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## Recovery Zinc and Manganese from Spent Battery Powder by Hydrometallurgical Route

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### Abstract

Spent Zn–MnO<sub>2</sub> battery electrode powder, containing 30.1% of Mn and 25.6% Zn was treated via reductive leaching by H<sub>2</sub>SO<sub>4</sub> and selective precipitation by NaOH at pH 13 for Mn(OH)<sub>2</sub> and then pH 10 for Zn(OH)<sub>2</sub>, and the hydroxides converted respectively to MnO<sub>2</sub> and ZnO by calcination. The effects of H<sub>2</sub>SO<sub>4</sub> concentration, leaching time, solid-liquid ratio, reaction temperature were investigated. H<sub>2</sub>SO<sub>4</sub> can totally dissolve Zn, but leaching rate of manganese is only 60% because of the existence of Mn (IV). Ascorbic, citric and oxalic acids were tested as the reducing agent, and ascorbic acid performs the better efficiency. The optimal reductive leaching condition were determined as 0.5 mol/L of H<sub>2</sub>SO<sub>4</sub>, 20 ml/g, 25°C, ascorbic acid dosage 10g/L for 2hours. Yielding up to 98% leaching efficiency of the two metals. The recovery rates are about 91% for Zn and 94% for Mn with high purity.

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**Keywords:** Ascorbic acid; electrode powder; reductive leaching; selective precipitation; Zn–MnO<sub>2</sub> battery.

### 1. Introduction

The demand of Zn-MnO<sub>2</sub> batteries is steadily increasing due to the popularity of electronic products from home appliances to personal portable. Since these batteries is easy to manufacture and safe to carry, the consumption of Zn-MnO<sub>2</sub> batteries is high compared to other batteries<sup>[1]</sup>. The annual consumption amount of Zn-MnO<sub>2</sub> batteries in Taiwan is about 9,000 to 10,000 tons<sup>[2]</sup>. According to Taiwan Recycling Fund Management Board report, it has reached the target of a 50% collection rate in 2009, which is as effective as in EU countries<sup>[3]</sup>. Zn-MnO<sub>2</sub> batteries

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have a stainless steel shell, zinc can as the anode,  $\text{MnO}_2$  powder as an active material of positive electrode. It also includes carbon rod,  $\text{NH}_4\text{Cl}$  solution,  $\text{ZnCl}_2$  solution and starch mixed into the electrolyte. In the recycle process, steel shell was recycled in the preliminary treatment. However, electrode powder with high Mn and Zn content were landfilled or incinerated, instead of being collected and recycled. It will cause many environmental problems [4]. The recycling of electrode powder from spent Zn- $\text{MnO}_2$  batteries not only enhances the environmental protection from reduced amount of hazardous wastes [5] but also reserves the application secondary resources.

There are two major recycling process, namely pyrometallurgy and hydrometallurgy, for treating Zn- $\text{MnO}_2$  battery. Pyrometallurgical processes are the most used in EU. The examples of such processes are BATREC, SNAM-SAVAN, and INMETCO [6, 7]. The process consists basically of selective volatilization of metals at elevated temperatures followed by condensation [8]. However, the disadvantage is the need for gas purification equipment, and large energy consumption [9]. Hydrometallurgical processes are considered environmentally suitable and economical for treating even materials of low metal grade at small scale. They can process secondary resources containing different impurities [10]. The first step of hydrometallurgy is physical treatment step includes crushing, magnetic separation, separated from plastic, iron scraps and paper residues, and electrode powder is accounted for 50% of total weight [11]. The next step is leaching by acidic solutions to convert the metals from the powder to the aqueous liquor. And then extract zinc and manganese by many methods. Since  $\text{MnO}_2$  is insoluble [12-13], reducing tetravalent manganese is the most important issue in acid leaching step. There are many reducing agent were studied. Carbohydrate such as glucose and sucrose [14-17], organic acid [18-20], sulfur dioxide [21-22], hydrogen peroxide [23] were used. After acid leaching, many kinds of methods that separate manganese and zinc from liquor have been studied such as chemical precipitation, solvent extraction [24-26] and electrolysis [27]. Hydroxide [28-29] was used to exact metals for chemical precipitation. Compared to other methods, chemical precipitation is a simpler and cheaper method to separate metals.

The previous studies show that it is an environmentally friendly and effective method to extract manganese and zinc from Zn- $\text{MnO}_2$  batteries when added reduce agent. A hydrometallurgical route is proposed in this study; the raw material is the electrode powder from Zn- $\text{MnO}_2$  batteries. In the reductive leaching experiment, sulfuric acid was the leaching agent. Ascorbic acid, citric acid and oxalic acid were tested as the reducing agent and find the best one. Subsequently, precipitating metals as zinc hydroxide and manganese hydroxide by sodium hydroxide. Finally, metal hydroxides converted into  $\text{MnO}_2$  and  $\text{ZnO}$  by calcination as final product for secondary raw material.

## 2. Experimental

### 2.1. Materials, reagents and instrument

The sample Zn- $\text{MnO}_2$  electrode powder was dissolved by sulfuric acid ( $\text{H}_2\text{SO}_4$ , Sigma-Aldrich 98%) is the leaching agent, ascorbic acid ( $\text{C}_6\text{H}_8\text{O}_6$ , Sigma-Aldrich 99.7% -100%), citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ , JT Baker ), oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ , Sigma-Aldrich 99%) are the reducing agent to reduce manganese(IV). Adjusting pH value by sodium hydroxide (NaOH, Showa 97%) to precipitate zinc and manganese.

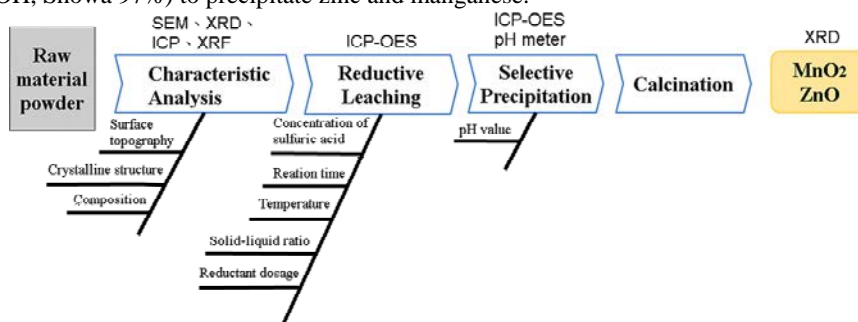


Fig. 1. Flow chart of experiment and parameter

Scanning electron microscope (SEM, Hitachi S-3000N) was used to observe powder particle size and surface microstructure; X-ray diffraction (XRD, Dandong, DX-2700) was used for determine crystalline phase of sample

and the final product. Inductively coupled plasma optical emission spectrometry (ICP-OES, Varian, Vista-MPX) for quantitative analysis of dissolved manganese and zinc. X-ray fluorescence analyzer (XRF, Spectro XEPOS) and elemental analyzer (EA, Elementar vario EL) were used as semi-quantitation analysis. The experiment consists raw material characteristic analysis, reductive leaching, selective precipitation and calcination. Fig. 1 shows the flow chart of experiment and parameters.

## 2.2. Reductive leaching

The electrode powder as raw material was first dissolved by sulfuric acid. The leaching parameters such as concentration, reaction time and solid-liquid ratio, temperature were investigated. Temperature was controlled by a heater equipped with magnetic stirrer (200 rpm). The dissolution reaction as follows:



Three different organic acids (ascorbic acid, citric acid and oxalic acid) were used as reducing agent to reduce manganese (IV) and compared for their effectiveness. The required stoichiometric dosages of reducing agents were calculated based on reactions (4) to (6), and Table 1 shows the parameters set in leaching experiment.

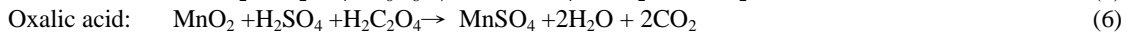
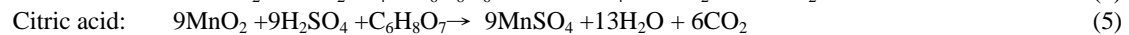


Table 1. Experiment parameter setting

Parameter	Parameter selection
Concentration(mol/L)	0.5, 1, 2, 3, 4, 5
Reaction time(min)	3, 9, 27, 81, 243
Temperature(°C)	25, 40, 60, 80
Solid-liquid ratio(ml/g)	5, 10, 20, 30, 40, 50

## 2.3. Selective precipitation and calcination

Precipitation experiments were carried out in the filtered liquor at different pH values. Solubility product constants ( $K_{sp}$ ) are used to describe saturated solutions of ionic compounds of relatively low solubility. A saturated solution is in a state of dynamic equilibrium between the dissolved, dissociated, ionic compound and the undissolved solid. The lower the number the more difficult to dissolve. Precipitation principle is that metal hydroxide has low  $K_{sp}$ , so we can separate them respectively. The  $K_{sp}$  of zinc and manganese hydroxide at 25°C as follows Eq. (7) and (8) [30]:



The liquors obtained at the optimal parameters in the study of the acid leaching step. The leaching liquor was treated with 1mol/L sodium hydroxide (NaOH) to adjust the pH value. Researching the precipitation rate changes follow by pH value. The  $\text{Mn(OH)}_2$  and  $\text{Zn(OH)}_2$  by selective precipitation were further calcined in air atmosphere to obtain  $\text{MnO}_2$  and  $\text{ZnO}$ .

## 3. Results and discussion

### 3.1. Characteristic analysis of raw material

The SEM image of a raw material powder which is mixture of the cathode (manganese oxides and graphite) and the anode (zinc oxides and electrolytic solution) materials was shown in Fig. 2. The particle diameter is 5 $\mu\text{m}$  to 100 $\mu\text{m}$  that has irregular shape and rough surface and many fine particles adhere to the larger particles.

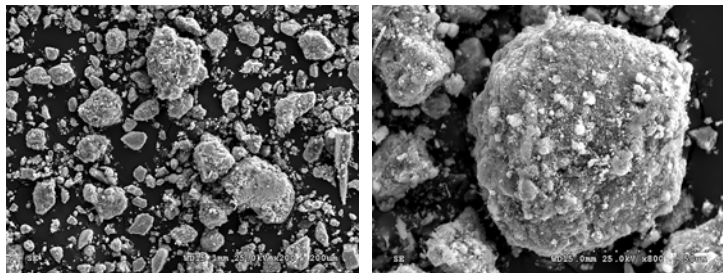


Fig. 2. Microstructure of raw material by scanning electron microscope

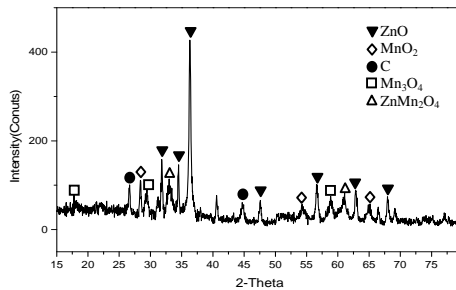


Fig. 3. The XRD pattern of raw material

Diffraction patterns (Fig. 3) shows the specific zinc oxide (ZnO) peak. It also reveals the raw material powder mainly containing manganese dioxide (MnO<sub>2</sub>), manganese tetroxide (Mn<sub>3</sub>O<sub>4</sub>), carbon (C), hetaerolite (ZnMn<sub>2</sub>O<sub>4</sub>) [31].

Table 2. Composition of raw material

Element	Mn	Zn	Fe	C	K	Cl
wt%	30.07%	25.62%	6.71%	5.12%	6.44%	4.53%

The raw material was dissolved by aqua regia at solid-liquid ratio of 1:50, 80°C for 6 hours, then analyzed by ICP-OES. Table 2 shows the results that manganese and zinc amount for about 30% and 25%, respectively, but with 6.7% of iron. The iron remain in the raw material was because of the incompletely magnetic separation. The potassium chloride is an electrolyte, may contribute to reduce the consumption of sulfuric acid in the acidic leaching step [9]. Carbon (graphite) is the inert electrode in the battery which can't dissolve in aqua regia.

### 3.2. Reductive leaching

Fig. 4 shows that the leaching rate of manganese continues to increase with acidity. However, the leaching rate of manganese can only reach about 60% even in 5mol/L sulfuric acid. According to the Eh-pH diagram of manganese [32], the reduction potential must be adjusted to reduce insoluble manganese (IV) to soluble manganese (II). In the other hand, zinc can be dissolve completely at low acidity.

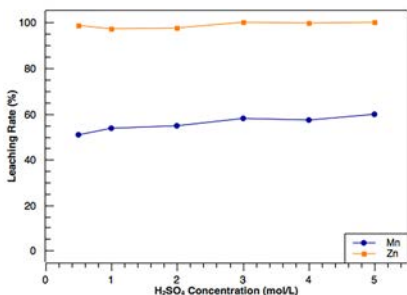


Fig. 4. The concentration of sulfuric acid(at 20 ml/g, 3hours, 25°C, 200rpm)

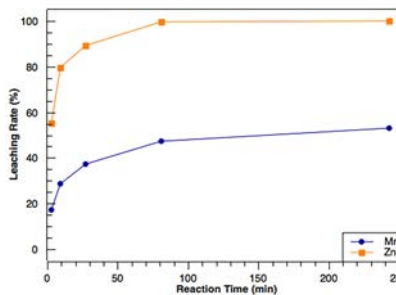


Fig. 5. Reaction time(at 0.5mol/L H<sub>2</sub>SO<sub>4</sub>, 20 ml/g, 25°C, 200rpm )

In Fig. 5, the results revealed that the leaching rate of manganese still increased between 81-243 minute, but the reaction is very slow. Therefore, the reaction time in this study was set up at three hours. Compared to manganese, zinc has reached 99% of leaching rate within 81 minutes.

Fig. 6(a) shows that the leaching rate of manganese was increased about 10% as the increasing temperature, zinc can be leached easily without heating. Fig. 6(b) shows the variation in leaching rate of manganese to determine the effect of acidity and temperature. It can be seen that when the temperature increased from 25 to 80°C, the leaching

rate of manganese increase from 50% to 60% at lower concentration. However, the efficiency increases from 56% to 76% when the temperature increased from 25 to 80 °C at the concentration of 4mol/L and 5mol/L. This result shows temperature effect plays a significant role in high concentration condition.

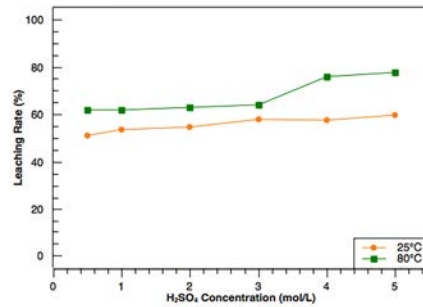
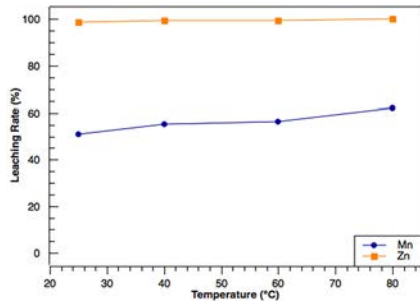


Fig. 6(a) Temperature (at 0.5mol/L H<sub>2</sub>SO<sub>4</sub>, 3hours, 20 ml/g, 200rpm) Fig. 6(b) Temperature and Concentration (at 3hours, 20 ml/g, 200rpm)

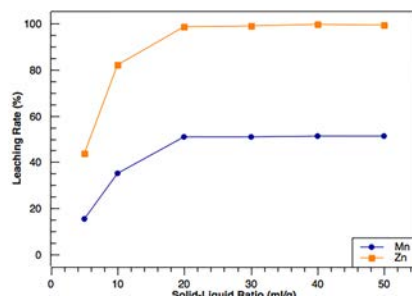


Fig. 7. Solid-liquid ratio(at 0.5mol/L H<sub>2</sub>SO<sub>4</sub>, 3hours, 25°C, 200rpm)

The reaction will be equilibrium with solid-liquid ratio at 20 ml/g, the efficiency keeps at a constant with higher ratio. Fig. 7 shows that 20 ml/g is the most moderate ratio under 0.5 mol/L H<sub>2</sub>SO<sub>4</sub>, which means that 0.01 mol of H<sub>2</sub>SO<sub>4</sub> is necessary for one gram of raw material to dissolve.

Since the leaching rate of manganese were increase slightly in sulfuric acid leaching experiment, due to the insoluble of Mn<sup>4+</sup> [32]. The reduction potential needs to be modified to turn Mn<sup>4+</sup> into Mn<sup>2+</sup>. The efficiency of reductive leaching by three different organic acids is shown in Table 3. The dosage was their stoichiometric requirement. The result indicated that ascorbic acid performed the highest leaching rate of manganese. Ascorbic acid and citric acid have almost the same results for zinc. Therefore, this study suggested ascorbic acid is the optimum reducing agent for reductive leaching. The effect of ascorbic acid will be studied in the following experiment.

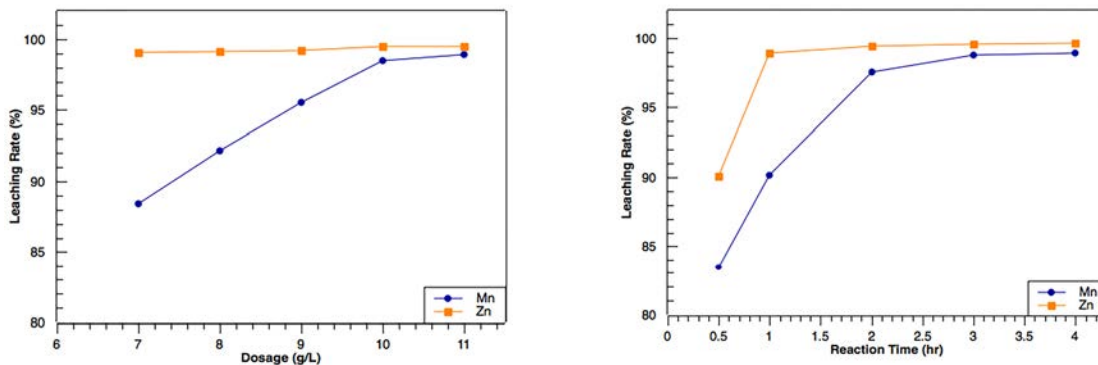
Table 3. The leaching rate of zinc and manganese by using different reductant (at 0.5mol/L H<sub>2</sub>SO<sub>4</sub>, 3hours, 20 ml/g, 25°C, 200rpm)

	Ascorbic acid	Citric acid	Oxalic acid
Mn	98.79%	91.59%	87.45%
Zn	99.51%	99.87%	96.43%

The effect of the leaching rate of manganese was carried out at different ascorbic acid dosages (7-11g/L) in Fig. 8(a). The results showed the effect of leaching rate of manganese increased distinctly while adding ascorbic acid at low acidity. 10g / L of ascorbic acid dosage was sufficient to leach almost all manganese from Zn-MnO<sub>2</sub>battery powder. In addition, the leaching rate of zinc was over 98% whether adding ascorbic acid or not.

Fig. 8(b) shows the leaching rate follow by time when ascorbic acid was added. The leaching time was modified in steps between 30 to 240 min. The leaching rate of manganese and zinc were 83% and 90% respectively at 30 min. The reaction was equilibrium at 120 min, and the leaching rate reached over 98% for two metals. Ascorbic acid not

only improved the leaching of manganese but also decreased the reaction time. Based on the above results, Table 4 shows the optimal parameters.



a. Ascorbic acid dosage (at 3 hours, 25°C)      b. Leaching time of ascorbic acid (at 10g/L)  
 Fig. 8. Ascorbic acid dosage (at 0.5mol/L H<sub>2</sub>SO<sub>4</sub>, 20 ml/g, 25°C, 200rpm)

Table 4. Optimal parameters of reductive leaching

Concentration (mol/L)	Time (hour)	Temperature (°C)	Solid-liquid ratio (ml/g)	Ascorbic acid (g/L)
0.5	2	25	20	10

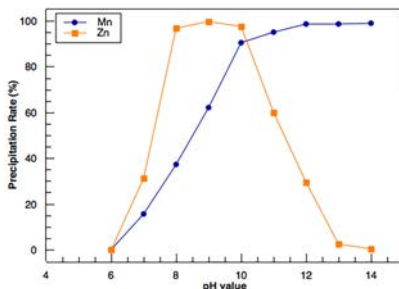


Fig. 9. Precipitation rate of zinc and manganese

Comparing to aforementioned study [14, 19-20, 23, 29], the results in this study revealed the higher leaching rate of manganese, the lower sulfuric acid dosage, the shorter reaction time.

### 3.3. Selective precipitation

The precipitation of manganese and zinc was investigated using the liquors obtained at the best operational conditions found in the study of the reductive leaching experiment. The changes in the zinc and manganese precipitation as function of pH values are shown in Fig. 9. Manganese and zinc did not separate at the pH value between 6 to 11. Manganese ion almost transferred to Mn(OH)<sub>2</sub> at pH = 11, and did not dissolve again. In contrast, zinc exhibits amphoteric character, it re-dissolves at the pH value greater than 10. The reaction is Zn(OH)<sub>2</sub> + 2OH<sup>-</sup> → Zn(OH)<sub>4</sub><sup>2-</sup> as zinc Eh-pH diagram shown [32]. According to the results, the pH should first adjust over 13 for manganese hydroxide to precipitate, then modified to 10 to precipitate zinc hydroxide.

### 3.4. Calcination

According to the reference [33-35], the hydroxides will convert to MnO<sub>2</sub> and ZnO by calcination. Therefore, this study calcined Mn(OH)<sub>2</sub> at 400 °C for 1hour and calcined Zn(OH)<sub>2</sub> at 600 °C for 1hour with air. The XRD pattern of



the final product  $\text{MnO}_2$  and  $\text{ZnO}$  is displayed in Fig. 10. Additionally, no impurity phase was found in the XRD pattern that revealed  $\text{MnO}_2$  and  $\text{ZnO}$  were high purity. In this study, the total recovery rate of zinc and manganese are about 91% and 94% respectively.

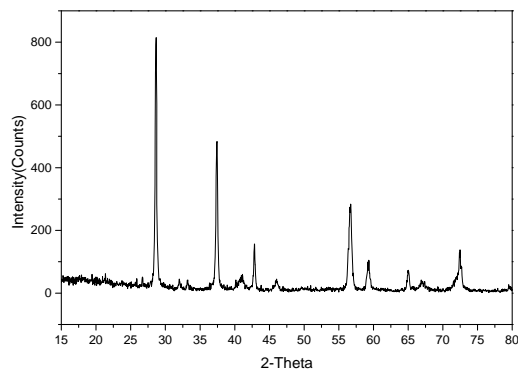


Fig. 10. (a) XRD pattern of  $\text{MnO}_2$

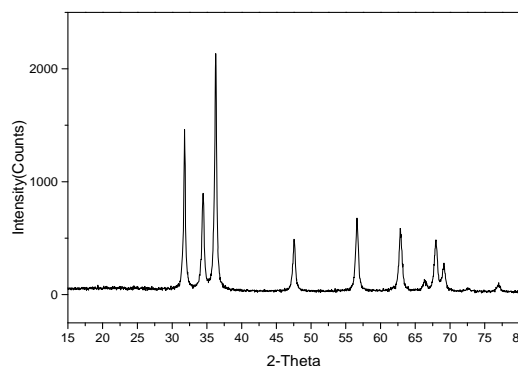


Fig. 10. (b) XRD pattern of  $\text{ZnO}$

#### 4. Conclusions

This study proposed a hydrometallurgical route to recovery zinc and manganese from the  $\text{Zn-MnO}_2$  battery electrode powder. The particle size of this powder is between  $5\mu\text{m}$  to  $100\mu\text{m}$ . It contains about 30.1% manganese, 25.6% zinc, 6% iron, 5% carbon, and the zinc oxide ( $\text{ZnO}$ ) and manganese tetroxide ( $\text{Mn}_3\text{O}_4$ ) were the main crystal phase in the sample. Zn can totally dissolve in low concentration of  $\text{H}_2\text{SO}_4$ . However, the leaching rate of Mn is only 60%. Using three organic acids as the reducing agent can increase the leaching rate of insoluble Mn(IV) significantly, especially ascorbic acid. The optimal condition was 0.5 mol/L of  $\text{H}_2\text{SO}_4$  with 10 g/L of ascorbic acid solid-liquid ratio of 20 ml/g in 2 hours and  $25^\circ\text{C}$ . Both zinc and manganese leaching rates are over 98%. The precipitation test revealed that it was not possible to separate manganese and zinc in neutral pH value. Therefore, the separation process is to adjust pH to 13 for manganese hydroxide precipitation. After removing manganese, adjust pH value to 10 to precipitate zinc hydroxide. Two kinds of metal hydroxides were calcined as  $\text{MnO}_2$  and  $\text{ZnO}$  with high purity. Above all, the total recovery rates are about 91% for Zn and 94% for Mn.

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