Recovery of Zn and Mn from spent zinc-manganese-carbon batteries

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Abstract

A lab-scale study was conducted for evaluating the recovery of valuable metals from spent zinc-manganese-carbon batteries (ZMCBs) by reductive acid leaching using different acids and reducing agents. In this study spent zinc-manganese-carbon batteries collected from a local recycling plant of spent batteries were subjected to various pre-treatments including battery discharge, crushing, sieving, and roasting. After pre-treatments, the powdered spent ZMCBs was first determined for its metal composition and then subjected to leaching using sulfuric acid, hydrochloric acid and nitric acid. Zinc and manganese were recovered from three acid leached solutions afterwards. In this work hydrogen peroxide, glucose and citric acid were used as reducing agents in acid leaching to enhance the recovery of zinc and manganese. Test results did confirm this. In addition, test results also showed that hydrogen peroxide outperformed glucose and citric acid in this regard. Under the optimal operating conditions, 100% of zinc and 100% of manganese were recovered using 4 M HCl and H_2O_2.

Keywords: Spent zinc-manganese-carbon batteries, Recovery of metals, Reductive acid leaching

Introduction

Batteries are used in many electrical and electronic products in our daily life. Major types of household small batteries include alkaline Zn–MnO_2, Zn–C, mercury-oxide, Ni–Cd, Ni–metal hydride and lithium-ion batteries etc. Zinc-manganese-carbon battery is one of common dry cell batteries (or dry batteries) that are closely related to modern life. The consumption of batteries has increased in the last 3-4 decades worldwide. In Taiwan, currently, it is estimated that about 10,000 metric tons of dry batteries are consumed annually. Depending on the battery type, dry batteries might contain zinc, manganese and other heavy metals such as mercury, cadmium and nickel posing a threat to the environment and human health. In addition to the said concern due to their potential toxicity, spent dry batteries might also cause a concern of recovery of valuable metals contained.

In early years spent batteries were landfilled and/or incinerated. Recycling of batteries would keep them out of landfill, where heavy metals may leak into the ground causing soil and water pollution when the battery casing corrodes. It also would keep them out of incineration with municipal solid waste preventing air pollution that might cause. During the last 20-30 years, battery recycling has gradually gained its popularity in many countries. For instance, recycling of spent dry batteries is mandatory in Taiwan according to Waste Disposal Act. A more comprehensive recycling program (known as Resource Recycling four-in One Program) for many types of municipal solid waste was established and implemented in Taiwan since 1997. Not until November 1999 all types of dry battery are included in the recycling program overseen by Taiwan EPA. During 2009-2013, on average 4,150 metric tons of dry batteries per year was recycled. It reflected that about 51% of spent dry batteries were recycled in 2013 in Taiwan [1]. On the other side of the world, in 2009 the United Kingdom adopted the EU's Batteries Directive through the Waste Batteries and Accumulators Regulations. The EU Directive sets a recycling target of 25% of all types of batteries sold by 2012 and 45% by 2016 [2].

In the literature, various unit operations in three methods have been used for battery recycling. These methods are mineral processing, hydrometallurgy, and pyrometallurgy [3]. In general, spent zinc-manganese-carbon batteries (ZMCBs) must be pretreated before pyrometallurgical and hydrometallurgical processes. Pretreatments may include battery discharge, roasting, crushing, sieving, etc. As compared with pyrometallurgical processes, generally, hydrometallurgical processes have several advantages such as low energy consumption, ease of operation, low emission of toxic gas, and lower costs [4]. In the literature, many researchers have conducted researches on extraction of zinc and manganese from alkaline and zinc-carbon spent batteries by acid leaching and reductive acid leaching [3,5-7].

As reported, the powder of spent zinc-manganese-carbon batteries contains zinc and manganese compounds, NH_4Cl/NH_3, carbon, starch and flour [6,7]. This powder can be treated by pyrometallurgical or hydrometallurgical methods. Hydrometallurgical methods generally involve the extraction of metallic parts in an acidic medium, but alkaline solutions (e.g., NaOH) can also be used for selective extraction of Zn [5,8]. It is almost a standard recycling scheme that leaching is followed by selective recovery involving cementation, solvent extraction, precipitation or electrochemical techniques [6,9]. Often, sulfuric acid, hydrochloric acid and nitric acid are used as leaching solutions for recovery of metallic values from dry batteries and lithium-ion batteries [9-11]. Several studies have focused on using hydrometallurgical processes for recycling of metals from spent dry batteries. For instance, an Italian research group has reported that nearly 99% of zinc and 20% of manganese are extracted after 3 h, at 80 °C with a pulp density of 10% (w/v) and 1.5 M H_2SO_4 [12]. Reductive acid leaching of manganese and zinc from spent alkaline and zinc–carbon batteries was also reported by separate Italian researchers [13]. In that study, for the sulfuric acid solution, 91% Mn and 112% Zn were achieved at 45 °C after 3 h of leaching by 10% pulp density, 30% oxalic acid (30% less than the stoichiometric requirement), 30% H_2SO_4. Also reported in the same study, for the hydrochloric acid solution, about 86% Mn and 95% Zn were obtained at 20% pulp density, 30% oxalic acid, 30% HCl, at 45 °C after 3 h of leaching. No matter spent dry batteries or lithium-ion batteries, in general, factors that affect the leaching efficiency of batteries powder include leaching solution concentration, reaction temperature, reaction time and solid-liquid ratio [14].

In addition, several researches have also demonstrated that by coupling acid solution and a reducing agent for leaching (known as reductive acid leaching) an enhanced leaching performance would be obtained [10,13]. However, to the best knowledge of the present authors, no one has reported a study for recycling of spent dry batteries on reductive acid leaching using three acids and three reductants in the same contribution for comparison. Thus, the main objective of this study was to fill this technology gap.

Materials and methods

Spent zinc-manganese-carbon batteries (ZMCBs) were obtained from a local recycling plant of spent batteries. Then spent ZMCBs were subjected to various pre-treatments including battery discharge, crushing, sieving, and roasting. More specifically, the spent batteries were first crushed and followed by magnetic separation and air classification to obtain the powder fraction of zinc oxides and manganese oxides. Then, the powder sample was subjected to sieving to obtain the screen undersize, namely < 4.07 mm fraction. The screen undersize was further subjected to roasting at 400 °C for 40 min to remove residual mercury if any.

The roasted specimen of screen undersize as such was then semi-quantitatively analysed for its elemental composition by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS). In this work the quantitative analysis of the composition of selected metals in the roasted specimen of screen undersize as such was also carried out. To meet this end, the said specimen was subjected to acid digestion using Taiwan EPA standard method NIEA M353.02C [15]. After solid/liquid separation, inductively coupled plasma atomic emission spectroscopy (ICP-AES) was employed for the elemental analysis in the filtrate.

In this study, sulfuric acid, hydrochloric acid, and nitric acid were selected as leaching agents while hydrogen peroxide (H_2O_2), glucose ($C_6H_{12}O_6$), and citric acid ($C_6H_8O_7$) were reducing agents in reductive acid leaching. Reductive acid leaching tests for the pretreated spent ZMCBs powder were carried out separately using a selected acid solution of 2-4 M in concentration at 80 °C coupled with one molar ratio of a selected reductant (based on the Mn concentration determined in the aforementioned acid digested sample) at the solid/liquid ratio of 1/100 for 60 min.

Analytical grade reagents and deionized water were used throughout this study whenever applicable.

Results and discussion

The analytical results of major elements contained in the pretreated spent ZMCBs are given in **Table 1**. In this work the determination of elemental composition was based on the results of SEM-EDS, as shown in **Fig. 1**. Also included in **Table 1** for comparison are the elemental compositions for spent dry batteries reported by other researchers. As noted, a great majority of researchers used X-ray fluorescence analysis for determination of the metal contents in spent dry batteries. It was also noticed that carbon was the most predominant element accounted for nearly 60 wt% of spent ZMCBs in this study. Other than carbon, zinc and manganese were found to the second and third predominant elements in spent ZMCBs. Other researchers, however, reported that manganese was the most predominant element, followed by zinc in their studies.

Table 1
The analysis of the elemental compositions in the solid phase of spent ZMCBs

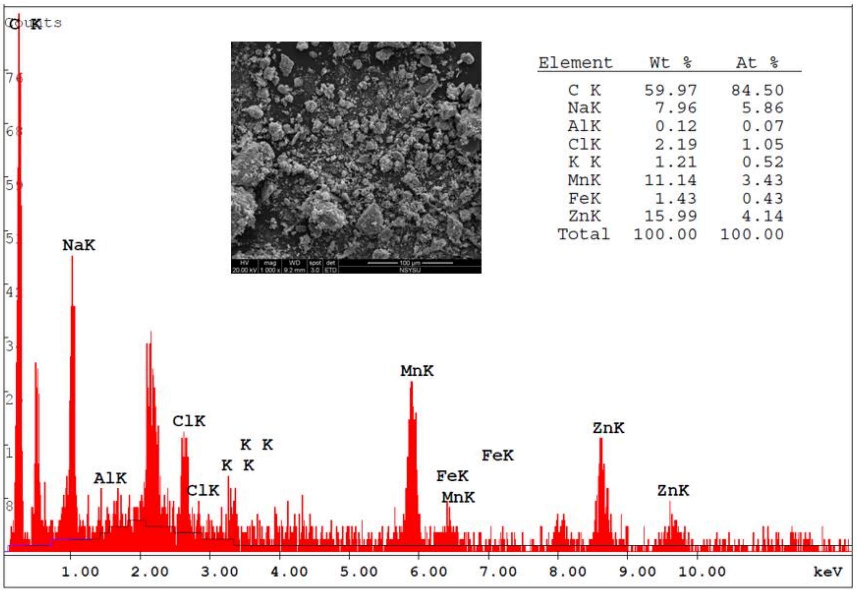
Elemental composition (wt%)								Reference (Year)
Zn	Mn	Fe	C	Na	K	Cl	Al	
9.86	37.45	1.04	41.81	N/A	3.57	4.38	0.49	[12][a] (2008)
20.86	22.44	0.39	N/A	N/A	N/A	5.14	0.05	[5][b] (2013)
19.20	27.20	0.53	5.70	1.20	3.40	2.75	N/A	[10][c] (2014)
15.99	11.14	1.43	59.97	7.96	1.21	2.19	0.12	This study[d] (2017)

[a] Determined by X-ray fluorescence.

[b] Determined by X-ray fluorescence

[c] Determined by X-ray fluorescence and X-ray diffraction.

[d] Determined by scanning electron microscopy with energy dispersive X-ray spectroscopy.



Element	Wt %	At %
C K	59.97	84.50
NaK	7.96	5.86
AlK	0.12	0.07
ClK	2.19	1.05
K K	1.21	0.52
MnK	11.14	3.43
FeK	1.43	0.43
ZnK	15.99	4.14
Total	100.00	100.00

Fig. 1. SEM micrograph and EDS analysis of the pretreated spent ZMCBs before acid leaching

As indicated above, acid digestion of the pretreated spent ZMCBs was also conducted to better understand the actual contents for selected elements (e.g., Zn and Mn), which were analyzed by ICP-AES. The results are given in **Table 2**. Evidently, Zn and Mn are the most abundant elements in the pretreated spent ZMCBs with a decreasing order of Zn > Mn > Fe > K > Na. In this study, this decreasing order of metal contents in the pretreated spent ZMCBs was found to be in good agreement with that of analyzed in the solid phase (as presented in **Table 1**) if the carbon content was disregarded.

Table 2
The analysis of the elemental compositions in the acid-digested phase of spent ZMCBs

Method	Elemental composition (mg/kg)				
	Zn	Mn	Fe	K	Na
NIEA M353.02C [15]	533,476	280,548	19,360	17,165	8,879

Determination of the optimal acid concentration to be used in acid leaching of spent ZMCBs is crucial. In this study, sulfuric acid was selected and tested for this purpose. As shown in **Fig. 2**, the leaching efficiency increased with increasing concentration in the range of 2-4 M for both zinc and manganese. Thus, 4M in concentration for sulfuric acid, hydrochloric acid, and nitric acid was selected in this study for all later leaching tests including reductive acid leaching.

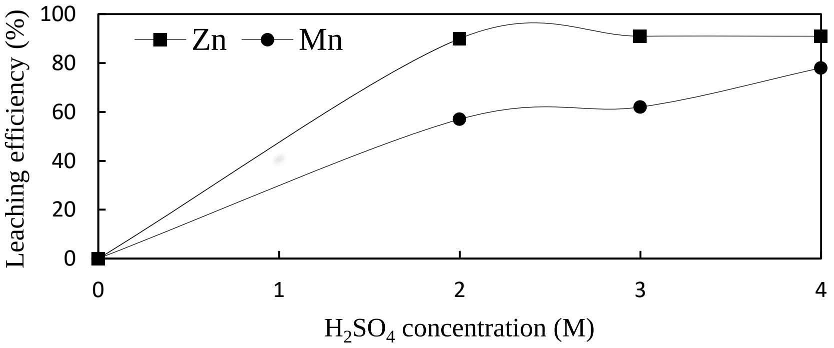
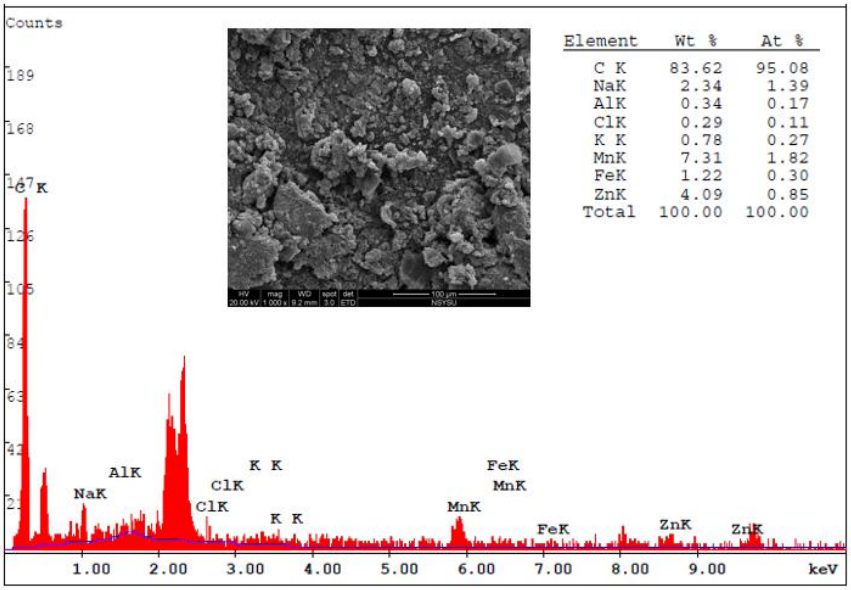


Fig. 2. Variation of leaching efficiency of Zinc and Mn with concentration of sulfuric acid for the pretreated spent ZMCBs

Fig. 3 further showed that SEM-EDS analysis for the solid residues of the pretreated spent ZMCBs after ordinary acid leaching by H_2SO_4. Comparing the elemental compositions before and after sulfuric acid leaching, it is obvious that a great percentage of target metals have been extracted.



Element	Wt %	At %
C K	83.62	95.08
NaK	2.34	1.39
AlK	0.34	0.17
ClK	0.29	0.11
K K	0.78	0.27
MnK	7.31	1.82
FeK	1.22	0.30
ZnK	4.09	0.85
Total	100.00	100.00

Fig. 3. SEM micrograph and EDS analysis of the pretreated spent ZMCBs after sulfuric acid leaching

Test results of reductive acid leaching using three acids (4 M in concentration) and three reductants are presented and compared in **Table 2**. In addition, the results of ordinary acid leaching are also included for comparison.

Table 2
Reductive acid leaching efficiency of the pretreated spent ZMCBs

Acid solution	Reductant	Leaching efficiency (%)	
		Zn	Mn
4 M H_2SO_4	-	91	78
	H_2O_2	89	100
	$C_6H_8O_7$	86	100
	$C_6H_{12}O_6$	85	100
4 M HCl	-	96	100
	H_2O_2	100	100
	$C_6H_8O_7$	85	100
	$C_6H1_2O_6$	85	100
4 M HNO_3	-	89	61
	H_2O_2	99	100
	$C_6H_8O_7$	85	100
	$C_6H_{12}O_6$	83	100

As compared with the ordinary acid leaching by 4 M H_2SO_4, reductive acid leaching with any of these three reductants has increased Mn leaching from 78% to 100%, whereas Zn leaching remained in the range of 85-91%. In the case of acid leaching by 4 M HCl, it yielded a very good leaching performance for both Zn and Mn, namely 96% for the former and 100% for the later. If H_2O_2 was added to HCl, 100% leaching efficiencies were obtained for both Zn and Mn. However, when glucose or citric acid was used as a reducing agent, the Zn leaching dropped to 85% even that the Mn leaching remained 100%. When the leaching was carried out by 4 M HNO_3 alone, as compared with other two acids, it yielded the poorest performance for the leaching of both Zn and Mn, namely 89% and 61%, respectively. But when H_2O_2 was added to HNO_3, the leaching efficiency of Mn increased to 100%, whereas the Zn leaching slightly declined to 83-85% for other two reductants.

Based on the results shown in **Table 2**, overall speaking, reductive acid leaching was fond to outperform its counterpart (i.e., ordinary acid leaching). By comparing three reductants tested, addition of H_2O_2 to any acid solution yielded the best leaching efficiencies for both Zn and Mn, followed by glucose and citric acid. In addition, the synergistic effect of HCl and H_2O_2 gave rise to 100% leaching efficiency for either Zn or Mn. **Table 3** further showed the results of acid leaching for various types of dry cell batteries obtained by different researchers for comparison. Evidently, the present study outperformed that of results obtained by others.

Table 3

Leaching of Zn and Mn from various types of spent dry batteries in different studies

Spent battery type	Leaching medium	Leaching time (min)	Temperature (°C)	Recovery (%)	Reference
Zn–Mn batteries	1-2 M HCl with 3% H_2O_2	50	50	Zn: 60–75	[16]
MnO_2–Zn dry cell batteries	2 M H_2SO_4	120	50	Zn: 74; Mn: 4.8	[17]
	2M HCl			Zn: 59; Mn: 5.1	
Alkaline Zn–MnO_2 and Zn–C batteries	0.5-2 M H_2SO_4 with 30% H_2O_2	60	60	Zn:63.1-97.2; Mn: 43.5-97.5	[10]
Alkaline and zinc–carbon batteries	0.5-2 M H_2SO_4	180	80	Zn:82.5 - 99.7; Mn: 13.7- 25.2	[12]
Zn-Mn-C batteries	2-4 M H_2SO_4, HNO_3 or HCl with H_2O_2, $C_6H_{12}O_6$, or $C_6H_8O_7$	60	80	Zn: 83-100; Mn: 61-100	This study

Conclusions

Based on the test results of ordinary acid leaching and reductive acid leaching of spent zinc-manganese-carbon batteries, it has again confirmed that reductive acid leaching is a preferred option to its counterpart. Among three acids tested, 4 M HCl yielded the highest leaching efficiencies for both Zn and Mn. Further, for three reductants tested, hydrogen peroxide was found to outperform glucose and citric acid. Under the optimal operating conditions, 100% of zinc and 100% of manganese were recovered using 4 M HCl and H_2O_2. However, precautions of potential risks caused by chlorine gas have to be made when acid leaching was conducted using HCl.

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