Solvent Extraction Separation of Silver(I) and Zinc(II) from Nitrate Leach Solution of Spent Silver Oxide Batteries with D2EHPA

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In this study, separation of silver(I) and zinc(II) from nitrate leach solution of spent silver oxide batteries were carried out by extraction and selective stripping. Di-(2-ethylhexyl) phosphoric acid (D2EHPA) was used to extract Zn(II) and Ag(I) in the equilibrium pH range of 0.99–1.34. The extraction of Zn(II) was more affected by the pH value than that of Ag(I). Zn(II) and Ag(I) loaded in D2EHPA was separated by selective stripping with a mixture of 0.01 mol/dm³ nitric acid and 1 mol/dm³ thiourea and 0.5 mol/dm³ nitric acid for Ag(I) and Zn(II), sequentially. A process flowsheet for the separation and recovery of Zn(II) and Ag(I) from the nitrate leach solution of spent silver oxide batteries was proposed. [doi:10.2320/matertrans.M2018394]

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1. Introduction

Silver oxide batteries are widely used in electronic products such as electric watches, portable medical monitors, calculators, digital thermometers, and toys.¹⁾ Spent silver oxide batteries resources is becoming an attractive proposition because of the depletion of natural resources and the increasing strictness of environmental policies.^{1–4)}

In the hydrometallurgical treatment of silver oxide batteries, Ag and Zn are dissolved with nitric acid (HNO₃) solution and fermentation liquor.^{5,6)} The separation of Ag and Zn from various media have been investigated via precipitation,⁵⁾ ion exchange followed by selective elution⁷⁾ and solvent extraction^{8–10)} among other methods. Di-(2-ethylhexyl) phosphoric acid (D2EHPA) has been used for the extraction/separation of Zn(II) from solutions containing diverse metal ions, some of which are summarized in Table 1. The sodium salt of D2EHPA (NaD2EHPA) has also been used to extract Zn(II) from sulfuric solutions.^{4,11)} To the best of our knowledge, little research has reported on the separation of Ag(I) and Zn(II) from the nitrate leach solutions of spent silver oxide batteries using D2EHPA.

In this study, extraction separation of Ag(I) and Zn(II) from the synthetic nitrate leach solution of spent silver oxide batteries was investigated by solvent extraction and stripping. For this purpose, D2EHPA was employed to study the extraction behavior of Ag(I) and Zn(II). The co-extracted Ag(I) and Zn(II) into the D2EHPA were separated by selective stripping with acidic thiourea and nitric acid solution. A process flowsheet for the separation and recovery of Zn(II) and Ag(I) from the nitrate leach solution of spent silver oxide batteries was proposed.

2. Materials and Methods

2.1 Reagents

AgNO₃ (99.8%, Daejung Chemicals and Metals Co., Ltd.) and Zn(NO₃)₂·6H₂O (98.0%, Daejung Chemical and Metals Co., Ltd.) were dissolved in distilled water to prepare the feed

solution. In all the experiments, the concentrations of Ag(I) and Zn(II) were maintained at 30 and 6 g/dm³, respectively, to mimic the leach solution.⁶⁾ HNO₃ (60%, Daejung Chemicals and Metals Co., Ltd.) was used to adjust the acidity of the solution.

Di-(2-ethylhexyl) phosphoric acid (D2EHPA) (95%, Alfa Aesar) was used without further purification. Pure kerosene (Daejung Chemicals and Metals Co., Ltd.) was used as a diluent. Thiourea (98%, Junsei Chemical Co., Ltd.) and HNO₃ (60%, Daejung Chemicals and Metals Co., Ltd.) were used in preparing the strippant solutions. Each strippant solution was prepared by dissolving the required amount of the reagent in the desired volume of distilled water.

2.2 Procedure

The general batch extraction and stripping experiment were carried out by mixing equal volumes (20 mL) of the aqueous and organic solutions for 30 min using a wrist shaker (Burrell, USA). All the experiments were performed at ambient temperature (25 ± 1°C). After equilibrium, the two phases were separated using separation funnels and the metal ion concentration in the aqueous phase was measured by ICP-OES (PerkinElmer Optima 8300). The metal ion concentration in the organic phase was calculated by mass balance. The pH value was measured before and after extraction with a pH meter (Thermo Orion star A211). The experimental chart for batch extraction and stripping experiments and the separation state of solution are shown in Figs. 1 and 2. The extraction percentage of metal ion is calculated as follows,

$$\begin{aligned}\text{Extraction percentage (\%)} &= (c_o/c_{a,1}) \times 100\% \\ &= [(c_{a,1} - c_{a,2})/c_{a,1}] \times 100\%\end{aligned}\quad (1)$$

where c_o is metal ion concentration in the loaded organic phase, $c_{a,1}$ and $c_{a,2}$ is metal ion concentration in the aqueous phase before and after extraction, respectively.

The stripping percentage of metal ion is calculated by eq. (2),

$$\text{Stripping percentage (\%)} = (c_{a,s}/c_o) \times 100\% \quad (2)$$

where $c_{a,s}$ is metal ion concentration in the aqueous phase

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Table 1 Literature survey for the separation/extraction of Zn(II) from various solutions.

Feed composition	Media	Conditions	Ref.
Zn, Cu	Perchlorate solution	Zn was extracted in the pH ranges 2.5–3.0 and 3.0–4.0 with D2EHPA and PC88A in toluene, respectively. Zn was stripped with 4.0 mol/dm ³ HCl. The probable extracted species was ZnR ₂ ·2HR for both extractants.	12)
Cu, Zn, Fe	Bioleaching of re-floated tailings	Cu was extracted with LIX984N; Fe was removed by precipitation; Zn was recovered by extraction with D2EHPA followed by stripping with H ₂ SO ₄ .	13)
Zn, Fe	Hydrochloric solution	99% of Zn was extracted by mixed extractant (0.58 mol/dm ³ TBP: 0.12 mol/dm ³ D2EHPA) at A/O ratio of 2/1 and equilibrium pH of 3. Stripping data was not available.	14)
Zn, Pb, Fe, Mn, Ni, Co, Ca	Sulfuric solution	Zn was extracted at pH 2.5 with 20% (w/w) D2EHPA in kerosene. Tributyl phosphate (TBP) as modifier, Na ₂ SO ₄ as salting-out agent increased the extraction of Zn.	15)
Zn, Cd, Co, Fe, Pb, Ca, Mg, Mn, Ni	Sulfuric solution	98% of Zn was extracted at pH 2.5 with 20% (w/w) D2EHPA, A/O = 1/1, in three stages. Stripping of Zn was obtained by 1.85 mol/dm ³ H ₂ SO ₄ at A/O = 1/4, in three stages.	16)
Zn, Cd	Phosphoric solution	The extraction mechanisms of Zn and Cd in 5.5 mol/dm ³ phosphoric acid solution were investigated.	17)

Fig. 1 The experimental flow chart for the batch extraction and stripping experiment.

after stripping, c_o is metal ion concentration in the loaded organic phase.

3. Results and Discussion

3.1 Effect of equilibrium pH on the extraction of metals

The effect of the equilibrium pH on the extraction of Ag(I) and Zn(II) was investigated by varying the initial pH of the feed solution from 0.66 to 3.07. The corresponding change in

equilibrium pH was from 0.63 to 1.47. The Ag(I) and Zn(II) concentrations in these experiments were fixed at 30 and 6.8 g/dm³, respectively, while the concentration of D2EHPA diluted in kerosene was maintained at 0.5 mol/dm³.

The results are represented as the extraction percentages of the metals as functions of the equilibrium pH in Fig. 3. The extraction of Ag(I) is 0~5% in all extraction experiments, and its extraction percentage is not evidently effected by varying the equilibrium pH. The extraction percentage of

Fig. 2 Separation state of the solution. Feed solution: Ag-30 g/dm³, Zn-6 g/dm³, HNO₃-0.1 mol/dm³; D2EHPA-0.5 mol/dm³ a) Feed solution b) Mixture of feed solution and D2EHPA after shaking for 30 min c) Raffinate after separation.

Table 2 The pH of solutions before and after extraction.

Initial pH	3.07	2.68	2.09	1.19	0.66
Equilibrium pH	1.47	1.34	1.11	0.99	0.63

Fig. 3 Effect of equilibrium pH on the extraction of metals using 0.5 mol/dm³ D2EHPA.

Fig. 4 Effect of D2EHPA concentration on the extraction of metals.

Zn(II) is increased with increasing equilibrium pH of the solution from 0.63 to 0.99, and kept nearly the same with further increasing equilibrium pH of the solution to 1.47. Therefore, it is possible to separate large part of Ag(I) from Zn(II) with D2EHPA when the equilibrium pH is >1 (initial pH of the feed solutions >0.99). The pH of the solution before and after extraction is summarized in Table 2. Decreasing pH indicates that the extraction of Zn(II) with D2EHPA follows a classical cationic extraction mechanism. Since D2EHPA exists as a dimer,¹²⁾ the extraction reaction can be represented as follows,

where $(\text{HR})_2$ denotes the dimer of D2EHPA.

3.2 Effect of D2EHPA concentration on extraction of metals

In order to investigate the effect of D2EHPA concentration on the extraction of metals, the concentration of D2EHPA

was varied from 0.3 to 1 mol/dm³. The concentration of HNO₃ in the feed solution was varied from 0.01 to 1 mol/dm³, while the concentrations of Ag(I) and Zn(II) were fixed at 30 and 6.8 g/dm³, respectively.

The results in Fig. 4 demonstrate the effect of the D2EHPA on the extraction percentages of Ag(I) and Zn(II) at various HNO₃ concentrations. The extraction percentages of Ag(I) in all these extraction experiments are 0~5%. For Zn(II), the extraction percentage of Zn(II) is increased with increasing D2EHPA concentration at a fixed acid concentration, but decreased with increasing HNO₃ concentration at a fixed D2EHPA concentration. In the case of feed solution with 0.01 mol/dm³ HNO₃ (initial pH = 1.98), the pH value of the solution after extraction varied from 1.45 to 1.32 with increasing D2EHPA concentration from 0.3 to 1 mol/dm³.

The results obtained in Fig. 4 indicated that D2EHPA was selective for the extraction of Zn(II) over Ag(I) at low HNO₃ concentrations. The separation of Ag(I) and Zn(II) with 1 mol/dm³ D2EHPA from 0.01 mol/dm³ HNO₃ was further investigated.

Fig. 5 McCabe–Thiele plot for extraction of Zn(II) with 1 mol/dm³ D2EHPA.

3.3 McCabe–Thiele plot for extraction of Zn(II) with D2EHPA

A McCabe–Thiele plot was constructed by varying the volume ratio of the aqueous to organic phases (A/O ratio) from 5/1 to 1/3 to determine the theoretical number of stages required for the complete extraction of Zn(II) from the feed solution containing 30 g/dm³ Ag(I) and 6.8 g/dm³ Zn(II). The concentrations of D2EHPA in the organic phase and that of HNO₃ in the feed solution were fixed at 1 and 0.01 mol/dm³, respectively. The extraction of Zn(II) increased from 30.8 to 66.2% (the concentration of Zn(II) in the raffinate solution decreased from 4.5 to 2.2 g/dm³) as the A/O ratio was decreased from 5/1 to 1/3. The extraction percentage of Ag(I) was lower than 6.8% for all studied A/O ratios (not shown in figure). The separation ratio of Zn(II) to Ag(I) decreased from 130.67 to 26.88 as the A/O ratio was decreased from 5/1 to 1/3. Figure 5 illustrates the McCabe–Thiele plot for Zn(II) extraction. The results indicate that three stages are required to obtain a quantitative extraction of Zn(II) using 1 mol/dm³ D2EHPA at the A/O ratio of 1/3.

Based on the results obtained from the McCabe–Thiele plot, a three-stage counter-current batch simulation test was performed at an A/O ratio of 1/3 using 1 mol/dm³ D2EHPA. For each stage, the initial pH was maintained at 2 (±0.05). After the three-stage counter-current extraction, 99.99% of Zn(II) and 6.78% Ag(I) were extracted from the aqueous solution, leaving most of Ag(I) in the raffinate. The Ag(I) and Zn(II) concentrations in the raffinate were 27.966 and 0.0068 g/dm³, respectively, indicating that the purity of Ag(I) was 99.98%. The Ag(I) and Zn(II) concentrations in the loaded D2EHPA were 0.678 and 2.264 g/dm³, respectively.

3.4 Selection of strippant for stripping of Ag(I) and Zn(II) from loaded D2EHPA

In order to recover Ag(I) and Zn(II) from the loaded D2EHPA, stripping experiments were performed by using HNO₃ and a mixture of 0.01 mol/dm³ HNO₃ and thiourea as strippants. Based on the hard and soft acid and base theory (HSAB theory), thiourea is a soft ligand and effective in stripping of Ag⁺ from the loaded organic phase. The

Fig. 6 Stripping of metals with various concentrations of HNO₃ solutions.

loaded D2EHPA was obtained by mixing the feed solution containing 30 g/dm³ Ag(I), 6.8 g/dm³ Zn, and 0.01 mol/dm³ HNO₃ with 1 mol/dm³ D2EHPA at an A/O ratio of 1/1. The concentrations of Ag(I) and Zn(II) in the loaded D2EHPA were 0.6 and 2.9 g/dm³, respectively. Then the loaded D2EHPA was mixed with HNO₃ and thiourea solutions of various concentrations, respectively.

Figure 6 shows the stripping percentages of Ag(I) and Zn(II) with various HNO₃ concentrations. The stripping percentages of both Ag(I) and Zn(II) are increased with increasing HNO₃ concentration. When the concentration of HNO₃ is higher than 0.2 mol/dm³, both Ag(I) and Zn(II) can be quantitatively stripped from the loaded D2EHPA. Thus, it is difficult to recover Ag(I) and Zn(II) separately by using HNO₃ as the strippant. The stripping reaction can be represented as follows,

where (HR)₂ denotes the dimer of D2EHPA.

For the stripping experiments using mixture of 0.01 mol/dm³ HNO₃ and thiourea as the strippant, the results (Fig. 7) show that the stripping percentage of Ag(I) is increased with increasing thiourea concentrations, and 84.5% stripping of Ag(I) is obtained with 1 mol/dm³ thiourea. In all studied thiourea concentration ranges, the concentration of Zn(II) in the obtained stripping solution is negligible. Therefore, the mixture of 0.01 mol/dm³ HNO₃ and 1 mol/dm³ thiourea was used in the following experiments to selectively strip Ag(I) from the loaded D2EHPA. The stripping reaction can be represented as follows,¹⁸⁾

where (HR)₂ and Th denotes the dimer of D2EHPA and thiourea, respectively.

3.5 McCabe–Thiele plot for stripping of Ag(I) with acidic thiourea

A McCabe–Thiele plot for the stripping of Ag(I) was constructed by varying the A/O ratio from 1/3 to 2/1 to estimate the number of stages and phase ratios to complete the stripping of Ag(I) from the loaded D2EHPA with a

Fig. 7 Stripping of metals with various concentrations of thiourea solution.

Fig. 9 McCabe-Thiele plot for stripping of Zn(II) with 0.5 mol/dm³ HNO₃ after removal of Ag(I). Fig. 8 McCabe-Thiele plot for stripping of Ag(I) with 1 mol/dm³ thiourea.

mixture of 0.01 mol/dm³ HNO₃ and 1 mol/dm³ thiourea. The above described loaded D2EHPA containing 0.6 g/dm³ Ag(I) and 2.9 g/dm³ Zn(II) was mixed with the mixture of 0.01 mol/dm³ HNO₃ and 1 mol/dm³ thiourea at varying A/O ratios. The stripping percentage of Ag(I) was increased from 51.1% to 90.8% as the A/O ratio increased from 1/3 to 2/1. The concentration of Zn(II) in the stripping solution was negligible. The results (Fig. 8) indicate that three counter-current stripping stages are required for the complete stripping of Ag(I) from the loaded D2EHPA at the A/O ratio of 1/1.

To verify the theoretical stripping stages obtained from the McCabe-Thiele plot, a batch simulation test was performed. The loaded D2EHPA was obtained by batch simulation experiments of three-stage counter-current extraction, and the concentrations of Ag(I) and Zn(II) were 0.68 and 2.26 g/dm³, respectively. The mixture of 0.01 mol/dm³ HNO₃ and 1 mol/dm³ thiourea was used as the strippant and the A/O ratio was maintained at 1/1. The results suggested that Ag(I) was completely stripped after the three-stage counter-current stripping, while the concentration of Zn(II) in the stripping solution was negligible. The concentration of Zn(II) was 2.26 g/dm³ in the loaded D2EHPA after removal of Ag(I).

3.6 McCabe-Thiele plot for stripping of Zn(II) with HNO₃ after removal of Ag(I)

Based on the results in Fig. 6, HNO₃ can strip Zn(II) from the loaded D2EHPA. Therefore, 0.5 mol/dm³ HNO₃ was selected as the strippant to recover Zn(II) from loaded D2EHPA after the removal of Ag(I).

A McCabe-Thiele plot for the stripping of Zn(II) was constructed by varying the A/O ratio from 1/3 to 5/1 to estimate the number of stages and phase ratios to complete the stripping of Zn(II) from the loaded D2EHPA with 0.5 mol/dm³ HNO₃. The loaded D2EHPA was prepared by mixing the feed solution containing Ag(I) and Zn(II) with 1 mol/dm³ of D2EHPA at 0.01 mol/dm³ of HNO₃. The A/O ratio was 1/1. Ag(I) was removed by three stages of counter-current stripping with 1 mol/dm³ thiourea. The concentration of Zn(II) in the loaded D2EHPA was 2.9 g/dm³. The results (Fig. 9) indicate that two counter-current stripping stages are required for the complete stripping of Zn(II) from the loaded D2EHPA at an A/O ratio of 1/1. D2EHPA can be regenerated after the complete stripping of Zn(II) with HNO₃.

To verify the theoretical stripping stages obtained from the McCabe-Thiele plot, a two-stage counter-current batch simulation of the stripping experiments was performed. The loaded D2EHPA was obtained by batch simulation experiments of the three-stage counter-current extraction. After removing the Ag(I) with the mixture of 0.01 mol/dm³ HNO₃ and 1 mol/dm³ thiourea, the concentration of Zn(II) in the loaded D2EHPA was 2.26 g/dm³. 0.5 mol/dm³ HNO₃ was used as a strippant and the phase ratio was maintained at 1/1. According to the batch simulation stripping experiments, Zn(II) was almost completely stripped from the loaded D2EHPA. The Zn(II) concentration in the obtained stripping solution was 2.26 g/dm³, while no Ag(I) was detected. This result indicated that the purity of Zn(II) was higher than 99.99% (determination limit: 0.01 mg/dm³).

In the literature,^{19,20} Ag(I) and Zn(II) from nitrate leaching solution of silver oxide batteries were precipitated using KCl/NaCl, which is a commonly used method. Its disadvantage of needing expensive equipment and precipitant (including flocculating agent) is avoided in the present

Fig. 10 Process flow sheet for the separation of Ag(I) and Zn(II) from nitrate leaching solution.

proposed process.²¹⁾ In addition, the present proceeding avoids using toxic chemicals and restricted disposal problems compared with that from cyanide medium.²²⁾ Thus, the present studied process is more environmentally friendly and has the potential to be applied in practice.

4. Conclusions

A liquid-liquid extraction process was developed for the separation of Ag(I) and Zn(II) from the nitrate leach solution of silver oxide batteries. The process flow sheet for the separation of Ag(I) and Zn(II) from the nitrate leach solution of silver oxide batteries is summarized in Fig. 10. The complete extraction of Zn(II) from the nitrate leach solution was achieved using 1 mol/dm³ D2EHPA in three stages at an A/O ratio of 1/3, leaving most of the Ag(I) in the raffinate. The co-loaded Ag(I) was removed by stripping with a mixture of 0.01 mol/dm³ HNO₃ and 1 mol/dm³ thiourea in three stages at a 1/1 A/O ratio. After the removal of Ag(I), Zn(II) loaded in D2EHPA was recovered by stripping with 0.5 mol/dm³ HNO₃ in two stages at an A/O ratio of 1/1. Finally, this process was verified by batch simulation experiments of counter-current extraction and stripping to obtain Ag(I) and Zn(II) solutions with high purities.

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