



Separation of zinc and nickel ions in a strong acid through liquid–liquid extraction

Young Jun Park*, Derek J. Fray*

Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, United Kingdom

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ABSTRACT

Many solid wastes contain both zinc and nickel at the same time. For recycling or recovery of metals, it is essential to separate materials. Among those materials, zinc and nickel are very difficult to be separated because there is not so much difference in the chemical and physical properties. This paper focuses on the separation of zinc and nickel ions in a diluted aqua regia solution. Liquid–liquid extraction by TBP, Cyanex 272 and Cyanex 301 was used and a distribution coefficient (D), a separation factor (S) and a relative purity (R) were induced to evaluate the degree of separation. All of the extractions were proportional to the concentration of the extractants, and zinc ions were extracted more easily than nickel ions. Among the extractants, Cyanex 301 showed the best characteristics regarding Zn/Ni separation. In particular, the extraction of zinc ions in the range of $\text{pH} \leq 6$ was constantly over 99 wt.%, whilst that of nickel ions was less than 20 wt.%, when 100 vol.% Cyanex 301 was used. The maximum $S_{\text{Zn,Ni}}$ value was about 21,700 at $\text{pH} 6.0$ and the highest relative purity (R) of zinc was about 99 wt.% without a pH control, $\text{pH} -1.1$.

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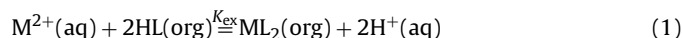
1. Introduction

Most electronic and electrical equipment contains printed circuit boards (PCB). Recently, waste PCB has become an environmental problem, as well as highlighting issues due to their valuable metal contents. Our previous papers suggested a new process, as shown in Fig. 1 [1]. In the process, iron and aluminum could be recovered through applying mechanical treatments, and the solder was separated by electrowinning after HBF_4 leaching [2]. Copper can also be removed by well established commercial processes [3]. The residues after copper removal are dissolved in aqua regia and the precious metals, such as gold, silver and palladium, can be recovered by liquid–liquid extraction and precipitation [1]. The last step in our process is the separation of zinc and nickel in a diluted aqua regia.

Previous work on selective nickel electrowinning gave the kinetics of nickel deposition after pH adjustment [4]. Some papers reported the selective extraction of zinc or nickel with organic solutions [5,6] and a few papers dealt with extraction of zinc or nickel from a sulphuric medium, respectively [7,8]. But none of them explored the separation of zinc/nickel in a concentrated HCl/HNO_3 solution. Therefore, this research aims to give basic and essential

information regarding zinc/nickel separation in a strong acid prepared from HCl and HNO_3 , which would be useful in the field of material recovery.

Liquid–liquid (L–L) extraction is an effective method of separating metal ions selectively. In particular, phosphorus acid (HL) groups have been reported as good extractants in acidic solutions [9–12]. The general reaction for the extraction of a divalent metal cation (M^{2+}) can be expressed in terms of the following equilibrium equation:



where K_{ex} is the extraction constant as follows:

$$K_{\text{ex}} = \frac{[\text{ML}_2]_{\text{org}}[\text{H}^+]_{\text{aq}}^2}{[\text{M}^{2+}]_{\text{aq}}[\text{HL}]_{\text{org}}^2} \quad (2)$$

Eq. (2) represents several factors which could have an influence on the extraction of metal ions, such as the type and concentrations of the extractants and the pH of the aqueous phase.

In this paper, zinc and nickel dissolved in a strong acid were separated by L–L extraction, in which three kinds of organic solutions – tri-*n*-butyl phosphate (TBP), Cyanex 272 and Cyanex 301 – were used as extractants.

* Corresponding authors. Tel.: +44 7972 222364.

E-mail addresses: yjp21@cam.ac.uk (Y.J. Park), djf25@cam.ac.uk (D.J. Fray).

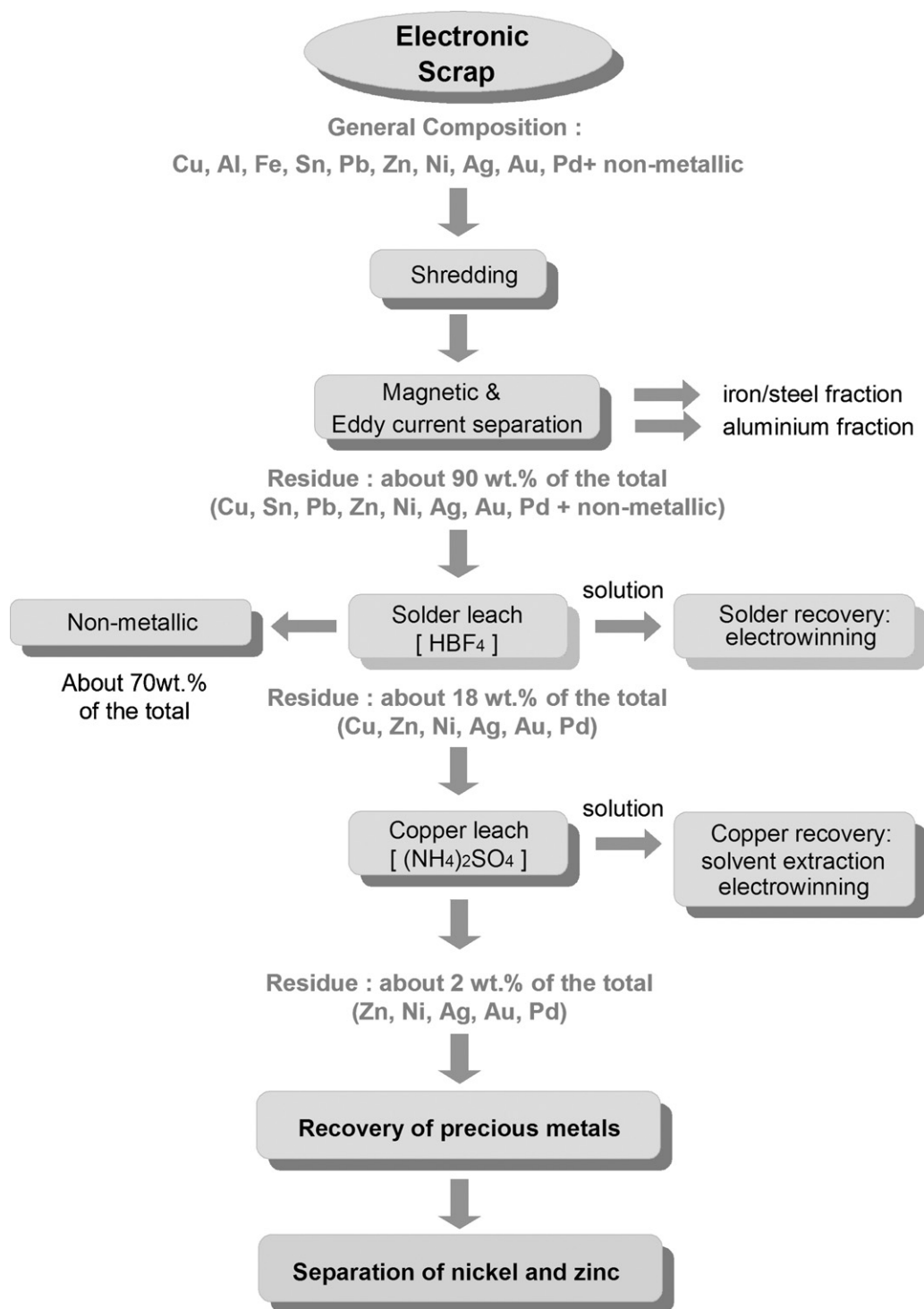


Fig. 1. A new recycling process of PCB metals.

2. Experimental

2.1. Dissolution of zinc and nickel

Aqua regia was freshly prepared by mixing ACS reagent grade concentrated hydrochloric with nitric acid. Zinc and nickel (2.5 g for each) were completely dissolved in the aqua regia (100 ml) for 4 h at $25 \pm 1^\circ\text{C}$. The solution was then diluted 2.5 times with deionized water, which made the solution suitable for the Zn/Ni separation

step in Fig. 1. In addition, the pH of the diluted aqua regia solution was -1.1 .

2.2. L-L extraction

Three kinds of organic solution – TBP (Merck), Cyanex 272 and Cyanex 301 (Cytec Industries Inc.) – were used as extractants. There were major two factors which could have a significant influence on the extraction efficiency. One is the concentration of extractants

and the other is the pH of the aqueous solution. Reagent grade kerosene was used as the diluent, and ACS reagent grade ammonium hydroxide solution (28.0–30.0% as NH_3) was used to control the pH of the aqueous phase.

Extraction tests were carried out at the temperature of 25 ± 1 °C with an aqueous:organic (A:O) ratio of 1:1 by volume. The two phases were mixed at 400 rpm for 20 min and kept stationary for 30 min to induce the phase separation.

2.3. Analysis and evaluation

The aqueous solutions, after coming into contact with the organic extractants, were analyzed using inductively coupled plasma-atomic absorption spectrometry (ICP-AAS, VARIAN LIBERTY-AX). The extracted amounts from the organic extractants were calculated through the concentration differences in the aqueous solutions before and after extraction.

The extraction efficiency was evaluated by the distribution coefficient (D_i):

$$D_{\text{Zn}} = \frac{C_{\text{Zn,org}}}{C_{\text{Zn,aq}}} \quad (3)$$

where $C_{\text{Zn,org}}$ and $C_{\text{Zn,aq}}$ are the concentrations of the zinc ions in the organic and the aqueous solution, respectively. In addition, $S_{\text{Zn,Ni}}$ is the separation factor of the zinc ions from the nickel ions.

$$S_{\text{Zn,Ni}} = \frac{D_{\text{Zn}}}{D_{\text{Ni}}} \quad (4)$$

The S value represents the tendency of the separation between the two species in an L–L extraction. Therefore, the relative purity ($R_{\text{Zn,Ni}}$) was also calculated by the following equation:

$$R_{\text{Zn,Ni}}(\text{wt.}\%) = \frac{C_{\text{Zn,org}}}{C_{\text{Zn,org}} + C_{\text{Ni,org}}} \times 100 \quad (5)$$

where $C_{\text{Zn,org}}$ and $C_{\text{Ni,org}}$ are the concentrations of zinc and nickel ions in the organic phase, respectively.

3. Results and discussion

3.1. Pre-experiment

The best way to recover a metal may be the simplest method and a paper reported that zinc and nickel ions in a sulphuric acid could be separated simply by a pH control [13]. Although the aqueous solution is different from that used in our research, it has the potential to separate the zinc and nickel ions through a simple treatment. Therefore, the pH of the solution which contained zinc and nickel ions in a diluted aqua regia was changed from -1.1 up to 12.5 with NaOH. However, there was no point at which these two metal ions were separated by selective precipitation.

3.2. L–L extraction with TBP

Fig. 2 shows the extraction of zinc and nickel ions when a TBP of 20 and 100 vol.% were used. With a TBP of 20 vol.%, the Zn and Ni extraction yields in the range of pH <6 were less than 20 wt.% and increased sharply up to 92 and 85 wt.% at pH 7.5, respectively. On the other hand, when 100 vol.% TBP was used as the extractant, the yields of zinc in the pH of 6 or less were 60–70 wt.% whilst those of nickel were less than 6 wt.%. The separation of materials requires a large difference in terms of the extraction yields. Accordingly, the results of Fig. 2 indicate that a 100 vol.% TBP is more effective in the separation than that of 20 vol.%. Figs. 3 and 4 show the D and S values according to the pH of the aqueous solution. In order to achieve an effective separation of the metal ions, it is essential that the values

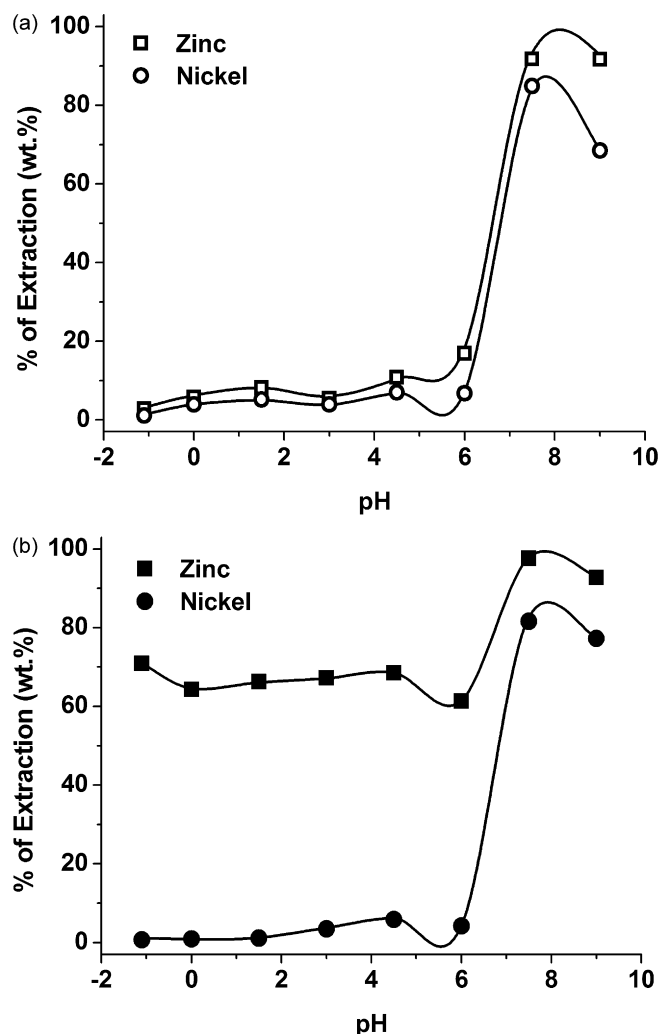


Fig. 2. Percentage extraction of zinc and nickel ions according to the pH of the aqueous solution by 20 (a) and 100 (b) vol.% TBP. The initial concentrations of zinc and nickel were 25 g/l, respectively.

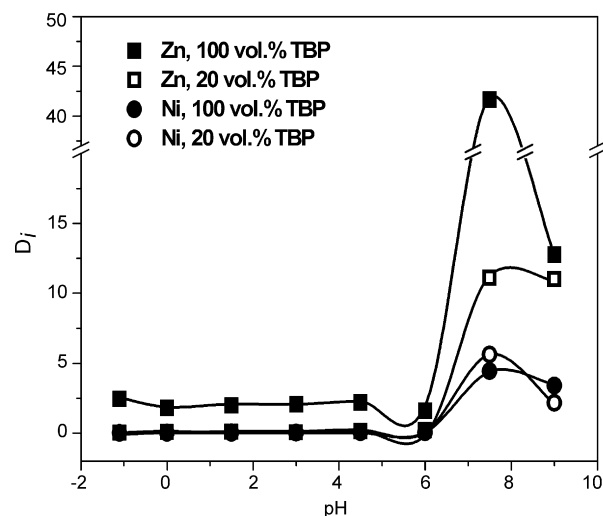


Fig. 3. Changes in the D_{Zn} and D_{Ni} values of 20 and 100 vol.% TBP according to the pH of the aqueous solution.

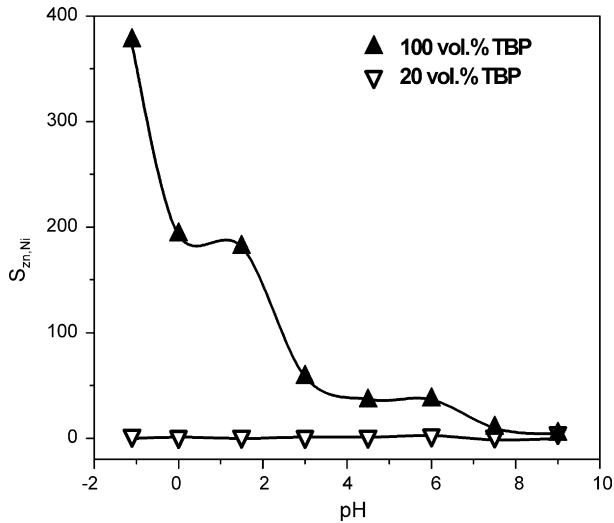


Fig. 4. Changes in the $S_{Zn,Ni}$ values of 20 and 100 vol.% TBP according to the pH of the aqueous solution.

of D and S are high at the same time. However, the D values were high at a pH of more than 7.5 (Fig. 3), whilst the S values were high at a pH of less than 1.5 (Fig. 4).

The separation with 40, 60 and 80 vol.% TBP, Cyanex 272 and Cyanex 301 showed a general tendency, proportional to the concentrations of extractants. Accordingly, the results of 40, 60 and 80 vol.% extractants were not mentioned because their values were between those of 20 and 100 vol.% extractants.

3.3. L–L extraction with Cyanex 272

Cyanex 272 is one of commercial extractants for the selective recovery of zinc. In this study, the extraction with 20 and 100 vol.% Cyanex 272 was investigated according to the pH of the aqueous solution. First of all, in the extraction test at pH 7.5, it took more than 2 h to separate the aqueous and organic phases, whilst the other separations were completed within 30 min. Thus, the parts of the pH 7.5 in Figs. 5–7 were shown as dotted lines. As the pH increased, the extraction of zinc showed a tendency to increase, but that of nickel in pH 6 was confined within 10 wt.% in both concentrations (Fig. 5(a) and (b)). In the case of pH 9 of 100 vol.% Cyanex 272, the percentage extractions of zinc and nickel were high at the same time, at about 99 wt.% for zinc and 96 wt.% for nickel.

The D values of the zinc were higher than those of the nickel throughout the pH. The maximum D value, except pH 7.5, was 171 at the pH 9, when the zinc ions were extracted with 100 vol.% Cyanex 272. However, the S value at this point was about 7, which was a relatively low value due to the amount of extracted nickel. Therefore, the relative optimum point for separation could be at pH 6.0 of 100 vol.% Cyanex 272, where the D and S values are 7.3 and 69.4, respectively. These results indicate that the zinc and nickel ions were not extracted sufficiently into the Cyanex 272 in pH 6 or less, and it is difficult to obtain a selective extraction at pH 9.

3.4. L–L extraction with Cyanex 301

The percentage extractions of the zinc and nickel ions from the aqueous solution to Cyanex 301 were examined as the pH of the aqueous solution changed. The overall patterns were similar, as shown in Fig. 8(a) and (b). The extraction of zinc in the 20 vol.% extractant was more than 85 wt.% whilst that of nickel was less than 20 wt.%, except for pH 7.5 and 9.0. In the case of the pH 7.5

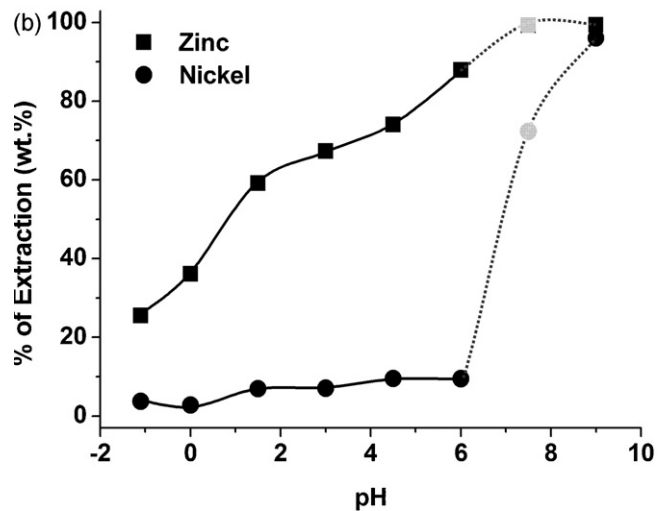
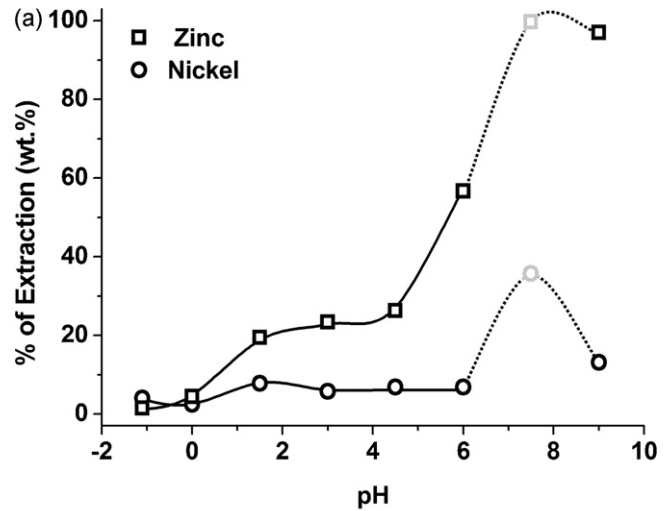


Fig. 5. Percentage extraction of zinc and nickel ions according to the pH of the aqueous solution by 20 (a) and 100 (b) vol.% Cyanex 272. The initial concentrations of zinc and nickel were 25 g/l, respectively.

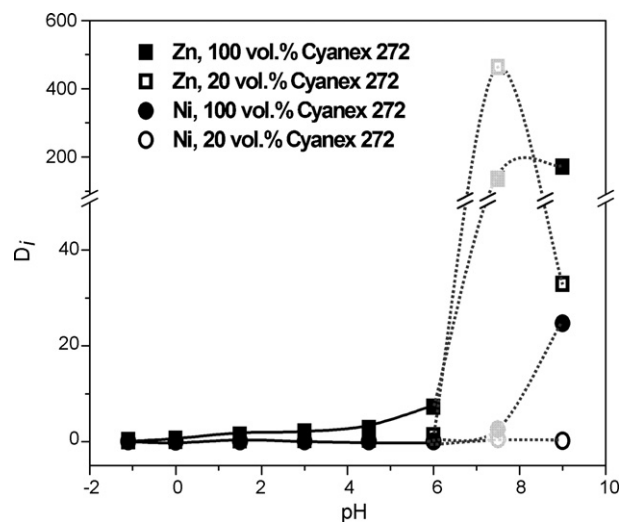


Fig. 6. Changes in the D_{Zn} and D_{Ni} values of 20 and 100 vol.% Cyanex 272 according to the pH of the aqueous solution.

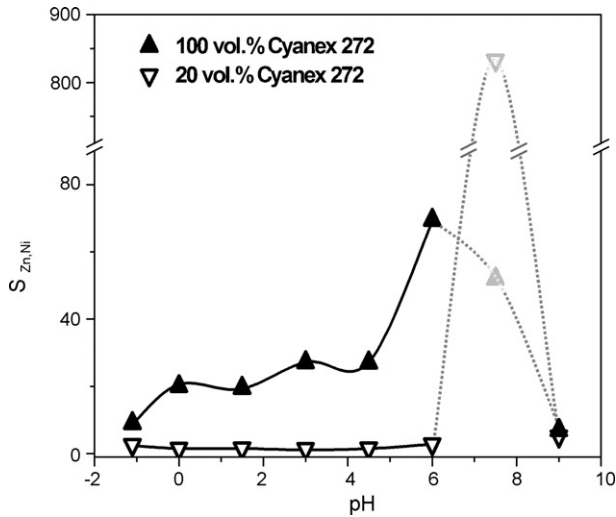


Fig. 7. Changes in the $S_{Zn,Ni}$ values of 20 and 100 vol.% Cyanex 272 according to the pH of the aqueous solution.

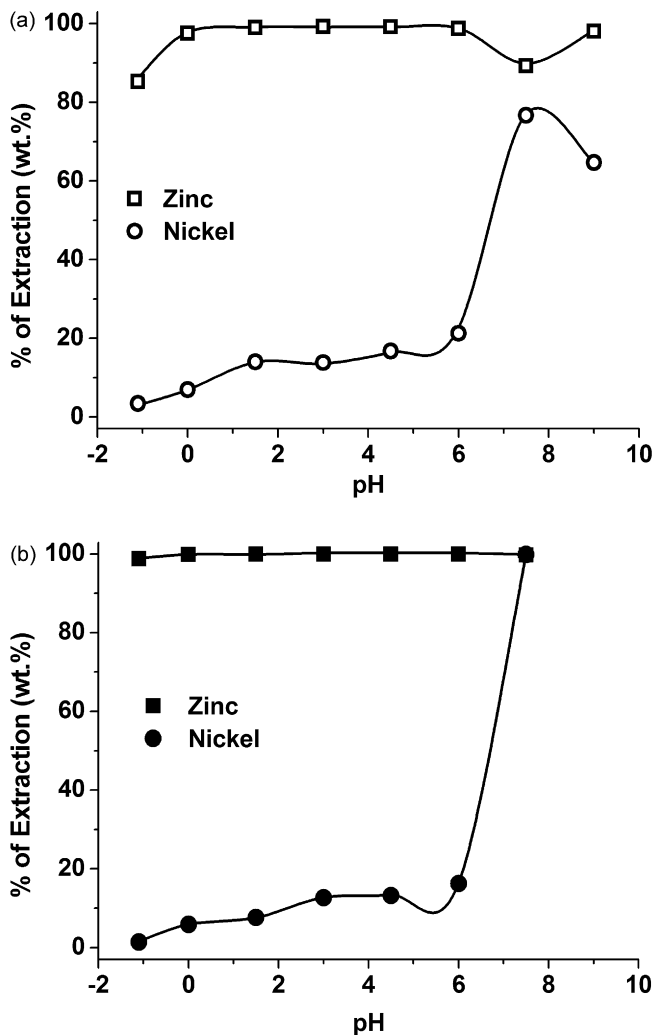


Fig. 8. Percentage extraction of zinc and nickel ions according to the pH of the aqueous solution by 20 (a) and 100 (b) vol.% Cyanex 301. The initial concentrations of zinc and nickel were 25 g/l, respectively.

Table 1

D values of 20 and 100 vol.% Cyanex 301 according to the pH of the aqueous solution

| pH | 20 vol.% Cyanex 301 | | 100 vol.% Cyanex 301 | |
|------|---------------------|----------|----------------------|----------|
| | D_{Ni} | D_{Zn} | D_{Ni} | D_{Zn} |
| -1.1 | 0.0 | 5.8 | 0.0 | 79.2 |
| 0.0 | 0.1 | 40.2 | 0.1 | 714.4 |
| 1.5 | 0.2 | 100.1 | 0.1 | 2132.0 |
| 3.0 | 0.2 | 131.9 | 0.1 | 2112.6 |
| 4.5 | 0.2 | 128.2 | 0.2 | 2122.3 |
| 6.0 | 0.3 | 82.0 | 0.2 | 4226.3 |
| 7.5 | 3.3 | 8.4 | 929.0 | 464.0 |
| 9.0 | 1.8 | 50.7 | N.S. ^a | N.S. |

^a Not separated.

and 9.0, the percentage extractions of the nickel ions were 77 and 65 wt.%, respectively (Fig. 8(a)). The extraction of the zinc ions in 100 vol.% Cyanex 301 was constantly high, at over 99 wt.%, and that of the nickel ions in the range of $pH \leq 6$ remained less than 20 wt.%. At pH 7.5, most of the zinc and nickel ions were extracted from the aqueous to the organic solution, which means that there was no selectivity in the extraction. In the extraction at pH 9.0, it was impossible to separate the phases (Fig. 8(b)).

From the results of the percentage extractions, it could be expected that the D values of zinc would be very high and show a big difference from that of the nickel. The D values of two ions are summarized in Table 1. At a pH of ≤ 6 , the D values of the nickel were confined within 0.3, whilst those of zinc varied from 5.8 at a pH -1.1 of 20 vol.% Cyanex 301 up to 4226.3 at a pH 6.0 of 100 vol.% Cyanex 301. Fig. 9 shows the S values of 20 and 100 vol.% Cyanex 301. Compared with the D values, it was found that the zinc ions could be extracted selectively around both pH 1.5 and 6.0. To examine the changes in the Zn extractions with the concentrations of the extractant in detail, the D and S values at these two pH values were investigated as the concentrations were changed from 20 to 100 vol.%. In order to facilitate observation of the changes, the Y axes in Figs. 10 and 11 were converted to logarithmic scales. The D_{Zn} values were proportional to the concentration whilst the D_{Ni} values were almost constant or slightly decreased (Fig. 10). The $S_{Zn,Ni}$ values were calculated and plotted from Eq. (4). The values at both pH 1.5 and 6.0 increased exponentially as shown in Fig. 11.

As stated above, the D and S values could represent the relative tendency of the extraction but it is difficult to show the quality of the

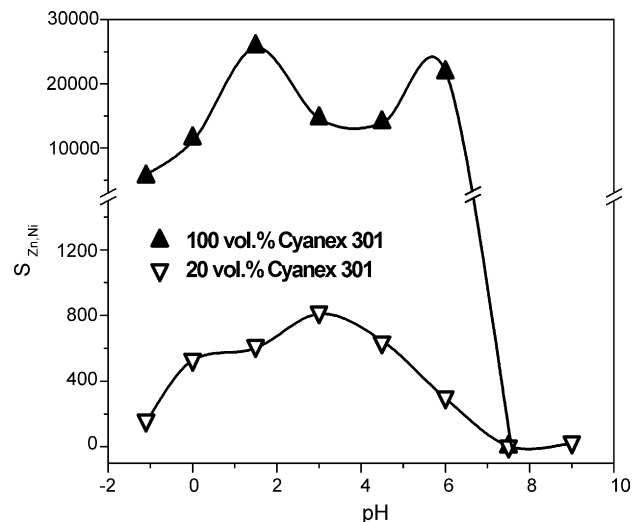


Fig. 9. Changes in the $S_{Zn,Ni}$ values of 20 and 100 vol.% Cyanex 301 according to the pH of the aqueous solution.

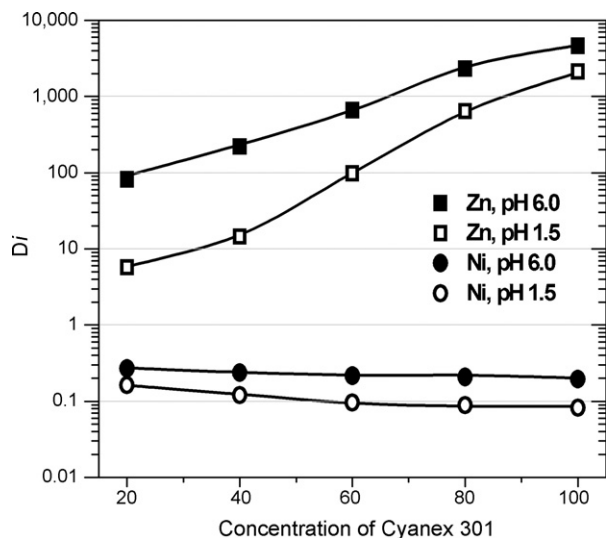


Fig. 10. Changes in the D_{Zn} and D_{Ni} values at pH 1.5 and 6.0 according to the concentration of Cyanex 301.

recovered material. Therefore, it is necessary to evaluate the purity of the final products in the recovery of materials from waste, which is directly related to economical efficiency. In addition, a relative purity in the organic phase reflects a purity of a metal product which could be obtained by the L–L extraction process. The relative purities (R) of zinc against nickel were calculated in proportion as the pH of the aqueous phase and the concentration of the organic phase. The R values showed the maximum at the pH –1.1 and decreased as the pH increased (Fig. 12). On the other hand, the values according to the concentration of Cyanex 301 increased slightly, as shown in Fig. 13. From the results stated above, it could be expected that zinc metal, with a purity of about 99 wt.%, could be obtained with 100 vol.% Cyanex 301 and without a pH control, pH –1.1.

The purities from 20 to 80 vol.% Cyanex 301 were also quite high as 96 and 98 wt.% at 20 and 80 vol.% Cyanex 301, respectively. In consideration of the workability and the economical efficiency, Cyanex 301 of less than 100 vol.% could be better because 100 vol.% Cyanex was a viscous solution and the price was higher than that of the diluent.

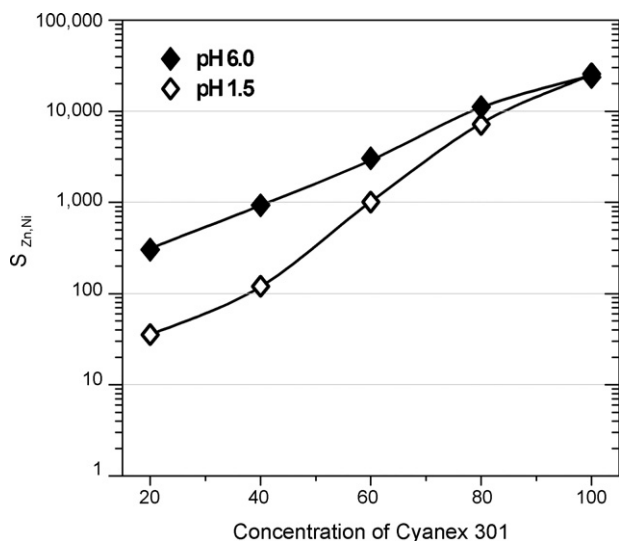


Fig. 11. Changes in the $S_{Zn,Ni}$ values at pH 1.5 and 6.0 according to the concentration of Cyanex 301.

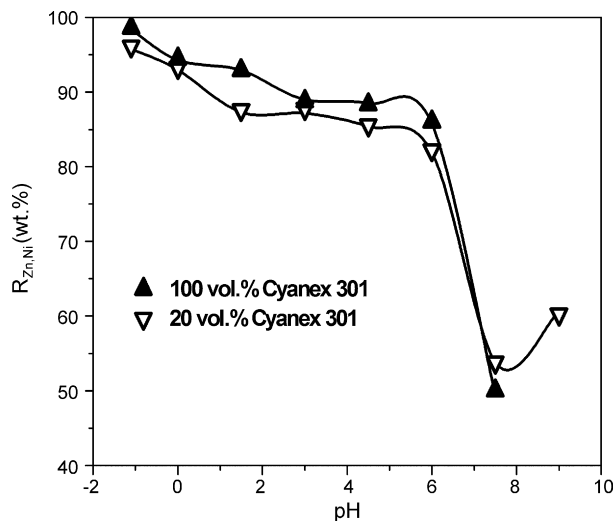


Fig. 12. Changes in the $R_{Zn,Ni}$ values of 20 and 100 vol.% Cyanex 301 according to the pH of the aqueous solution.

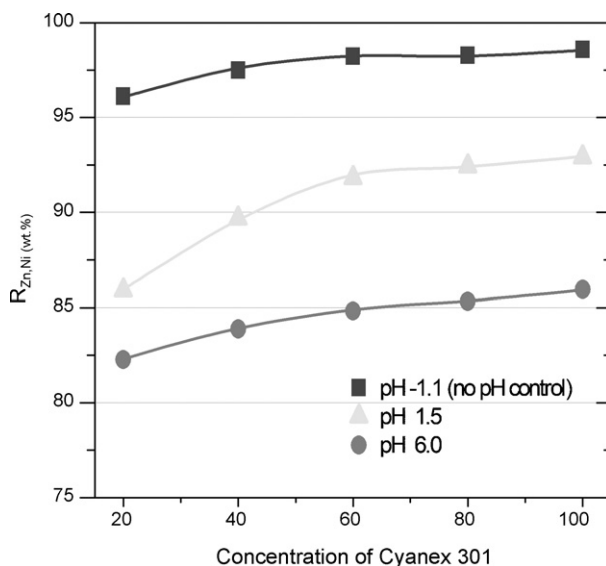


Fig. 13. Changes in the $R_{Zn,Ni}$ values according to the concentration of Cyanex 301 at pH –1.1, 1.5 and 6.0.

4. Conclusions

Zinc and nickel ions could be separated by L–L extraction. TBP, Cyanex 272 and Cyanex 301 were used as extractants, and the aqueous:organic ratio was fixed at 1:1 by volume. The extraction of zinc prevailed against that of nickel throughout the experiments. In addition, the extractants with higher concentrations showed better extraction characteristics.

When 100 vol.% TBP was used as the extractant, the extraction of zinc in a pH range of less than 6 was relatively low, 60–70 wt.%, whilst that of nickel remained below 6 wt.%. In the case of Cyanex 272, the optimum condition was at pH 6.0 of the 100 vol.% Cyanex 272, where the extracted zinc and nickel ions were about 88 wt.% and 10 wt.%, respectively. Cyanex 301 showed the excellent characteristics of Zn/Ni separation in this study. In the range of $pH \leq 6$, the extraction of the zinc ions in the 100 vol.% Cyanex 301 was constantly over 99 wt.%, whilst that of the nickel ions was less than 20 wt.%. In the aspect of separation, the Zn extraction at pH 6.0 showed the highest S value of about 21,700. The relative purity of

the organic extractant could make it possible to obtain zinc metal of about 99 wt.% without a pH control, when 100 vol.% Cyanex 301 is used as the extractant.

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