

## Cyanex 272를 이용한 폐산화은배터리 침출액으로부터 Ag 및 Zn의 분리

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### Separation of Ag and Zn from Nitrate Leachate of Spent Silver Oxide Batteries by Solvent Extraction with Cyanex272

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#### 요 약

폐산화은 전지의 질산 침출액으로부터 Ag(산화상태)와 Zn(산화상태)의 분리를 위해 cyanex272를 추출제로 사용하여 용매추출 실험을 수행했다. Ag와 Zn의 추출은 질산과 추출제의 농도에 영향을 받았다. Cyanex272는 HNO<sub>3</sub> 농도가 0.1 mol/L보다 낮을 때 Ag보다 Zn을 선택적으로 추출되었다. 공동 추출된 Ag는 1 mol/L thiourea로 탈거하여 제거했다. Ag를 제거한 후 0.5 mol/L HNO<sub>3</sub>를 사용하여 추출된 Cyanex272에서 Zn을 탈거했다. Cyanex272를 사용한 Zn의 추출, thiourea를 사용한 Ag의 탈거, HNO<sub>3</sub>를 사용한 Zn의 탈거에 대한 McCabe-Thiele 다이어그램이 각각 구성되었다. 위 결과는 시뮬레이션 된 계수 전류 추출 및 탈거 실험을 통해 검증되었다. 마지막으로 산화은 전지에서 Ag와 Zn을 분리하는 공정이 제안되었다.

**주제어** : 은, 아연, 질산, Cyanex272, 분리

#### Abstract

The separation of Ag and Zn from the nitrate leachate of spent silver oxide batteries using Cyanex272 as an extractant was investigated. The extraction of Ag and Zn was affected by the concentrations of nitric acid and the extractant. Cyanex-272 selectively extracted Zn over Ag when the HNO<sub>3</sub> concentration was lower than 0.1 mol/L. The co-extracted Ag was removed by stripping with 1 mol/L thiourea. Stripping of Zn from the loaded Cyanex-272 was accomplished using 0.5 mol/L HNO<sub>3</sub> after the removal of Ag. The McCabe-Thiele diagrams for the extraction of Zn with Cyanex-272, the scrubbing tripping of Ag with thiourea, and the stripping of Zn with HNO<sub>3</sub> were constructed. The results were verified by simulated counter-current extraction and stripping experiments. Finally, a process for the separation of Ag and Zn from silver oxide batteries was proposed.

**Key words** : Ag, Zn, HNO<sub>3</sub>, cyanex272, separation

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## 1. Introduction

Silver oxide batteries are applied in a range of electronic products from military applications to medical devices, watches, calculators, and toys<sup>1)</sup>. Spent silver oxide batteries are important resources for Zn and Ag recovery, considering the shortage of this material resource, environmental contamination, and the decline in the cost of waste treatment<sup>1-4)</sup>.

Among of various recovery process, silver oxide batteries are generally dissolved with nitrate acid, cyanide solution, and fermentation liquor<sup>5-7)</sup>. In case of nitrate leachate, Ag and Zn were precipitated by using chloride salts, such as KCl or NaCl<sup>8)</sup>. Expensive equipment and precipitants (including flocculating agent) are inevitable for these methods<sup>9)</sup>. Solvent extraction with various extractants, such as LIX63, D2EHPA, Cyanex471X, were also used to separate Zn and Ag from nitrate leachates of silver oxide batteries<sup>10-13)</sup>. Compared with other metal separation/recovering methods, solvent extraction has an advantage on easy handing and high process efficiency<sup>14,15)</sup>.

In this study, bis(2,4,4-trimethylpentyl) phosphinic acid (cyanex272) was used to separate Ag and Zn from nitrate leachate of silver oxide batteries. The effects of acid and extractant concentrations, phase ratio on the extraction of them were examined. Stripping agent and phase ratio on the stripping of Ag and Zn was also studied. Simulated count-current extraction and stripping experiments were also performed to validate the results.

## 2. Materials and Methods

The aqueous solution was prepared by dissolving AgNO<sub>3</sub> (99.8%, Daejung Chemicals and Metals Co., Ltd.) and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (98.0%, Daejung Chemical and Metals Co., Ltd.) in distilled water. For extractant, Cyanex272 was used without further purification. Kerosene (90% distillation at 265 °C; Daejung) was used as the diluent.

In batch extraction experiments, equal volumes (20 mL) of leachate and extractant were mixed in a sealed bottle (100 mL) and shaken for 30 min using a wrist-action shaker (Model 75, Burrell, USA) at ambient temperature. Then the two phases were separated by using a separation funnel. Stripping experiments were performed through the same procedure by mixing the loaded extractant and stripping solution. The concentration of metals in the solution was measured via inductively coupled plasma optical emission spectrometry (ICP-OES; PerkinElmer Optima 8300).

## 3. Results and Discussions

### 3.1. Effect of HNO<sub>3</sub> concentration on extraction of metals

To investigate the effect of HNO<sub>3</sub> concentration on extraction of metal ions, the concentration of HNO<sub>3</sub> in the feed solution was varied from 0.01 to 5 mol/L, the concentrations of Zn and Ag were kept at 0.0015 and 0.0028 mol/L, respectively. The concentration of cyanex272 was maintained at 0.5 mol/L, and the volume ratio of feed solution to extractant was fixed at 1:1.

The results in Fig. 1 show the effect of HNO<sub>3</sub> concentration in the feed solution on the extraction percentages of metal ions. The extraction percentage of

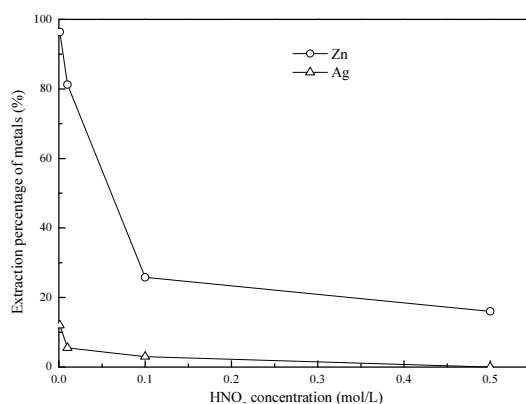
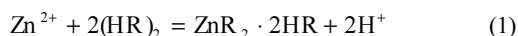


Fig. 1. Effect of acid concentration on the extraction of metals.

both of Zn and Ag decreased with increasing the concentration of  $\text{HNO}_3$  in the feed solution. Cyanex272 selectively extracted Zn over Ag in the  $\text{HNO}_3$  concentration range lower than 0.1 mol/L. when the concentration of  $\text{HNO}_3$  was 0.01 mol/L, the extraction percentage of Zn and Ag was 81.25% and 5.5%.

The extraction reaction can be represented as follows,



where  $(\text{HR})_2$  denotes cyanex272.

### 3.2. Effect of cyanex272 concentration on extraction of metals

Effect of cyanex272 concentration on the extraction of metals was investigated by varying the concentration of cyanex272 in the extractant from 0.1 to 1 mol/L. The concentration of Zn, Ag and  $\text{HNO}_3$  in the feed solution was maintained at 0.0015, 0.0028 and 0.01 mol/L, respectively.

The results in Fig. 2 show that the extraction percentage of Zn increased sharply when increasing the concentration of cyanex272 from 0.1 to 0.5 mol/L then slowed down

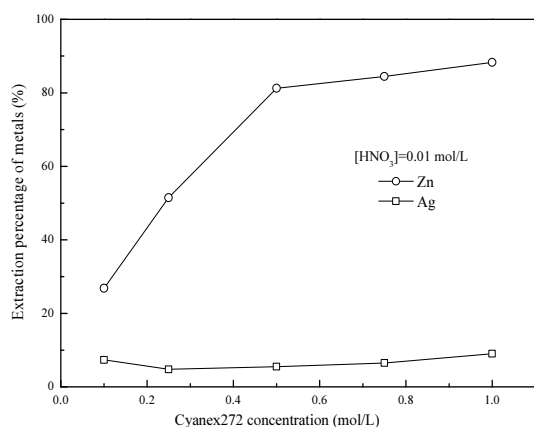


Fig. 2. Effect of extractant concentration on the extraction of metals.

with further increasing it to 1 mol/L. While the extraction percentage of Ag was lower than 10% in all the studied extractant concentration range. These results indicate a possibility to separate Ag and Zn by extraction with cyanex272.

### 3.3. Effect of phase ratio on the extraction

In order to know the theoretical stages needed for the complete extraction of Zn from the leachate, extraction experiments with 1 mol/L cyanex272 was constructed by varying the volume ratio of extractant to leachate from 1:5 to 5:1. The results are given as the McCabe-Thiele plot for the extraction of Zn. (In the case of Ag, the extraction efficiency was ranged 3~10% and was not given in the figure.) The results in Fig. 3 suggest that 3 stages are needed to completely extract Zn from the leachate with 1 mol/L of cyanex272 at an extractant to leachate ratio of 1.

A two-stage countercurrent batch simulation test was carried out at 1:1 volume ratio of cyanex272 to leachate. For each stage, the initial pH was maintained at 2 ( $\pm 0.05$ ). The concentration of Zn in the raffinate after three stages extraction was  $< 0.01$  mg/L. The concentrations of Ag in the loaded cyanex272 was 0.25 mmol/L (27 mg/L).

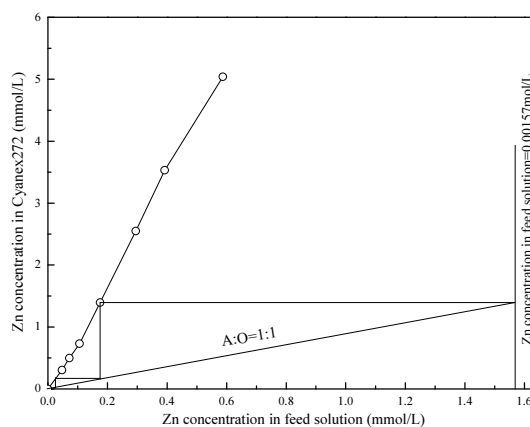


Fig. 3. Effect of O/A ratio on the extraction of Zn with 1 mol/L Cyanex272.

### 3.4. Stripping agent and removal of Ag

The experiments for removal of Ag from the loaded cyanex272 were carried out by using various concentrations of HNO<sub>3</sub> and thiourea. Loaded cyanex272 was prepared by mixing a feed solution containing Zn (0.0015 mol/L), Ag (0.0028 mol/L), and HNO<sub>3</sub> (0.01 mol/L), with 1 mol/L cyanex272, as described in Section 2. The loaded cyanex272 was mixed with each strippant at an A/O ratio of 1:1.

The results of stripping of the metals with HNO<sub>3</sub> are presented in Fig. 4. The stripping percentage of Zn increased with increasing the concentration of HNO<sub>3</sub> from 0.1 to 5 mol/L. In the case of Ag, the stripping percentage increased in a small grade and all the stripping percentages were lower than 20% in the studied HNO<sub>3</sub> concentration range.

When thiourea was used in the stripping experiments

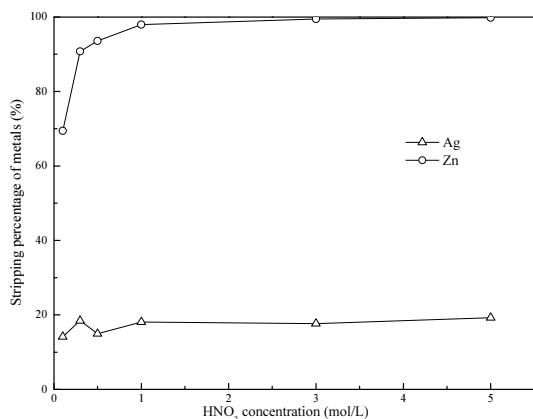


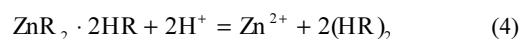
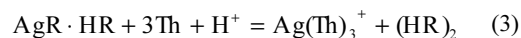
Fig. 4. Effect of HNO<sub>3</sub> concentration on the stripping of metals from loaded Cyanex272.

Table 1. Stripping of metals from loaded cyanex272 with various concentration of thiourea

Thiourea concentration (mol/L)	Stripping percentage (%)	
	Ag	Zn
0.1	15	0
0.5	58	0
0.7	69	0
1	83	0

(see Table 1), more than 80% of the Ag loaded in cyanex272 was stripped when the concentration of thiourea was higher than 1 mol/L. While the concentration of Zn was little changed before and after stripping process. Thus, 1 mol/L of thiourea was selected to selectively strip Ag from loaded cyanex272 containing both Zn and Ag.

The stripping reaction can be represented as follows,



where (HR)<sub>2</sub> and Th denotes cyanex272 and thiourea, respectively.

Furthermore, based on the results in Figs. 4 and Table 1, the loaded cyanex272 could be regenerated by stripping of Ag with thiourea, followed by stripping of Zn with HNO<sub>3</sub> solution.

### 3.5. Effect of phase ratio on the stripping of Ag

Effect of phase ratio on the stripping of Ag was investigated by varying the A/O ratio (1 mol/L thiourea to loaded cyanex272) from 1:3 to 2:1. The loaded cyanex272 was obtained by mixing 1 mol/L of cyanex 272 and the mixture of Zn and Ag prepared in 0.01 mol/L HNO<sub>3</sub>. The loaded cyanex272 containing 1.337 mmol/L Zn and 0.227 mmol/L Ag was mixed with 1 mol/L thiourea at varies A/O ratios. A McCabe-Thiele plot for the stripping of Ag was constructed in Fig. 5. The stripping percentage of Ag was increased from 43% to 90% as the A/O ratio increased from 1:3 to 2:1. The concentration of Zn in the stripping solution was negligible. The results indicate that three counter-current stripping stages are required for the complete stripping of Ag from the loaded cyanex272 at the A/O ratio of 1:1

To verify the above results, a batch simulation stripping experiments were performed. The loaded cyanex272 was obtained by batch simulation experiments of three-stage counter-current extraction, and the concentrations

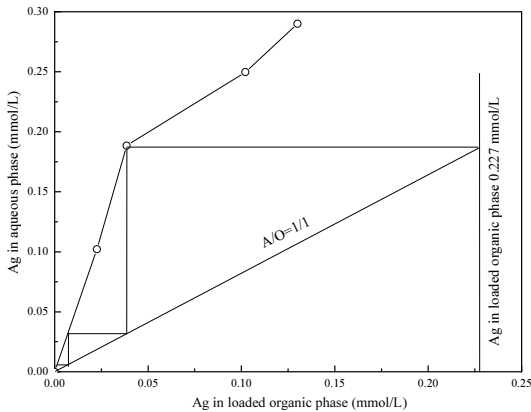


Fig. 5. Effect of O/A ratio on the stripping of Ag with 1 mol/L thiourea.

of Ag and Zn were 0.25 mmol/L and 0.0015 mol/L, respectively. 1 mol/L thiourea was used as the strippant and the A/O ratio was maintained at 1:1. The results suggested that Ag was completely stripped after the three-stage counter-current stripping, while the concentration of Zn in the stripping solution was negligible.

### 3.6. Effect of phase ratio on the stripping of Zn after removal of Ag

Effect of phase ratio on the stripping of Zn with  $\text{HNO}_3$  was investigated by varying the A/O ratio from 1:3 to 5:1. The loaded cyanex272 obtained from the counter-current stripping experiment in part 5 was used. The concentration of Zn in the loaded cyanex272 was 0.0015 mol/L. 0.5 mol/L  $\text{HNO}_3$  was used as stripping agent.

The results given in Fig. 6 indicate that three counter-current stripping stages are required for the complete stripping of Zn from the loaded cyanex272 at an A/O ratio of 1:1.

A three-stage counter-current batch simulation of stripping experiments of Zn was performed to verify the obtained results. The phase ratio was maintained at 1:1. According to the batch simulation stripping experiments, Zn concentration in the obtained stripping solution was 97.4 mg/L, indicating 99.9% stripping percentage of Zn

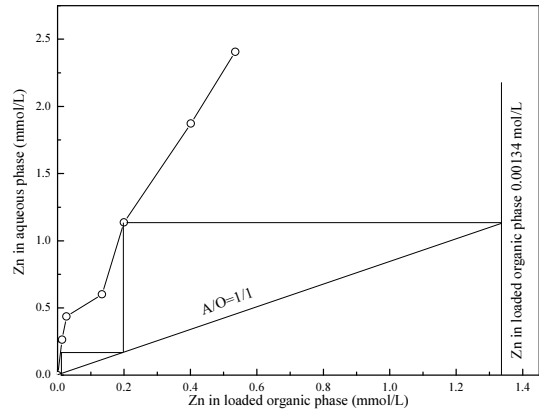


Fig. 6. Effect of O/A ratio on the stripping of Zn with 0.5 mol/L  $\text{HNO}_3$ .

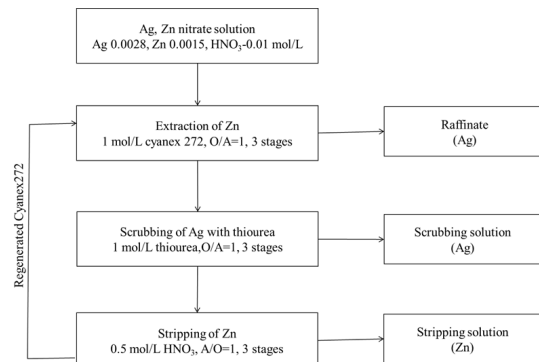


Fig. 7. Flow sheet for the proceeding of separation of Ag and Zn from leachate of spent silver oxide batteries with Cyanex272.

from the loaded cyanex272.

## 4. Conclusions

A solvent extraction process was developed for separation of Ag and Zn from the nitrate leachate of silver oxide batteries. The proposed flow sheet is summarized in Fig. 7. Zn and small amount of Ag were extracted with cyanex272 when the concentration of acid in leachate lower than 0.1 mol/L. The co-extracted Ag was removed by stripping with 1 mol/L thiourea. Zn in the loaded cyanex272 after removal of Ag was recovered by stripping with 0.5 mol/L  $\text{HNO}_3$ . Moreover, the feasibility of the proposed process was verified by

performing batch simulation counter-current extraction and stripping experiments.

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