

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

Student number: 12M18100 Name: Kazuma NAKAMURA Supervisor: Ryuichi EGASHIRA

カルボン酸抽出剤を用いた溶媒抽出法による有価金属のリサイクル

中村 数馬

安価であり分子中にリンを含まないことで廃溶媒の焼却処分が可能なカルボン酸の一種であるネオデカン酸を抽出剤として、希土類磁石構成金属元素であるジスプロシウム、ネオジム、コバルト、および鉄の回分平衡抽出を行った。他の金属と比較して鉄の分配比は著しく高く容易に除去でき、この性能は現在工業的に利用されている有機リン酸系抽出剤の場合に比較して高かった。また、有機溶媒相からの金属の逆抽出に利用する酸の量を低減できた。最後に、希土類磁石リサイクルにおけるカルボン酸抽出剤の利用を提案した。

## 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<sup>[1][2]</sup>. 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. **Table1** shows the typical composition of Nd-Fe-B magnets<sup>[3]</sup>. 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 has phosphor in their structure. Moreover, due to their strong affinity with major impurity,  $\text{Fe}^{3+}$ , the recovery of  $\text{Fe}^{3+}$  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  $\text{Fe}^{3+}$  was easier than that with organophosphorous ester extractants<sup>[1]</sup>.  $\text{Fe}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Co}^{2+}$  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.

**Table1** Typical composition of Nd-Fe-B magnets

	Fe	B	Co	Cu	Rare earth			
					Nd	Dy	Pr	Tb
ave[wt%]	66	1	2	0	23	5	3	0
					31			
max	69.6	1.11	3.66	0.23	27.6	7.67	6.48	1.61
min	61.6	0.95	0.54	0.11	18.6	2.97	0.26	0

## 2. EXPERIMENTAL

The experimental conditions of extraction equilibrium 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  $\text{HNO}_3$  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.

**Table2** Experimental conditions of batch extraction equilibrium

Solute	$\text{M}^{n+}(\text{Fe}^{3+}, \text{Dy}^{3+}, \text{Nd}^{3+}, \text{Co}^{2+})$ chloride
Extractant	Neo-decanoic, naphthenic (NA) PC-88A, D2EHPA
Diluent	kerosene
Initial metal concentration in aqueous phase, $C_{i,\text{aq},0}$ [kmol·m <sup>-3</sup> ]:	0.001
Extractant concentration in organic phase [vol%]:	10~30

**Table3** Experimental conditions of stripping experiment

Solute	$\text{M}^{n+}(\text{Fe}^{3+}, \text{Dy}^{3+}, \text{Nd}^{3+}, \text{Co}^{2+})$ chloride
Extractant	Neo-decanoic acid, PC-88A
Stripping agent	HCl, $\text{HNO}_3$
Initial metal concentration in organic phase, $C_{i,\text{org},2}$ [kmol·m <sup>-3</sup> ]:	0.001
Initial extractant concentration in organic phase [vol%]:	10
Initial concentration of stripping agent, $C_{\text{HCl},\text{aq},2}$ or $C_{\text{HNO}_3,\text{aq},2}$ [kmol·m <sup>-3</sup> ]:	0.01~7

### 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,

$$\begin{aligned} C_{i,aq,0}V_{aq} + C_{i,org,0}V_{org} &= C_{i,aq,1}V_{aq} + C_{i,org,1}V_{org} \\ C_{i,aq,2}V_{aq} + C_{i,org,2}V_{org} &= C_{i,aq,3}V_{aq} + C_{i,org,3}V_{org} \end{aligned}$$

The distribution ratio, extraction yield, and stripping yield of component  $i$ , were defined respectively as,

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

$$E_i = \frac{C_{i,org,1}V_{org}}{C_{i,aq,0}V_{aq}} \quad \text{Eq(2)}$$

$$Y_i = \frac{C_{i,aq,3}V_{aq}}{C_{i,org,2}V_{org}} \quad \text{Eq(3)}$$

$C_{i,org,1}$  and  $C_{i,org,3}$  were calculated with an assumption that the volumes of aqueous and organic phases were constant before and after the experiment.

The separation factor of component  $i$  relative to component  $j$ ,  $\beta_{i,j}$  was defined as,

$$\beta_{i,j} = \frac{D_i}{D_j} \quad \text{Eq(4)}$$

The half extraction  $pH$  values ( $pH_{1/2}$ ) for the extraction with single metal solutions with various extractant are listed in **Table 4**. The  $pH_{1/2}$  was defined as the  $pH$  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  $Nd^{3+}$ .

**Table4** List of  $pH_{1/2}$  with each extractant (10vol%) on extraction of  $Fe^{3+}$ ,  $Dy^{3+}$ ,  $Nd^{3+}$ ,  $Co^{2+}$ .

	Neo-decanoic	NA	PC-88A	D2EHPA
$Fe^{3+}$	2.36	2.21	-0.15	-0.48
$Dy^{3+}$	4.64	4.47	0.54	0.09
$Nd^{3+}$	5.01	4.89	1.29	0.60
$Co^{2+}$	6.39	6.21	3.37	2.79

#### 3.2. Extraction equilibrium with neo-decanoic acid

As reported in previous paper<sup>[4]</sup>, extraction equilibrium with carboxylic acid can be represented by 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 dimer in the organic solution. The extraction equilibrium constant can be expressed as,

$$K_{ex,i} = \frac{[(M_i R_{n_i} \cdot m_i RH)_{x_i}][H^+]^{n_i x_i}}{[M_i^{n_i+}]^{x_i} [(RH)_2]^{\frac{(n_i+m_i)}{2}}} \quad \text{Eq(6)}$$

Eq. (6) can be written as,

$$\log C_{i,org,1} = x_i (\log C_{i,aq,1} + n_i pH) + \log(x_i K_{ex,i,1}) + \frac{(n_i+m_i)}{2} \log C_{RH,org,1} \quad \text{Eq(7)}$$

In this experiment, the concentrations of metal were much lower than that of extractant,  $C_{RH,org}$  were assumed to be a constant. The  $\log C_{i,org}$  was plotted against  $(\log C_{i,aq} + n_i pH)$  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,

$$\log D_i - n_i pH = \frac{n_i+m_i}{2} \log C_{RH,org} + \log K_{ex,i} \quad \text{Eq(8)}$$

The  $m_i$  and  $K_{ex,i}$  could be obtained from the slope and intercept of the plots of  $\log D_i - n_i pH$  against  $\log C_{RH,org}$ , (**Fig. 1. (b)**) and they are listed in **Table 5**.

Eq(4) can be rewrite using  $K_{ex,i}$  as,

$$\beta_{i,j} = \frac{K_{ex,i}}{K_{ex,j}} \times (C_{RH,org,1})^{\frac{1}{2}(n_i-n_j)} \times (C_{H,aq,1})^{(n_j-n_i)} \quad \text{Eq(9)}$$

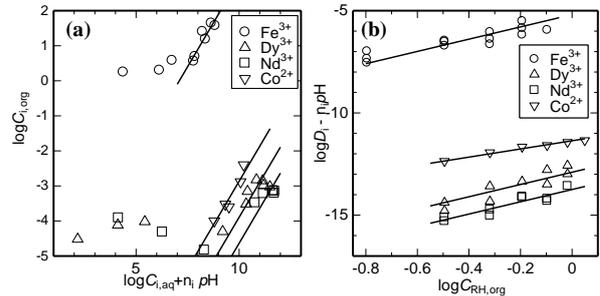
Separation factor can be obtain by substitute  $K_{ex,i}$  and  $n_i, n_j$ .

$$\beta_{Fe,Dy} = \frac{K_{ex,Fe}}{K_{ex,Dy}} = 5.10 \times 10^7$$

$$\beta_{Dy,Nd} = \frac{K_{ex,Dy}}{K_{ex,Nd}} = 7.24$$

$$\begin{aligned} \beta_{Nd,Co} &= \frac{K_{ex,Nd}}{K_{ex,Co}} \times (C_{RH,org,1})^{\frac{1}{2}} \times (C_{H,aq,1})^{-1} \\ &= 2.25 \times 10^6 \text{ (obtained by substitute } C_{RH,org}=0.32, pH=5) \end{aligned}$$

The separation factor of  $Fe^{3+}$  to  $Dy^{3+}$ , and that of  $Nd^{3+}$  to  $Co^{2+}$  were enough large to be possible to separate each other.  $Dy^{3+}$  and  $Nd^{3+}$  can be separated by using multistage extraction system.



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

**Table5.** Composition of extracted species and obtained  $K_{ex,i}$

i	Extracted species	$K_{ex,i}$
$Fe^{3+}$	$FeR_3 \cdot 3RH$	$6.43 \times 10^{-6}$
$Dy^{3+}$	$DyR_3 \cdot 3RH$	$1.26 \times 10^{-13}$
$Nd^{3+}$	$NdR_3 \cdot 3RH$	$1.74 \times 10^{-14}$
$Co^{2+}$	$CoR_2 \cdot 2RH$	$4.37 \times 10^{-12}$

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

Extraction of binary metal solution in some representative systems, such as (i)  $Fe^{3+}$  and  $Dy^{3+}$ , (ii)  $Fe^{3+}$  and  $Co^{2+}$ , (iii)  $Dy^{3+}$  and  $Nd^{3+}$ , (iv)  $Dy^{3+}$  and  $Co^{2+}$  were carried out to investigate the effect of coexistence metal on extraction equilibrium.

F.M.Doyle et al.<sup>[5]</sup> reported that extraction of some metal ions ( $Ni^{2+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$  etc) increased with  $Fe^{3+}$  extraction in sulfuric acid solution at high acidity re-

gion 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  $\text{Co}^{2+}$  increased with distribution of  $\text{Fe}^{3+}$  and  $\text{Dy}^{3+}$  in high acidity region and separation efficiency was reduced. It means that  $\text{Co}^{2+}$  is co-extracted with other metal such as  $\text{Fe}^{3+}$ ,  $\text{Dy}^{3+}$ , and  $\text{Nd}^{3+}$ .

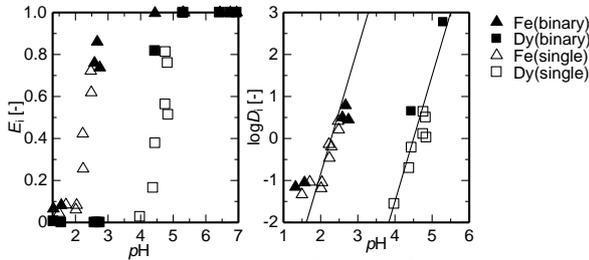


Fig. 2 Extraction behavior of  $\text{Fe}^{3+}$  and  $\text{Dy}^{3+}$  from binary or single metal solution by using neo-decanoic acid

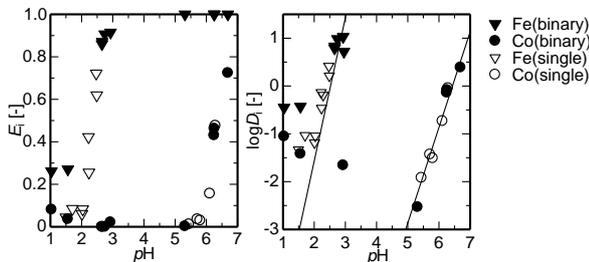


Fig.3 Extraction behavior of  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$  from binary or single metal solution by using neo-decanoic acid

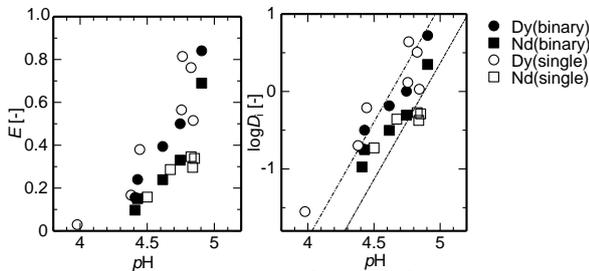


Fig.4 Extraction behavior of  $\text{Dy}^{3+}$  and  $\text{Nd}^{3+}$  from binary or single metal solution by using neo-decanoic acid

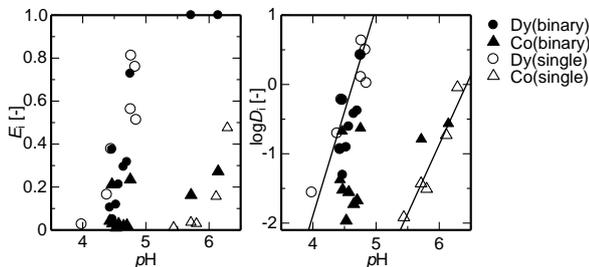


Fig.5. Extraction behavior of  $\text{Dy}^{3+}$  and  $\text{Co}^{2+}$  from binary or single metal solution by using neo-decanoic acid.

### 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  $\text{Fe}^{3+}$  and  $\text{Dy}^{3+}$  from

neo-decanoic acid solution was larger than that from PC-88A solution. The yields of  $\text{Co}^{2+}$  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  $\text{Fe}^{3+}$  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.

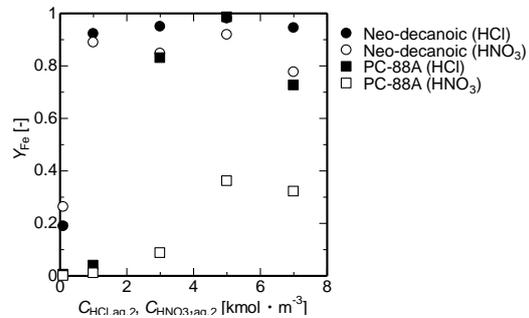


Fig.6 The effect of acid concentration on stripping yield of  $\text{Fe}^{3+}$ . Stripping reagent: HCl,  $\text{HNO}_3$

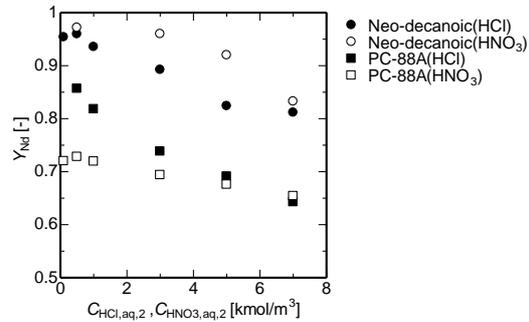


Fig.7 The effect of acid concentration on stripping yield of  $\text{Dy}^{3+}$ . Stripping reagent: HCl,  $\text{HNO}_3$

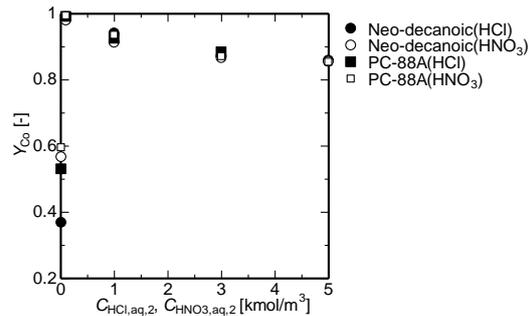


Fig.8 The effect of acid concentration on stripping yield of  $\text{Co}^{2+}$ . Stripping reagent: HCl,  $\text{HNO}_3$

### 3.5. Separation process

From the experimental results, we made a proposal of the separation process of  $\text{Fe}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Co}^{2+}$  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,  $\text{Fe}^{3+}$ , first, (iv) to separate  $\text{Dy}^{3+}$  and  $\text{Nd}^{3+}$  in the last stage because it's

the most difficult in this process, (v) to consider the effects of co-extraction of  $\text{Co}^{2+}$  with  $\text{Fe}^{3+}$ .

After leaching the magnet scrap with 0.1~1.0M HCl, the major impurity,  $\text{Fe}^{3+}$ , and  $\text{Co}^{2+}$  are removed at pH2~2.5.  $\text{Co}^{2+}$  is co-extracted with  $\text{Fe}^{3+}$ . After stripping them, NaOH are added to the aqueous solution and  $\text{Fe}(\text{OH})_3$  are precipitated and  $\text{Co}^{2+}$  remain in the aqueous solution.  $\text{Dy}^{3+}$  and  $\text{Nd}^{3+}$  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  $\text{Fe}^{3+}$  from other valuable metals ( $\text{Dy}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Co}^{2+}$ ) easier than using PC-88A.
- Separation factor between  $\text{Dy}^{3+}$  and  $\text{Nd}^{3+}$  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.
- $\text{Co}^{2+}$  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	[ $\text{kmol} \cdot \text{m}^{-3}$ ]
$K_{\text{ex},i}$	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	[ $\text{m}^3$ ]
$t$	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	
<b>&lt;Subscript&gt;</b>		
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	$\text{Fe}^{3+}$	
Dy	$\text{Dy}^{3+}$	
Nd	$\text{Nd}^{3+}$	
Co	$\text{Co}^{2+}$	
H	Hydroxide	
HCl	Hydrochloric acid	
$\text{HNO}_3$	Nitric acid	
NaCl	sodium chloride	
i	Solute i	
j	Solute j	

#### References

- [1] 小山和也, 田中幹也; レアアースの最新技術動向と資源戦略, 第三章, 2(工場内)磁石廃材の湿式リサイクル技術 127-131
- [2] 禰田榮一: リサイクル金属資源回収プロセスにおける溶媒抽出, レアメタル資源の分離回収技術と溶媒抽出, 化学工学シンポジウムシリーズ60 101-110
- [3] 平成22年度 廃棄物資源循環学会 レアメタルリサイクルに関する合同講演会 資料
- [4] J.S.Preston, Solvent extraction of metals by carboxylic acids, Hydrometallurgy, 14(1985) 171-188
- [5] F.M.Doyle, D.pouillon, Solvent extraction of metals with carboxylic acid acid-coextraction of base metals with  $\text{Fe}(\text{III})$  and characterization of selected carboxylate complexes, Hydrometallurgy, 19(1988)289-308

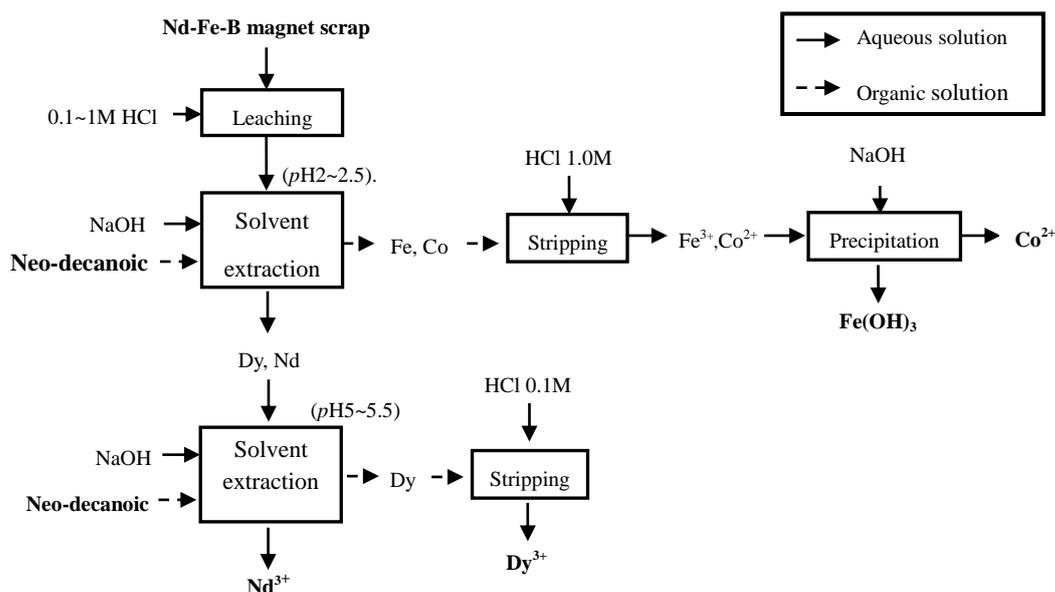


Fig.9. Separation process of  $\text{Fe}^{3+}$ ,  $\text{Dy}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Co}^{2+}$  from Nd-Fe-B magnet scrap.