Simultaneous Recovery of Zinc and Manganese from Cadmium-Containing Mixed-Battery Leachate by Separation and Purification Process

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A study on the simultaneous separation of Zn and Mn from a feed solution containing various types of dissolved battery wastes was carried out by a solvent extraction process using D2EHPA. The selective recovery of Zn and Mn from feed solutions containing Cd ions is difficult due to their similar physicochemical behavior. Therefore, 99.9% of Zn, 99.8% of Mn, and 99.9% of Cd were extracted using the optimum conditions of 40 vol% D2EHPA, 40 vol% NaOH concentration, 2-stage countercurrent extraction, and an O/A ratio of 2. The Co-extracted Co could be scrubbed using pH 2 sulfuric acid at an O/A ratio of 1, and Cd was then scrubbed using 0.5 M Na₂S₂O₃. The results of the Cd scrubbing experiments indicated that the optimum conditions were 3-stage countercurrent scrubbing and an O/A ratio of 2, and the scrubbing efficiency of Cd was approximately 99.9%. The Zn and Mn that remained in the loaded organic could be enriched by increasing the O/A ratio of the stripping stage to 6. From this concentrated solution, high purity zinc manganese sulfate powder, which can be used as a raw material for fertilizer for crop cultivation, was manufactured. [doi:10.2320/matertrans.M2019033]

(Received January 29, 2019; Accepted March 12, 2019; Published April 19, 2019)

Keywords: hydrometallurgy, recycling of mixed battery wastes, cadmium, simultaneous zinc and manganese recovery, zinc manganese sulfate

1. Introduction

As the use of various electronic devices increases in the modern era, the demand for batteries, which are essential for the operation of such electronic devices, is also rapidly increasing. The increase in battery usage has spontaneously led to an increase in the generation of battery waste. In South Korea, 11,630 thousand tons of manganese/alkaline batteries, 483 thousand tons of nickel-cadmium batteries (Ni-Cd batteries), 195 thousand tons of nickel metal hydride batteries (NiMH batteries), and 300 thousand tons of lithium primary batteries were collected as waste in 2017.¹⁾ These battery wastes still contain valuable metals such as Zn, Mn, Co, Ni, and Li, and these elements can be recovered and used to synthesize various compounds for many types of industry. In particular, zinc manganese sulfate can be manufactured from Zn and Mn recovered from various resources, including battery wastes. This compound is used as a fertilizer for the cultivation of various crops such as fruits and grains.^{2,3)} However, battery wastes contain a typical heavy metal, Cd, in addition to the other valuable metals. If battery wastes are buried or incinerated without significant metallurgical processing, the Cd in the waste may cause air, soil, and water pollution. In addition, the Cd content of zinc manganese sulfate fertilizer must be controlled, because Cd adversely affects the cultivation of crops. Therefore, Cd should be removed during the metallurgical processing of battery wastes. Several studies have been conducted on the recovery of Zn, Mn, and Cd from various battery wastes.

De Michelis *et al.* recovered Zn and Mn from spent alkaline and zinc-carbon batteries by leaching. Zn and Mn were 99% and 96% dissolved through a countercurrent leaching process, respectively.⁴⁾ De Souza and Tenorio recovered Zn and Mn simultaneously from household

alkaline batteries using a hydrometallurgical process consisting of leaching and electrowinning. However, the leaching efficiency of Mn was quite low at 40%.⁵⁾ Salgado *et al.* tried to recover Zn and Mn from spent alkaline batteries by solvent extraction with Cyanex 272. 90% of the Zn was extracted, whereas only 7% of the Mn was extracted.⁶⁾ Shin *et al.* studied the recovery of Zn and Mn from alkaline manganese batteries. Most of the Zn and Mn were leached using sulfuric acid in the presence of the reducing agent H₂O₂.⁷⁾ Chen *et al.* recovered Zn and Mn from spent Zn-MnO₂ battery electrode powder. The electrode powder was treated by reductive sulfuric acid leaching, and then Zn(OH)₂ and Mn(OH)₂ were precipitated by increasing the pH using NaOH. These hydroxides were calcined and converted into their oxide forms. The recovery efficiencies of Zn and Mn were 91% and 94%, respectively.⁸⁾ Zhu *et al.* recovered Cd by vacuum distillation at the high temperature of 1173 K over 3 hours at 10 Pa, and Umesh and Hong recovered 88% of Ni and 84% of Cd from Ni-Cd battery wastes by a chemical method using ferric sulfate solution.^{9,10)} Mahandra *et al.* studied the recovery of Zn and Cd from Zn-C batteries and Ni-Cd batteries, respectively. However, each metal was recovered separately without mixing the two types batteries by solvent extraction using Cyphos IL 104.¹¹⁾ The BATENUS process is used for the recovery of metals from mixtures of zinc-carbon, alkaline manganese, lithium, and Ni-Cd cells. This process consists of mechanical treatment and hydrometallurgical processing, finally recovering Zn, Cu, Ni, Cd, and Mn. However, this process was discontinued because it was not economical.¹²⁾ Tanong *et al.* studied the recovery of Zn, Mn, Cd, Co, and Ni from spent mixed batteries by sequential hydrometallurgical processing. After applying a leaching process to the spent mixed battery powder, Zn was first extracted using Cyanex 272 and TBP. Mn and Cd were then simultaneously extracted using D2EHPA and TBP. After stripping Mn and Cd from the loaded organic, Cd was

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recovered as a metal by electrodeposition, and Mn was precipitated as MnCO_3 .^{13,14)}

In addition, various studies have been carried out to separate and recover Zn, Mn, and Cd from sources other than battery wastes. Kumbasar studied the recovery of Cd from a zinc plant leaching solution by an emulsion liquid membrane using trioctylamine (TOA). The recovery of Cd reached 95% under the optimum conditions, but about 1.4% of the Zn was also extracted.¹⁵⁾ Gupta *et al.* extracted Cd using Cyanex 923 from a hydrochloric acid medium also containing Al, Fe, In, Mn, Co Ni, Cu, Zn, and Pb. Selective recovery of more than 98% of Cd was achieved.¹⁶⁾ Haghighi *et al.* studied the separation of Zn from Mn, Mg, Ca, and Cd using D2EHPA. The optimum conditions were 3-stage counter-current extraction and an O/A ratio of 1, and the extraction efficiency of Zn was 89%. By scrubbing using a ZnSO_4 solution, the trace concentrations of Fe, Mn, Ca, and Cd in the loaded organic were rejected, and finally an 88.8 g/L Zn solution was obtained.¹⁷⁾ Daryabor *et al.* studied the solvent extraction of Cd and Zn from sulfate solutions using D2EHPA by comparing mechanical agitation and ultrasonic irradiation. In the presence of only the ultrasound system, both the Cd and Zn extraction efficiencies increased, so its selectivity was lower than that of the mechanical stirring system. Using both the mechanical and ultrasonic systems, on the other hand, Zn was extracted selectively from Cd by D2EHPA.¹⁸⁾

Until now, most studies have focused on the recovery of valuable metals from a single type of battery waste, which is a way to minimize the effects of other impurities on the recovery of the desired elements. In addition, research has yet to be conducted on the possibility of applying products obtained through such recycling processes to other types of industry. In this study, therefore, zinc manganese sulfate, which is a raw material for fertilizer applied in other industries, i.e., agriculture, was produced by simultaneously recovering Zn and Mn from the mixed battery wastes. Moreover, the Cd in the mixed battery wastes, which has an adverse effect on zinc manganese sulfate, was separated from Zn and Mn through a hydrometallurgical process.

2. Experimental Procedure

2.1 The preparation of feed solution for solvent extraction

The feed solution for the co-extraction of Zn and Mn was prepared by leaching with 1 M sulfuric acid at the optimum conditions after heat treatment of the mixed batteries at a certain ratio as in the previous study.¹⁹⁾ Figure 1 shows the distinctions between the previous study and the present study as a process flow sheet. In the leaching solution, impurities such as Fe, Al, and Cu were precipitated by adding NaOH to raise the pH. The elemental contents of the feed solution used for solvent extraction are shown in Table 1.

2.2 Solvent extraction

The extractant used for solvent extraction was di-2-ethylhexyl phosphoric acid (D2EHPA), which is well-known as a representative cationic extractant. First, a pH isotherm experiment was carried out to derive the pH range in which

Fig. 1 Process flow sheets of previous (left) and present (right) study.

Table 1 Concentrations of elements and pH of feed solution for solvent extraction (mg/L).

Component in feed solution	Concentration
Zn	9261
Mn	11242
Cd	2238
Co	10081
Ni	9175
Li	1714
Fe	1
Al	18
Cu	2
pH	5.56

Zn and Mn can be simultaneously extracted. In the pH isotherm experiment, 40 vol% D2EHPA and the feed solution were added to a beaker at an O/A ratio of 1 and stirred at 250 rpm with a magnetic stir bar. The pH was increased from 1.5 to 8.0 at intervals of 0.5 with NaOH and sampled at equal intervals. After sampling, the raffinate was analyzed to determine the metal ion extraction efficiency. The D2EHPA was diluted with kerosene and its concentration was fixed at 40 vol% without purification. The extraction tendency of the metal was investigated using concentration of NaOH from 0 vol% to 50 vol%, and the optimum concentration of NaOH was determined by calculating the distribution ratio and separation factor. A McCabe Thiele diagram for the countercurrent multi-stage extraction under the optimum conditions was constructed after the experiment according to the O/A ratio.

2.3 Scrubbing and stripping experiment

The optimization of the scrubbing process to remove the co-extracted impurities, especially Co and Cd, was carried out using pH-adjusted sulfuric acid, ethylenediaminetetraacetic acid (EDTA), and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$). The pH was adjusted to pH 2, 3, 4, or 5 using sulfuric acid. The concentrations of EDTA and $\text{Na}_2\text{S}_2\text{O}_3$ used were 0.01, 0.05, 0.1, 0.5, and 1.0 M for EDTA and 0.1, 0.3, 0.5, 0.7, and 1.0 M for $\text{Na}_2\text{S}_2\text{O}_3$. The O/A ratio of all the scrubbing experiments was 1. A countercurrent multi-stage scrubbing experiment was conducted for the complete removal of Cd using a McCabe Thiele diagram scheme for Cd scrubbing. In order to enrich and strip all of Zn and Mn from the loaded organic, stripping was carried out using 2-stage countercurrent stripping at an O/A ratio of 6 using 1.5 M sulfuric acid. All separation and purification experiments were carried out on a batch scale, and the organic and aqueous phases were mixed at 250 rpm using an automatic shaker (model SI-600R, Jeiotech, South Korea). After the reaction, the organic and aqueous phases were separated in a separation funnel, and the aqueous phase was filtered and analyzed by atomic absorption spectroscopy (model AA-7000, Shimadzu Corp., Japan).

2.4 Vacuum evaporation

Vacuum evaporation was carried out by adding a zinc manganese sulfate solution to a 1 L round-bottom flask. The reaction was performed at 80 rpm and 80°C using a mechanical stirrer (model R-215, BÜCHI, Switzerland) to remove the moisture as steam, and zinc manganese sulfate powder was obtained.

3. Results and Discussions

3.1 pH isotherm experiment

The purpose of the pH isotherm experiment was to identify the pH conditions in which the Zn and Mn in the feed solution could be simultaneously separated and purified and the impurities could be co-extracted. The results of pH isotherm experiment are shown in Fig. 2 and Table 2. The extraction of metal ions in the feed solution followed the order $\text{Zn} > \text{Mn} > \text{Cd} > \text{Co} > \text{Ni} > \text{Li}$. In particular, Cd

Fig. 2 pH isotherm experiment for 40 vol% D2EHPA.

Table 2 Concentrations of elements with equilibrium pH of the raffinate for solvent extraction (mg/L).

Equilibrium pH	Concentration of Elements* ¹					
	Zn	Mn	Cd	Co	Ni	Li
1.5	1213	7344	1809	9677	8891	1677
2	352	5369	1468	9609	8874	1677
2.5	83	3207	1065	9390	8787	1650
3	28	2118	718	9090	8715	1548
3.5	9	1141	399	7545	8471	1591
4	9	760	191	6226	7974	1559
4.5	N.D	534	152	4404	7824	1591
5	N.D	414	129	3161	7075	1586
5.5	N.D	337	119	2404	6189	1559
6	N.D	317	111	2327	5322	1557
6.5	N.D	298	103	2206	4982	1542
7	N.D	293	110	1965	4247	1484
7.5	N.D	256	122	1378	3605	1452
8	N.D	247	156	1237	2587	1447

*¹ Not Detected

could be extracted as an impurity when extracting Mn. The ΔpH_{50} value, which represents the difference in the pH value when 50% of the two metal ions are extracted, indicates the separation behavior of the two elements. If the value of ΔpH_{50} is low, the extraction behavior of the two elements is similar, and separation of the two elements by solvent extraction will be difficult. Based on the pH isotherm experiment, the ΔpH_{50} value between Mn and Cd is 0.5. This means that Cd can be easily co-extracted in the pH range used to extract Mn. It also indicates that it is difficult to separate Mn from Cd by only the solvent extraction process. Therefore, from this solvent extraction process, conditions for the simultaneous extraction of Zn, Mn, and Cd were derived.

3.2 Effect of NaOH concentration

The equilibrium pH range of the aqueous solution in solvent extraction is an important factor in the separation and purification of metal ions. D2EHPA, which is an acidic extracting agent, exchanges hydrogen ions into aqueous solution when extracting metal ions, so that the pH of the aqueous solution is decreased after extraction. Eventually, the extraction of the metal ions no longer occurs since the concentration of hydrogen ions in the aqueous solution is increased. Therefore, it is necessary to adjust of pH value using NaOH to suppress the generation of hydrogen ions and to maintain a stable equilibrium pH. In order to extract Zn, Mn, and Cd with D2EHPA, the effect of the adjusting the concentration of NaOH on the extraction efficiency of the metal was examined at 40 vol% D2EHPA. The extraction efficiencies of Zn, Mn, and Cd increase with the concentration of NaOH. The addition of NaOH prevented a significant drop in the pH during the solvent extraction process.

Table 3 Distribution ratio (D_M) and separation factor values for $\beta_{((Zn+Mn+Cd)/Co)}$ and pH at different concentration of NaOH (M: Zn, Mn, Co, Ni, Cd).

Concentration of NaOH, vol. %	Distribution ratio, D_M					Separation factor, $\beta_{((Zn+Mn+Cd)/Co)}$	pH
	Zn	Mn	Co ($\times 10^{-2}$)	Ni ($\times 10^{-2}$)	Cd ($\times 10^{-2}$)		
0	5.43	0.38	5.63	0.00	1.32	103	1.27
10	12.2	0.63	3.88	2.58	4.19	332	1.54
20	35.8	1.17	8.26	4.77	31.5	451	1.81
25	60.7	1.58	7.65	5.90	53.8	821	2.04
30	114	2.40	9.54	8.15	85.4	1229	2.26
40	499	4.91	17.6	9.46	228	2876	2.86
50	999	11.0	41.3	11.8	583	2460	3.41

On the other hand, Co and Ni were hardly extracted because the equilibrium pH was maintained at about 3.4 even when the concentration of NaOH was 50 vol%. Since some Co was extracted, however, the separation factor of Co with respect to Zn, Mn, and Cd for different concentration of NaOH should be considered to derive the optimum conditions. The separation factor can be derived from the distribution ratio, which represents the ratio of the concentrations present in the organic phase and aqueous phase. The distribution ratio and separation factor of Co with regards to Zn, Mn, and Cd was calculated as follows:

$$D_M = \frac{[M]_{org}}{[M]_{aq}} \quad (1)$$

$$\beta_{((Zn+Mn+Cd)/Co)} = \frac{D_{Zn} + D_{Mn} + D_{Cd}}{D_{Co}} \quad (2)$$

Table 3 lists the distribution ratios (D) of the elements for each concentration of NaOH and the separation factor of Co compared with those of Zn, Mn, and Cd. The value of the separation factor was the highest (2,876) at 40 vol% NaOH concentration. Although more Zn and Mn were extracted at 50 vol% NaOH concentration, the relative co-extraction of Co was also greater. This means that the separation of Co from Zn, Mn, and Cd is more difficult at 50 vol% NaOH concentration. Therefore, the separation factor at 40 vol% NaOH concentration was lower than that at 50 vol% NaOH concentration. As a result, the optimum concentration of NaOH for the solvent extraction of Zn, Mn, and Cd was 40 vol%.

3.3 McCabe Thiele diagram for the extraction of Zn, Mn, and Cd

In order to simultaneously extract Zn, Mn, and Cd, a 40 vol% of concentration of NaOH and a 40 vol% D2EHPA concentration were set as the optimal conditions. However, since not all of the Zn, Mn, and Cd in the feed solution could be extracted in a single stage under these conditions, adjustment of the O/A ratio and countercurrent multi-stage extraction should be considered. As the extraction proceeds in the countercurrent direction, the extraction efficiency of the desired metal can be improved through the crowding

Fig. 3 McCabe Thiele diagram for the extraction of zinc, manganese and cadmium.

Table 4 The concentrations of the elements in the loaded organic and raffinate and their extraction efficiency after 2-stage counter-current extraction (O/A ratio = 2).

Element	Feed solution, mg/L	Raffinate, mg/L	Loaded organic, mg/L	Extraction efficiency, %
Zn	9261	N.D	4630	99.9
Mn	11242	18	5612	99.8
Co	10081	10070	5.5	0.1
Cd	2238	N.D	1118	99.9
Ni	9175	9177	N.D	-
Li	1714	1713	N.D	-

effect.²⁰⁾ The optimal O/A ratio and number of stages can be determined from a McCabe Thiele diagram. Therefore, the McCabe Thiele diagram for Zn, Mn, and Cd was plotted and is shown in Fig. 3. According to the McCabe Thiele diagram, it is possible to extract the Zn, Mn, and Cd in the feed solution from a 4-stage countercurrent extraction process at operating line 1, i.e., O/A = 1, and using 2-stage counter-current extraction at operating line 0.5, i.e., O/A = 2. When the operating line is increased, the usage of solvent is decreased, but the number of stages is increased. Lowering the operating line reduces the number of stages but increases the O/A ratio and thus amount of solvent required. Also, when the O/A ratio increases, the concentration of loaded metal ions is diluted. In this study, the solvent extraction of Zn, Mn, and Cd was carried out using 2-stage countercurrent extraction at an O/A ratio of 2, which increased the economic efficiency of the process by reducing the number of stages. The metal diluted by the increased O/A ratio of the extraction step can be re-concentrated by adjusting the O/A ratio in the stripping process. Table 4 shows the contents of the elements in the final raffinate and the extraction efficiency after 2-stage countercurrent solvent extraction. In the loaded organic, Zn, Mn, and Cd were present in concentrations of 4.6 g/L, 5.6 g/L, and 1.1 g/L, respectively. The Co present

Table 5 Concentrations of the elements in the loaded organic and in each scrubbing solution (O/A ratio = 1) (mg/L).

Scrubbing solution	Element	Zn	Mn	Cd	Co
	Loaded organic	4630	5612	1118	5.5
H ₂ SO ₄	pH 2	4.02	10.0	8.08	5.48
	pH 3	0.38	5.73	3.49	4.59
	pH 4	0.26	2.41	0.53	0.28
	pH 5	0.25	2.32	0.51	0.22
	0.01 M	66.4	263	363	-
EDTA ^{*1}	0.05 M	308	986	730	-
	0.1 M	763	1394	829	-
	0.5 M	4320	5029	833	-
	1.0 M	-	-	-	-
	0.1 M	N.D	N.D	73.1	-
Na ₂ S ₂ O ₃ ^{*1}	0.3 M	N.D	N.D	939	-
	0.5 M	N.D	N.D	1045	-
	0.7 M	N.D	N.D	1100	-
	1.0 M	N.D	N.D	1127	-

^{*1} Performed after scrubbing Co using a pH-adjusted H₂SO₄ solution

could easily be scrubbed because its concentration in the loaded organic was very low at 5.5 mg/L.

3.4 Co and Cd scrubbing experiment

In order to recover only Zn and Mn from the loaded organic solution containing Zn, Mn, Co, and Cd, Co and Cd must scrubbed. The scrubbing results are shown in Table 5. At first, scrubbing experiments were carried out using pH-controlled sulfuric acid. When the pH-controlled sulfuric acid was used as the scrubbing solution, Zn, Mn, and Cd were scarcely scrubbed over the entire pH range tested, but the Co in the loaded organic was completely scrubbed by a sulfuric acid solution adjusted to pH 2. The reaction and the Gibbs free energy of scrubbing the loaded metal ions at 25°C by the pH controlled sulfuric acid solution were calculated as follows using data from the HSC Chemistry database.²¹⁾

As shown in the above reactions, Co, Zn, Mn, and Cd can all be scrubbed using sulfuric acid. Therefore, Zn, Cd, and Mn can be lost in the scrubbing reaction. Since the concentration of Co is relatively low, however, Co can be completely scrubbed without large losses of Cd, Mn, and Zn. The scrubbing of Co was carried out using only a single stage, rather than a multi-stage scrubbing procedure, to prevent the losses of Cd, Mn, and Zn from increasing.

The scrubbing of Co from the loaded organic by pH adjusted sulfuric acid was followed by the Cd scrubbing process. EDTA solution and Na₂S₂O₃ solution were both

used to scrub Cd in order to select the scrubbing solution that best minimized the losses of Zn and Mn and could completely scrub Cd from the loaded organic. In the case of EDTA, loss of Zn and Mn also occurred, making it unsuitable as a scrubbing solution. In general, EDTA is known as a chelating agent that forms a complex with ions such as Cd²⁺, Mn²⁺, and Zn²⁺, and these complexes can be stable in the scrubbed solution.²²⁾ In the scrubbing experiment using 1.0 M EDTA, precipitation occurred during the experiment and the scrubbing efficiency could not be calculated. On the other hand, no loss of Zn and Mn was observed for Na₂S₂O₃; only Cd was scrubbed. Na₂S₂O₃ is known to be an excellent scrubbing solution for Cd.²³⁾ Like EDTA, Na₂S₂O₃ is a chelating agent that complexes with cations such as Cd. In particular, Na₂S₂O₃ forms Cu²⁺, Ag⁺, and Hg²⁺ complexes in addition to Cd²⁺ complexes, and does not form complexes with Zn²⁺ and Mn²⁺ ions.^{24,25)} This is because the stability constants of Zn²⁺ and Mn²⁺ ions with S₂O₃²⁻ ions are smaller than that with Cd²⁺ ion.^{26,27)} The reaction of Cd²⁺ ions with Na₂S₂O₃ is shown below using data from the HSC Chemistry database.²¹⁾

Another solution that can scrub the loaded Cd is NH₄Cl.²³⁾ Like Na₂S₂O₃, the Cd scrubbing with NH₄Cl forms complexes with NH₃ or Cl⁻ ions. Since NH₄Cl can also form complexes of Zn amine, however, it was not applied to Cd scrubbing in this study.²⁸⁾ When 0.5 M Na₂S₂O₃ was used, only 91% of the Cd was scrubbed. The McCabe Thiele diagram for the countercurrent multi-stage scrubbing of Cd using this concentration of Na₂S₂O₃ was prepared to increase the scrubbing efficiency of Cd scrubbing by varying the O/A ratio, and is shown in Fig. 4. According to the McCabe Thiele diagram, Cd requires 3-stage countercurrent scrubbing at operating line 2, i.e., an O/A ratio of 2, and 2-stage countercurrent scrubbing at operating line 1, i.e., an O/A ratio of 1. Therefore, multi-stage countercurrent scrubbing was performed under the above two conditions, and the results are shown in Table 6. Even after the multi-stage countercurrent scrubbing experiment, Zn and Mn were not scrubbed at all, and only Cd was scrubbed. However, about

Fig. 4 McCabe Thiele diagram for scrubbing cadmium.

Table 6 Results of counter-current simulation batch test for Cd scrubbing.

Scrubbing experiment condition	Element	Scrubbing solution, mg/L	Scrubbing efficiency, %
2-stage countercurrent scrubbing	Zn	N.D	-
	Mn	N.D	-
	Cd	1082	97.5
3-stage countercurrent scrubbing	Zn	N.D	-
	Mn	N.D	-
	Cd	2231	100

2.5% of the Cd was not scrubbed using an O/A ratio of 1 and 2-stage countercurrent scrubbing; thus, 3-stage countercurrent scrubbing at an O/A ratio of 2 was set as the optimum condition. Since $\text{Na}_2\text{S}_2\text{O}_3$ does not scrub Co at all, it was not used for Co scrubbing.²³⁾ Therefore, a separate scrubbing stage with pH-adjusted sulfuric acid is required for scrubbing Co.

3.5 Zn and Mn stripping procedure and the manufacture of zinc manganese sulfate

The stripping of Zn and Mn was carried out using 1.5M sulfuric acid and setting the O/A ratio as high as 6. The purpose of the high O/A ratio is to concentrate Zn and Mn into the aqueous phase in order to produce ZnMnSO_4 from

the final stripping solution. When the O/A ratio of the stripping process is increased, however, the concentration of the stripped metal ions increases but the stripping efficiency is decreased. Therefore, in order to increase the stripping efficiency, stripping was carried out using a 2-stage countercurrent stripping procedure. The resulting stripping efficiency for Zn and Mn was more than 99%, and both were enriched in the final stripped solution, which contained 27.7 g/L of Zn and 33.6 g/L of Mn. The used solvent can be regenerated via a water- and acid-washing process. The mass balance of each element in the solvent extraction, scrubbing, and stripping processes is shown in Fig. 5. Vacuum evaporation was performed using 200 ml of the final stripping solution, and zinc manganese sulfate powder was obtained. The compositional analysis result of this powder and its XRD peaks are shown in Table 7 and Fig. 6, respectively. No other impurities were present, and the powder contained 16.1 mass% Mn and 18.4 mass% Zn. The zinc manganese sulfate XRD peak was not present, but the $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ peak and the $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ peak overlapped. The purity of the zinc manganese sulfate is 99.9%, which is sufficient for use as a fertilizer for crop cultivation.

4. Conclusion

In this study, the simultaneous recovery of Zn and Mn from a feed also containing Cd, Co, Ni, and Li was carried

Fig. 5 Mass balance of each element in the hydrometallurgical process.

Table 7 Elemental composition of zinc manganese sulfate (mass%).

Elements of Zinc manganese sulfate	Composition
Zn	18.4
Mn	16.1
Cd	N.D
Co	N.D
Ni	N.D
Li	N.D
Fe	N.D
Al	N.D
Cu	N.D

Fig. 6 XRD results of the zinc manganese sulfate.

out through a hydrometallurgical process. The final results of this research are the following:

- (1) A feed solution for solvent extraction that contained Zn, Mn, Cd, Co, Ni, and Li was obtained from various kinds of battery wastes mixed at a certain ratio through stable heat treatment, physical treatment, and a leaching process under the optimum conditions of a previous experiment.
- (2) The pH isotherm experiment showed that it is difficult to separate Mn and Cd based on the ΔpH_{50} value calculated for the two elements. Therefore, Zn, Mn, and Cd were extracted simultaneously. The optimum conditions were 40 vol% D2EHPA, a 40 vol% NaOH concentration, and 2-stage countercurrent extraction at an O/A ratio of 1. Under these conditions, more than 99% of the Zn, Mn, and Cd were extracted, and Co was slightly co-extracted as an impurity.
- (3) The co-extracted Co was scrubbed using an O/A ratio of 1 by sulfuric acid adjusted to pH 2. The loaded organic that had been scrubbed of Co was completely scrubbed of Cd in a 3-stage countercurrent process using 0.5 M $\text{Na}_2\text{S}_2\text{O}_3$ at an O/A ratio of 2. There was no loss of Zn or Mn during the scrubbing of Cd.
- (4) Stripping of Zn and Mn was carried out using a 2-stage countercurrent process, an O/A ratio of 6, and 1.5 M sulfuric acid. The Zn and Mn were concentrated by the high O/A ratio, and finally a 27.7 g/L Zn and a 33.6 g/L Mn solution were obtained.
- (5) Zinc manganese sulfate powder can be manufactured by vacuum distillation from the highly concentrated Zn and Mn sulfate solution. The final product contains 16.1 mass% Mn and 18.4 mass% Zn, and can be utilized as a source of fertilizer.
- (6) The remaining elements in the raffinate, such as Co, Ni, and Li will be recovered separately. After the recovery of Zn, Mn, and Cd, the remaining organic will be washed with water and acid and then regenerated to recover metals. The metallurgical process described in this study can be applied to other complex minerals and urban mines having similar compositions.

Acknowledgments

This study was supported by the R&D Center for Valuable Recycling (Global-Top R&D Program) of the Ministry of Environment. (Project No.: 2016002220001)

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