



Fluoride removal from Double Leached Waelz Oxide leach solutions as alternative feeds to Zinc Calcine leaching liquors in the electrolytic zinc production process

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ABSTRACT

The most important limitation of leached Waelz Oxide from the pyrometallurgical treatment of Electric Arc Furnace Dust (EAFD) is its high fluorine content. This work deals with the reduction of the harmful effects of the Double Leached Waelz Oxide fluorine content in the hydrometallurgical process for electrolytic zinc production process when it is used as raw material directly in the leaching stage. The resulting process is a purification treatment of Double Leached Waelz Oxide leach solution to remove the dissolved fluoride in this unpurified zinc liquor. Leached fluorides from this liquor are precipitated in order to reduce their concentration until the specified values, avoiding cathode corrosion in the electrowinning cells. In this paper a selective precipitation process to maximize the fluoride removal and to minimize the zinc losses is presented, achieving the industrially specified solution composition when the Zinc Calcine is the used raw material. The formation of aluminium-fluoride complexes and the variation of their solubilities with the pH evolution are the basis of the proposed treatment. In addition, this fluoride removal has also been improved and optimized in order to be integrated in the overall industrial hydrometallurgical process and the obtained results are presented and discussed proving the viability of this improved stage.

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1. Introduction

The steelmaking industry produces around 1.606 million tons of steel every year. 40% of the processed steel is obtained from recycled electric arc furnace waste (World Steel Association, 2014) in order to reduce the need for iron ore extraction. This fabrication process generates a solid waste called Electric Arc Furnace Dust (EAFD), which contains a considerable concentration of zinc, ranging from 22% to 28% (Núñez et al., 1992). The percentage of zinc is so high because galvanized steel scrap is used as feeding of the melting process. EAFD residues appear mainly during the filtration to clean the flue gas from steel melting and refining operations (Machado et al., 2006; Saleh, 2004). This dust must be treated to recycle some heavy metals for economical reasons and to prevent environmental impacts (Alguacil et al., 2007; Orhan, 2005). In this steel recycling process, approximately 15 kg of EAFD per ton of obtained steel are generated (Dutra et al., 2006). The Waelz process is the most used technology for this purpose, generating a solid, which is a mix of zinc and lead oxides with several impurities called Waelz Oxide (WO). An industrial Waelz furnace treats approximately 160,000 tons of EAFD/year, obtaining 50,000 tons of WO/year (Befesa Zinc S.A.-Aser, 2013). The aim of the current development of the process

is to expand the market of the WO into the zinc business and to raise the products value designing sustainable processes (Lozano Blanco et al., 1999; Kumar et al., 2001).

Zinc is the fourth most common metal in use, trailing only iron, aluminium, and copper with an annual production of about 12 million tons. China is the largest producer country in the world, followed by Peru and Australia (Tolcin, 2011). About 70% of the world's zinc originates from mining, while the remaining 30% comes from secondary zinc recycling. The level of recycling is increasing each year, in step with progress in the technology of zinc production and zinc recycling. Today, over 80% of the zinc available for recycling is indeed recycled (International Zinc Association, 2014). Today, over 90% zinc is produced hydrometallurgically in electrolytic plants (International Zinc Association, 2014).

Nowadays, the WO is useful as one of the raw materials for metallic zinc production in the Imperial Smelting Furnace, but some impurities limit its use in the leaching stage of the industrial electrolytic process. Some impurities in the electrolyte severely affect the zinc adherence in the electrolysis, being the strong effect of F^- ions the most damaging one and as a result fluorides the most problematic species which the WO leach solutions contain, because they also cause the corrosion of the aluminium cathodes (Andrienne et al., 1980; Buarzaiga, 1999). The fluoride ions content in the zinc solutions cause problems with the removal of the metallic zinc from aluminium blanks. Different studies indicated that the mechanism responsible for adherence was mainly

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due to two factors. First of all the fluoride attack the passivated surface of the aluminium cathode (Al_2O_3), exposing metal and allowing direct zinc deposition and metal to metal bonding (Zn–Al). Secondly, the corrosive attack is non-uniform and the pits which are also formed provide sites for the mechanical keying of the zinc (O'Keefe and Han, 1992). The accepted fluoride concentration in the liquor to be feed to the cells must be controlled to be less than 50 mg/L (De Goicoechea y Gandiaga et al., 1999). The halogens quantity in the zinc concentrates degrade the product value (Guozhu et al., 1999), specifically a high fluorine concentration is more detrimental than other impurities, for instance cobalt, nickel or cooper (García-Carcedo et al., 1999). So far, there are different strategies to purify the WO, the double leaching with sodium carbonate (Dañobeitia et al., 1996; De Goicoechea y Gandiaga, 1996) is the important one. This process was developed in order to reduce the content of halogens and alkaline compounds, producing a more purified product called Double Leached Waelz Oxide (DLWO).

The goal of this paper is to present the development of an improvement of a fluoride removal step to be integrated in the electrolytic process for metallic zinc production from WO. For this purpose, a selective precipitation of dissolved fluorides from the DLWO leach solution has been studied by formation of aluminium–fluorine complexes and their removal occurs within the low solubility range of the formed AlF_x^{x-} complexes ($4 \geq \text{pH} \geq 12$) minimizing the dissolved zinc losses. The reduction of the fluoride concentration in the zinc liquor could allow the use of DLWO as raw material directly in the leaching stage of the electrolytic zinc production process. A simplified block-diagram of the developed treatment for fluoride removal into the electrolytic process using DLWO as raw material is presented in Fig. 1.

2. Materials and methods

The sample of Double Leached Waelz Oxide under study originates from the BEFESA ZINC ASER S.A. plant (Spain) and it was used as received. The reactants used during the experimental works are aluminium chloride 6-hydrate (pure, Panreac) and aluminium sulphate 18-hydrate (pure, Panreac) as aluminium source and sulphuric acid 95% technical grade (Panreac), hydrochloric acid 37% p.a. (Panreac) and sodium hydroxide pellets pure (Panreac) as pH modifiers.

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, precipitation and washing stages was carried out automatically by acid/alkali addition through a peristaltic pump controlled by the A329. A 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 DLWO sample and the generated solid waste were carried out using a microwave acid digestion procedure and

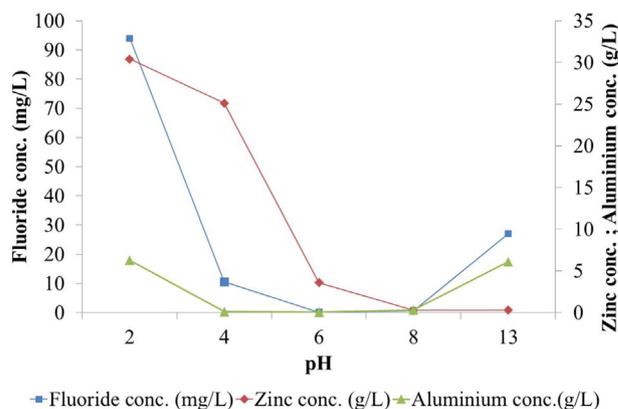


Fig. 2. Zinc, fluoride and aluminium concentrations as functions of the pH using a 50 g/L aqueous solution of $\text{Al}_2(\text{SO}_4)_3$ as leaching liquor, controlling the pH with NaOH (aq) or H_2SO_4 (aq) at 25 °C.

the subsequent 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 titration (Crison 8661 Titromatic) was used to measure the chloride concentration and a fluoride ion selective electrode (Crison 9655) was used for fluoride analysis. Solid residues obtained in the leaching stage were also analysed by X-ray diffraction (using a Bruker D8 Advance Diffractometer), equipped with a primary germanium monochromator with Bragg–Brentano geometry and with a $\text{CuK}\alpha 1$ wave-length of 1.5406 Å.

3. Results and discussion

3.1. The influence of the pH and temperature on the fluoride solubility in aluminium presence

The DLWO was leached (with a S/L Ratio = 1/17 and at 25 °C during 100 min) using different aluminium salt solutions controlling the pH of the leaching stage. The solubility of the fluorine and the zinc contained in the DLWO in aluminium presence as function of the pH of the leaching liquor is studied.

From the obtained results (see Figs. 2 and 3) a difference between Zn^{2+} and F^- solubilities can be observed within some pH ranges. Hence, a methodology of fluoride removal by selective precipitation was designed taking into account the formation of aluminium–fluoride complexes and the modification of their solubilities. The formation of these aluminium–fluoride complexes could also be observed as the aluminium (using two different aluminium salt solutions as leaching agent) and fluoride concentrations follow the same solubility profile within the pH studied range. Industrially, a sulphuric media is more

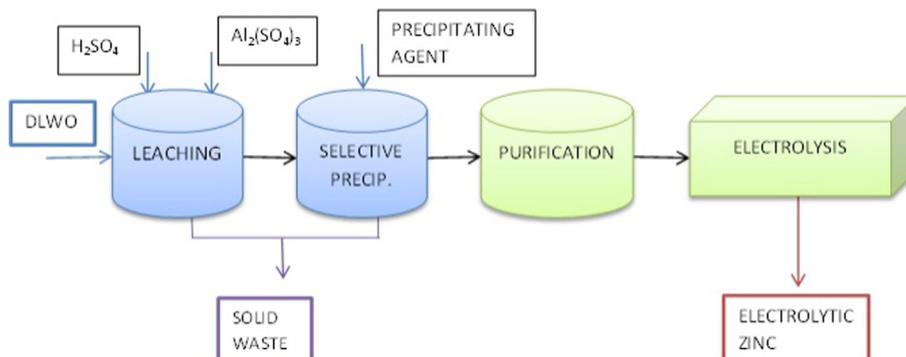


Fig. 1. Proposed flow sheet for the zinc electrolytic process with the improvement of the selective precipitation step.

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