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Selective process of zinc extraction from spent Zn–MnO_2 batteries by ammonium chloride leaching

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ABSTRACT

Recycling of spent Zn–MnO_2 batteries by hydrometallurgy is usually carried out by leaching in acid media, mainly with sulphuric acid solutions. Another type of leachant was used in this work, specifically solutions of concentrated ammonium chloride. The development of this study has relied on the prediction of the chemical behavior of the constituting phases based on data obtained from theoretical and experimental equilibrium values. The assessment of the effects of factors on leaching efficiency was also done.

It was concluded that about 70% of zinc, as ZnO, can be selectively extracted using this media, under optimized conditions such as 4–5 M NH_4Cl, 90–100 °C and 4 h, the remaining zinc namely that corresponding to the spinel form $ZnO\cdot Mn_2O_3$ being insoluble. All other manganese species were also almost insoluble, besides iron, holding up that ammonium chloride leaching is a very selective process for zinc recovery from batteries. The factors temperature, leachant concentration and time are indicate to be very significant in leaching, while stirring velocity was less relevant. The apparent activation energy was calculated based on the initial velocity differential method and the value achieved (5.7 ± 0.7 kcal mol^{-1}) showed a mixed control process. This indicates that, although the surface chemical reaction is still playing an important role in the leaching mechanism, the contribution of diffusion phenomena shall not be disregarded at all.

1. Introduction

Spent batteries are a significant waste stream requiring adequate management. Recycling is recognized as the most effective way to manage this waste, allowing simultaneously recovering metal values, saving primary raw-materials and minimizing the impact on the environment, thus contributing to its protection and preservation.

In portable battery market, Zn–MnO_2 systems (alkaline and zinc–carbon or saline) are still a share of typically 70–80 wt.% constituting therefore an important parcel of batteries to be taken into account. Main components of these spent batteries with economic value are the electrodes, containing essentially zinc in its oxide form (ZnO) and manganese in Mn_3O_4 and MnO_2 forms (Linden, 1995), besides other possible constituting solid phases.

Hydrometallurgy is one of the treatment processes suitable for recycling this type of residue. Last years, research on this field has been carried out, as explained in bibliography (Bernardes et al., 2004; Espinosa et al., 2004; Sayilgan et al., 2009a), and also some industrial processes were implemented. The existing technology is mainly based on the aqueous dissolution of metals, mainly using acids with or without additional reagents. Preliminary mechanical treatment is necessary (Cabral et al., 2008) to open the battery cases and expose the electrode particles to the reactants. This step normally includes several unit operations as shredding with hammer or cutting mills, and size classification or magnetic separation for removing steel and plastic scraps.

Leaching with sulphuric acid solutions is the most common process (El-Nadi et al., 2007; Ferella et al., 2008; Salgado et al., 2003; Souza and Tenório, 2004; Souza et al., 2001; Veloso et al., 2005), allowing attaining high zinc recoveries, usually above 95%. Manganese recovery is always lower, since manganese in the oxidation state IV is only soluble in acid media with the presence of a reducing agent. Studies performed by many researchers showed that the manganese solubilization by acid leaching is small, but the range of values attained is broad, namely up to 5–8% (El-Nadi et al., 2007; Veloso et al., 2005), 20% (Ferella et al., 2008), and 30–45% (Salgado et al., 2003; Souza and Tenório, 2004; Souza et al., 2001). These processes generate leachates containing high zinc concentration and lower manganese concentration, requiring further purification prior to metal recovery.

To improve manganese recovery in hydrometallurgical processes with sulphuric acid, it is necessary to apply for reductive conditions by using several optional reducers. Hydrogen peroxide (Kim et al., 2009) allows leaching practically all the manganese. The use of carbohydrates such as glucose or sucrose (Furlani et al., 2009) was also efficient to

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