Recovery of Metal Values from Spent Battery Leach Solutions by Solvent Extraction

By Chu Yong Cheng

ABSTRACT

The recovery of metal values using solvent extraction technologies from leach solutions of lithium-ion and zinc-carbon batteries has been investigated and flowsheets have been developed.

A mixed solvent extractant system was developed for the purification of cobalt and lithium in spent lithium-ion battery leach solutions. The addition of Acorga M5640 to the Ionquest 801 organic solution generated a significant pH isotherm shift for copper with a $\Delta pH_{50}$ value of 3.45 pH units. This indicates that the separation of Fe(III), Al and Cu from Co, Li and Ni could easily be realised with the mixed solvent extractant system. The slow extraction kinetics of aluminium was increased by increasing the temperature from room temperature to 40°C. The slow stripping kinetics of iron can be overcome by stripping the iron with higher acid concentration. A process flowsheet is proposed for recovering cobalt and lithium from spent lithium-ion battery leach solutions using the mixed Ionquest 801 and Acorga M5640 system in the first solvent extraction circuit and Cyanex 272 in the second solvent extraction circuit.

An organic system consisting of Ionquest 801 and TBP in Shellsol D70 was used to purify zinc-carbon battery leach solutions. It was shown that two theoretical stages are needed for the extraction of iron and zinc with the system containing 30% (v/v) Ionquest 801 at an A/O ratio of 1:1, pH 3.0 and 40°C. The extraction kinetics of iron and zinc were very fast and their extractions reached 99% and 93% within one minute, respectively. Less than 1% of the manganese was extracted in two minutes. The selective stripping of zinc from iron could be achieved at pH 0.5. Iron cannot be stripped effectively with the stripping solution containing 40 g/L zinc and 170 g/L H$_2$SO$_4$. An organic bleed stream may be needed to strip the iron with 400 g/L sulphuric acid. A process flowsheet has been proposed for the recovery of zinc and manganese from spent zinc-carbon battery leach solutions using the Ionquest 801/TBP system.
What is Synergistic SX (SSX)?

In normal solvent extraction (SX) processes, the organic solution consists of:

1. An extractant for selectivity (essential)
2. A diluent (essential in most cases)
3. A modifier (optional)

In SSX or mixed solvent systems, another reagent is added to improve selectivity.
The minerals industry needs highly selective reagents. However:

1. Development new reagents very costly
2. Commercialisation of new reagents very expensive
3. New reagents face small application, leading to high price

Solution: Synergistic Solvent Extraction (SSX) – The use of mixed solvent extractants to improve metal selectivity
DEVELOPMENT OF SSX SYSTEMS

Our Responses

• Develop new SSX systems based on fundamental understanding, and

• Apply SSX systems to industry using commercially available reagents

• The SX group of CSIRO Minerals has developed novel SSX systems for the application in metal purification, separation and recovery.
INTRODUCTION

The CSIRO SSX systems

1. Versatic 10 / 4PC for separation of Ni and Co from Mn/Mg/Ca (Test work with BHP Billiton, Australia)
2. Versatic 10 / LIX63 for separation of Co from Mn/Mg/Ca (Pilot plant operations by Baja Mining, Canada)
3. Versatic 10 / LIX63 / TBP for separation of Ni and Co from Mn/Mg/Ca (Pilot plant operations for Rio Tinto, Australia)
4. Cyanex 272 / LIX84 for separation of Cu/Fe/Zn from Ni/Co (Pilot plant operations for Minara Resources, Australia)
5. Ionquest 801 / Acorga M5640 for Co and Li purification (Test work with very good results)
6. Novel SSX systems to recover Cu/Ni from high chloride concentration solutions
7. Novel SSX systems to recover Co/Zn from high chloride concentration solutions
8. Novel SSX systems to separate Cu from Fe and recover Cu from high chloride concentration solutions
DEVELOPMENT OF AN SSX SYSTEM TO PURIFY COBALT AND LITHIUM

Aqueous solution:
A synthetic sulphate solution to mimic a spent battery leach solution.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Co</th>
<th>Li</th>
<th>Cu</th>
<th>Ni</th>
<th>Fe(III)</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>16.80</td>
<td>3.80</td>
<td>0.40</td>
<td>0.15</td>
<td>0.65</td>
<td>0.70</td>
</tr>
</tbody>
</table>

Organic solution:
Ionquest 801 (phosphonic acid) and Acorga M5640 (hydroxyoxime) as mixed extractant system. Shellsol D70 as diluent (aliphatic solvent, containing 0.3% aromatics).
DEVELOPMENT OF AN SSX SYSTEM TO PURIFY COBALT AND LITHIUM

Ionquest 801: 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester, cationic extractant

$$R\quad \text{RO} - \quad P - \quad O \quad \text{OH}$$

$$R = \text{CH}_2\text{CH(C}_2\text{H}_5\text{(CH}_2\text{)_3CH}_3$$

Acorga M5640: 5-nonylsalicylaldoxime, hydroxyoxime extractant

$$\text{C}_9\text{H}_{19}$$

$$\text{N}$$

$$\text{OH}$$

$$\text{NOH}$$
DEVELOPMENT OF AN SSX SYSTEM TO PURIFY COBALT AND LITHIUM

Metal extraction pH isotherms

7% Ionquest 801 alone, A/O ratio 2:1, room temp.

Fe(III) >> Al >> Cu >> Co, Ni, Li

7% Ionquest 801 & 2% Acorga M5640, A/O ratio 2:1, room temp

Fe(III) >> Cu >> Al >> Co, Ni, Li

pH_{50} = pH value at 50% extraction
DEVELOPMENT OF AN SSX SYSTEM TO PURIFY COBALT AND LITHIUM

Metal extraction pH isotherms

<table>
<thead>
<tr>
<th>Metal</th>
<th>7% Ionquest 801</th>
<th>7% Ionquest 801 2% Acorga M5640</th>
<th>ΔpH&lt;sub&gt;50&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH&lt;sub&gt;50&lt;/sub&gt;</td>
<td>pH&lt;sub&gt;50&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>Fe(III)</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>Nil</td>
</tr>
<tr>
<td>Al</td>
<td>3.15</td>
<td>3.20</td>
<td>-0.05</td>
</tr>
<tr>
<td>Cu</td>
<td>5.45</td>
<td>2.00</td>
<td>3.45</td>
</tr>
</tbody>
</table>

In the Ionquest/Acorga system, Fe/Cu/Al can be completely separated from Co/Li/Ni

pH<sub>50</sub>=pH value at 50% extraction

ΔpH<sub>50(M)</sub>=metal pH<sub>50</sub> difference
At an A/O ratio of 2:1 and pH 4.0, three theoretical extraction stages are needed to yield a raffinate containing a few ppm of copper.
DEVELOPMENT OF AN SSX SYSTEM TO PURIFY COBALT AND LITHIUM

<table>
<thead>
<tr>
<th>Element</th>
<th>A/O Ratio</th>
<th>Concentration (mg/L)</th>
<th>Extraction (%)</th>
<th>Sepn. Factor (M/Co) (×10^4)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Aqueous</td>
<td>Organic</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>1:2</td>
<td>0</td>
<td>336</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>0</td>
<td>680</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>2</td>
<td>1343</td>
<td>99.7</td>
</tr>
<tr>
<td></td>
<td>5:1</td>
<td>5</td>
<td>3280</td>
<td>99.3</td>
</tr>
<tr>
<td>Al</td>
<td>1:2</td>
<td>0</td>
<td>344</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>1</td>
<td>680</td>
<td>&gt;99.8</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>31</td>
<td>1341</td>
<td>95.5</td>
</tr>
<tr>
<td></td>
<td>5:1</td>
<td>414</td>
<td>1397</td>
<td>42.0</td>
</tr>
<tr>
<td>Cu</td>
<td>1:2</td>
<td>3</td>
<td>238</td>
<td>99.4</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>3</td>
<td>419</td>
<td>99.2</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>50</td>
<td>734</td>
<td>88.0</td>
</tr>
<tr>
<td></td>
<td>5:1</td>
<td>282</td>
<td>870</td>
<td>38.2</td>
</tr>
<tr>
<td>Co</td>
<td>1:2</td>
<td>13362</td>
<td>1183</td>
<td>15.1</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>15781</td>
<td>483</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>2:1</td>
<td>16236</td>
<td>19</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td>5:1</td>
<td>16450</td>
<td>8</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Metal extractions and separation factors over cobalt at pH 4.0

Separation factors of Fe/Cu/Al over Co > 12000 at pH 4 and A/O ratio 2:1 indicates their very good separation from Co/Li/Ni

SF>100, good separation
SF>1000, very good separation extractions
SF>10000, excellent separation
Copper stripping McCabe-Thiele diagram

With 80 g/L H₂SO₄ at A/O ratio 1:8, two theoretical stripping stages are needed to yield a stripped organic solution containing low level of Cu.
DEVELOPMENT OF AN SSX SYSTEM TO PURIFY COBALT AND LITHIUM

Metal extraction kinetics at 22°C

<table>
<thead>
<tr>
<th>Metals</th>
<th>Extraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>33.2</td>
</tr>
<tr>
<td>Cu</td>
<td>77.5</td>
</tr>
</tbody>
</table>

Metal extraction kinetics increased with increasing temperature. At 40°C, the metal extraction kinetics is acceptable. Adding TBP did not increase Al extraction kinetics.
DEVELOPMENT OF AN SSX SYSTEM TO PURIFY COBALT AND LITHIUM

Separation of Co, Li & Ni with Cyanex 272

Cyanex 272: Phosphinic acid, cation exchange extractant

R=CH₂CH(CH₃)(CH₂C(CH₃)₂CH₃

Metal pH isotherms using Cyanex 272 at A/O ratio 1:2 and 22°C

pH₅₀(Ni)=4.35, pH₅₀(Co)=7.25, pH₅₀(Li)=8.6
ΔpH₅₀(Ni-Co)=2.9, ΔpH₅₀(Li-Co)=4.25 pH units.
At pH 5.5-6.0, Co can be easily separated from Ni & Li
A conceptual process flowsheet for the recovery of Co, Li and Ni from spent battery leach solutions

1. Separation of Co/Li/Ni from Fe/Cu/Al: Ionquest 801 / Acorga M5640
2. Separation of Co from Li/Ni: Cyanex 272
2. Separation of Ni from Li: Ion exchange resin Dowex M4915
1. The addition of 2% (v/v) Acorga M5640 to 7% (v/v) Ionquest 801 generated a significant pH isotherm shift for Cu, with a $\Delta pH_{50}$ of 3.45 pH units, indicating easy separation of Fe(III), Al and Cu from Co, Li and Ni.

2. Three theoretical stages are needed for the extraction of Fe, Al & Cu at an A/O ratio of 2:1, pH 4.0.

3. Two theoretical stages are required to achieve a very good stripping of Al & Cu at an A/O ratio of 1:8 using a stripping solution containing 80 g/L H2SO4.

4. The extraction kinetics of Fe & Cu was very fast, but slow for aluminium. The Al extraction kinetics increased substantially at 40°C.
Parker Centre/CSIRO Process Science and Engineering/CSIRO Minerals Down Under National Research Flagship

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Thank you