

Article

Hydrometallurgical Process and Economic Evaluation for Recovery of Zinc and Manganese from Spent Alkaline Batteries

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Abstract: An innovative, efficient, and economically viable process for the recycling of spent alkaline batteries is presented herein. The developed process allows for the selective recovery of Zn and Mn metals present in alkaline batteries. The hydrometallurgical process consists of a physical pre-treatment step for separating out the metal powder containing Zn and Mn, followed by a chemical treatment step for the recovery of these metals. Sulfuric acid was used for the first leaching process to dissolve Zn(II) and Mn(II) into the leachate. After purification, Mn was recovered in the form of MnO₂, and Zn in its metal form. Furthermore, during the second sulfuric acid leaching, Na₂S₂O₅ was added for the conversion of Mn(IV) to Mn(II) (soluble in the leachate), allowing Mn to be recovered as MnCO₃. Masses of 162 kg of Zn metal and 215 kg of Mn (both in the form of MnO₂ and MnCO₃) were recovered from one ton of spent alkaline batteries. The direct operating costs (chemicals, labor operation, utilities, energy) and indirect costs (amortization, interest payment) required for a plant treating 8 tons of spent batteries per day was calculated to be \$CAD 726 and \$CAD 534 per ton, respectively, while the total revenue from the sale of the metals was calculated at \$CAD 1359.6 per ton of spent batteries. The development of this type of cost-effective industrial process is necessary for a circular economy, as it contributes to addressing environment- and energy-related issues, and creates opportunities for the economic utilization of metals.

Keywords: spent alkaline battery; recycling; leaching; electrowinning; hydrometallurgy; techno-economic evaluation; metal recovery

1. Introduction

The use of electronic compact devices with batteries such as remote controls, watches, electric toys, and pocket lamps has become an integral part of our society. Furthermore, these batteries have a certain lifetime, and the increase in volume of spent batteries over the last few years requires an innovative recycling process. Findings from research into metal recovery in recent years indicate the importance of recycling spent batteries [1–8]. In Canada, Call2recycle collected more than 2.5 kt of batteries for recycling in 2017 and 2.7 kt in 2018, of which 78% consisted of alkaline and Zn–C batteries [9]. However, the collected quantity only represents approximately 20% of all batteries sold in the market [10]. Alkaline batteries consist of a negative zinc metal electrode and a positive manganese dioxide (MnO₂) electrode with an alkaline potassium hydroxide electrolyte, instead of the acidic ammonium chloride electrolyte used in zinc–carbon batteries. After collection, batteries are separated by type and sent to appropriate processing plants. Alkaline and carbon zinc batteries are sent to Retrieval (Trail, BC, Canada), Inmetco (Elwood City, PA, USA), Raw Materials Company

(Port Colborne, ON, Canada), and Battery Solutions Recovery (Brighton, MI, USA), where the batteries are treated by pyrometallurgical processes [10,11]. These processes separate metals by volatilization and melting, and, therefore, require high-energy consumption and, due to the release of toxic gases, require an additional collection/cleaning system. By contrast, hydrometallurgical processes usually have a lower energy consumption and lower environmental impacts than pyrometallurgical processes. Hydrometallurgical processes consist of metal leaching followed by the separation, purification, and recovery of valuable metals through various techniques including, among others, precipitation, solvent extraction, and electrowinning. Numerous studies have used leaching processes under various conditions for the leaching of Zn and Mn from battery powder (Table 1).

Table 1. Leaching yields of Zn and Mn from alkaline battery by acid leaching.

Leaching Agent	Auxiliary Agent	Conditions	Metal Removal (%)		Ref.
			Zn	Mn	
H ₂ SO ₄ 0.54 M	H ₂ O ₂ 4% (v/v)	2 h, 55 °C, 1/30 w/v	100	95.7	[12]
H ₂ SO ₄ 0.54 M	H ₂ O ₂ 4% (v/v)	2 h, 55 °C, 1/10 w/v	53.8	42.8	
H ₂ SO ₄ 0.5 M	Ascorbic acid 10 g/L	3 h, 25 °C, 1/20 w/v	99.5	98.8	[13]
H ₂ SO ₄ 0.5 M	Citric acid 10 g/L		99.9	91.6	
H ₂ SO ₄ 0.5 M	Oxalic acid 10 g/L		96.4	87.5	
H ₂ SO ₄ 1.5 M	-	3 h, 80 °C, 1/10 w/v	90	<20	[14]
H ₂ SO ₄ 1.0 M		Microwave 1 cycle, 30 s	94	<20	
H ₂ SO ₄ 1.0 M		Ultrasonic, 2 min, 0.1 pulse, 20% amplitude	92	<20	
H ₂ SO ₄ 1.5 M	Lactose twice of stoichiometry	3 h, 90 °C, 1/10 w/v	100	98	[15]
Bio-generated H ₂ SO ₄	H ₂ O ₂ 5 vol.% or Na ₂ SO ₃ 1 wt.% Calcine 2 h, 750 °C	2 h, 30 °C, 1/25 w/v	99	90–98	[16]

Notably, the respective reaction time, temperature, acid concentration, and solid/liquid (S/L) ratio should be compared, as these parameters vary across the different studies. Sulfuric acid is commonly used either singly or in combination with an auxiliary agent. For example, the addition of H₂O₂ (4% v/v) in a sulfuric acid solution was used to remove 100% of Zn and 95.7% of Mn from battery powder [12]. In another study, the combination of ascorbic acid with sulfuric acid led to the dissolving of 99.5% of Zn and 98.8% of Mn [13]. Although the use of an auxiliary agent is key to dissolving Mn in sulfuric acid, results from a study where no auxiliary agents were used indicate a 90% removal of Zn and less than 20% removal of Mn in a sulfuric acid medium [14]. Furlani et al. (2009) studied the use of carbohydrates, primarily lactose, as reducing agents for the leaching of manganese from the zinc alkaline battery powder [15]. The carbohydrates reduced Mn(IV) and Mn(III) oxides to acid-soluble Mn(II), and approximately twice the stoichiometric amount of lactose was used for complete leaching [15]. Gallegos et al. (2018) proposed a process using biogenerated sulfuric acid with 5 vol.% H₂O₂ or 1 wt.% Na₂SO₃ for the leaching of Zn and Mn in a single step [16]. In their study, 99% of Zn and 90–98% of Mn was extracted after 2 h of leaching at 30 °C and 0.04 g/mL [16]. Sodium metabisulfite (Na₂S₂O₅) was also used as a reducing agent for the dissolution of metals from a mixture of spent batteries. In their research, Tanong et al. (2017) obtained 94 and 99% removal yields for Mn and Zn, respectively, by adding 0.45 g Na₂S₂O₅/g to battery powder in H₂SO₄ 1.34 M in a single leaching step, with an S/L ratio of 10.9% for 45 min at ambient temperature [6]. In other studies, a thermal pre-treatment was added to increase the efficacy of leaching. For example, Petranikova et al. (2018) investigated the effects of a thermal treatment at 300–950 °C of battery powder on the acid leaching (0.5 M H₂SO₄ at 25 °C for 60 min) [17]. In general, these studies indicate that sulfuric acid leaching allows for the complete dissolving of Zn and partial extraction of Mn (MnO, Mn₂O₃,

and Mn_3O_4). The total dissolving of Mn (including MnO_2) demands an auxiliary agent to reduce MnO_2 to MnO, soluble in sulfuric acid. Therefore, the leaching process can dissolve Zn and Mn simultaneously in a single step or via selective leaching in a two-step process. Selective leaching allows for the use of different techniques for recovery.

After leaching, the second challenge in the hydrometallurgical process is the efficient recovery of metals at high purities. The metals present in the leachate can be recovered by precipitation in the form of hydroxides, sulfides, or carbonates according to their respective pH and redox potential. Sobianowska-Turek et al. [18] used NH_4HCO_3 3 M and NH_4OH 1 M to recover almost 100% of manganese, iron, cadmium, and chromium, as well as 98.0% of cobalt, 95.5% of zinc, and 85.0% of copper and nickel from the solution after reductive acidic leaching ($H_2SO_4 + C_2H_2O_4$) [18]. Furthermore, Sayilgan et al. used KOH 2 M and NaOH 2 M for the selective precipitation of manganese and zinc, with complete precipitation obtained for Zn at pH 7–8 and Mn at pH 9–10 [19].

In industry, zinc is usually recovered in metallic form by electrowinning. In a study by Alfantazi and Dreisinger (2003), electrowinning experiments were conducted at an 80 min plating time, 500 A/m² current density, and temperature of 38 °C with zinc-containing electrolyte zinc and H_2SO_4 concentrations of 62 and 170 g/L, respectively [20]. In this study, 90% of zinc was recovered by using an Al cathode and Pb anode. Similar results were recorded by Ivanov (2004) with an electrolyte containing 45–55 g Zn/L, 5–6 g Mn/L, and traces of other metals including, among others, Ni, Sb, and Ge [21].

In our study, in addition to developing an efficient battery recycling process, relevant economic factors were also considered. Economic factors generally include processing and operating costs, as well as transport and residue disposal costs. For example, Gasper et al. (2013) evaluated the economic viability for recycling alkaline batteries using mechanical separation [22]. Although the mechanical process developed in their study was cheaper than other reported processes (\$US529/ton), it was still not economically feasible, due to the low end-product value. The revenue of the end products was \$US 383/ton of batteries that consisted of brass, Zn/ZnO powder, mixed Mn oxides powder, and KOH powder. In our study, we developed and described a complete hydrometallurgical process including the recovery of Zn by electrowinning and Mn by precipitation from alkaline battery powder. The process included dismantling, magnetic separation, leaching, and metal recovery. Furthermore, an economic evaluation was carried out to assess the feasibility on a global scale, especially for applications in Quebec (Canada), where an alkaline battery recycling process is not yet available.

2. Materials and Methods

2.1. Process Description

Figure 1 represents a flow sheet of the entire process for the recovery of Zn and Mn from spent alkaline batteries for this study. The globally relevant process includes two steps, namely, a physical pre-treatment step and a chemical treatment step. After dismantling, a representative sample of batteries is subjected to the attrition process followed by filtration and rinsing to remove any metallic powder attached to the coarse fraction. In addition to the separation of battery products, the removal of alkaline-soluble salts during this process reduces acid consumption in the following step. The coarse fraction is then transferred to the magnetic separator, allowing the magnetic fraction to be recycled as ferrous material and the non-magnetic fraction containing nylon, carton, and plastic to be used as energy sources.

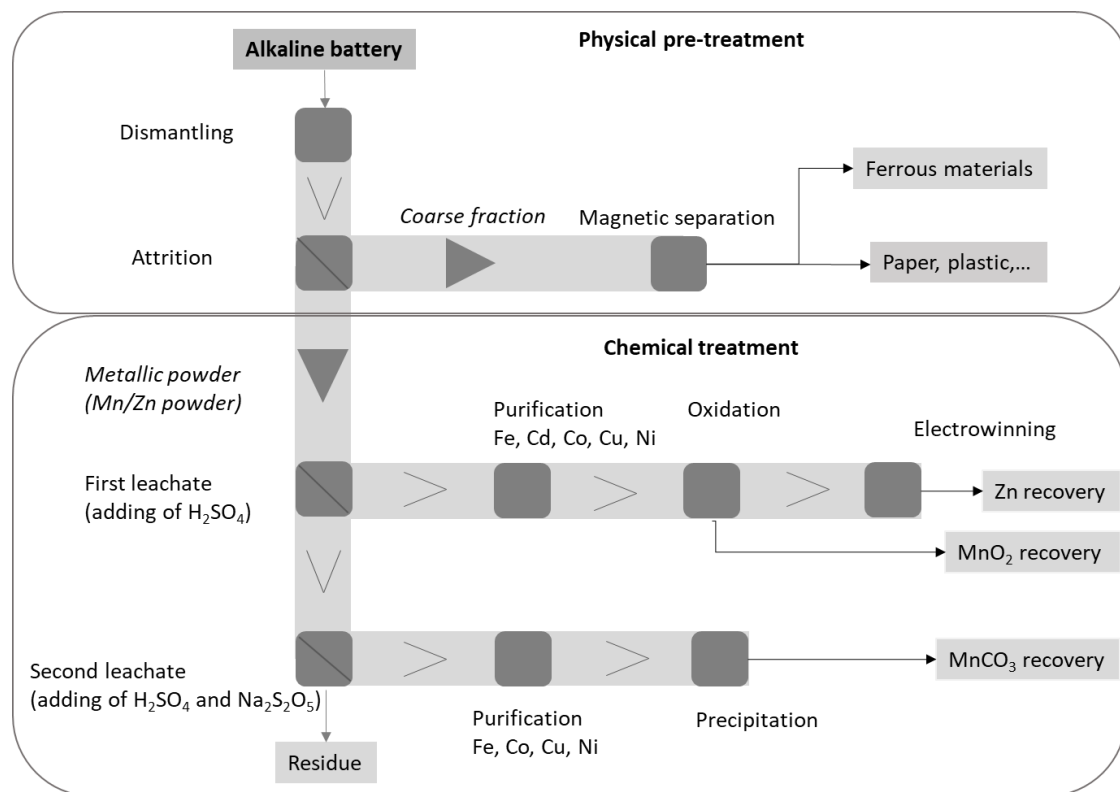
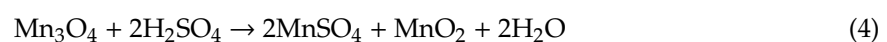
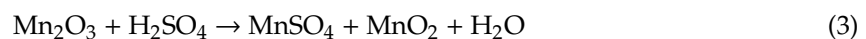
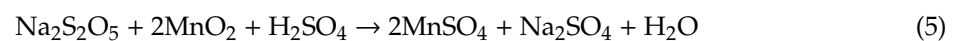


Figure 1. Detailed flow sheet of the hydrometallurgical route to treat the spent alkaline batteries.

The fine fraction containing manganese and zinc described as “metallic powder” is transferred to the chemical treatment, where zinc is dissolved during the first leaching step using sulfuric acid (Equation (1)). A portion of manganese, in the form of MnO , Mn_2O_3 , and Mn_3O_4 , is also dissolved according to Equations (2) to (4) as follows:



As MnO_2 is insoluble in sulfuric acid, sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) is added during the second leaching step to reduce Mn(IV) to Mn(II) [6]. During this leaching step, MnO_2 in metallic powder is transferred in the leachate solution according to Equation (5):



After precipitation for the removal of iron, and cementation for the removal of trace metals such as Ni and Cu, the first pregnant leach solution (PLS-1) is treated using sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) to oxidize manganese for MnO_2 recovery. Then, zinc is reduced by electrodeposition, resulting in a high-purity zinc metal. Furthermore, the second pregnant leach solution (PLS-2) is treated for the removal of iron and zinc followed by the precipitation of manganese as MnCO_3 . While the water used during this process can be reused through a counter-current mode, the final carbon-rich residue can be used for the fabrication of new batteries.

2.2. Physical Pre-Treatment

2.2.1. Sampling and Pre-Treatment

The sample of spent alkaline Zn-MnO₂ and Zn-C batteries was obtained from Laurentide Re-Resources Inc. (Victoriaville, QC, Canada). This company receives used batteries from various collection centers located throughout the Province of Quebec (Canada). During physical pre-treatment, spent alkaline batteries were shredded to approximately 1 cm × 4 cm fractions using a mechanical grinder (Muffin Monster, model 30005, JWC Environmental[®], Santa Ana, CA, USA).

2.2.2. Attrition Process

The neutral attrition consisted of three 20 min steps with a solid/liquid (S/L) ratio fixed at 30% (*w/w*) and 700 rotations per minute (rpm). The high rotation speed accelerates the separation of fine powder from other parts of the battery including carton pieces, ferrous scraps, and plastic. This step is also useful in removing soluble potassium hydroxide from the battery powder. Attrition experiments were carried out using a 40 L stainless tank reactor equipped with three internal baffles. For each experiment, 3 kg of shredded battery material was combined with 10 L tap water for 20 min at ambient temperature. After each step, S/L separation was carried out using 1.7 mm sieves. The remaining coarser fraction was then rewashed until three attrition stages were complete. The metallic powder was removed from the liquid phase after 2 h of settling. The water used for the washing process was recycled via counter-current mode, the result will show the media after three cycles.

2.3. Chemical Treatment

2.3.1. Leaching Process

After washing, the metal powder was collected and different conditions were used to leach a maximum amount of zinc and manganese from the metallic powder. The challenge within this process is to obtain a high leaching efficiency and a PLS zinc concentration ≥ 40 g/L. This is important for avoiding energy loss during the electrowinning process. The selective leaching process was carried out in two stages in a 40 L stainless steel reactor. The water was recycled three times (LC 1 to 3) as presented in Figure 2. During the first cycle (LC 1), leaching was conducted with 4 kg of metallic powder in 2 M H₂SO₄ and an S/L ratio fixed at 40% (*w/v*) for 45 min at ambient temperature. For the second and third cycles (LC 2 and 3, respectively), leaching was conducted with 2 kg of metallic powder, and an S/L ratio of 20% in 1 M H₂SO₄, using the recycled solution after electrowinning (approximately 35–40 g Zn/L).

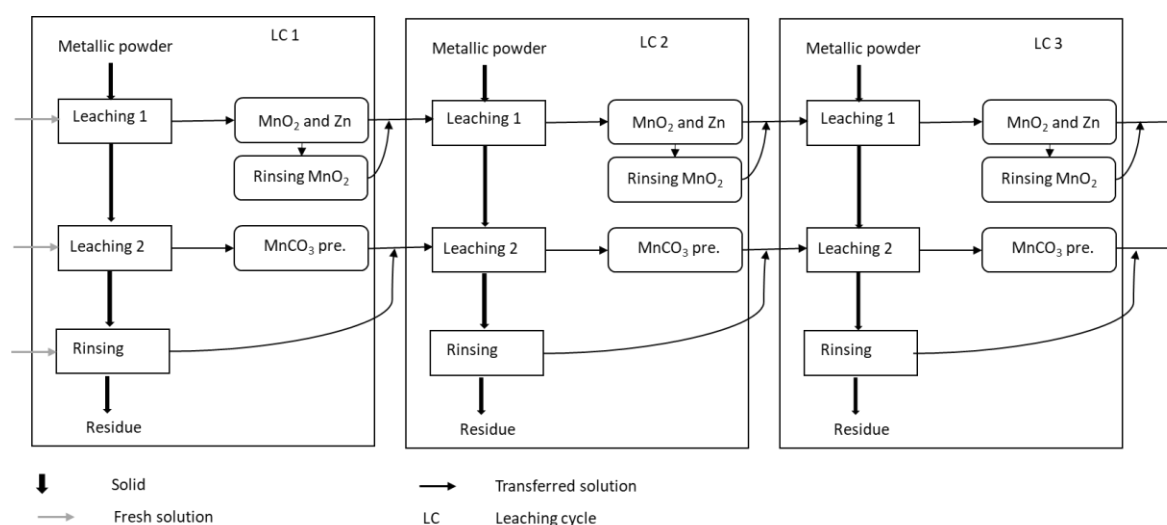


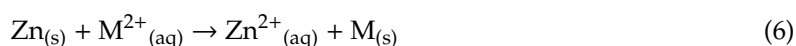
Figure 2. Schematic representation of the counter-current leaching and recovery process including rinsing steps performed on metallic powder.

During the second leaching step, 0.45 g Na₂S₂O₅ per gram of metallic powder was added to reduce Mn(IV) to Mn(II), soluble in 1.34 M H₂SO₄, with an S/L ratio of 14% for 45 min at ambient temperature. The PLS-2 obtained from the second leaching step contained a significant proportion of manganese. Following each leaching step, S/L separation was carried out by filtration.

2.3.2. Purification

Both PLS-1 and PLS-2 were purified prior to zinc and manganese recovery. The iron removal from PLS-1 was carried out at pH 4.0–4.5 by the addition of sodium hydroxide (NaOH) and hydrogen peroxide (H₂O₂). The added H₂O₂ dose was 1.5 times that of the stoichiometric molar ratio (SMR) of the total iron concentration (approximately 2 mM for PLS-1 and 30 mM for PLS-2).

After iron removal, the solution was purified by cementation using Zn powder to remove metal traces, such as Ni, Cu, and Co via the following equation:



where M represents metal traces such as Ni, Cu, and Co.

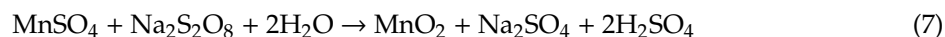
In our study, a quantity of Zn metal powder equal to 20 times the impurity of metals (around 200 mg/L) was added, and cementation was conducted at 80 °C at pH 4.0–4.5 for 30–120 min.

Using the same principle, iron was also removed from PLS-2. Thereafter, the Zn residual (about 0.1 mol/L) in the PLS-2 was precipitated out using sodium sulfide (Na₂S) at pH 4.0–5.0. The SMR values of 1, 2, and 3 were used during these experiments. The ZnS precipitate was then returned to the first leaching step and the PLS-2 was transferred to the MnCO₃ recovery step.

2.3.3. Metal Recovery from PLS-1

Oxidation—MnO₂ Recovery

The recovery of MnO₂ was performed by manganese oxidation using sodium persulfate (Na₂S₂O₈) according the following equation:



The purified solution of ZnSO₄ and MnSO₄ from the previous step was used to recover MnO₂. The kinetic reaction was carried out with 1 SMR Na₂S₂O₈ at 60 °C (nearby 0.6 M of Mn), and the pH increased in the range of 2–4 by adding NaOH. The S/L separation was carried out by filtration and the resulting liquid was transferred to the next step for Zn recovery. The MnO₂ precipitate was washed with an S/L ratio of 10% for 10 min (200 rpm) to obtain high-purity MnO₂.

Electrowinning—Zn Recovery

An acrylic reactor, 8.5 cm (width) × 70 cm (length) × 15 cm (depth), was used for electrodeposition experiments. The electrode sets consisted of 14 aluminum cathodes and 15 Pb/Ag anodes, each with a surface area of 119 cm² (4.5 cm (width) × 10 cm (height) × 1 cm (thickness)). Electrodes were placed in parallel, 1 cm apart. The cathodes and anodes were connected to the negative and positive outlets of a DC power supply, respectively, Xantrex XFR (ACA TMetrix, Mississauga, ON, Canada). The working volume was fixed to 5 L at ambient temperature for all electrowinning experiments. Assays were conducted in batch mode with continuous mixing using a water recirculation system in the reactor. The purified solution of ZnSO₄ (pH = 2) after MnO₂ precipitate recovery was used in the electrowinning experiments, in which Zn was deposited on the cathode surface with a current density between 250 and 750 A/m² and an electrowinning time of 180 min. In this condition, the potential was dropped from 5.6 to 5.2 V. Samples of electrolyte were taken after 15, 30, 45, 60, 90, and 180 min to analyze the residual metal concentration.

2.3.4. Metal Recovery from PLS-2: MnCO_3 Precipitation

Sodium carbonate (Na_2CO_3) was used to precipitate manganese from PLS-2 (a quantity of 90 g Na_2CO_3 was added for 1 L of PLS-2). The MnCO_3 precipitate was rinsed using an S/L ratio of 10% for 10 min for a moderate-speed mixing (200 rpm) to eliminate dissolved sulfur and sodium from the MnCO_3 powder after precipitation. All precipitation experiments were carried out at ambient temperature.

2.4. Analytical Methods

Liquid samples were filtered using G6 glass fiber paper (Fisher brand, Fisher Scientific, Ottawa, ON, Canada, pore size = 1.5 μm) to remove solid particles, and stored in 5% HNO_3 before analysis. Solid samples were dissolved with nitric and hydrochloric acid (HNO_3 and HCl , respectively) before analysis. Metal mobility in the final residual (after the second leaching step) was evaluated using the toxicity characteristic leaching procedure (TCLP)—Method 1311. The metal concentrations in all samples were determined using an inductively coupled plasma-optical emission spectrometer (ICP-OES) (model 725-ES, Agilent Technologies, Santa Clara, CA, USA).

2.5. Techno-Economic Evaluation of the Hydrometallurgical Process

The economic simulation for a battery recycling plant required a large number of parameters (variables) in order to estimate the economic performance of the process. For this study, a computer model was developed to evaluate both direct and indirect costs of the proposed recycling process. This model included more than 260 input variables to define, among others, the various processing steps, capitalization, and operating parameters. The techno-economic analysis was based on parameters and efficiency values obtained from pilot-scale experiments, but increased to a basis of 2800 tons of batteries processed per year ($\text{t}\cdot\text{y}^{-1}$). This capacity represents the actual amount of batteries collected in Canada. Therefore, the capacity plant was developed for 8 tons per day ($\text{t}\cdot\text{d}^{-1}$), with a running time of 8 h per day, and annual operation of $350\text{ d}\cdot\text{y}^{-1}$. Once the capacity of the plant was established, it was possible to adjust the dimensions of the required equipment, according to the specific process. The total cost was established based on variable equations including dimensions and capacity of equipment, purchase costs and transport of equipment, electric and thermal requirements, as well as energy consumption, as recorded in previous studies [23]. Depreciation and annual interest charges were estimated using a 20-year equipment lifetime, as well as a working capital of 15% of fixed capital costs. In addition, used market parameters were defined as follows: An inflation rate of 2%, an annual interest rate of 5%, and an annual discount rate of 6%. Table 2 presents the basic operating parameters taken from the Canadian market and relevant literature [23–25].

Table 2. Basic operating parameters, market parameters, and capitalization parameters of the techno-economic model for recycling spent alkaline batteries.

Parameters	Values	Units
Basic operating parameters	-	-
Operating period	350	d/yr
Processing capacity of a plant	8	t/d
Daily operation period	8	h/d
Factor of safety (for equipment)	20	%
Market parameters	-	-
Annual inflation rate	2.0	%/yr
Annual interest rate	5.0	%/yr
Annual discount rate	6.0	%/yr
Income tax	30	% of gross income
Exchange rate	1.25	\$/US/\$CAD
Chemical Engineering Plant Cost Index	603.1	dec-18

Table 2. Cont.

Parameters	Values	Units
Capitalization parameters	-	-
Amortization period	20	yr
Lifetime of equipment	20	yr
Direct (dir.) costs	-	-
Equipment	-	-
Insulation installation equipment	19	%
Instrumentation and control	3	%
Piping and pipeline systems	7	%
Electrical system	8	%
Building process and services	18	%
Landscaping	3	%
Facilities and services	14	%
Indirect (indir.) costs	-	-
Engineering and supervision	32	%
Construction spending	10	%
Construction management fees	9	% cap. (dir. + indir.)
Contingent fees	26	% cap. (dir. + indir.)
Working capital	15	% fixed capital costs

3. Results and Discussion

3.1. Mass Balance for Physical Pre-Treatment

After three stages of attrition, samples were divided into the following two parts: Coarse fraction (larger than 1.7 mm) and fine fraction (smaller than 1.7 mm). The coarse fraction consisted of a ferrous fraction (22%) and non-ferrous fraction (4%), while the fine fraction contained graphite carbon with metallic powder. Water used for the initial washing contained soluble electrolytes, primarily KOH (4%). According to our results, 1924 g of metallic powder (68% of total mass) was recovered from 2833 g of battery waste with a mass balance of 98.9%. During attrition with water, the pH decreased slightly to 12.8 (stage 1), 11.4 (stage 2), and 10.3 (stage 3).

Table 3 presents the average composition of batteries after physical pre-treatment with recirculated water. This distribution corresponds to results from an investigation on the composition of spent AA alkaline batteries by Almeida et al. [26]. Findings from their study reported alkaline batteries to consist of 2.9% plastic and paper, which is equivalent to the non-ferrous fraction of our study; 21.8% metal and brass, which is equivalent to the ferrous fraction; and 75.3% anode and cathode, which is equivalent to KOH and metallic powder. Although slight differences may be attributed to the sampling method and technical separation, these results indicate the high efficacy of washing for obtaining metallic powder.

Table 3. Composition of the battery after separation by attrition and magnetic separation (physical pre-treatment).

Characteristics	Fraction	Mass (g)	Proportion (%)
Initial		2833 ± 29	
>1.7 mm fraction	Ferrous fraction	639 ± 16	22.4 ± 0.6
	Non-ferrous fraction	124 ± 12	4.4 ± 0.4
<1.7 mm fraction	Metallic powder	1924 ± 16	67.5 ± 0.6
	Soluble fraction (KOH, ...)	115 ± 6	4.0 ± 0.2

The chemical composition of the resulting metallic powder from the attrition process is shown in Table 4. The quantities of zinc and manganese are 240 and 326 g per kg of metallic powder, respectively. The high concentration of potassium (25.5 g/kg) is associated with the high quantity of alkaline

3.2.2. PLS-2 Leachate

Notably, the weight of solids was reduced after the first leaching by the dissolving of metals in PLS-1, with the mass of metal powder decreasing from 400 to 284 g after the first leaching. The addition of $\text{Na}_2\text{S}_2\text{O}_5$ (0.45 g $\text{Na}_2\text{S}_2\text{O}_5$ for 1 g metallic powder) in the second leaching resulted in more than 96% of Mn being dissolved. The S/L ratio had a negative impact on the leaching of Mn with a decrease in the S/L ratio from 35 to 9%, resulting in an increase in Mn extraction rate from 72 to 96%. The S/L ratio of 14.1% made it possible to extract 96.5% of Mn (49.1 g/L). Under these conditions, the concentration of Zn in PLS-2 was 5.87 g/L (a 94.5% solubilization of Zn). Table 5 represents the classification of PLS-1 and PLS-2. Our results confirm the important role of $\text{Na}_2\text{S}_2\text{O}_5$ as the reducing agent for dissolving Mn in the leachate (PLS-2). In an H_2SO_4 solution, the leaching yield of Mn increased from 22 to 96.5% with the addition of $\text{Na}_2\text{S}_2\text{O}_5$. The residue mass decreased from 284 to 140 g after the second leaching.

Table 6 represents the mass distribution for the leaching process for 1 kg of metallic powder and also the global efficiency of the leaching process. The composition of metals (in mg/kg of residue) in residue is also represented in Table 6. The combination of $\text{Na}_2\text{S}_2\text{O}_5$ with sulfuric acid led to the dissolving of not only Zn and Mn, but also other metals (Co, Cu, Ni) of more than 98.4%.

Table 6. Composition of metals in different fractions for each step of leaching.

Samples	Mn	Zn	Fe	Cd	Co	Cu	Ni
Metallic powder (g)	326	240	14.5	0.041	0.045	0.22	0.65
PLS-1 (g)	71.3 ± 8.8	209 ± 2	0.33 ± 0.03	0.042 ± 0.007	0.034 ± 0.006	0.11 ± 0.02	0.41 ± 0.02
PLS-2 (g)	246 ± 3	29.4 ± 1.6	13.8 ± 1.2	<0.0002	0.013 ± 0.002	0.11 ± 0.01	0.24 ± 0.02
Leaching 1 efficiency (%)	21.9 ± 2.7	87.0 ± 0.8	2.3 ± 0.2	101 ± 17	74.3 ± 14.1	48.8 ± 6.9	63.3 ± 2.8
Global leaching efficiency (%)	97.2 ± 2.6	99.3 ± 1.0	97.2 ± 8.3	101 ± 17	102 ± 14	98.4 ± 0.9	101 ± 1.5
Residue (mg/kg)	26.7 ± 2.4	6.8 ± 1.2	4.2 ± 0.5	5.6 ± 3.2	3.2 ± 1.2	20.5 ± 6.9	110 ± 24

3.2.3. Final Residue

A TCLP test was conducted on the final residue in order to validate the effectiveness of the leaching process and residue valorization capacity. Table 7 presents the TCLP results for the residue obtained in our study across three cycles with the recycling of water. All results were below USEPA limits for the potential hazards of waste [27]. The residue obtained after the second leaching is not considered hazardous and could, therefore, be used for other applications, such as a material for the production of batteries.

Table 7. Metal concentration in leachate by toxicity characteristic leaching procedure (TCLP) for final residue.

Elements	US EPA (mg/L)	Residue From		
		LC1	LC2	LC3
As	5.0	<0.01	<0.01	<0.01
Ba	100	0.11	0.19	0.12
Cd	1.0	0.22	0.14	0.47
Cr	5.0	<0.0006	<0.0006	0.01
Pb	5.0	<0.005	<0.005	<0.005
Hg	0.2	0.05	0.01	0.003
Se	1.0	0.07	0.05	0.03
Ag	5.0	0.02	<0.01	<0.01
Ni	250	5.2	3.7	6.9
Cu	250	1.8	0.56	0.19

3.3. Purification and Recovery of Metals

3.3.1. Recovery of MnO₂ from PLS-1 Solution

Purification

Iron precipitation tests were carried out under the same conditions as those used in a study by Blais et al. (2016) with 1.5 times SMR of H₂O₂ for oxidizing Fe²⁺ ions to Fe³⁺ at pH = 4, T = 25 °C, and stirring rate = 200 rpm [28]. Under these conditions, 98% of Fe in the PLS-1 was precipitated. A concentration of 131 mg Fe/L was recorded in the PLS-1 and a 2.99 mg Fe/L was measured after Fe removal (Table 5). In this step, the concentration of Cu decreased from 42.9 to 26.6 mg/L. After iron removal, cementation was used to remove impurities such as Cd, Co, and Ni. The impurities more electropositive than Zn could be removed by adding metal Zn powder and controlling the pH and temperature of the solution [29]. The most efficient removal of Cd (100%), Co (53%), Cu (100%), and Ni (86%) was obtained after 120 min. The low rate of Co removal in our study corresponds to observations made in other studies [29,30]. Furthermore, these studies also mention the difficulty of removing Co due to the small potential difference between Zn and Co–Zn alloys. In addition, the low concentration of cobalt (13.4 mg/L) also makes it more difficult to remove. Notably, Cd and Cu can be removed at lower temperatures (25–40 °C) and at a pH between 2.0 and 2.5. However, a temperature of 80 °C and a pH of 4–5 are necessary for the cementation of Ni [30]. The slight increase in Mn (from 28.5 to 31.3 mg/L) and Zn (83.6 to 85.2 mg/L) concentration can be explained by the evaporation of water during the cementation process at 80 °C.

Precipitation of MnO₂

Across all experiments, 1 SMR of Na₂S₂O₈ was used for the oxidation of Mn²⁺ to MnO₂. As suggested by Demopoulos et al. (2002), this reaction was performed at 60 °C and at a controlled pH to investigate the oxidation kinetics of Mn²⁺ ions in MnO₂ at a pH between 2 and 4 [31].

The residual concentration of Mn at pH 2, pH 3, and pH 4 was investigated. According to our results, the oxidation at pH = 3 gave a good oxidation yield (93%). After 120 min, Mn concentration in the solution decreased from 31.3 to 2.03 g/L (Table 8). An amount of 2 g Mn/L in the solution had a positive effect on the next step of Zn electro-deposition [32]. Notably, traces of Co co-precipitated with MnO₂, whereas Ni did not precipitate with MnO₂ (Table 8).

Table 8. Oxidation kinetics of Mn²⁺ to MnO₂ in different pHs.

pH	Temps. (min)	Conc. (g/L)		Conc. (mg/L)	
		Mn	Zn	Co	Ni
	Initial	31.3	85.2	5.99	21.8
2	15	22	85.2	5.87	21.9
	30	19	84.9	5.95	21.8
	60	14	84.9	4.02	21.7
	120	5	83.9	3.09	21.9
3	15	18	84.2	5.13	21.6
	30	16	84.1	4.38	21.9
	60	8	83.6	2.01	21.1
	120	2.03	83.1	ND	20.7
4	15	31.3	84.2	4.35	21.2
	30	24.1	83.7	ND	19.4
	60	3.01	82.5	ND	15.2
	120	ND	79.3	ND	15.1

3.3.2. Electrowinning for Recovery of Zn Metal from PLS-1 Solution

The effect of current density on the electrowinning of Zn was evaluated by measuring the residual concentration of Zn between 250 and 750 A/m² for 180 min. The results clearly indicate that the deposition efficiency of Zn increased with an increase in current density. The high concentration of Mn (>5 g/L) in the solution decreased the faradic yield [32], while a lower concentration (between 1 and 5 g/L) had a positive effect on oxidation, thereby protecting the electrodes and increasing the purity of the deposited Zn [32]. At a high current density (750 A/m²), a decrease in Mn concentration was observed (from 2.03 to 0.22 g/L), which is consistent with the results obtained by Poinsignon et al. [33], where Mn oxidized at the anode and precipitated as MnO₂. The largest Zn deposit was obtained with a current density of 500 A/m². Under these conditions, Mn concentration remained stable (from 2.03 to 1.92 g/L).

Figure 4 shows the changes in Zn deposition as a function of time at a current density of 500 mA/m². In the figure, two different zones can be distinguished, with the yield of Zn deposits increasing linearly with time until 90 min. After 90 min, the rate of Zn deposits decreased significantly. Notably, at the start of the electrowinning process, Zn concentration was relatively high (83.1 g/L) and, accordingly, the Zn deposit rate was subjected to current control. As the Zn deposit achieved a certain thickness and the Zn concentration was below a certain level (approximately 40 g/L), we conclude that the Zn deposit rate is limited by mass transfer control. This explains why the Zn deposit rate remained constant with time. Figure 4 also presents the change in energy consumption as a function of time, indicating that energy consumption increased linearly to 156 kWh/m³ after 180 min. It has been established that Zn deposition efficiency is affected by reaction time and the cost of the electrowinning process. In view of reducing power use and increasing Zn deposits, a time of 90 min was selected for the process. Under these conditions, the residual concentration of Zn in the solution was 36.1 g/L. The solution was also recirculating for the first leaching (S/L ratio of 40%) and, consequently, an S/L ratio of 20% was used for the second cycle.

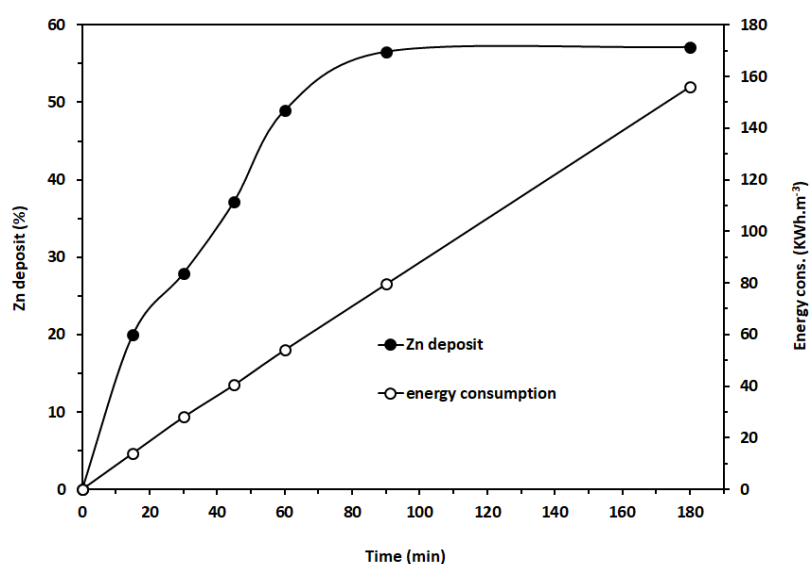


Figure 4. Variation in residual Zn concentration and effect of energy consumption as a function of time applying a current density of 500 A/m².

3.3.3. Recovery of MnCO₃ from PLS-2 Solution

Using the same principle, iron precipitation assays were carried out with 1.5 SMR of H₂O₂ for the oxidation of Fe²⁺ ions to Fe³⁺ at pH = 4 and ambient temperature. Within this context, nearly 99.9% of Fe in PLS-2 was precipitated. A concentration of 2754 mg Fe/L was recorded in PLS-2 and a concentration of 2.33 mg Fe/L was measured after Fe removal (Table 5). In this step, the concentration

of Co remained stable, while all Cu was removed and the concentration of Ni decreased from 48.4 to 24.1 mg/L.

To obtain a pure manganese solution, zinc precipitation was achieved by adding Na_2S (2 SMR of Na_2S at pH 4–5). Under these conditions, up to 100% of zinc was precipitated (Table 5) and the obtained ZnS could be added to the first leaching stage for PLS-1 rich in Zn.

The precipitation of MnCO_3 was achieved by the addition of Na_2CO_3 . The quantity of Na_2CO_3 was calculated for 1 SMR, with pH 4.5–5.0 and at ambient temperature. After rinsing, the collected MnCO_3 had a purity of 95%.

3.4. Economic Evaluation

Table 9 presents the direct and indirect costs, as well as profit for a basic plant that recycles 8 tons of batteries per day. In this simulation, the cost of shredding was not considered. However, the non-magnetic fraction (plastic, carton, etc.) and the final residue were considered waste products that would need to be transported over 50 km with a disposal cost of \$CAD 75 per ton of residue. This cost included loading, transport, and landfill calculated at \$CAD 28.2 per ton of batteries. In addition to chemical products, labor costs and utilities costs were the two other important parameters, from an economic point of view, which accounted for 18.5 and 10.0% of the total direct costs, respectively.

A total cost of \$CAD 1260 per ton was calculated, of which the direct and indirect costs were calculated as \$CAD 725.7 and \$CAD 534.5 per ton, respectively. Regarding the cost simulation, cost distribution was dominated by indirect costs including amortization (9.6%), financing (15.8%), and marginal social benefits (1.5%). The revenue was calculated as \$CAD 1359.6 per ton, whereas Zn, MnO_2 , and MnCO_3 values were estimated as \$CAD 527.4, \$CAD 451.6, and \$CAD 357.8 per ton, respectively.

Figure 5 illustrates the variation in cost as a function of the recovery capacity of the plant. Indirect costs showed an influence on total cost, and costs decreased with the increase in recovery capacity. Total costs were evaluated to be \$CAD 1015 and \$CAD 913 per ton for treatment capacities of 16 and 24 t/day, respectively, equivalent to 40 and 60% of batteries sold in the Canadian market.

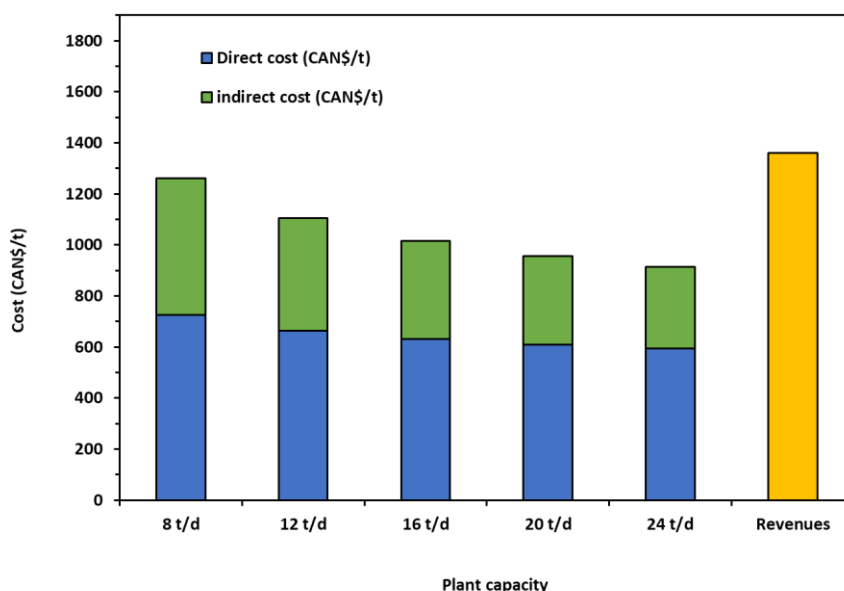


Figure 5. Exploitation costs and revenues depending on the processing capacity of the recovery plant.

Table 9. Parameters related to hydrometallurgical recovery in spent alkaline battery.

Parameters	Values	Units	Cost/profit (\$CAD/t)
Direct operating costs	-	-	-725.7
Chemicals	-	-	-
H ₂ SO ₄	0.21	\$CAD/kg	-129.0
NaOH	0.35	\$CAD/kg	-89.3
Na ₂ CO ₃	0.21	\$CAD/kg	-14.7
H ₂ O ₂	1.60	\$CAD/kg	-15.6
Na ₂ S ₂ O ₈	0.30	\$CAD/kg	-18.6
Na ₂ S ₂ O ₅	0.31	\$CAD/kg	-86.9
Na ₂ S	0.90	\$CAD/kg	-45.7
Labor	-	-	-
Unit cost	25.0	\$CAD/h	-115.9
Supervision	20.0	% (labor cost)	-23.2
Utilities			
Unit cost of electricity	0.07	\$CAD/kWh	-27.5
Unit cost of water process	0.50	\$CAD/m ³	-2.6
Unit cost of fuel	3.50	\$CAD/M Btu	-20.7
Residue management	-	-	-
Loading and transport cost	2.50	\$CAD/t	-3.3
Transportation cost (estimate of 50 km)	0.15	\$CAD/t/km	-
Unit cost of landfill or treatment	75.0	\$CAD/t	-24.9
Maintenance and repairs	2.00	% fixed capital costs/yr	-66.1
Current materials	0.75	% fixed capital costs/yr	-24.8
Laboratory charges	10	% operating labor	-11.6
Patents and royalties	5.00	\$CAD/t	-5.0
Indirect and General costs			-534.5
Marginal social benefits	22.0	% operating labor + supervision	-30.6
Amortization	-	-	-189.9
Financing (interest redemption)	-	-	-314.0
Metal revenues	-	-	1359.6
Fe	0.10	\$CAD/kg	22.8
134 kg of MnO ₂ (85.6 kg Mn)	3.37	\$CAD/kg	451.6
286 kg of MnCO ₃ (136.5 kg Mn)	1.25	\$CAD/kg	357.8
162 kg of Zn metal	3.25	\$CAD/kg	527.4
Profit	-	-	98.3

4. Conclusions

In this study, we established a pilot process for the recycling of metals in spent alkaline batteries, including physical separation techniques and hydrometallurgical steps. Spent batteries were crushed and attrited to separate out and collect the metallic powder. Metallic powder was then treated using sulfuric acid leaching. The first leaching for zinc and a part of manganese included the use of 2 M H₂SO₄ for 45 min at ambient temperature and a solid content of 40% (*w/v*). Under these conditions, up to 87% of zinc was solubilized. In the second leaching step, 0.45 g Na₂S₂O₅ was added per 1 g metallic powder in 1.34 M H₂SO₄, resulting in up to 97% of manganese being dissolved. The dissolved manganese was recovered by precipitation in the form of MnO₂ and MnCO₃, whereas zinc was recovered in metallic form by electrowinning. Notably, the leaching efficacy remained high, even after three cycles of processing with recirculated water. Furthermore, results from our technical and economic simulation indicate that the suggested process for recycling spent alkaline batteries is economically competitive and feasible. It is necessary to highlight that the profits from the process greatly depend on the market

price of zinc, manganese (IV) oxide, and manganese carbonate. However, despite economic challenges, the process of recycling alkaline batteries reduces negative environmental impacts.

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