1. Introduction

Electroless nickel plating is one of the most popular plating techniques. This process, however, generates a large amount of spent bath. Although this spent bath is treated mainly by alkaline precipitation, the stringency of the landfill space and recent high nickel price motivate us to develop a less sludge generation and effective nickel recycling technique. We previously reported high recovery efficiencies of nickel (99.9%) from the model spent baths by a new recovery process with solvent extraction using a mixer-settler extractor \(^1\). It was observed that the extraction efficiency was affected by the operation parameters such as the flow rates of the aqueous and organic phases and the number of extraction stages. In this study, these effects were quantitatively studied on the basis of the extraction rate equation together with the hydrodynamics in the mixer. Then an engineering model was established for simulating the extraction efficiency of nickel during a multistage countercurrent extraction.

2. Experimental methods

Holdup of the dispersed phase (organic phase) was measured using the same mixer-settler as described in our previous paper \(^1\) (MX-4G, Tokyo Rikakikai Co.). The size of the mixer part was 7.0×7.0×7.0 cm\(^3\). A disk turbine-type impeller with a 2.8 cm diameter was situated 1 mm from the mixer bottom. The aqueous phase used in the present experiment was a 0.1 kmol m\(^{-3}\) \(\text{H}_2\text{SO}_4\) solution, while the organic phase was the same as that in the previous nickel extraction experiments \(^1\) which contained 20 vol% LIX84I and 2 vol% PC88A. Each of the aqueous and organic phases was pumped to the mixer bottom by a diaphragm pump, mixed at 1300 rpm and discharged from the settler. The holdups were measured at ambient temperature \((T=296-300\text{K})\) under the two series of conditions \((Q_w=2\times10^{-7}\text{ m}^3\text{ s}^{-1} \text{ and } Q_o=Q_w)\), which were the same as those in our previous continuous extraction experiments \(^1\). Here \(Q_w\) and \(Q_o\) are the flow rates of the aqueous and organic phases, respectively. After the system reached a steady state, a small portion of the liquid mixture in the mixer was drawn out by a 2.5-cm\(^3\) syringe at a specified distance from the mixer bottom, \(H\), in order to measure the weight of each phase in the portion. This sampling was done at least three times during each run. The holdups were calculated from the measured weights and the densities of both phases.

3. Results and discussion

3.1 Holdup and specific interfacial area in the mixer

The dispersed phase holdups below the impeller, \(\phi^d\), were higher than those above the impeller, \(\phi^u\). For the part below the impeller, the discharge rate of the dispersed phase can be expressed by Eq. (1)\(^2\),

\[
Q_o = (Q_o + Q_w) \phi^u + K_A (\phi^c - \phi^u)
\]
where $K$ is the transfer coefficient and $A$ is the cross-sectional area of the flow path around the impeller.

In the upper part of the mixer, the velocity of the dispersed phase relative to the continuous phase, $v_r$, can be expressed as

$$v_r = \frac{Q_o}{(\phi^U A)} - \frac{Q_w}{[(1 - \phi) A]}$$  \hspace{1cm} (2)

The average values of $K$ and $v_r$ were determined to be $1.5 \times 10^{-3}$ m s$^{-1}$ and $2.2 \times 10^{-4}$ m s$^{-1}$, respectively.

The values of $\phi^U$ and $\phi^L$ can be calculated from Eqs. (1) and (2) using the obtained $K$ and $v_r$ values, and thus the overall holdup, $\phi$, can be obtained from

$$\phi = \frac{d_{32}}{D} \cdot e^{-0.72\left(V^L \phi^L / Q_o\right)}$$  \hspace{1cm} (3)

Here, $D$ is the impeller diameter, and $We$ is the Weber number ($We = n^2 D^3 \rho_c / \gamma$), where $n$, $\rho_c$ and $\gamma$ are the rotation speed of the impeller, density of the continuous phase and interfacial tension, respectively.

The specific interfacial area between the aqueous and organic phases in the mixer, $a$, is given by Eq.(4):

$$a = 6\phi / d_{32}$$  \hspace{1cm} (4)

where $d_{32}$ is the Sauter mean diameter of the dispersed phase droplet. Eq. (5)$^2$ was employed in the present calculation.

$$d_{32} / D = 0.86We^{-0.72}\left(V^L \phi^L / Q_o\right)^{-0.36}$$  \hspace{1cm} (5)

The final calculated results indicates that the specific interfacial area increases with the organic phase flow rate (Figs. 1 and 2).

### 3.2 Interfacial extraction rate constant of nickel

The mass balance for the organic phase in one mixer-settler in the steady state is given as:

$$Q_o C_{in} + R = Q_o C_{out}$$  \hspace{1cm} (6)

where $C$ is the molar concentration of nickel, $R$ is the amount of nickel transferred from the aqueous phase to the organic phase in unit time, and $V$ is the total volume.

Based on the assumption of complete mixing and interfacial reaction control, $R$ is given by Eq. (7) according to the pseudo-first-order reaction model$^3$:

$$R = k_f^0 a V C_{out} - k_b^0 a V C_{eq}$$  \hspace{1cm} (7)

where $k_f^0$ and $k_b^0$ are the interfacial reaction rate constants of the forward and backward extractions, respectively. Under equilibrium conditions, $R = 0$; thus,

$$k_b^0 = k_f^0 C_{eq} / C_{eq}$$  \hspace{1cm} (8)

where the subscript eq denotes equilibrium. By considering the total mass balance for the mixer-settler in the steady state as

$$Q_w C_{in} + Q_o C_{in} = Q_w C_{out} + Q_o C_{out}$$  \hspace{1cm} (9)

the following equation is derived:

$$a V \left(\frac{C_{in} - Q_o C_{out}}{C_{in} - C_{eq}}\right) = \frac{1}{k_f^0} Q_o$$  \hspace{1cm} (10)

where $Y$ is defined as the left side of Eq. (10). The
Y values for different temperatures and flow rates, obtained from the experimental data in our previous study (Figs. 2 and 3 in Ref. (1)) and the equilibrium concentrations calculated using our extraction equilibrium model⁴, were plotted versus Q₀ as shown in Fig. 3, and the straight lines were fitted by the least squares method. The k₀ value of (3.3±0.6)x10⁻⁷ m s⁻¹ was obtained as the inverse of the slope of the line when T=299-303K and Qₓ=2x10⁻⁷ m³ s⁻¹. Likewise, the k₀ value of (2.5±0.3)x10⁻⁷ m s⁻¹ was obtained when T=295-299K and Q₀=Qₓ.

The calculated values of the overall extraction rate coefficient, k₀a, are in the range of 2.6x10⁻³-7.3x10⁻⁷ s⁻¹ and 3.2x10⁻³-1.0x10⁻² s⁻¹ when Qₓ=2x10⁻⁷ m³ s⁻¹ and Q₀=Qₓ, respectively, which are close to the value obtained in our previous batch shaking-out study³ (3.4x10⁻³ s⁻¹).

3.3 Calculation of the extraction efficiency of nickel

The total extraction efficiency of the countercurrent multistage operation, E, was calculated by combining the model in 3.2 with the material balance in each stage. The calculated results under the condition of Qₓ=2x10⁻⁷ m³ s⁻¹ show that the calculated E value increases with Q₀ (Fig. 4). Although the calculated E values cannot completely reproduce the experimental E values, the agreement is generally good. One possible reason for the small discrepancy between these two values is that we used a constant value for the interfacial tension (γ= 19.0 mN m⁻¹) of the 0.1M H₂SO₄-organic phase system employed in the holdup investigation, which would be different from the γ values of the real extraction experiments using the model spent bath-organic phase system. By considering the variation of γ in the model, the agreement between the calculations and the experimental results would be improved.

4. Conclusions

Our previous experimental results for the solvent extraction of nickel from the model spent electroless nickel plating bath using the mixer-settler have been analyzed by considering the hydrodynamic variation and pseudo-first-order reaction rate. The calculated extraction efficiencies of multistage processes are in good agreement with the experimental results, which indicates that the present model can be utilized for the engineering prediction of the nickel extraction behavior during a multistage recovery operation.

References