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Development of a combined solid and liquid wastes treatment integrated into a high purity ZnO hydrometallurgical production process from Waelz oxide

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ABSTRACT

Electric Arc Furnace Dust (EAFD) is an important hazardous waste from the steel production industry, due to its heavy metals content. It is recycled through a pyrometallurgical process to generate a Zn and Pb concentrate called Waelz oxide. This concentrate can be processed hydrometallurgically in order to obtain high purity ZnO. But this hydrometallurgical process also generates as wastes different solid residues with high content of heavy metals and a liquid waste stream with significant concentrations of ammonia and heavy metals. This is why the objective of this work is to design a process that can simultaneously treat these solid and liquid wastes. In the developed process, an alkaline solution is used to leach solid residues so as to produce an inert final waste. After filtration, the leaching liquor is mixed with the liquid waste in order to increase its pH and to enhance the ammonia evaporation by air stripping. This stripped stream can be recycled to the leaching stage of the Waelz oxide treatment process. Furthermore, the ammonia stripping precipitates the dissolved heavy metals as a zinc concentrate that can be commercialized as a raw material for the metallic zinc production industry. Therefore, the developed process reduces by more than half the wastes generation, increases the Zn recycling yield > 5% and recovers > 75% of the needed ammonia for the fresh leaching liquor.

1. Introduction

Steel is one of the most widely used metallic materials in our modern world, because of the adaptability and durability of its products. Hence, steelmaking industry produces approximately 1.6 billion tons of steel every year to meet worldwide consumption demand. 40% of the processed steel is obtained from recycled waste in electric arc furnace (World Steel Association, 2014). During the melting of scrap in the furnace, the electric arc furnace dust (called EAFD) is generated and collected by bag filters or electrostatic precipitators (De Araujo et al., 2014). In the most developed countries this dust is classified as hazardous waste due to its toxic heavy metals content. Obviously, for economic reasons and to prevent environmental impacts, this dust must be treated in order to recycle part of its heavy metals (Gupta et al., 1990; Orhan, 2005). An average steelworks facility generates approximately 15 kg of EAFD per ton of steel (Dutra et al., 2006).

Nowadays, Waelz process is acknowledged as the Best Available Technology (BAT) in order to treat EAFD, according to Reference Document for Non-Ferrous Metal Industries (Industrial Emission Directive, 2010). The product of Waelz process, named Waelz oxide, is a mix of mainly zinc and lead oxides with several impurities.

Waelz oxide is sold to zinc concentrator companies to produce high-purity zinc products, basically, metallic zinc and zinc compounds such as zinc oxide and zinc sulphate (International Lead and Zinc Study Group, 2011). High-purity zinc oxide is the most produced and widely used zinc compound. It is used in rubber vulcanization as a catalyst for its manufacture. It is also employed in ceramics, paints, animal food, pharmaceuticals and in many other products and processes. In addition, special grade of zinc oxide has long been used in photocopiers. This oxide is also used in varistors, providing protection against over-voltages. ZnO market supposes 100,000 tonnes per year. It is fabricated through three different technologies: French process, American process and Hydrometallurgical process (Klingshirn, 2007). Even today, the most used technologies are American and French processes (Pyrometallurgical processes), although they require purer raw materials (zinc ingot, zinc mattes, zinc ashes, and so on) on the contrary of the Hydrometallurgical ones. This last alternative uses ammonium carbonate and ammonia solutions as leaching liquors to purify Waelz oxide and it has been investigated by different researchers (Núñez, 2005; Meseguer et al., 1996; Ruíz et al., 2007).

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The main conclusion of these previous works is that a very promising ZnO production yield can be obtained from the hydrometallurgical treatment of Waelz oxide, but the ammonia and heavy metals discharge and solid wastes disposal make impossible its industrial application. So, further research is required to get this process closer to its industrialization.

Firstly, in this study a hydrometallurgical process to high-purity zinc oxide production using ammoniacal solutions as leaching liquors was optimized. Once zinc is dissolved from Waelz oxide with other impurities (i.e. iron, lead, cadmium and copper), these are eliminated from the zinc solution through purification stage: i) via oxidation with air (iron removal) and ii) via cementation with metallic zinc powder (removal of other metallic impurities). The purified zinc solution is precipitated through CO_2 (g) injection at room temperature obtaining zinc carbonate species. Then, it is calcined to yield zinc oxide of a high grade (ZnO of purity higher than 99.0%). Nevertheless, the final industrial development must include the exhausted liquor recycling and wastes treatment technologies. Therefore, the main aim of this work is to develop a new chemical process, that combines solid and liquid residues treatment from the previously described ZnO hydrometallurgical process, in order to achieve a technoeconomically feasible and environmentally benign technology to convert Waelz oxide into commercial high-purity zinc oxide.

The solid wastes generated by the ZnO hydrometallurgical production process stages (leaching, oxidation and cementation) are categorized as dangerous and hazardous industrial wastes (Boreiko, 1991). The main problem of these waste products lies in their disposal due to the high concentration of heavy metals such as cadmium, lead, chromium, mercury and zinc. As these metals tend to bio-accumulate they are extremely toxic even at low concentrations. For zinc dosses between 225 and 450 mg/day are considered as severe toxicity (World Health Organization, 2011). Regarding the liquid waste stream generated in this high-grade ZnO production process, pH, dissolved ammonia and heavy metals content must be controlled. Ammonia can simultaneously be in two forms at an equilibrium mostly governed by pH and temperature. This forms are NH_3 (un-ionized ammonia) and NH_4^+ (ionized ammonia or ammonium). The sum of these two forms is called total ammonia. The NH_3 form is particularly harmful for aquatic organisms, being limited its discharge. The maximum permissible concentrations of metals in natural waters are recommended and regulated by several environmental protection agencies for the human health. This implies that they must be removed from industrial wastes streams. For this reason, the intended combined process must allow to inertize the solid residue, recovering the highest possible proportion of metals in order to increase the metallic yield and profitability of the plant. In the same way, dissolved ammonia in the exhausted liquor must be recovered so as to reuse it as a reagent in the leaching liquor formulation. This recovery generates a zinc concentrate by-product from the liquid waste treatment stage. Thus, this study deals with the design of solid and liquid hazardous wastes treatment process integrated in a hydrometallurgical plant producing high grade ZnO from Waelz oxide. This improvement reduces environmental impact and increases techno-economic viability of the zinc recycling. The developed technology could be applied to other metallurgical processes with similar wastes (e.g. Ni, Cu or Co via Sherritt Gordon Process).

2. Materials and methods

The Waelz Oxide sample under study (used as raw material) originates from the BEFESA ZINC ASER S.A. plant (Spain) and it was used as received.

The reactants used during the experimental works are ammonium carbonate (ACS grade, SIGMA-ALDRICH) and liquid ammonia 25% (ACS grade, SIGMA-ALDRICH) to prepare the leaching liquor, zinc powder as cementation agent (pure, SIGMA-ALDRICH), CO_2 gas (ALPHAGAZ 2, AIR LIQUIDE) as precipitation agent and sodium hydroxide pellets pure (Panreac) as pH modifier.

All experiments were carried out in a 2 L glass reactor with mechanical stirring. The reactor worked in a thermostatic bath and it was operated closed in order to avoid water losses by evaporation. An Orion Star A329 Multiparameter apparatus was used as pH and temperature controller. The pH control of the leaching stage was carried out automatically by acid/alkali addition through a peristaltic pump controlled by the A329. The ammonia stripping experiments were carried out in the 2 liter glass reactor with mechanic stirring. In this case, the stirrer was perforated in order to permit the gas injection. The gas was injected from the laboratory compressed air line and using a Dwyer serie STFO as a flowmeter. The reactor worked in a thermostatic bath and the cover had a gas extraction system. The stripped ammonia was recovered in an absorption reactor. Millipore ASME - MU High pressure filter, YT30-142HW model, was used for solid/liquid separation so as to take the samples which were analysed.

Chemical analysis of the used Waelz oxide sample and the generated solid wastes and treated solid residues were carried out using a microwave acid digestion procedure and the subsequence analysis of the metal contents with an ICP - AES Perkin Elmer 2000 - DV model. The metallic ions concentrations in the liquid samples of the obtained zinc liquors were also analysed by ICP - AES (Perkin Elmer 2000 - DV model). Argentometry tritration (Crison 8661 Titromatic) was used to measure the chloride concentration and a fluoride ion selective electrode (Crison 9655) was used for fluoride analysis. Dissolved ammonia was analysed using a high-performance ammonia ion selective electrode (Orion Ammonia gas sensing electrode) and a carbon dioxide ion selective electrode (Orion Carbon dioxide electrode 952BNMP) was used in the analysis of total carbonates present in the liquid samples. Zinc concentrate obtained in the ammonia recovery stage was also analysed by X ray diffraction (using a Brucker D8 Advance Diffractometer), equipped with a primary germanium monochromator with Bragg-Brentano geometry and with a CuKα1 wave-length of 1.5406 Å. Thermogravimetric analysis was carried out using a microThermogravimetric Analizer with small furnace TGA 2 Mettler Toledo.

3. Results and discussion

3.1. Characterization of raw material and treated solid and liquid wastes

First of all, the patented industrial process to produce high-purity zinc oxide from Waelz oxide, using aqueous solutions of ammonium carbonate and liquid ammonia as leaching liquor (Alguacil et al., 1998), was improved and optimized. In this work, all the hydrometallurgical stages were further studied with the purpose of improving ammonia recovery and final quality of the product (ZnO). In addition, ammonia losses and energy consumption (new design without evaporation stage) were minimized.

The characterization of the Waelz oxide used as raw material in this study is shown in Table 1.

Table 1
Composition of Waelz oxide supplied by Befesa S.A.

Element	Weigh (%)	Element	Weigh (%)
Zn	55–58	S_{total}	0.7–1.0
Pb	7–10	F	0.15–0.18
Cd	0.3–0.5	Cl	4.5–6.1
Cr	0.1–0.3	Ni	0.03–0.12
Cu	0.2–0.6	C_{total}	1.0–2.0
Sn	0.1–0.2	FeO	5–7
Al_2O_3	0.1–0.4	MnO	0.4–0.7
SiO_2	0.5–1.5	Na_2O	1.1–1.5
CaO	0.3–1.0	K_2O	1.5–2
MgO	1.5–2.5	Hg (ppm)	3–30