Continuous Liquid-Liquid Extraction of Nickel from Simulated Electroless Nickel Plating Liquid Wastes by Using a Counter Current Emulsion Flow Extractor

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Simulated electroless nickel plating liquid wastes have been processed by using an emulsion flow extractor of a counter current type with a special focus on the influence of dilution of the liquid wastes on the extraction performance. The emulsion flow extractor provides efficient liquid–liquid extraction without the need for additional stirring or shaking. The solvent used in the present study was a Shellsol D70 solution containing LIX84-I as the extractant for nickel and PC88A as an accelerating agent. As a result, it was found that increasing the degree of dilution with water resulted in an improvement in nickel extractability obtained from the emulsion flow experiments with a maximum value of 96% as well as those obtained from batch experiments. Droplet sizes at the lower and the upper parts of the emulsion phases, estimated by using high-speed microscope, were 214 ± 36 µm and 415 ± 110 µm, respectively.

1. Introduction

Electroless nickel plating (hereinafter termed “EN”) is a surface finishing method that deposits a uniform thickness of a protective nickel coating onto product surfaces regardless of their shapes by chemical reduction, not by electricity, and has been widely applied to various industrial fields such as automobile manufacture or electronics. Separation and recovery of nickel from spent EN liquids can reduce the volume of waste waters and save resources [1-3], and is expected to contribute to the establishment of a recycling-based society. Solvent extraction is considered to be a promising candidate for the treatment of EN liquid wastes [4-6], because it enables the selective recovery of nickel from the liquid wastes without sludge generation. An effective solvent extraction system, which contains a chelating extractant with a small amount of an accelerating agent, has been used for the selective extraction of nickel [7-9].

Continuous liquid-liquid extraction for industrial waste waters has been conducted by using conventional apparatus such as mixer-settlers, centrifugal extractors and spray extraction columns. We have recently developed a new type of apparatus, called the emulsion flow extractor [10-12]. This apparatus can provide a flow of the emulsified mixture of aqueous and organic solutions (hereinafter termed “emulsion flow” or “EF”) without the need for additional stirring or shaking. It also allows continuous treatment of a large volume of waste waters with high recovery efficiency, low fabrication/running cost, and low waste generation.

EN liquid wastes contain reducing agents and complexing agents [1]. Since these agents are
considered to inhibit nickel extraction as masking agents [9], the extraction performance can be improved if the concentrations of the masking agents are reduced by dilution of the EN liquid wastes with water. In the present study, we first conducted batch experiments to evaluate the effect of the dilution for simulated EN liquid wastes. Then, we carried out EF experiments to examine the applicability of a counter current EF extractor to processing the simulated EN liquid wastes with a special focus on the practical use of dilution effect. In addition, we conducted in-situ observation of the emulsion phases in the EF extractor by using a high-speed microscope to examine the droplet sizes.

2. Experimental

2.1 Outline of the counter current emulsion flow extractor

Figure 1 shows the outline of a desktop counter current EF extractor used in the present study. The apparatus is mainly composed of three sections: an extraction section at the center of the apparatus and two phase-separation sections located at the top and bottom of the extraction section without any partition. A head for spraying the aqueous phase, located at the upper side of the extraction section, was a polypropylene hollow cylinder with several small holes in its side wall. On the other hand, another head for spraying the organic phase, located at the lower side of the extraction section, was a commercial sintered-glass plate bound onto one end of a hollow cylinder.

Prior to operation of the counter current EF extractor, the apparatus was filled with aqueous and organic solutions, the boundary of which was set in the middle between the two heads. Using a pump, the organic solution was withdrawn from the upper phase-separation part, and sprayed into the aqueous solution through the lower head, while the aqueous solution in the reservoir tank was sprayed into the organic solution through the upper head. In the emulsion phase, the aqueous and organic phases came into contact with each other, and target elements in the aqueous phase were extracted into the organic phase. When the emulsion phase reached the upper or lower phase-separation section, it disappeared, and separated into the bulk aqueous or organic phases, respectively. The solvent separated in the upper section was sent again to the lower spray head and re-circulated. On the other hand, the aqueous raffinate separated in the lower section was removed for continuous treatment.

2.2 Preparation of simulated nickel electroless liquid wastes

EN liquid wastes contained nickel ion, reducing agents, complexing agents and a pH adjuster [1]. Table 1 shows the chemical composition of the simulated Ni liquid waste in the present study (hereinafter termed “Model Liquid A” [8]), which was prepared from commercially available reagents. Model Liquid A was adjusted to pH6.5 with NaOH solution (50w/v% NaOH solution, Wako, 47~53w/v%), and was diluted
two and four times with deionized water to prepare Model Liquids B and C, respectively. The solvent was a Shellsol D70 (Shell Chemicals) solution containing 0.65 mol/L 2-hydroxy-5-nonylacetophenone oxime (LIX84-I) (Cognis) as the extractant for Ni and 0.062 mol/L 2-ethylhexyl-2-ethylhexylphosphonic acid (PC88A) (Daihachi Chemical Industry) as an accelerating agent [7, 8]. When LIX84-I is represented as RH, the chemical reaction extracting Ni$^{2+}$ from aqueous solutions in the present study is given by,

$$2RH_{(org)} + Ni^{2+}_{(aq)} \rightleftharpoons R_2Ni_{(org)} + 2H^+_{(aq)}.$$  (1)

This reaction is very slow, but is significantly accelerated by adding a small quantity of accelerating agents such as PC88A to attain the equilibrium within 20 minutes [7, 8].

### 2.3 Liquid-liquid extraction experiments

At first, batch experiments were conducted at room temperature (18–23 °C) to determine the distribution ratios of Ni at equilibrium. The simulated EN liquid waste and the solvent at a volume ratio of 1:1 were shaken in a propylene tube with a shaking machine for 20 minutes, the aqueous phase was separated with a centrifuge machine (5 minutes and 3000 rpm), and the Ni concentration in the aqueous phase was analyzed.

Next, continuous liquid-liquid extraction experiments were carried out for Model Liquids A, B and C at room temperature (18–23 °C) by using the counter current EF extractor. Initially, the apparatus was filled with deionized water and the solvent, and then the two phases were circulated in the apparatus before

### Table 2. Chemical composition of Model Liquid A.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentration (mol/L)</th>
<th>Reagents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>2.35</td>
<td>(1) Na$_2$SO$_4$, Wako (≥99%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+ (4), (5)</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>0.08</td>
<td>(2) Ni$_2$SO$_4$·6H$_2$O, Kishida (99–102%)</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>0.51</td>
<td>(3) H$_2$SO$_4$, Wako (≥95%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>+ (1), (2)</td>
</tr>
<tr>
<td>H$_2$PO$_4^-$</td>
<td>0.23</td>
<td>(4) NaH$_2$PO$_4$·H$_2$O, Kishida (≥99%)</td>
</tr>
<tr>
<td>HPO$_3^{2-}$</td>
<td>0.70</td>
<td>(5) Na$_2$HPO$_4$·5H$_2$O, Kishida (≥95%)</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>0.30</td>
<td>(6) Lactic acid, Kishida (85–92%)</td>
</tr>
</tbody>
</table>

dilution

### Table 2. Experimental conditions for the EF extraction method for Model Liquids A, B and C.

<table>
<thead>
<tr>
<th></th>
<th>Model Liquid A</th>
<th>Model Liquid B</th>
<th>Model Liquid C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous phase$^a$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feed volume (L)</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Feed rate (L/h)</td>
<td>1.64</td>
<td>1.59</td>
<td>1.56</td>
</tr>
<tr>
<td>Solvent$^{b,c}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volume (L)</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Circulation rate (L/h)</td>
<td>9.6-16.8</td>
<td>12-19.2</td>
<td>12-14.4</td>
</tr>
</tbody>
</table>

$^a$: head of polypropylene tube with 3 holes of 1.0 mm in diameter or with 4 holes of 0.5 mm in diameter.

$^b$: 20 vol% Lix84I and 2 vol% PC88A dissolved in Shelsol D70.

$^c$: head of sintered glass plate with a pore size of 0.04 mm in diameter.
the introduction of the Model Liquids until the emulsion phase reached a steady state. In the present
experiments, feed volumes and rates of the aqueous phase were 5 L and ~1.6 L/h, respectively (Table 2).
Circulation rates of the organic phase were 9.6-19.2 L/h (Table 2). The aqueous raffinate from the apparatus
was sampled every 0.5 L and the Ni concentrations in the raffinate were determined. Batch and EF
experiments were conducted four times and twice, respectively, for each Model Liquid. Concentrations
of Ni were analyzed with an inductively coupled plasma mass spectrometer (ICP-MS; NexION 300X, Perkin
Elmer). The standard solution for Ni was prepared from a multi-elements stock solution (XSTC-13; SPEX
CertiPrep, Inc.). In addition, a scandium solution prepared from scandium nitrate was added to the
analytical samples as an internal standard.

2.4 Observation of emulsion droplet

In-situ observation of the emulsion phases was conducted by using a high-speed microscope
(VW-9000, Keyence) that had a camera unit (VW-600C) and a high-performance zoom lens (VH-Z20W).
A rectangular column was used as the extraction section to facilitate the in-situ observation. When the
solvent reacted with the Ni model liquid, its color soon changed to greenish black, which made it difficult
to observe the steady-state emulsion phase. Therefore, the EF extractor was initially filled with the solvent
and a Ni-free aqueous solution, in which Ni alone was excluded from Model Liquid B, instead of deionized
water. After the emulsion phase reached steady state by circulation of the aqueous and organic phases,
Model Liquid B was introduced into the apparatus. The upper and lower parts of the emulsion phase were
observed with the high-speed microscope for 5-10 seconds before the greenish black coloration of the
solvent hampered the observation. Video images were captured at the following conditions; lens
magnification of 50 or 100, frame rate of 125 fps and resolution of 640×480. Still images were generated
from the videos using a software package (Keyence, Motion Analyzer), and the droplet sizes in the still
images were analyzed with another software package (Keyence, Album).

3. Results and Discussion

3.1 Distribution ratios of Ni

In order to evaluate extraction performance in the batch experiments, the initial Ni concentrations
($C_0$) in the Model Liquids and Ni ($C$) in the aqueous solutions after extraction were analyzed by using
ICP-MS, and the nickel distribution ratio ($D$) and extractability ($E$%) were determined as follows:

$$D = \frac{(C_0 - C)}{C}. \quad (2)$$

$$E = \frac{(C_0 - C)}{C_0} \times 100. \quad (3)$$

The Ni distribution ratios for Model Liquids A, B and C from the batch experiments were determined to be
58 ± 5, 735 ± 60 and 2197 ± 244, respectively, (Table 3), and they clearly increased with increasing dilution

| Table 3. Results of the batch experiments for Model Liquids A, B and C. |
|----------------|----------------|----------------|
|                | Model Liquid A | Model Liquid B | Model Liquid C |
| Initial pH     | 6.5            | 6.6            | 6.7            |
| Equilibrium pH | 6.0            | 6.0            | 6.0            |
| Ni Distribution ratio | 58 ± 5 | 735 ± 60 | 2197 ± 244 |
| Ni extractability (%) | 98.30 ± 0.14 | 99.86 ± 0.01 | 99.95 ± 0.01 |
of the Model Liquids with water. As shown in Table 3, the improvement in the Ni distribution ratios was independent of the equilibrium pH (~6.0). Also, since two LIX84-I molecules are required for the extraction of one Ni$^{2+}$ molecule as represented in equation (1), the present solvent containing 0.65 mol/L LIX84-I can extract up to 0.325 mol/L Ni$^{2+}$. Initial Ni$^{2+}$ concentrations in Model Liquids A, B and C corresponded, respectively, to 25%, 12% and 6% of half the LIX84-I concentration in the present solvent, and therefore it is probable that the reduction of the initial Ni$^{2+}$ concentrations with the increase in the degree of dilution was responsible for the improvement in the Ni$^{2+}$ distribution ratios. In addition, since Ni extraction from EN liquid wastes is considered to be inhibited by the presence of masking agents such as HPO$_3^{2-}$ or lactic acid [9], the decrease in the concentration of the masking agents in the Model Liquids by the dilution with water will reduce the masking effect on the Ni extraction and hence result in an improvement in the Ni distribution ratios.

3.2 Formation of emulsion flow

Both pre-filled deionized water and solvent were circulated in the apparatus prior to introduction of the Model Liquids. At first, the solvent was sprayed upwards into the aqueous phase through the lower spray head, and a dense cloudy emulsion phase with white turbidity formed above the head. On the other hand, each droplet of the aqueous phase sprayed around the upper head was so coarse compared with that of the solvent as to be visible to the naked eye. The emulsion phase formed above the lower spray head gradually moved upwards, as it absorbed falling droplets of the aqueous phase, up to the upper spray head, where the droplets of the solvent in the emulsion phase rapidly expanded, bursting around the top end of the emulsion phase and eventually disappearing. In this way, the formation of the emulsion phase reached a steady state, in which the dense emulsion phase with white turbidity was contained mainly between the two heads. At this stage, the circulation of the pre-filled aqueous phase was terminated and the Model Liquids were introduced into the extractor.

Since the height of the emulsion phase varied slightly after introduction of the Model Liquids, it was adjusted by the circulation rate of the organic phase to be 35-40 cm, which corresponded to a volume of 0.74-0.85 L for the emulsion phase (Table 3). Judging from the fact that the boundary of the pre-filled aqueous and organic solutions was set in the middle between the upper and lower spray heads, and that the emulsion phase was maintained mainly between the two heads, the emulsion phase is considered to be a mixture of the aqueous and organic solutions with a volume ratio of around 1:1. This suggests that the volume occupied by the aqueous phase in the emulsion phase would be roughly half of its total volume although the circulation rates of the two phases were quite different. In an earlier stage of the EF experiments, the lower
phase-separation part was slightly cloudy due to leakage of fine droplets of the organic phase, but it became transparent after ~3 L of feed volume.

Figure 2 shows still images of the emulsion phase, generated from videos by using the high-speed microscope. Both upper and lower parts of the emulsion phase are crammed full of spherical droplets of the solvent. The sizes of the droplets, which clearly exhibited spherical shapes, were analyzed. As a result, the average size of 22 droplets at the upper part of the emulsion phase (Figure 2 (a)) was 415 ± 110 µm, while that of 25 droplets at the lower part (Figure 2 (b)) was 214 ± 36 µm. This demonstrates that solvent droplets generated around the lower spray head were growing as they moved upward.

3.3 Extraction performance of the EF extractor

In order to evaluate the extraction performance of the EF extractor, initial Ni concentrations \(C_0\) in the Model Liquids and the Ni concentration \(C\) in an aliquot of raffinate sampled every 0.5 L were analyzed with ICP-MS, and the extractability \(E\%\) of nickel was determined by equation (3). Figure 3 shows the nickel extractabilities for Model Liquids A, B and C as a function of feed volume. At the initial feeding stage, the extractabilities are ~100% due to the drainage of the pre-filled deionized water, but then they gradually decrease and eventually reach almost constant values after ~4 L of feed volume, which corresponds to 2.5 times the volume of the pre-filled aqueous phase. Average extractabilities for Model Liquids A, B and C from 4 to 5 L of feed volume were 56-62%, 84-89% and 95-96% (Table 4), respectively, and they are quite small compared to those from the batch experiments (Table 3). This suggests that the extraction reaction in the EF experiments did not attain equilibrium because of mild emulsion formation in the apparatus.

Figure 3 also shows that the EF extractor has a higher extraction performance as the dilution of the Model Liquids with water was increased. As shown in Table 4, the higher extraction performance associated with the dilution did not depend on the pH of the aqueous phases after extraction. The extraction efficiency of the EF method is considered to be influenced by the quality and quantity of the emulsion phase, which are linked to the operation condition of the EF extractor, and also by the extraction reactivity.

### Table 4. Results of the EF experiments for Model Liquids A, B and C.

<table>
<thead>
<tr>
<th>Item</th>
<th>Model Liquid A</th>
<th>Model Liquid B</th>
<th>Model Liquid C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pH</td>
<td>6.5</td>
<td>6.6</td>
<td>6.7</td>
</tr>
<tr>
<td>Drainage pH at 5 L</td>
<td>6.2</td>
<td>6.2</td>
<td>6.3</td>
</tr>
<tr>
<td>Emulsion quantity (L)</td>
<td>0.80</td>
<td>0.73</td>
<td>0.73</td>
</tr>
<tr>
<td>Residence time (min)</td>
<td>14.6</td>
<td>13.8</td>
<td>14.0</td>
</tr>
<tr>
<td>Ni extractability (%) at 4-5 L</td>
<td>56-62</td>
<td>84-89</td>
<td>95-96</td>
</tr>
<tr>
<td>Free LIX84-I (mol/L) at 5 L</td>
<td>0.40-0.43</td>
<td>0.47-0.48</td>
<td>0.55</td>
</tr>
</tbody>
</table>
such as the distribution ratio and reaction rate. However, differences in the degree of packing or sizes of the droplets in the emulsion phases among the three Model Liquids could not be seen by the naked eye. Moreover, all Model Liquids had similar residence times (~14 minutes), which were estimated from the half volumes of the emulsion phases divided by the feed rates (Table 3). These results suggest that contact areas and times of the aqueous and organic phases in the emulsion phases were equivalent regardless of the dilution ratios of the Model Liquids.

Based on the assumption that Ni$^{2+}$ was extracted during the EF experiments at almost constant extractabilities in Table 4, we can estimate the concentrations of free LIX85-I remaining in the solvents. Judging from the results at 5 L of feed volume in Table 4, the increasing dilution degree of the Model Liquids tends to increase the amount of free LIX84-I in the solvents, as well decreasing the Ni$^{2+}$ and masking agent concentrations in the Model Liquids. All these conditions of aqueous and organic solutions are favorable for improving the Ni$^{2+}$ extractabilities obtained in the EF experiments. Therefore, the dilution of EN liquid wastes with water directly influences Ni extractabilities in the continuous liquid-liquid extraction by using the EF apparatus.

4. Conclusion

In the present study, we examined the applicability of a counter current EF extractor for the extraction of nickel from simulated EN liquid wastes, and demonstrated that dilution of the EN liquid wastes with water was a promising method for practical use of the EF extractor. To enhance reliability of this method for EN liquid wastes, further investigation is required with respect to the influence of the dilution on the mechanisms or kinetics of the present extraction reaction.

References