**Processing of spent zinc-MnO2 dry cells in various acid 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 oC 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) striping 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.

**RESULTS AND DISCUSSION**

**Composition of the dried electroactive components**

Table 1 presents the average composition of the solid after milling and drying the active components of spent zinc-MnO2 dry cells. It must be emphasized that lead has been found in detectable amounts only in Brazilian Leclanché cells.13,22,45

**Leaching results**

The reproducibility of leaching was determined to be about ± 4%. Manganese and zinc were leached with high yields (> 95 wt.%, Table 2) after 1 h (HF) or 3 h (HCOOH and H2SO4). These results are comparable to the best ones reported in the literature20 using strong acids. Leaching with H2SO4 was somewhat longer than the average time reported in the literature,5,7,14,16 but temperature was higher in such studies (40-90 oC) than in the present work and carbon was not eliminated.

Iron and aluminum were especially leached by HF probably due to formation of complexes36,44 such as [AlF6]3- and [FeF6]3-). Calcium, barium and lead were not found in HF and H2SO4 leachates because their fluorides/sulfates are insoluble or very sparingly soluble in water.36,37,44 Soluble silicon (as [SiF6]2- ions) was found when HF + H2O2 was the leachant.36,37,44

**CONCLUSIONS**

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 oC) 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.