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RECOVERY OF MANGANESE AND ZINC FROM SPENT Zn-C AND ALKALINE BATTERIES IN ACIDIC MEDIUM

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The anode and the internal paste of spent Zn-C and alkaline batteries were leached with 2 mol L^{-1} H_2SO_4 at 80 ^oC for 2 h. Solid/liquid ratio was 1/10 (g mL^{-1}). The leachate was treated with Na_2S in order to precipitate Hg, Cd and Pb. Zn was quantitatively isolated at pH 1,5-2 by adding Na_2S. Mn can be precipitated at pH close to 7. Na_2S may be replaced by oxalic acid. Zn precipitated at pH around 0, whereas Mn was quantitatively recovered at pH ≥ 4. Acidity control is a critical parameter. Na_2SO_4 and carbon are the end products.

Keywords: zinc; manganese; spent batteries.

INTRODUCTION

Two great demands for portable sources of energy arose in the XXth century: the arrival of the portable radio in the 1920s and the burst of small electroelectronic devices since the 1980s. This second reason explains why batteries are widely used nowadays. For instance, alkaline and zinc–carbon batteries are used in radios, recorders, toys, remote controls, watches, calculators, cameras, and in many other objects where small quantities of power are required. These batteries are not rechargeable and must be replaced from time to time.

Brazil produces around 1,2 billion batteries per year,[1] whereas China's production surpasses 15 billion batteries.[2] The great demand for batteries in Brazil began in the 1970s. The Brazilian market is nowadays dominated by Zn-C batteries (70%), the first ones to be produced in the country since 1951, whereas the alkaline batteries began to be produced in 1978.[3] In the United States and Europe alkaline batteries are predominant (over two thirds of the overall market).[2,3] On an average basis, 6 batteries per person are consumed in Brazil, whereas this consumption reaches 10-15 units in developed countries.[2]

Most Zn-C and alkaline batteries are landfilled or even incinerated in Europe.[4-6] More than 1 billion spent batteries are discarded every year in Brazil and South Korea.[3,7] In November 2008 a new directory for batteries was approved (Directory 401 from the National Brazilian Environmental Council).[8] It is in force since July 2009 and is very close to the European Directory 2006/66/EC. It states that if the amount of Hg, Cd and Pb in each battery is below 0,0005, 0,010 and 0,20 wt %, respectively, this battery may be discarded in licensed municipal landfills. However, only a little more than 10% of Brazilian municipalities present licensed landfills. Since collection of spent batteries is still incipient in the country, most of them are discarded improperly in the environment. Simulation of natural leaching of spent batteries disposed of in landfills[5,9] demonstrates that spent batteries can impact the environment due to the release of zinc and manganese and the change of the pH of ground. These materials should be regarded as dangerous wastes. Incineration is also not a good practice. Recent studies demonstrate that they may release mercury, zinc and lead to the atmosphere.[6]

Perhaps the definite solution to the question of spent batteries (as well as other spent materials such as waste electrical and electronic equipment (WEEE) and catalysts) is to develop recycling processes for these materials. The known zinc reserves will be depleted in 20-40 years.[10,11] The price of this metal has reached record values in the last years.[12] Therefore, this material could be regarded as a secondary source of this metal (as well as manganese).[2,7,12] Literature shows that much attention has been paid to processing of spent alkaline and Zn-C batteries in the last 5 years.

Classical (and commercial) recovery methods applicable to spent batteries are pyrometallurgical ones. They are simple and do not require battery dismantling, but are high energy consuming, may release toxic gaseous effluents and are not as versatile as other recovery methods.[2] Most laboratory studies have been employing hydrometallurgical routes. These processes require more steps and consumption of chemicals and also generate final liquid effluents.[2,7,13] Sulfuric acid is the most employed leachant. It has been demonstrated that this acid is more efficient than hydrochloric acid.[14] It may be employed alone,[2,4,15] where zinc is preferably leached over manganese, or together with a reductant: H_2O_2,[1,2,7,13] SO_2,[13] oxalate[16] or carbohydrates.[17] In this case, manganese is reduced from + 4/+3 to + 2 state (Mn^{2+}, soluble and stable in acidic medium). Leaching of these two elements is usually high (> 95 wt %). Recovery of both metals can be accomplished by several methods. Liquid-liquid extraction has been cited as suitable to recover zinc from acidic solutions.[2,14] Electrowinning and classical precipitation methods are also alternatives.[2,15] This latter technique is relatively simple and cheap. However, metals present in small amounts may influence the purity of final products. The most current way is to treat the acidic leachate with strong alkali base (KOH or NaOH), keeping the pH above 13. Manganese precipitates as $Mn(OH)_2$, which is readily oxidized to $MnO(OH)_2$, whereas zinc remains soluble as $[Zn(OH)_4^{2-}]$ ions. Separation in acidic medium is relatively difficult because most manganese/zinc salts present about the same solubility.[1]

Besides acid leaching, another leaching procedure is based on the use of aqueous NaOH. Zinc is solubilized to a considerable extent (80-90 wt %), whereas manganese remains in the solid residue together with other metal impurities and some zinc.[3,13] Alternatively, the whole battery may be worked in a process called vitrification:[18] spent alkaline batteries are transformed into inert substances. This process allows recovery of iron, manganese and zinc.

In the present study, leaching with sulfuric acid was performed in order to solubilize as much as possible all metals present in the anode and the internal paste of spent alkaline and Zn-C batteries. Recovery of the main metals (Mn and Zn) and other elements present in small amounts (particularly iron, usually the major contaminant of the leachate[16]) was performed by a three-step separation procedure in acidic medium. The overall route presented in this work was compared to those published in the literature about the processing of spent batteries in acidic medium.

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EXPERIMENTAL

Raw materials

Twenty spent AA alkaline (two manufacturers) and twenty spent AA Zn-C batteries (two manufacturers) were employed in this work. The AA format is the most current size employed in Brazil. Their expiry date was between August-December 2008. Samples were manually dismantled (using gloves, glasses and dust masks) in order to recover the internal paste and the anode. Other components such as plastic and paper films, ferrous and non-ferrous scraps were identified and separated.

Leaching of the anode + internal paste

The mixed material was ground for 30 min by a ball mill. A fraction of the final mass was dried for 24 h at 40 ºC in order to measure humidity by weight difference.

Leaching was performed at around 80 ºC under magnetic stirring (200 rpm) with 2 mol L^{-1} sulfuric acid for 2 h. 10 g of the solid were mixed with 100 mL of the acidic solution (solid/liquid ratio 1/10). H_2O_2 (30 wt %) was added from time to time to reduce Mn(IV) to Mn(II). It also converts Fe(II) to Fe(III). Water was added during leaching to keep volume constant.

The dark insoluble residue was separated from the leachate by filtration and washed with deionized water (5 mL g^{-1} solid). This solid was dried for 3 h at 110 ºC and weighed, after which it was calcined (600 ºC, 3 h). The ash was analyzed for metals.

Metals separation

2 mol L^{-1} sulfuric acid was added to adjust free acidity to 1.1 mol L^{-1}. The leachate was then treated with 2 mol L^{-1} Na_2S at 90 ºC, added dropwise, under stirring (200 rpm). A black powdered solid was obtained, which was filtered and washed. The solution presented a pale-pink color, due to Mn^{2+} ions. The pH was adjusted to 1.8 by adding 12.5 mol L^{-1} NaOH. 2 mol L^{-1} Na_2S was added dropwise at 90 ºC under magnetic stirring (200 rpm). pH must be kept between 1.5-2.0 by adding 2 mol L^{-1} H_2SO_4 from time to time (a pH meter was used during the experiments). A white precipitate was obtained and filtered. H_2O_2 (30 wt %) was added to oxidize residual sulfide ions to sulfate species. The new filtrate was treated at room temperature (200 rpm) with 12.5 mol L^{-1} NaOH in order to adjust pH to 7. Manganese precipitated as $Mn(OH)_2$. It was converted to $MnO(OH)_2$ after addition of H_2O_2 (which also oxidized soluble Mn^{2+} to MnO_2). The brown solid was filtered and washed (5 mL g^{-1}) to remove Na^+ and SO_4^{2-} ions. Figure 1 presents the overall scheme for processing metals in the leachates.

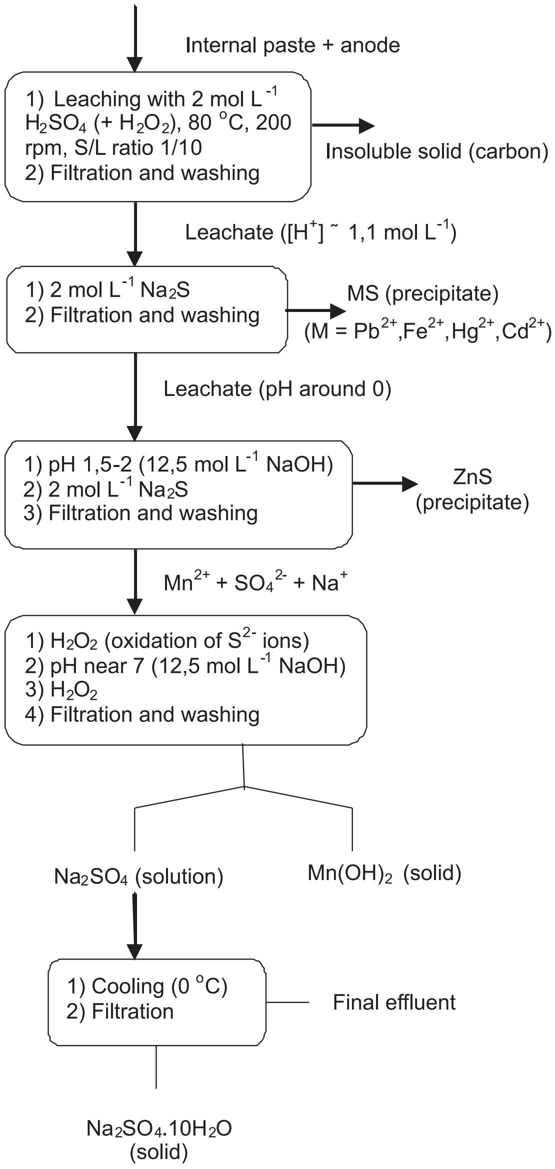

Figure 1. *General scheme for recovery of Zn, Mn and other metals from spent Zn-C and alkaline batteries after leaching with 2 mol* L^{-1} H_2SO_4 *(+* H_2O_2*)*

Analytical methods

The whole spent battery, the components obtained during sample dismantling and the solids obtained during leaching and separation steps were weighed in an analytical balance. Solubilized metals (Mn, Zn, Fe, Pb, Cd and Hg) were analyzed by ICP-OES spectrometry. The Zn-C and alkaline battery powders, the ash isolated after calcining the insoluble matter in H_2SO_4 and the solids obtained during separation procedure were also analyzed by x-ray fluorescence (XRF).

RESULTS AND DISCUSSION

Composition of batteries

The average composition of the batteries is shown in Table 1. These results are in agreement with composition data found in the literature.[2,3,12,13] After drying the anode + internal paste at 40 ºC the mass was reduced from 10.00 to 7.98 g for Zn-C batteries (loss of mass 20.2 ± 0.5 wt %) and from 10.06 to 8.26 g for alkaline ones (loss of mass 17.9 ± 1.1 wt %). This last result is consistent with previous studies on moisture content in the components processed in this study.[2]

Leaching of internal paste + anode

Table 2 presents metals concentration in the leachates. Data for manganese and zinc are comparable to other literature studies.[2,16] The amount of manganese is higher in alkaline batteries, whereas zinc is more abundant in Zn-C ones.[2] The amount of iron is relatively low. This result agrees with literature data,[2,16] but it must be emphasized that no appreciable corrosion of the external case (made of steel) was found in the samples examined. Therefore it is worth processing spent batteries as quickly as possible since introduction of high amounts of iron due to corrosion of the external case in the anode + internal paste is unavoidable. This makes zinc and manganese recoveries more difficult due to chemical interference.[2]

Table 1. Masses (g) of the spent AA batteries and their components

Battery type	Whole battery	Internal paste + anode*	External case	C or metal rod	Other components	Losses
Alkaline I	22.89 ± 0.13 (100 wt %)	10.00 ± 0.80 (43.7 wt %)	11.65 ± 0.84 (50.9 wt %)	0.20 ± 0.01 (0.9 wt %)	0.99 ± 0.05 (4.3 wt %)	- (0.2 wt %)
Alkaline II	23.93 ± 0.33 (100 wt %)	10.06 ± 0.53 (41.8 wt %)	12.22 ± 0.99 (51.1 wt %)	0.16 ± 0.02 (0.7 wt %)	1.46 ± 0.09 (6.1 wt %)	- (0.3 wt %)
Zn-C I	17.92 ± 0.27 (100 wt %)	10.90 ± 0.30 (60.8 wt %)	6.00 ± 0.21 (30.5 wt %)	0.94 ± 0.07 (5.2 wt %)	0.59 ± 0.11 (3.3 wt %)	- (0.1 wt %)
Zn-C II	18.23 ± 0.03 (10 wt %)	11.55 ± 0.73 (63.4 wt %)	6.50 ± 0.33 (25.5 wt %)	0.96 ± 0.87 (5.3 wt %)	1.02 ± 0.10 (5.6 wt %)	- (0.2 wt %)

*before drying at 40 °C

Table 2. Metallic ions in the leachates

Battery type	Mn^{2+} (g L^{-1})	Zn^{2+} (g L^{-1})	Fe^{3+} (mg L^{-1})	Pb^{2+} (mg L^{-1})	Cd^{2+} (μg L^{-1})	Hg^{2+} (μg L^{-1})
Alkaline I	36.4 ± 0.9	16.2 ± 0.5	3.4 ± 0.4	1.8 ± 0.4	35.1 ± 0.2	7.8 ± 0.2
Alkaline II	34.2 ± 0.3	16.8 ± 0.8	1.6 ± 0.7	2.0 ± 0.6	40.2 ± 0.3	8.6 ± 0.3
Zn-C I	27.2 ± 0.3	17.2 ± 0.4	12.0 ± 0.5	9.8 ± 0.3	49.2 ± 0.3	3.0 ± 0.4
Zn-C II	29.2 ± 0.6	17.2 ± 0.7	10.7 ± 0.8	9.1 ± 0.2	43.2 ± 0.5	3.8 ± 0.4

Table 3. Average metals composition (wt %) of the sulfides precipitated at pH ≈ 0

Battery type	Pb	Cd	Hg	Fe	Zn	Mn
Alkaline I	34.5	0.7	0.2	64.1	0.4	negligible
Alkaline II	55.7	1.1	0.3	42.9	< 0.1	negligible
Zn-C I	45.8	0.2	< 0.1	54.0	< 0.1	negligible
Zn-C II	48.4	0.4	< 0.1	50.6	0.5	negligible

The insoluble residue after leaching with sulfuric acid is essentially carbon. It corresponds to 25.0 ± 0.8 wt % of the internal paste + anode after drying and 20.0 ± 0.3 wt % before this step in all samples studied. After calcining this solid, the ash recovered corresponds to 1.2 ± 0.3 wt % of the dried mass. XRF showed the presence of manganese and zinc only. The Mn/Zn mass ratio is about 2.1 (alkaline batteries) and 1.7 (Zn-C batteries). This result agrees with the mass ratio found in the leachates (Table 2). On the other hand, the amount of zinc and manganese present in the ash corresponds to less than 1 wt % of the amount present in the leachates.

This result confirms that sulfuric acid is a good leachant to treat spent batteries, as stated in the literature.[2,15] However, this is only true if manganese is solubilized via conversion to Mn(II) by adding a reducing agent.[1,7,13,16,17] Otherwise, manganese leaching is partial. In separate experiments leaching was performed under the conditions described in the experimental section, except that no hydrogen peroxide was added. Manganese leaching reached only 25 ± 2 wt %, about ¼ of the yield obtained when the reducing agent was added. Leaching of all other metals was also lower in the experiments without hydrogen peroxide, as already shown in the literature.[13] Under these circumstances neither the leachate nor the solid residue can be regarded as raw material for zinc and manganese recoveries, respectively. Other metals are present, requiring further separation (precipitation) steps. This effort is concentrated only in the leachate when a reducing agent is employed. The free acidity of the leachates is 1.06 ± 0.02 mol L^{-1}.

Separation of metals in the leachates

As seen in Figure 1, the first step is the precipitation of a dark solid. XRF showed the presence of Pb and tiny amounts of Zn, Cd, Fe and Hg (Table 3). Manganese was not found in this precipitate in all samples.

Iron and lead are the most abundant metals in the leachates after zinc and manganese (Table 2). Despite their low amounts in the leachates, Hg and Cd sulfides (as well PbS) present very low K_{sp} values (below 10^{-27}), belonging to the group of the acid-insoluble sulfides. Iron was reduced to +2 state by sulfide ions, being precipitated thereafter. More than 90 wt % of iron was removed in this precipitate.

$$M^{2+} + H_2S \rightarrow MS\downarrow + 2\,H^+ \;(M^{2+} = Pb^{2+}, Cd^{2+}, Hg^{2+}) \qquad (1)$$

$$2\,Fe^{3+} + 3\,H_2S \rightarrow FeS\downarrow + S\downarrow + 6\,H^+ \qquad (2)$$

The absence of manganese is reasonable since K_{sp} of its sulfide is much higher than that of ZnS.[19] pH of 2 mol L^{-1} Na_2S is around 14, so its addition to the leachate tends to increase pH which is deleterious to the separation scheme shown in Figure 1. However, only few drops were necessary in this step since metals concentration (Pb^{2+}, Cd^{2+}, Hg^{2+} and Fe^{2+}) is very low in the leachates (Table 2). The pH of these leachates was not significantly modified after precipitation.

Acidity plays an important role on the sulfide ion concentration: the more acidic the solution the lower the concentration of such ions. Only very insoluble sulfides precipitate at very low pH values. Although Mn^{2+} and Zn^{2+} ions are much more abundant in the leachates (Table 2), the K_{sp} of their sulfides cannot be reached at pH 0 with the concentrations given in Table 2.[19] This feature allows removal of almost all metals present in small amounts before recovery of zinc and manganese. This is not possible when conventional precipitation techniques are employed. When zinc is leached by aqueous sodium hydroxide,[3,13] some lead can be solubilized (as $Pb(OH)_4^{2-}$ ions) together with $Zn(OH)_4^{2-}$,[19,20] whereas manganese remains in the solid residue with other elements.

When pH was adjusted to 1.5-2.0 for the second precipitation step, ZnS was isolated with very good purity (Table 4) from all leachates. The remaining soluble iron was precipitated together with zinc, but it did not influence purity of ZnS since iron was mainly isolated (> 95 wt %) in the previous step. When pH was shifted to higher values (up to 5), a mixture of ZnS and MnS was obtained (Table 4). The color of the precipitate changed from white (pH < 2) to pink (pH ≥ 4). Zinc was not completely precipitated at pH below 1.5. It was quantitatively recovered (≥ 99.9 wt %) at pH ≥ 1,5, but manganese precipitation rapidly increased when pH was above 3 (it was quantitatively precipitated only in pH > 7). The purity of ZnS is maximum at pH < 2.

On the basis of the K_{sp} of MnS and ZnS (2×10^{-11} and 2.3×10^{-23}, respectively[19]), and using the expression $[H^+]^2[S^{2-}] = 1.1 \times 10^{-22}$, it is possible to calculate pH where both sulfides dissolve in acidic medium. $[Zn^{2+}]$ and $[Mn^{2+}]$ can be obtained from data in Table 2. For Zn^{2+} (≈ 0.25 mol L^{-1}), $[H^+] = 1.03$ mol L^{-1}, whereas, $[H^+] = 1.8\text{-}2.0 \times 10^{-6}$ mol L^{-1} (pH 5.7) for Mn^{2+} (0.55-0.60 mol L^{-1}). 99.9 wt % Zn^{2+} was precipitated (residual $[Zn^{2+}] = 2.5 \times 10^{-4}$ mol L^{-1}), at pH 1.5. If pH is shifted to 1.9, 99.99 wt % Zn^{2+} was precipitated (residual $[Zn^{2+}] = 2.5 \times 10^{-5}$ mol L^{-1}). From data in Table 4, pH must be in the narrow range 1.5-2.0 in order to isolate Zn quantitatively and with good pu-

Table 4. Amount of metals (wt %)* precipitated by 2 mol L^{-1} Na_2S under constant pH (0.5 to 5)

Metal	pH 0.5	pH 1	pH 1.5	pH 2	pH 3	pH 4	pH 5
Zn	55	97	99.5	> 99.9	> 99.9	> 99.9	> 99.9
Mn	negligible	negligible	negligible	0.1	1	11	43

*Present in the leachates of alkaline and Zn-C batteries

rity. Addition of the precipitating agent must be dropwise to ensure pH control (pH is kept constant by adding H_2SO_4). This procedure also reduces release of toxic gases, H_2S and SO_2 (from oxidation of H_2S by sulfuric acid).

It must be also emphasized that stirring (200 rpm) is essential in order to avoid co-precipitation of MnS. For instance, when stirring was only 50 rpm, manganese content in the precipitate at pH 3 increased six fold.

The acidic solution containing only manganese can be easily processed. H_2O_2 oxidizes the remaining SH^- ions to sulfate species according to the reaction:

$$SH^- + 4\,H_2O_2 \rightarrow SO_4^{2-} + 4\,H_2O + H^+ \tag{3}$$

Addition of 12.5 mol L^{-1} NaOH precipitates manganese(II) hydroxide as follows:

$$Mn^{2+} + 2\,OH^- \rightarrow Mn(OH)_2\downarrow \tag{4}$$

This precipitate is readily oxidized by air:

$$Mn(OH)_2 + \tfrac{1}{2}\,O_2 \rightarrow MnO(OH)_2\downarrow \tag{5}$$

This reaction explains why the solid gets a brownish color along time. Addition of hydrogen peroxide avoids ranging the pH to alkaline zone, where $Mn(OH)_2$ is quantitatively precipitated.[1]

$$Mn^{2+} + H_2O_2 \rightarrow MnO_2\downarrow + 2H^+ \tag{6}$$

$$Mn(OH)_2 + H_2O_2 \rightarrow MnO(OH)_2\downarrow + H_2O \tag{7}$$

From Equation 6, pH tends to decrease as H^+ ions are produced. Hydrogen peroxide reduces Mn(IV) if pH is below 4. Therefore, addition of 12.5 mol L^{-1} NaOH is necessary to keep pH near 7. 99.5 wt % of manganese was isolated. Zinc was not found in this precipitate.

Is it possible to replace sulfide ions?

The first step (Figure 1) of the separation scheme (precipitation of sulfides at pH ≈ 0) is of utmost importance to obtain an acidic solution containing essentially only Mn^{2+} and Zn^{2+} ions. However, it is also clear that the reactant (Na_2S) is very toxic. Therefore it was attempted to replace it by another precipitating anion in the second precipitation step. The key condition is that the difference between K_{sp} of manganese and zinc salts is as great as possible like in the case of their sulfides.

Most salts have close K_{sp} values.[19] However, oxalate ions were investigated as a possible alternative for Zn-Mn separation in acidic medium ($K_{sp}MnC_2O_4$ – 5 x 10^{-6}, $K_{sp}ZnC_2O_4$ – 1.5 x 10^{-9}). Taking into account the K_a values for oxalic acid ($K_{a1} = 1.4 \times 10^{-2}$, $K_{a2} = 5.5 \times 10^{-5}$) and the average concentration of both metals in the leachates (Table 2), it is possible to calculate pH where the oxalates will dissolve in acidic medium:

$$XC_2O_4\downarrow + 2\,H^+ \rightleftharpoons X^{2+} + H_2C_2O_4 \quad (X^{2+} = Zn^{2+}, Mn^{2+}) \tag{8}$$

The equilibrium constant is:

$$K = K_{sp}XC_2O_4/(K_{a1} \times K_{a2}) = [X^{2+}] \times [H_2C_2O_4]/[H^+]^2 \tag{9}$$

From Equation 8, $[X^{2+}] = [H_2C_2O_4]$. Thus

$$K = [X^{2+}]^2/[H^+]^2 \tag{10}$$

$$[H^+] = [X^{2+}]/K^{1/2} \tag{11}$$

All parameters are known, so $[H^+]$ can be estimated in order to avoid precipitation of each oxalate. $[X^{2+}]$ can be obtained from data in Table 2. For Zn^{2+}, $[H^+] = 5.9$ mol L^{-1}, whereas $[H^+] = 0.2$-0.25 mol L^{-1} (pH around 0.6) for Mn^{2+}. Therefore, at pH 0 ($[H^+] = 1$ mol L^{-1}), zinc oxalate precipitates but manganese oxalate does not.

The experimental procedure is similar to the general scheme with Na_2S (Figure 1). The best technique is to add dropwise aqueous hot (50 °C) 2 mol L^{-1} $H_2C_2O_4$ under magnetic stirring (200 rpm) and moderate heating (50 °C). The most insoluble oxalate (ZnC_2O_4) quickly precipitated. 99.0 ± 0.5 wt % of zinc oxalate was precipitated at pH 0-0.3. The increase of the acidity does not affect precipitation yield. After zinc removal, manganese may be precipitated as hydroxide, as seen earlier. However, it is also possible to recover it as oxalate, by adjusting pH to ≥ 4; the oxalic acid is added as described earlier. MnC_2O_4 (pink precipitate) was obtained:

$$Mn^{2+} + H_2C_2O_4 \rightarrow MnC_2O_4\downarrow + 2H^+ \tag{12}$$

It contains more than 99.5 wt % of the element. Zinc was not detected. pH control is essential since acidity tends to increase when Mn is precipitated (reaction 12). If pH is below 4, Mn is not completely precipitated as oxalate. Addition of 12.5 mol L^{-1} NaOH ensures pH control.

Final wastes management

The final effluent may be neutralized with NaOH and is essentially an aqueous solution containing sodium sulfate. Metals concentration is below the detection limits of the analytical methods used in this work. This effluent is the main final waste (about 15 mL g^{-1} anode + internal paste processed). This amount is 50% higher than the original liquid/solid ratio during leaching (10 mL g^{-1}). This is basically due to the washing of insoluble matter after leaching (carbon) and precipitation of zinc and manganese. The first precipitation step employs small amounts of aqueous sodium sulfide. Washing of precipitates under vacuum[21] would reduce the amount of water employed and would increase Na_2SO_4 concentration in the effluent.

The concentration of Na_2SO_4 (about 1.4 mol L^{-1} according to XRF data) allows a partial recovery of this salt by crystallization (as a decahydrate) at 0 °C (the solubility of this salt is about eight times lower at this temperature than at 25-30 °C[20]). After drying at 180 °C for 3 h, about 59 wt % of the original mass was lost. This result is close to the theoretical value for the decahydrate (55.9 wt %), allowing about 40 wt % of Na_2SO_4 to be recovered. The final effluent was still very saline. Partial (slow) evaporation of the solvent would increase Na_2SO_4 recovery but this depends on the energy cost.

This salt may also be converted into $NaHSO_4$ by adding the calculated amount of concentrated sulfuric acid.[19,20] $NaHSO_4$ is about three times less soluble in water than the normal salt at 25-30 °C.[20] The yield of the acid salt was much higher (~80 wt %) when the solution was cooled at 0 °C. This procedure greatly reduced the salinity of the final effluent. $NaHSO_4$ is a valuable industrial product since it is widely used in metal finishing and cleaning products, to lower the pH of water for effective chlorination (including swimming pools) and in the manufacture of food products (including beverages, dressings, sauces, and fillings). It is also widely used in meat and poultry processing and most recently in browning prevention of fresh cut produce.[21]

Carbon and the solid obtained after precipitation at pH around 0 correspond to 11-15 and 0.2 wt % of the whole spent battery, respectively. Carbon can be co-processed as an alternative fuel, according to the Directory 264/99 from the National Brazilian Environmental Council (CONAMA).[22] The final solid waste that must be sent to industrial dumps corresponds to a small mass fraction of the original battery.

CONCLUSIONS

More than 99 wt % of metals present in the anode and in the internal paste of spent alkaline and Zn-C batteries was leached with 2 mol L^{-1} sulfuric acid (solid/liquid ratio = 1/10) in the presence of hydrogen peroxide at 80-90 °C after 2 h. Carbon is basically the insoluble matter after leaching.

It is possible to isolate the main metals present in the leachates by a sequential precipitation procedure under controlled pH: (i) free acidity 1.1 mol L^{-1} – Hg, Cd, Pb and most Fe were precipitated by adding sodium sulfide; (ii) pH between 1.5-2.0 – Zn (and traces of Fe) was precipitated by adding sodium sulfide; (iii) pH near 7 - Mn can be precipitated after adding sodium hydroxide and hydrogen peroxide. The critical condition to ensure a well-succeeded separation is to keep the pH rigorously constant in all precipitation steps. Reactants must be added slowly, under stirring. Sodium sulfate can be partially recovered from the final effluent as such or as sodium hydrogenosulfate by cooling it near 0 °C. This process avoids working at high pH (above 13) to separate manganese and zinc, thus reducing consumption of chemicals (such as NaOH and water) and generation of final wastes.

Sulfide ions are versatile for separation purposes but they are hazardous species. They are essential in the first precipitation step, but may be replaced in the other steps by oxalate ions, which appear to be a useful reactant. Although they are also toxic, they are much easier to handle. Zinc oxalate was quantitatively precipitated at pH around 0, whereas manganese oxalate was quantitatively recovered at pH ≥ 4. Acidity control is, once again, extremely critical for the success of the separation procedure.

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