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

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Outline

- Introduction
- Objective
- Materials and methods
- Results and discussion
- Conclusions

Introduction (1/2)

- Batteries are used in many electrical and electronic products in our daily life. 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.
- Various unit operations in three methods have been used for battery recycling. These methods are mineral processing, hydrometallurgy, and pyrometallurgy (Espinosa et al., 2004). In general, spent zinc-manganese-carbon batteries (ZMCBs) must be pretreated before pyrometallurgical and hydrometallurgical processes.

Introduction (2/2)

- 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 (Yazici et al., 2013).
- 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 (Espinosa et al., 2004; Ferella et al., 2010; Buzatu et al., 2014).

Objective (1/1)

- The objective of this study was to compare with reductive acid leaching using three acids and three reductants.

Materials and methods (1/3)

- 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.
- Different concentrations of H_2SO_4, HCl and HNO_3 were used as leaching agents while H_2O_2, glucose, and citric acid were used as reductants in various leaching tests at 80℃ for the aforementioned spent batteries.

游曜銘

Materials and methods (2/3)

- Taiwan EPA standard method NIEA M353.02C

1 gram sample → 10 mL (1:1)HNO_3 Heat and refluxed 15 min → Cool down → 5 mL HCl Heat and refluxed 30 min (no brown fume) → Cool down → 2 mL DI water and 3 mL 30% H_2O_2 Heat slowly → refluxed 120 min → Cool down → 10 mL HCl Heat and refluxed 15 min → Cool down → quantitative to 100 mL

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游曜銘3 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.And the chemical composition was analysis by standard method.

游曜銘; 13/6/2017

Materials and methods (3/3)

Sample

- 1 g of ZMCBs powder

Leaching

- 2 - 4 M H_2SO_4 , 4 M HCl , and 4 M HNO_3
- H_2O_2 , $C_6H_{12}O_6$, and $C_6H_8O_7$
- 60 min and 80℃

Analysis

- ICP-AES and ESEM/EDS

Results and discussion (1/5)

- 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 1**.

Table 1
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	533,476	280,548	19,360	17,165	8,879

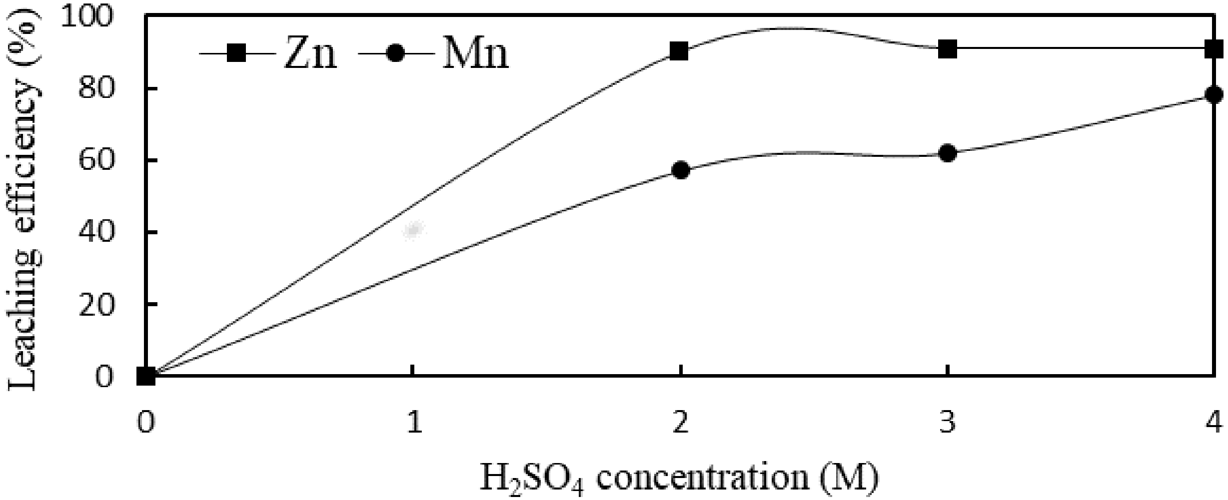

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Fig 1. Variation of leaching efficiency of Zinc and Mn with concentration of sulfuric acid for the pretreated spent ZMCBs

Results and discussion (3/5)

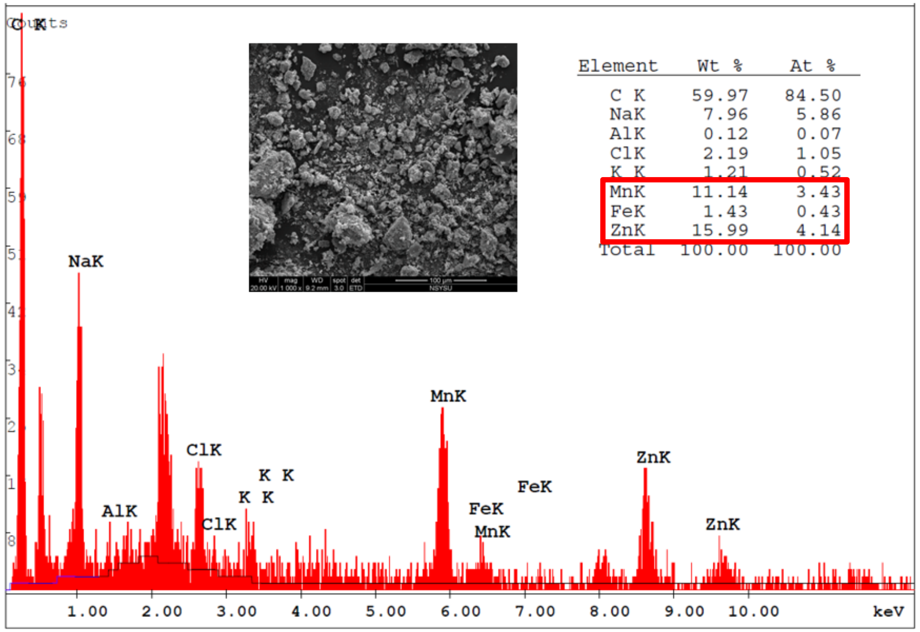

Fig 2. SEM micrograph and EDS analysis of the pretreated spent ZMCBs before acid leaching

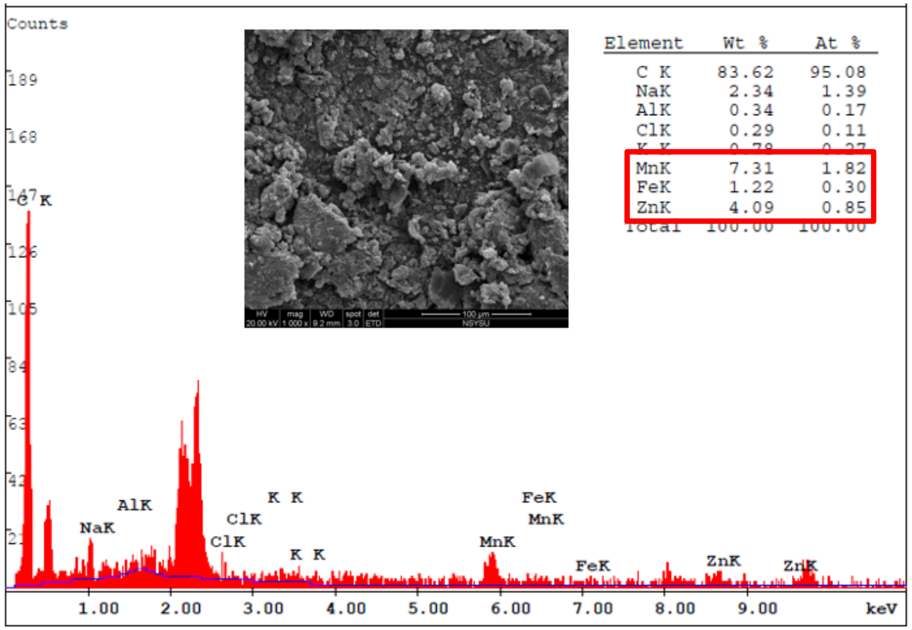

Fig 3. SEM micrograph and EDS analysis of the pretreated spent ZMCBs after sulfuric acid leaching

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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

leaching

ic acid.

Table 3

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

Battery type	Reagents	Leaching time (min)	Temperature (°C)	Recovery (%)	Reference
Zn–Mn batteries	1-2 M HCl with 3% H_2O_2	50	50	Zn: 60–75	Li, Y et al., 2005
MnO_2–Zn dry cell batteries	2 M H_2SO_4 2M HCl	120	50	Zn: 74, Mn: 4.8 Zn: 59, Mn: 5.1	El Nadi et al., 2007
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	Buzatu et al., 2007
spent alkaline and zinc–carbon batteries	0.5-2 M H_2SO_4	180	80	Zn:82.5 - 99.7, Mn: 13.7- 25.2	Ferella et al ., 2008
Zn- Mn- C batteries	2-4M H_2SO_4, HNO_3, HCl with $C_6H_{12}O_6$, $C_6H_8O_7$, H_2O_2	60	80	Zn: 83- 100, Mn: 61- 100	This study

Conclusions (1/2)

- Among three acids tested, 4 M HCl yielded the highest leaching efficiencies for both Zn and Mn.
- 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.

Conclusions (2/2)

- Further, for three reductants tested, hydrogen peroxide was found to outperform glucose and citric acid. However, precautions of potential risks caused by chlorine gas have to be made when acid leaching was conducted using HCl.

Thanks for your attention