

Characterization of used alkaline batteries powder and analysis of zinc recovery by acid leaching

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Abstract

This paper discusses the spent alkaline batteries characterization and leaching stage experiments results with sulfuric acid as leachant, as part of a complex system, involving purification and electrolytic stages, aiming the Zn recovery. After dismantling batteries by mineral processing techniques, the black powder sample produced was submitted to X-ray diffraction and atomic absorption spectrophotometry in order to identify its composition. Batch laboratory experiments were conducted for acid leaching procedure to determine appropriate leaching conditions from the viewpoint of maximum zinc extraction. On these tests an amount of dry powder was added to sulfuric acid at different conditions and after leaching and filtration, the aqueous solutions were submitted to atomic absorption spectrophotometry analysis to verify the Zn content. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the last 30 years the amount of domestic refuse and industrial waste has continuously risen. The growth of world population and demand for a higher standard of life increase the consumption of raw materials and waste produced. The large amount of waste is a true problem everywhere. The storage capacity of landfills and special waste dumpsites is limited, and the disposal costs become very high. Therefore, concepts of reutilization and recycling of materials are appearing in order to minimize the wastes. Wastes often offer economical benefits to industries through the reuse of possible valuable materials present in them. In other words, minimizing production costs through substitution of raw materials by cleaned recyclable products leading to the preservation of raw materials, and must be a goal for our society, since the resources on earth are limited and recycling means their preservation as well as environmental protection.

Large amounts of materials which are considered waste could be recovered. Recycling rates for commonly used materials are growing in many industrial countries. Most of them, such as Japan and Germany have created successful

official recycling programs with collection centers located across the country. The community participates in the program involving separation of household refuse in many countries such as Europe, Japan and United States.

The features of the batteries make them an efficient portable power source. Different sizes and models are available. The consumption of batteries has increased because of the versatility, low maintenance, reduced cost and its requirements by the electronics industry. The average battery consumption per year in Brazil is approximately 759.5 million units and the manufacturer's sales forecast of alkaline type is about 25–30% of the total of consumed batteries [1]. In comparison with zinc–carbon and Leclanché types, alkaline batteries offers best performance due to its lower discharge rate with a useful life of five to six times higher than that of zinc–carbon battery. One manufacturer estimates that 30% of the household batteries sold in the world today are zinc–manganese dioxide alkaline batteries [2]. In USA, for instance, sales of zinc–carbon cells are decreasing and alkaline type dominates the market for primary batteries [3].

All battery components contribute to the pollution of the environment when improperly discarded mainly due to the metallic content, being considered as hazardous waste. The results of toxic metals analysis found in solid wastes in USA forecast that spent batteries are going to be the main source

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of metals in solid waste by year 2000 [4]. In Brazil, the final disposal for spent batteries include sanitary and industrial landfill for hazardous waste respectively for domestic and industrial waste, and an environmental law was recently approved regarding the responsibilities that manufactures of batteries must have for collection and disposal of used batteries. This obligation must be extended to minimize waste production and also the amount of toxic substances added inside the batteries.

Currently, the manufacturers dispose off all waste batteries removed from manufacturing plants in industrial landfills. However, the major manufactures are making efforts to minimize and remove toxic metals from batteries.

The collection of used batteries could be made by separating them from household wastes. Unfortunately, there is no systematic collection scheme in some countries and no method for sorting if they are collected. Sometimes this task cannot be feasible due to educational problems and economical concerns. One way of reducing the solid waste volume of discarded batteries is by using rechargeable (secondary) alkaline batteries, which can be recharged and consequently giving a life cycle greater than the non-rechargeable type. Battery manufacturers explain the advantages of this kind of batteries, which can be reused many times before discarding. However, the disposal concern remains to be figured out.

2. Recycling process for spent household batteries

Some of the battery components are organic, such as paperboard and carbon/graphite and do not cause a serious environmental impact. Otherwise, other components, including steel, plastic, zinc and toxic metals are going to increase the volume of a landfill, since they decompose slowly, remaining into the environment. Coarse parts such as steel casings, paper, carbon, brass, and others could be reclaimed by means of mechanical treatment, while the remaining powder, could be treated in a process involving metallurgical procedures, aimed at the recovery of Zn used as the anode in alkaline cells.

Batteries have a great number of components, which can be technically extracted and reused. The recovered component materials proportion offer some advantages in an economical concern meaning that it could be returned to the production of process of the batteries as raw material or be used for other purposes. Plated steel scrap can be marketed in high-density bundles and sold to steel mills; manganese can be sold to the steel industry and recovered zinc to metallurgical industries. While recycling is not still used frequently as a method of solving the problem of spent batteries, the best solution is to dispose them properly in a landfill.

Household batteries are disposed along with other household waste, although used batteries can be considered as secondary raw materials source. Treatment methods had been developed in many countries mainly due to environ-

mental law restrictions regarding to toxic metal content in soil and water stream. Some proposed process for battery treatment has been described by Hurd et al. [5], which have pyrometallurgical and/or hydrometallurgical routes such as INMETCO, Metallurgy 101, MEREKO, SNAM/SAVAM, SABNIFE AB, and RECYTEC.

Recycling and recovering can be an alternative way for solving disposal and treatment problems while decreasing the amount of wastes to be disposed in a landfill and in some cases providing economic savings. Separation of different types of batteries needs some developments and this segregation could select the appropriate treatment and disposal and the proposal of an efficient recycling process. Some techniques are being proposed for recycling this type of waste not only to protect the environment but also to bring economic advantages of recovering metals.

2.1. Hydrometallurgical process

The processing of metals using hydrometallurgical techniques is becoming a well-established and efficient method for recovering metals from raw materials. It is chosen as an extraction process and environmental control as well, since the metal extracted will avoid the waste production. Hydrometallurgy has some benefits compared with pyrometallurgical techniques such as low cost requirements, possible recovery of leachants and decrease of air pollution as there are no particles produced.

While producers had not made efforts to reduce some mercury content, pyrometallurgical operation were the techniques chosen for removing metals from used batteries despite its high costs. Hydrometallurgical processes have contribute to research in metals recovery, and their use have increased, compared to that of pyrometallurgical methods. Many patented processes have already been developed mainly for treatment of dry cell batteries as BATENUS for a mixture of batteries [6], PLACID, for mercury recovery [7], RECYTEC for simultaneous recovering of zinc and manganese dioxide [4] and HYDROMETAL SPA [8] for lead-acid batteries.

This study proposes the use of hydrometallurgical process for the treatment of batteries. The soluble portion (dry powder), resulting from mechanical treatment and isolated from others coarse components, was chosen to be treated as it contains the metals. The metals recovery proposition includes as first stage an acid leaching procedure followed by purification step to remove impurities, such as iron, and in sequence the metals recovery from aqueous solution through electrolytic deposition step.

3. Household batteries — alkaline type

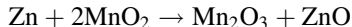
Household batteries are those used to power small and portable devices as flashlights, radios and toys and approximately 90% of the battery-operated devices require AA, C or

D battery sizes. The zinc–carbon and alkaline batteries are included in this group as non-rechargeable batteries (primary cells), which are designed to be fully discharged only once, and then discarded.

The alkaline cell uses the same electrochemical system of zinc–carbon/Leclanché cells, with zinc and manganese dioxide as anode and cathode, respectively. The alkaline cell only differs from the latter one as that includes a strong electrolyte of KOH (potassium hydroxide) solution. The anode contains powdered zinc with corrosion inhibitor and the compacted cathode of manganese dioxide is mixed with carbon/graphite and acetylene black. The electrolytically produced manganese dioxide used in alkaline batteries provide capacity and higher reactivity than the natural ores used for the cathode in zinc–carbon battery.

The cell is totally enclosed in a high-density steel can with both edges covered with plated steel. A separator made from non-woven fabric is used inside to separate the anode and cathode from electrolyte solution. An asphalt insulator is added to prevent any leakage from batteries and an adhesive plastic coated is added for finishing operations. An average initial composition of alkaline batteries is given in Table 1 [9].

During discharging, batteries change their previous chemical formulations resulting from anode and cathode reaction mechanisms. The overall chemical reaction could be expressed as



This is the most probable reaction but sometimes the products may change depending on the battery discharging conditions [10].

The metal zinc is one of the most important components in batteries, being used as anode due to its electrochemical features and low costs. For alkaline cells, zinc is used in powdered form and must be of high purity (99.85–99.00%) and it is usually produced by electrowinning or distilling. Otherwise, zinc has limited natural sources on earth. Data from US Bureau of Mines inform that zinc mineral supplies will be exhausted in about 20–40 years worldwide. Compared to its other uses, as in alloys and protection of steelwork, the amount of zinc used in the production of batteries is small. Therefore, approximately 16% of Zn included in each battery, which means 18% of world production [11].

Table 1
Alkaline battery average formulation

Battery component	Percentage
Manganese electrolytic	32–38
Graphite	3–5
Zinc	11–16
Steel	19–23
Potassium hydroxide	5–9
Barium sulfate	<5
Water, paper, plastic, other	Balance

4. Experimental studies

The experimental study made use of a mixture of different sizes of spent cylindrical alkaline batteries (AAA, AA, C, and D) from different manufacturers, supposing a similar feature of the waste batteries in found the wastestream.

4.1. Pre-treatment

The used batteries were treated by applying mineral processing methods to provide the fine powder for experimental procedure.

First, the batteries were fed to a hammer mill for dismantling. Magnetic separator removed the magnetic fractions; the non-magnetic fraction was screened in sieve with openings of 10 mesh (2.0 mm). The coarse fraction was separated while the undersize portion was picked up and dried to be submitted through next treatment stages. A second magnetic separation was carried out to remove the ferrous materials, which remains in the sample. In sequence, this last non-magnetic fraction was added to a ball mill for increasing the size reduction and afterwards screened in sieve with openings of 65 mesh (0.208 mm). The undersize portion was carefully sampled. The sampling methodology was made by using of a Jones riffle, consisting of an assembly comprising an even number of equally sized chutes, adjacent chutes discharging at opposite sides, and the divided portion was used for characterization and leaching tests.

The sample was submitted to X-ray diffraction method and atomic absorption spectrophotometry to qualitative and quantitative analysis, respectively.

4.2. Batch laboratory leaching tests

A series of batch laboratory leaching tests was conducted to define the efficiency of Zn extraction. Different conditions of solid/liquid ratio (weight sample/leaching solution volume), temperature, sulfuric acid concentration and leach times were chosen for this purpose. These experiments were conducted as one stage of a more complex hydrometallurgical process aimed at the recovery of zinc and manganese present in this kind of battery.

In the bench scale leaching process, dry powder was fed into a glass vessel, containing dilute sulfuric acid. A magnetic variable mixer with heating system was available to provide a good contact area between sample and leaching solution and temperature control as well. pH and temperature were monitored with a bench pH meter and a simple mercury thermometer. After leaching test, the leached suspension was filtered with paper filter in Büchner funnel. The solid residue, which is composed of manganese dioxide, graphite and other metals, remained in the paper filter. This was recovered and subsequently dried. The filtrate was a clean liquid with Zn soluble in a zinc sulfate (ZnSO₄) form.

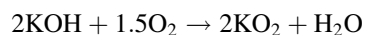
Tests were carried out at temperatures between 25 and 50°C. Sulfuric acid concentrations in the range of 0.3–0.7% were used in compliance with zinc hydrometallurgy. The pH observed at some other different conditions had variable values between 1 and 5. A total leach time in the range 1–3 h were used for these experiments.

5. Results and discussion

5.1. Characterization

The resulting X-ray diffraction spectrum is shown in Fig. 1 and the quantitative composition determined by atomic absorption spectrophotometry is shown in Table 2.

As the discharge overall reaction suggest, the electrolyte KOH is non-variant and zinc oxide is being formed as the solid reaction product. The quantitative analysis results revealed a potassium oxide form (KO₂ — named potassium superoxide or peroxide). The existence of superoxides of alkali metals was reported by Volv'nov [12]. The author observed the formation of potassium superoxide via the reaction of KOH and atomic oxygen:



The oxidation of KOH might occur during the mechanical treatment procedure and dehydration steps, when dismantled batteries are being handling and in contact with atmosphere.

In the commercial batteries, the mercury content was kept between 4 and 8% in the past [13], but nowadays the trend is to lower the concentration. The major producers inform that they are manufacturing batteries with a “mercury-free” formula. The small amount of Hg and Cd found in the

Table 2

Average composition of dry powder from alkaline batteries after dismantling

Compounds	Composition (wt.%)
ZnO	25.6
Mn total	44.2
KO ₂	8.6
Fe ₂ O ₃	1.4
Pb total	0.06
Hg total	0.0001
Cd total	0.000006
Others miscellaneous parts ^a	20.5

^a Graphite and acetylene black are included.

sample's analysis go toward the producer's information about their compromise in eliminating these toxic metals from alkaline batteries, while maintaining the features that the consumers demand. Otherwise, there is no information available from the manufacturers regarding the Pb content in alkaline batteries, but is also known that often 0.04–0.06% is added in zinc powder anode formulation in order to prevent zinc corrosion [14]. The battery producers do not mention about Pb either in a toxicity perspective, or as a trend to eliminate it from the composition of alkaline batteries. The Pb content found in the sample analyzed could also be originated as one of the impurities in the electrolytic manganese dioxide used as cathode.

The iron oxide content observed in the results might have its origins either from the friction of the whole batteries with mill hammers in the crushing stage, producing small particles of ferrous material, which caused the contamination of the sample or from corroded or oxidized batteries, due to its storage conditions. Furthermore, cell component parts of batteries such as steel, which probably

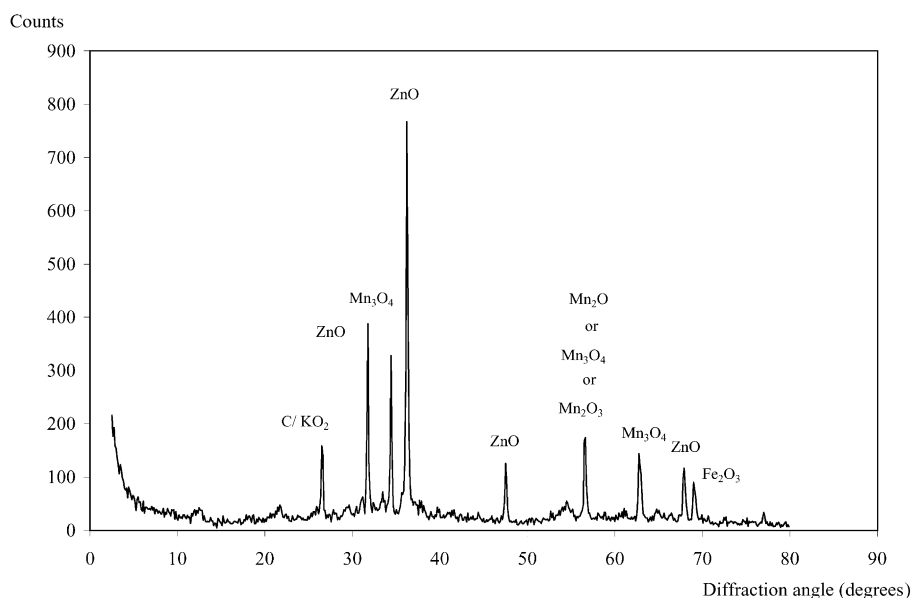


Fig. 1. X-ray diffraction spectra of dry powder from spent alkaline battery.

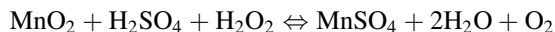
had shredded in the mechanical treatment process, remained as fine particle.

The mechanism of the cathode reaction in the alkaline MnO_2 -zinc system was studied and the results are presented in a series of papers, as described by Heise and Cahoon [15]. Some authors examined the cathode reaction and found different stages in the cell discharge with electrolytic MnO_2 , developing different manganese oxide phases. Others report that the electrochemical oxidation of the electrode could be affected by electrolyte concentration, consequently reducing MnO_2 to a different species. The forms of manganese oxides detected in the sample by X-ray diffraction analysis are in agreement with these observations, and these results stress that complex reaction mechanism during the discharge process still needs further information and elucidation.

5.2. Leaching process

5.2.1. Different chemical reactions

In the leaching stage, the following reactions may occur during the dissolution process at dilute sulfuric acid concentrations:



The analysis of the filtrate remaining after filtration stage revealed that Mn, K, and Fe were also leached with zinc. Zinc oxide is readily soluble in dilute sulfuric acid and the tests could be probably carried on a lower temperature and shorter leaching time if only this element was soluble; however, the zinc extraction can be affected by the presence of other elements since there are different chemical reactions occurring concurrently with sulfuric acid and contesting with each other. Otherwise, the amount of sulfuric acid remained was enough to react with the majority of compounds.

5.2.2. Acid solution concentration

Zinc is currently produced hydrometallurgically on a continuous scale by industry. Zinc ores must be roasted and treated by acid leaching with sulfuric acid. The tests were carried on using four sulfuric acid concentration: 0.3, 0.4, 0.5 and 0.7% (vol.%). These concentrations were chosen since the leaching stage with dilute sulfuric acid in a concentration range of 0.3–0.5% is commonly used to dissolve ZnO compounds originated from roasting process stage in compliance with zinc metallurgy [13]. The increase of Zn extraction was observed with increasing sulfuric acid

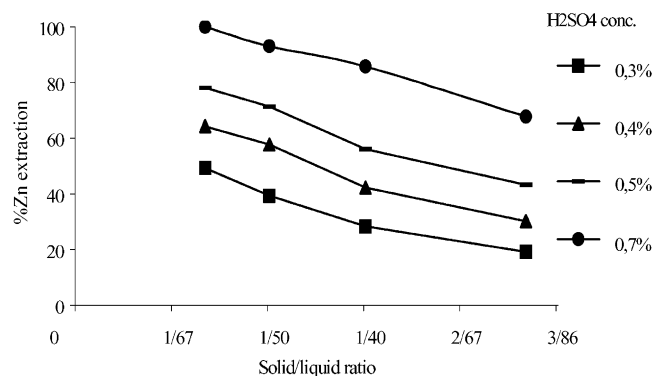


Fig. 2. Zinc extraction behavior for dilute acid concentration and solid/liquid ratio (test conditions: temperature = 50°C, time = 2 h).

concentrations, as shown in Fig. 2. At lower acid concentrations, the efficiency of Zn extraction is low. The alkaline battery black powder has compounds other than ZnO, which probably can cause a decrease on the active contact surface with the solvent, making dissolution of Zn difficult at lower concentrations, usually recommended in literature on zinc. Dilute acid concentrations were used for Zn extraction with good extraction efficiency, reaching up to 100% of zinc in a solid/liquid ratio of 1/60 for 0.7% sulfuric acid concentration.

5.2.3. pH

Zinc extraction increases with a decrease of pH in any leachant concentration and solid/liquid ratio. The potential–pH equilibrium diagram for the zinc–water system (Pourbaix diagram) [16] can predict the existence of the various chemical species and it shows that Zn^{2+} are readily dissolved for pH up to 5.5. On these bench-leaching experiments, the pH did not exceed this value, with good results of Zn extraction: the increase is much more evident at low end-points pH.

5.2.4. Temperature

At higher temperatures the zinc extraction increased, as shown in Fig. 3. From these results, it can be seen that temperatures above 50°C do not have any influence on Zn

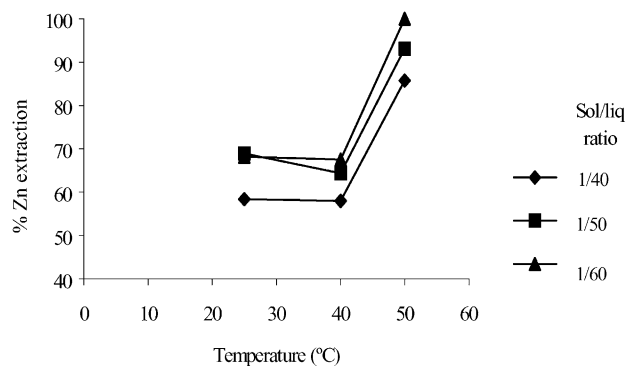


Fig. 3. Relationship between temperature and zinc extraction (test conditions: H_2SO_4 concentration = 0.7%, time = 2 h).

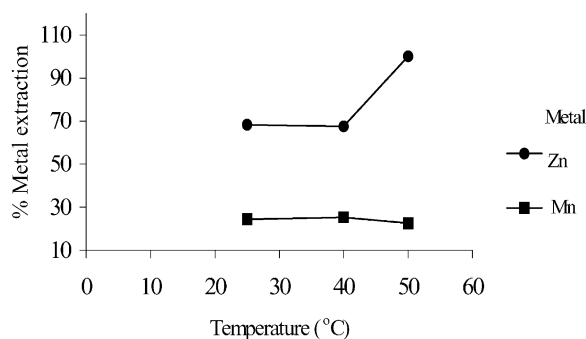


Fig. 4. Comparison between zinc and other elements leached (test conditions: H_2SO_4 concentration = 0.7%, time = 2 h, solid/liquid ratio = 1/60).

extraction, since a great amount of Zn was extracted up to this temperature. As observed by Gilchrist [17], and noticed from the experiments, the ambient temperature leaching is inherently slow and the rate of the chemical reaction involving zinc increases and so its solubility increase as the temperature is raised. The amount of ZnO leached increase with increasing the solid/liquid ratio, but on the other hand, the increase on the solid/liquid ratio also causes leaching of other undesirable compounds.

5.2.5. Time

Batch leach data for dry powder indicate the increase of zinc extraction with time for leaching times up to 3 h. The leaching rate increases, since the concentration of the product increases with time as the concentration of the reactant decreases.

5.2.6. Effect of manganese

Manganese is also dissolved into solution to almost 30% (Fig. 4). This might be due to two reasons. (a) The presence of a reduction agent, hydrogen peroxide, H_2O_2 , produced by reaction of the superoxide KO_2 with water and acid. So MnO_2 is the main manganese compound in the sample, and manganese dioxide compounds can be attacked readily by this reducing agent at any sulfuric acid concentration. (b) The possible reaction of sulfuric acid with other manganese compounds as Mn_2O_3 and Mn_3O_4 . Further, these two reactions can take place either simultaneously or not.

6. Conclusions

The battery manufacturers have progressed in mercury and cadmium reduction; however, other metals as lead and zinc still remain in consumer batteries disposed off in the wastestream. The cumulative amount of these metals in the environment caused by conventional disposal procedures as landfilling still need special attention. Not only the environmental public groups, but also the industries and government must join their forces to find solutions to the issues

concerning used disposal of batteries and also feasible and cost-effective recycling and recovering process.

This paper discusses and demonstrates the use of acid leaching as a zinc recovery process from batteries dry powder. A bench scale leaching process was developed and the results of the experimental study indicate that leaching with dilute sulfuric acid is suitable for recovering Zn by considering as variables: (a) the acid concentration; (b) the temperature of the leaching solution; (c) the solid/liquid relation during leaching; and (d) the process time. The dilute sulfuric acid at lower concentration is capable of dissolving ZnO with the increase of temperature and leaching times with a high solid/liquid ratio. The bench scale leaching process aimed at Zn extraction is feasible with removal of almost 100% of Zn as soluble form ZnSO_4 . A purification step is necessary to remove the impurities from the solution as Fe contents. Afterwards, a second leaching stage can also be proposed both for manganese extraction into soluble form and an electrolytic deposition process stage for Zn and Mn metal recovery. This analysis is not developed in this paper but can be explored in future studies.

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