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Short communication

Studies on impurity iron removal from zinc electrolyte using MnO_2–H_2O_2

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ABSTRACT

This paper is focused on the iron removal from sulphuric acid–zinc liquors obtained from double leached Waelz oxide. The initial iron concentration in the liquor was around 80 mg/L which must be removed prior to complementary purification stages and zinc electrowinning. Different oxidation agents were studied, operating at room temperature and atmospheric pressure. It was observed that the most suitable oxidation agent was a mixture of MnO_2–H_2O_2. During 20 min at pH 4.5 while adding 2 mL H_2O_2 and 1.2 g MnO_2/L of liquor, an iron removal around 99.6% was achieved, reducing the iron concentration in the liquor to 0.3 mg/L. The proposed process operates well at room temperature and energy saving is achieved with respect to conventional oxidation processes using O_2 or H_2O_2 as oxidation agents, in which temperatures of at least 60–80 °C must be used.

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1. Introduction

Due to the restrictive environmental regulations and the increasing environmental awareness, recycled zinc represents around 30% of the world zinc production (Frias, 2009). The most common way to produce metallic zinc is by electrolysis of zinc sulphate liquors (Habashi, 1997). To obtain these electrolytes, different zinc concentrates are usually roasted or pressure leached and treated with sulphuric acid solutions and then purified from impurities. The generation of these liquors have been extensively studied (Herrero et al., 2010; Dvorak and Jandova, 2005).

To prevent electrode corrosion and to ensure high zinc purity, these electrolytes must fulfil some minimum requirements related to chloride, fluoride and metallic impurities concentrations. One of the most important metallic impurities is iron, because it is one of the major impurities. The maximum iron concentration tolerated in the electrolytic liquor is 10 mg/L (Tsakiridis et al., 2010). As a result of this restriction, the liquor obtained in the leaching stage must be treated to remove most of this iron.

There are three main traditional processes used to remove iron species from electrolytic liquors: the jarosite process, the goethite process and the hematite process (Gordon and Pickering, 1975). However, none of these can remove low amounts of iron which generally remains as iron(II) and this is the reason why processes that focus on the use of different oxidation agents are under study. In most cases, after partial oxidation of Fe^{2+} to Fe^{3+}, partial neutralization with NaOH or other neutralizing agents removes most of the iron. However, when the liquor is sent to electrolysis, the allowable concentration of sodium, potassium or other alkali cation species is very limited. So, alkali additions are not recommended.

The most economic oxidation agent is oxygen and very high yields of iron removal can be achieved, around 99%. The best results using oxygen are obtained at 220 °C and with a partial pressure of oxygen of 709 kPa (Ruiz et al., 2007). However, to improve the oxidation yield under atmospheric pressure using oxygen, Barakat et al. (2006) also added MnO_2. In this case, 99.6% Fe was removed at a temperature of 60–80 °C when the working pH was in a range of 4.5–5.2. Although, the presence of manganese in the electrolyte can lead to lower electrolytic zinc purity, some manganese is required to condition the anodes and provide a MnO_2 coating to minimise lead contamination of the cathode. Excess manganese can be removed from the liquor in an additional purification stage if necessary.

Other oxidation agents such as hydrogen peroxide or manganese dioxide have been also studied. Adding hydrogen peroxide to the liquor at pH 4–5 removes almost 99.95% Fe (Baik and Fray, 2000), while using manganese dioxide at pH 4.5 removes 98.9% Fe (Koleini and Moradi, 2004). In both cases, the temperature was around 70 °C. Finally, Tsakiridis et al. (2010) removed 99.9% Fe through chemical precipitation with lime and aeration at 95 °C.

In all the previously cited works, the oxidation stage was carried out at temperatures higher than room temperature. Processes working at lower temperatures could offer energy savings in the operation. In this paper, the oxidation of iron present in a sulphuric acid liquor obtained from double leached Waelz oxide is studied in detail. This oxide is a complex oxide of zinc and lead with lower chloride–fluoride concentration than the Waelz oxide. All the experiments have been performed at room temperature and atmospheric pressure, studying different oxidation agents such as

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hydrogen peroxide, manganese dioxide and a mixture of them. Oxygen has not been studied as an oxidation agent because it has been proved that to achieve high enough iron oxidation it is necessary to work at high temperatures (Vraçar, 1997).

1.1. Oxidation pH theoretical study

The oxidation pH is one of the critical parameters involved in the oxidation. It not only affects the oxidation of iron(II) to iron(III), but also the precipitation of iron as $Fe(OH)_3$ or related compounds. In the experimental studies in which the optimum oxidation pH was determined, H_2O_2 was used as an oxidation agent, adding 1 mL/L liquor. So, the main reaction which took place was reaction (1).

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \quad (1)$$

$$\frac{\left[Fe^{3+}\right]^2}{[Fe^{2+}]^2[H_2O_2][H^+]^2} = exp\frac{\left(E^0 - E\right)nF}{RT}.$$

Applying the Nernst equation to the reaction (1), it is observed that low pH favours the iron oxidation, while high pH improves iron (III) hydroxide precipitation, reaction (2). So, it is necessary to reach an acceptable equilibrium between them. While it is possible to carry out the oxidation–precipitation in separate stages, this would involve higher neutralizing agent additions.

$$2Fe^{2+} + H_2O_2 + 4H_2O \rightarrow 2Fe(OH)_3\downarrow + 4H^+. \quad (2)$$

1.2. Oxidation mechanism theory

Hydrogen peroxide and manganese dioxide were studied as oxidation agents. It was observed that by adding H_2O_2 alone, a sufficiently high yield of iron removal was achieved. The problem in this case is that NaOH is needed to keep the pH constant, and sodium is a restricted parameter in zinc sulphate electrolytic liquors. This is why manganese dioxide was considered with 2 g MnO_2 added/L of liquor.

$$MnO_2 + 2Fe^{2+} + 2H_2O + 2OH^- \rightarrow Mn^{2+} + 2Fe(OH)_3\downarrow \quad (3)$$

$$MnO_2 + Fe^{2+} + H_2O + H^+ \rightarrow Mn^{3+} + Fe(OH)_3\downarrow \quad (4)$$

$$3MnO_2 + 4Fe^{2+} + 12H_2O \rightarrow Mn^{2+} + 2Mn^{3+} + 4Fe(OH)_3\downarrow. \quad (5)$$

As shown in reactions (3–5), the manganese present in MnO_2 is reduced to Mn(II) or Mn(III) or to a mixture of both. Reactions (3 and 4) show that if MnO_2 is reduced to Mn^{2+} the pH decreases, while if it is reduced to Mn^{3+} the pH increases. In the case of the reaction (5), the pH increases if the ratio Mn^{3+}/Mn^{2+} is greater than 2. It was experimentally observed that the pH during the oxidation clearly increased, which indicates that the Mn^{3+}/Mn^{2+} ratio in the liquor was greater than 2. To keep the pH constant at the chosen value of pH 4.5 during the oxidation, sulphuric acid solution (10% v/v) was added. After analysing the solid residue by XRD it was observed that MnO_2 was reduced to hausmannite ($MnO \cdot Mn_2O_3$), (see Fig. 1). The presence of γ-Mn_3O_4 is attributed to a later partial hydrolysis of Mn (II)/Mn(III) in the presence of water.

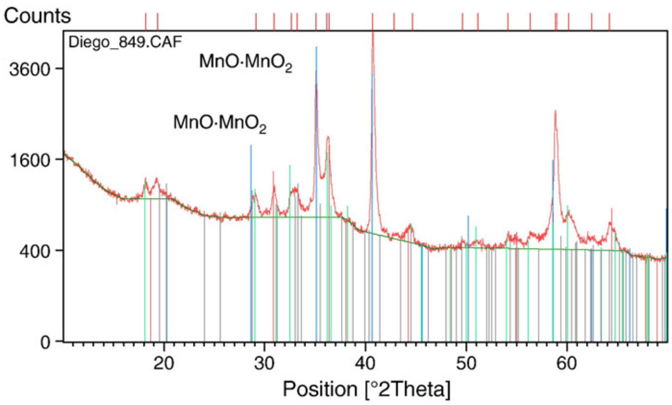

Fig. 1. XRD pattern of the solid obtained in the oxidation stage by adding MnO_2.

2. Experimental

2.1. Experimental procedures

The oxidation experimental studies were carried out in a 5 L glass reactor with a magnetic (VELP Scientifica ARED) and mechanical stirrer system (Heidolph RZR-2000). A DIGIMED pH Analyser TH-404 was used to keep the pH constant by adding basic or acidic solution. Hydrogen peroxide (30% v/v, Rieder-de Haën) additions were studied in a range of 0.5–2.0 mL/L liquor. Manganese dioxide (60% w/w, Panreac) addition was studied in a range of 0.3–1.2 g/L liquor. All the initial studies, until the oxidation time were optimized, were carried out over 30 min.

In order to separate liquid samples from the solid residue, a pressure filter Millipore YT30-142HW was used. The samples obtained during the oxidation were analysed in a liquid state using a Perkin Elmer ICP-AES Model 2000-DV. The solid residues were digested in an aqua regia-HF mixture. Solid samples were 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 $CuK_{\alpha1}$ wave-length of 1.5406 Å. To carry out the semi-quantitative analysis, an internal standard of 50% corundum α-Al_2O_3 was used and the ratio of the highest intensity peak of the represented phase and the corundum was measured.

The chloride–fluoride anion concentrations determination was performed by ion chromatography, using a DIONEX ICS 3000.

2.2. Double leached Waelz oxide and leach liquor composition

The raw material used to obtain the liquor is the double leached Waelz oxide, a product obtained after a double leaching of the Waelz oxide with sodium bicarbonate solutions. The main metallic species in the double leached Waelz oxide is zinc along with significant concentrations of iron, lead, cadmium, copper and manganese as shown in Table 1.

When the double leached Waelz oxide was analysed by XRD, the main species observed was zinc oxide together with some zinc ferrite (see Table 2 and Fig. 2) However, because this material comes from a pyrometallurgical Waelz process, where EAF dusts are treated, other species derived from the fluxes such as the $CaCO_3$ or CaF_2 are present (Ma, 2006).

Table 1
DLWO composition determined by ICP.

	DLWO composition (%)
Copper	0.17
Nickel	0.00
Cadmium	0.16
Iron	2.17
Lead	6.47
Zinc	64.77
Manganese	0.28
Tin	0.05
Chromium	0.03

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