthesis of hydrotalcites, and the inert cake for the preparation of inorganic glasses, thus leading to the complete consumption of the solid components comprising the hazardous waste, as summarised in Fig. 1.

2.1.3. Synthesis of hydrotalcites

The synthesis of Mg/Al hydrotalcites was based on conventional co-precipitation (exposed to air without ageing) with sodium hydroxide (1 mol/l) for 2 h at 80 °C and pH 10. The Mg/Al molar ratios were 3:1, 3.5:1 and 4:1. The required mass of Mg^{2+} was mainly supplied by magnesium chloride (reagent grade from

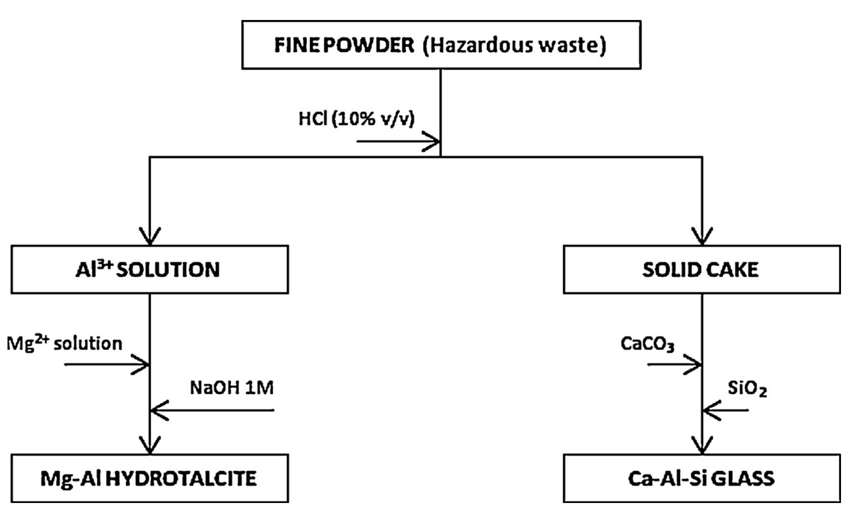

Fig. 1. Procedure for full recovery of a hazardous waste trapped in filter sleeves in the tertiary aluminium industry.