

Processing of spent ZINC-MnO₂ DRY cells in various acidic media

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This paper describes a route for recovering manganese and zinc from spent zinc-MnO₂ dry cells via acid leaching. Sulfuric, hydrofluoric and formic acids were used as leachants. Hydrogen peroxide was added as reductant, except for formic acid since it is itself a reductant. Experiments were run at 25-40 °C for 1-3 h. Under the best optimal conditions, over 95 wt.% of zinc and manganese were leached irrespective of the leachant. Leaching of contaminants was strongly dependent on the leachant due to the insolubility of salts or complexing reactions. Zn(II) was best extracted with D2EHPA diluted in n-heptane at pH > 1, particularly from the leachates of weak acids. Mn(II) was much more co-extracted from sulfuric leachates, but was easily scrubbed with dilute leachant (~2 mol L⁻¹). Zn(II) stripping was possible using 5 mol L⁻¹ H₂SO₄. Manganese was isolated as MnO₂ carrying the leached contaminants. High-purity sodium salts of the anions of the leachants were recovered after slow evaporation of the final solution [1-15].

Over 95 wt.% of zinc and manganese were leached from the electroactive components of spent zinc-MnO₂ dry cells under mild experimental conditions in the presence of a weak acid and a reductant. Formic acid effectively served the dual role of leachant and reductant as HF or H₂SO₄ + H₂O₂ mixtures. Leaching was fastest in the presence of hydrofluoric acid. Precipitation and complexation reactions influenced leaching of minor elements present in the electroactive components. The insoluble matter corresponded to carbon and non-leached elements except for formic acid, where an additional volatile mass was found.

More than 95 wt.% of Zn(II) was extracted by D2EHPA in one stage (6 vol.%, A/O = 1 v/v, 25 °C) at pH 2 following the order HF > HCOOH > H₂SO₄. Mn(II) extraction from leachates of weak acids was the lowest. Therefore, hydrofluoric or formic acids are alternative leachants for processing spent zinc-MnO₂ dry cells. The effect of pH and D2EHPA concentration on Zn(II) extraction were the same regardless of the leachant. Extracted Mn(II) was easily scrubbed with 2 mol L⁻¹ leachant. Zn(II) stripping was only possible using a strong

acid (5 mol L⁻¹ H₂SO₄). High purity crystalline sodium salts of the anions of the leachants were obtained after precipitation of Mn(II) and pH adjustment of the final solution followed by slow evaporation. Recovery of these salts reduced the amount of final wastes.

References

- [1] BISWAS, R. K.; KARMAKAR, A. K.; KUMAR, S. L. Recovery of manganese and zinc from spent Zn-C cell powder: Experimental design of leaching by sulfuric acid solution containing glucose. **Waste Management**, Amsterdam, v. 51, [s.n.], p. 174-181, 2016.
- [2.] BISWAS, R. K.; KARMAKAR, A. K.; KUMAR, S. L. Recovery of manganese and zinc from waste Zn-C cell powder: Mutual separation of Mn(II) and Zn(II) from leach liquor by solvent extraction technique. **Waste Management**, Amsterdam, v. 51, [s.n.], p. 149-156, 2016.
- [3] IPPOLITO, N. M. et al. Utilization of automotive shredder residues in a thermal process for recovery of manganese and zinc from zinc-carbon and alkaline spent batteries. **Waste Management**, Amsterdam, v. 21, [s.n.], p. 182-189, 2016.
- [4] OWAIS, A.; GEPREEL, M. A. H.; AHMED, E. Production of electrolytic zinc powder from zinc anode casing of spent dry cell batteries. **Hydrometallurgy**, Amsterdam, v. 157, [s.n.], p. 60-71, 2015.
- [5]. KARNCHANAWONG, S.; LIMPITEEPRAKAN, P. Evaluation of heavy metal leaching from spent household batteries disposed in municipal solid waste. **Waste Management**, Amsterdam, v. 29, n. 2, p. 550-558, 2009.
- [6] XARÁ, S. M.; ALMEIDA, M. F.; COSTA, C. Life cycle assessment of three different management options for spent alkaline batteries. **Waste Management**, Amsterdam, v. 43, [s.n.], p. 460-484, 2015.
- [7] DEEP, A. et al. A facile chemical route for recovery of high quality zinc oxide nanoparticles from spent alkaline batteries. **Waste Management**, Amsterdam, v. 51, [s.n.], p. 190-195, 2016.
- [8] MA, Y. et al. Reclaiming the spent alkaline zinc manganese dioxide batteries collected from the manufacturers to prepare valuable electrolytic zinc and LiNi_{0.5}Mn_{1.5}O₄ materials. **Waste Management**, Amsterdam, v. 34, n. 10, p. 1793-1799, 2014.
- [9] KOMILIS, D. et al. The influence of spent household batteries to the organic fraction of municipal solid wastes during composting. **Science of Total Environment**, Amsterdam, v. 409, n. 13, p. 2555- 2566, 2011.
- [10] CÂMARA, S. C. et al. Simulation of natural weathering of zinc-carbon and alkaline batteries. **Química Nova**, São Paulo, v. 35, n. 1, 2012. Não paginado.
- [11] NOGUEIRA, C. A.; MARGARIDO, F. Selective process of zinc extraction from spent Zn-MnO₂ batteries by ammonium chloride leaching. **Hydrometallurgy**, Amsterdam, v. 157, [s.n.], p. 13-21, 2015.
- [12] KIM, T. H. et al. Reductive acid leaching of spent zinc-carbon batteries and oxidative precipitation of Mn-Zn ferrite nanoparticles. **Hydrometallurgy**, Amsterdam, v. 96, n. 1/2, p. 154-158, 2009.
- [13] SAYILGAN, E. et al. A review of technologies for the recovery of metals from spent alkaline and zinc-carbon batteries. **Hydrometallurgy**, Amsterdam, v. 97, [s.n.], p. 158-166, 2009.
- [14] QUINTANILHA, C. L. et al. Recovery of manganese and zinc via sequential precipitation from spent zinc-MnO₂ dry cells after fusion with potassium hydrogensulfate. **Journal of Power Sources**, Amsterdam, v. 248, [s.n.], p.596-603, 2014.