Recycling of valuable metals by solvent extraction using carboxylic acid as extractant

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1. INTRODUCTION

Recovery of valuable metals such as rare metals is greatly attracted because of increasing their demands and escalating their prices. But recycling them is difficult and costly. Therefore, large number of research activities has been reported to improve the recycling technology [1][2]. The recovery of valuable metals from Nd-Fe-B magnets scrap is a representative example, and the solvent extraction with acidic organophosphorous ester as extractant has been intensively studied. Table 1 shows the typical composition of Nd-Fe-B magnets [3]. Acidic organophosphorous ester, such as PC-88A and D2EHPA are most popular extractants in the industrial application and they have high selectivity between rare earth metals, but they cause waste water pollution because they have phosphor in their structure. Moreover, due to their strong affinity with major impurity, Fe$^{3+}$, the recovery of Fe$^{3+}$ from the loaded organic solution should require large amount of acids.

In this study, the recovery of valuable metals in Nd-Fe-B magnet was studied by the solvent extraction with carboxylic acid as extractant. Carboxylic acid can be incinerated, and stripping of Fe$^{3+}$ was easier than that with organophosphorous ester extractants [1]. Fe$^{3+}$, Dy$^{3+}$, Nd$^{3+}$ and Co$^{2+}$ were selected as representative elements in the magnet to investigate the solvent extraction with neo-decanoic acid, one of carboxylic acid. The extraction equilibria of single and binary metal solutions were measured to study the effects of the experimental conditions on the extraction and stripping behaviors for the purpose to make the valuable metal recycle process from Nd-Fe-B magnet scrap by using carboxylic acid as extractant.

2. EXPERIMENTAL

The experimental conditions of extraction equilbrium are shown in Table 2. Neo-decanoic and naphthenic acids are mixtures of carboxylic acids. PC-88A (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) and D2EHPA (Bis(2-ethylhexyl) phosphoric acid) are acidic organophosphorous ester extractants. Kerosene was used as the diluent of the extractant. The aqueous solutions of the metals were prepared by dissolution of metal chloride in deionized water. The pH in the aqueous phase was adjusted by NaOH and HCl. The experimental condition of stripping equilibrium is shown in Table 3. The feed organic phases of 10vol% extractant loaded by single metal ion were prepared by extracting the metal from the aqueous solution. HCl or HNO$_3$ was used as stripping reagent.

All experiments were carried out in a 50mL conical flask with screw top. Equal volumes (10mL) of aqueous and organic solutions were stirred with thermostatic bath for 3hours at 303K to attain the equilibrium. After equilibrium, these two phases were separated by separating funnel. The pH value in the aqueous phase was measured by digital pH meter (F-52, HORIBA). The concentration of metal in aqueous phase was determined using ICP-AES (SPS7800, SII Nano Technology), and that in organic phase was calculated by material balance.

Table 1 Typical composition of Nd-Fe-B magnets

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>B</th>
<th>Co</th>
<th>Cu</th>
<th>Rare earth</th>
</tr>
</thead>
<tbody>
<tr>
<td>ave[wt%]</td>
<td>66</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>23</td>
</tr>
<tr>
<td>max</td>
<td>69.6</td>
<td>1.11</td>
<td>3.66</td>
<td>0.23</td>
<td>27.6</td>
</tr>
<tr>
<td>min</td>
<td>61.6</td>
<td>0.95</td>
<td>0.54</td>
<td>0.11</td>
<td>18.6</td>
</tr>
</tbody>
</table>

Table 2 Experimental conditions of batch extraction equilibrium

<table>
<thead>
<tr>
<th>Solvent</th>
<th>M$^{3+}$(Fe$^{3+}$, Dy$^{3+}$, Nd$^{3+}$, Co$^{2+}$) chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractant</td>
<td>Neo-decanoic, naphthenic (NA)</td>
</tr>
<tr>
<td>Diluent</td>
<td>Kerosene</td>
</tr>
<tr>
<td>Initial metal concentration in aqueous phase, C$_{i,aq}$[kmol·m$^{-3}$]:</td>
<td>0.001</td>
</tr>
<tr>
<td>Extractant concentration in organic phase [vol%]:</td>
<td>10--30</td>
</tr>
</tbody>
</table>

Table 3 Experimental conditions of stripping experiment

<table>
<thead>
<tr>
<th>Solvent</th>
<th>M$^{3+}$(Fe$^{3+}$, Dy$^{3+}$, Nd$^{3+}$, Co$^{2+}$) chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractant</td>
<td>Neo-decanoic acid, PC-88A</td>
</tr>
<tr>
<td>Stripping agent</td>
<td>HCl, HNO$_3$</td>
</tr>
<tr>
<td>Initial metal concentration in organic phase, C$_{i,org}$[kmol·m$^{-3}$]:</td>
<td>0.001</td>
</tr>
<tr>
<td>Initial extractant concentration in organic phase [vol%]:</td>
<td>10</td>
</tr>
<tr>
<td>Initial concentration of stripping agent, C$<em>{i,org}$ or C$</em>{i,aq}$ [kmol·m$^{-3}$]:</td>
<td>0.01--7</td>
</tr>
</tbody>
</table>
3. RESULTS AND DISCUSSION

3.1. Solvent extraction with various extractant

The material balance equations for extraction and stripping equilibrium measurements can be expressed as,

\[ C_{\text{aq},0}V_{\text{aq}}+C_{\text{org},0}V_{\text{org}} = C_{\text{aq},1}V_{\text{aq}}+C_{\text{org},1}V_{\text{org}} \]

\[ C_{\text{aq},2}V_{\text{aq}}+C_{\text{org},2}V_{\text{org}} = C_{\text{aq},3}V_{\text{aq}}+C_{\text{org},3}V_{\text{org}} \]

The distribution ratio, extraction yield, and stripping yield of component \( i \) were defined as,

\[ D_i = \frac{C_{\text{org},i}}{C_{\text{org},i}} \quad \text{Eq}(1) \]

\[ E_i = \frac{C_{\text{org},i}}{C_{\text{org},i}} \quad \text{Eq}(2) \]

\[ Y_i = \frac{C_{\text{org},i}}{C_{\text{org},i}} \quad \text{Eq}(3) \]

The separation factor of component \( i \) relative to component \( j \) was defined as,

\[ \beta_{ij} = \frac{D_i}{D_j} \quad \text{Eq}(4) \]

The half extraction \( \text{pH} \) values (pH\(_{1/2}\)) for the extraction with single metal solutions with various extractants are listed in Table 4. The pH\(_{1/2}\) was defined as the \( \text{pH} \) value at \( D_i=1 \). Neo-decanoic acid could preferably extract Fe\(^{3+}\) in the range of high acidity relative to other metal ions, such as Dy\(^{3+}\), Nd\(^{3+}\) and Co\(^{2+}\). PC-88A showed the better performance to separate Dy\(^{3+}\) and Nd\(^{3+}\).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Fe(^{3+})</th>
<th>Dy(^{3+})</th>
<th>Nd(^{3+})</th>
<th>Co(^{2+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA</td>
<td>2.36</td>
<td>4.64</td>
<td>5.01</td>
<td>6.39</td>
</tr>
<tr>
<td>PC-88A</td>
<td>2.21</td>
<td>4.47</td>
<td>4.89</td>
<td>6.21</td>
</tr>
<tr>
<td>D2EHPA</td>
<td>-0.15</td>
<td>0.54</td>
<td>1.29</td>
<td>3.37</td>
</tr>
<tr>
<td></td>
<td>-0.48</td>
<td>0.09</td>
<td>0.60</td>
<td>2.79</td>
</tr>
</tbody>
</table>

3.2. Extraction equilibrium with neo-decanoic acid

As reported in previous papers, extraction equilibrium with carboxylic acid can be represented by Eq(5).

\[ x_iM^{m_i+} + \frac{1}{2}(n_i+m_i)(RH)_{2} = [M]R_{m_i} \cdot m_iR_{n_i} + n_iH^+ \quad \text{Eq}(5) \]

where \( x_i \), \( m_i \), and \( n_i \) stand for polymerization number of extracted species, solvation number of extractant to extracted species, valence of metal, respectively. The extractants were assumed to exist as dimmer in the organic solution. The extraction equilibrium constant can be expressed as,

\[ K_{ex,i} = \frac{[M]R_{m_i} \cdot m_iR_{n_i}}{[M]^{x_i} \cdot (RH)_{2}^{n_i} \cdot m_i} \quad \text{Eq}(6) \]

Eq. (6) can be written as,

\[ \log C_{\text{org},i} = x_i (\log C_{\text{org},i} + n_i \text{pH}) + \log [M]R_{m_i} \cdot m_iR_{n_i} \quad \text{Eq}(7) \]

In this experiment, the concentrations of metal were much lower than that of extractant, \( C_{\text{org},i} \) were assumed to be a constant. The \( \log C_{\text{org},i} \) was plotted against \( (\log C_{\text{aq},i} + n_i \text{pH}) \) in Fig. 1(a), and \( x_i \) was decided as unity. However, the plot of Fe\(^{3+}\), Dy\(^{3+}\) and Nd\(^{3+}\) results didn’t follow the slope in high acidity region. Different reaction might occur and the extraction was enhanced in this region. When \( x_i=1 \), Eq(7) can be written as,

\[ \log [M]R_{m_i} \cdot m_iR_{n_i} = \frac{n_i+m_i}{2} \log C_{\text{org},i} + \log C_{\text{aq},i} \quad \text{Eq}(8) \]

The \( m_i \) and \( K_{ex,i} \) could be obtained from the slope and intercept of the plots of \( \log D_i \cdot n_i \text{pH} \) against \( \log C_{\text{RH},org} \).

Table 4. List of \( \text{pH}_{1/2} \) with each extractant (10vol%) on extraction of Fe\(^{3+}\), Dy\(^{3+}\), Nd\(^{3+}\), Co\(^{2+}\).

3.3. Extraction of binary metal solution with neo-decanoic acid

In this binary system, the concentrations of metal were much lower than that of extractant, \( C_{\text{org},i} \) were assumed to be a constant. The \( \log C_{\text{org},i} \) was plotted against \( (\log C_{\text{aq},i} + n_i \text{pH}) \) in Fig. 1(a), and \( x_i \) was decided as unity. However, the plot of Fe\(^{3+}\), Dy\(^{3+}\) and Nd\(^{3+}\) results didn’t follow the slope in high acidity region. Different reaction might occur and the extraction was enhanced in this region. When \( x_i=1 \), Eq(7) can be written as,

\[ \log D_i = \frac{n_i+m_i}{2} \log C_{\text{RH},org} + \log C_{ex,i} \quad \text{Eq}(8) \]

The \( m_i \) and \( K_{ex,i} \) could be obtained from the slope and intercept of the plots of \( \log D_i \cdot n_i \text{pH} \) against \( \log C_{\text{RH},org} \).

Fig.1. (a) Extraction of Fe\(^{3+}\), Dy\(^{3+}\), Nd\(^{3+}\) and Co\(^{2+}\) with neo-decanoic acid as extractant.

Table 5. Composition of extracted species and obtained \( K_{ex,i} \).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Extracted species</th>
<th>( K_{ex,i} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(^{3+})</td>
<td>FeR(_3) \cdot 3RH</td>
<td>6.43 \times 10^6</td>
</tr>
<tr>
<td>Dy(^{3+})</td>
<td>DyR(_3) \cdot 3RH</td>
<td>1.26 \times 10^13</td>
</tr>
<tr>
<td>Nd(^{3+})</td>
<td>NdR(_3) \cdot 3RH</td>
<td>1.74 \times 10^14</td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>CoR(_2) \cdot 2RH</td>
<td>4.37 \times 10^12</td>
</tr>
</tbody>
</table>

3.3. Extraction of binary metal solution with neo-decanoic acid

Next, the extraction of some metal ions (Ni\(^{2+}\), Zn\(^{2+}\), Cu\(^{2+}\) etc) increased with Fe\(^{3+}\) extraction in sulfuric acid solution at high acidity.
region when neo-decanoic acid was used as extractant.

Figures 2–5 show the effects of the acidity on the extraction yield and distribution ratio of metals. White and black plots represent the extraction results with single metal solution, and binary solution, respectively. Distribution of Co$^{3+}$ increased with distribution of Fe$^{3+}$ and Dy$^{3+}$ in high acidity region and separation efficiency was reduced. It means that Co$^{3+}$ is co-extracted with other metal such as Fe$^{3+}$, Dy$^{3+}$, and Nd$^{3+}$.

![Fig. 2](image1.png)

**Fig. 2** Extraction behavior of Fe$^{3+}$ and Dy$^{3+}$ from binary or single metal solution by using neo-decanoic acid

![Fig. 3](image2.png)

**Fig. 3** Extraction behavior of Fe$^{3+}$ and Co$^{3+}$ from binary or single metal solution by using neo-decanoic acid

![Fig. 4](image3.png)

**Fig. 4** Extraction behavior of Dy$^{3+}$ and Nd$^{3+}$ from binary or single metal solution by using neo-decanoic acid

![Fig. 5](image4.png)

**Fig. 5** Extraction behavior of Dy$^{3+}$ and Co$^{2+}$ from binary or single metal solution by using neo-decanoic acid

3.4. Stripping

Figures 6–8 show the effect of acid concentration on the stripping yields with neo-decanoic acid and PC-88A. The stripping yield of Fe$^{3+}$ and Dy$^{3+}$ from neo-decanoic acid solution was larger than that from PC-88A solution. The yields of Co$^{3+}$ were same between neo-decanoic acid and PC-88A. It means that stripping from neo-decanoic acid solution was easier than that from PC-88A. Stripping of Fe$^{3+}$ from PC-88A solution required higher acidity solution. However higher acidity solution should degrade the quality of organic solution and corrosion-resistance equipment should be necessary.

![Fig. 6](image5.png)

**Fig. 6** The effect of acid concentration on stripping yield of Fe$^{3+}$

Stripping reagent: HCl, HNO$_3$

![Fig. 7](image6.png)

**Fig. 7** The effect of acid concentration on stripping yield of Dy$^{3+}$

Stripping reagent: HCl, HNO$_3$

![Fig. 8](image7.png)

**Fig. 8** The effect of acid concentration on stripping yield of Co$^{2+}$

Stripping reagent: HCl, HNO$_3$

3.5. Separation process

From the experimental results, we made a proposal of the separation process of Fe$^{3+}$, Dy$^{3+}$, Nd$^{3+}$ and Co$^{3+}$ from Nd-Fe-B magnets by using neo-decanoic acid as extractant, as shown in Figure 9. This separation process was proposed by the following rules; (i) to use low amount of NaOH or HCl to adjust the pH, (ii) to use relatively weak acid to strip the metal from organic phase, (iii) to remove major impurity, Fe$^{3+}$, first, (iv) to separate Dy$^{3+}$ and Nd$^{3+}$ in the last stage because it’s
the most difficult in this process, (v) to consider the effects of co-extraction of Co\(^{3+}\) with Fe\(^{3+}\).

After leaching the magnet scrap with 0.1–1.0M HCl, the major impurity, Fe\(^{3+}\), and Co\(^{2+}\) are removed at pH2–2.5. Co\(^{2+}\) is co-extracted with Fe\(^{3+}\). After stripping, NaOH are added to the aqueous solution and Fe(OH)\(_3\) are precipitated and Co\(^{2+}\) remain in the aqueous solution. Dy\(^{3+}\) and Nd\(^{3+}\) are separated by solvent extraction at pH5–5.5. Dy can be recovered from organic phase by stripping with 0.1M HCl.

4. CONCLUSION

- Using neo-decanoic acid as extractant could remove Fe\(^{3+}\) from other valuable metals (Dy\(^{3+}\), Nd\(^{3+}\), Co\(^{3+}\)) easier than using PC-88A.
- Separation factor between Dy\(^{3+}\) and Nd\(^{3+}\) was enough for separation.
- Stripping from metal loaded organic solution of neo-decanoic acid using hydrochloric acid or nitric acid was easy and it will suppress the decreasing of quality of organic solution.
- Co\(^{3+}\) was co-extracted with other metals.
- From the above, we made proposal of the separation process of valuable metals from Nd-Fe-B magnet using neo-decanoic acid as extractant.

Acknowledgement

PC-88A was supplied by Daihachi chemical industry corporation.

Nomenclatures

\[ C_i \] Concentration of \(i\) [kmol \(\cdot\) m\(^{-3}\)]
\[ K_{ex,i} \] Extraction equilibrium constant of \(i\) [-]
\[ D_i \] Distribution ratio of \(i\) [-]
\[ E_i \] Extraction yield of \(i\) [-]
\[ Y_i \] Stripping yield of \(i\) [-]

\[ \beta \] Separation factor [-]
\[ V \] Volume [m\(^3\)]
\[ t \] time [min]
\[ T \] Temperature [K]
\[ x_i \] Polymerization degree of extract species of \(i\)
\[ n_i \] Valence of \(i\)
\[ m_i \] Solvation number of extract species of \(i\)

<Subscript>

0 at initial state of batch extraction experiment
1 equilibrium state of batch extraction experiment
2 at initial state of stripping experiment
3 equilibrium state of stripping experiment
aq Aqueous phase
org Organic phase
RH Extractant
Fe Fe\(^{3+}\)
Dy Dy\(^{3+}\)
Nd Nd\(^{3+}\)
Co Co\(^{2+}\)
H H\(_2\)O
HCl Hydrochloric acid
HNO\(_3\) Nitric acid
NaCl sodium chloride
i Solute \(i\)
\(j\) Solute \(j\)

References

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Fig.9. Separation process of Fe\(^{3+}\), Dy\(^{3+}\), Nd\(^{3+}\) and Co\(^{2+}\) from Nd-Fe-B magnet scrap.