Reaction Kinetics of Sulfidation of Heavy Metals with H₂S Introduced into Plating Wastewater

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Abstract: Sulfidation treatment of heavy metals with hydrogen sulfide (H₂S) was proposed to recover heavy metals from plating wastewater. In sulfidation treatment, heavy metals can be selectively separated and thus recovered by precise control of pH value. As samples, model wastewaters containing either single metal (single-metal system) or three metals (multi-metal system) were used, and the pH value was controlled at pH=1.5 for Cu, pH=4.5 for Zn or pH=(6.5-7.0) for Ni. Moreover, selectivity of metal precipitation and reaction kinetics of Cu, Zn and Ni sulfidation were investigated.

As a result, it was found that an amount of H₂S equimolar to a given metal was sufficient to achieve almost complete precipitation of the metal. Further, the selectivity of the precipitation was found to be higher than 95% for all three metals used in this study. It was also found that the sulfidation reaction proceeded in accordance with Higbie’s penetration theory and reaction rate constants and mass-transfer coefficients were determined for various experimental conditions.

Keywords: Sulfidation, Hydrogen sulfide, Reaction kinetics, Plating wastewater, Metal sulfide

1. INTRODUCTION

In the electroplating industry, wastewater containing valuable metals such as copper, zinc and nickel is discharged when an extra plating solution is rinsed out of the surface of electroplated products. Currently, metal-containing wastewater is treated with alkaline hydroxide such as sodium hydroxide (NaOH) and calcium hydroxide (Ca(OH)₂). Consequently, metals dissolved in the plating wastewater are precipitated as metal hydroxides and discharged as metal containing sludge. The metal hydroxide sludge is characterized by low filterability and is usually disposed of to a landfill without any attempt to achieve metal recovery. However, the metal consumption is still growing, which leads to a decrease in reserve-production ratio and ultimately to an increase in the cost of these metals. Therefore, an investigation towards heavy metals recovery is essential.

In this study, a sulfidation treatment of heavy metals using hydrogen sulfide (H₂S) was proposed to replace the presently used hydroxide treatment. The advantage of sulfidation treatment inheres in the possibility to selectively precipitate/recover heavy metals by precise control of the pH during sulfidation treatment. To further develop this method, an attempt was made to determine sulfidation rates of heavy metals with H₂S. In the experiments, the parameters such as H₂S flow rate, H₂S concentration and bubble diameter were changed. Then, sulfidation rates of heavy metals as well as corresponding mass-transfer coefficients were determined.

2. EXPERIMENTAL

2.1 Sulfidation treatment with H₂S

The experimental apparatus is schematically shown in Fig. 1. The model wastewater was prepared by dissolving metal sulfates of CuSO₄·5H₂O, ZnSO₄·7H₂O, and NiSO₄·6H₂O in distilled water. The metal concentration in model wastewater was set at 100 mg/dm³. In the experiment, the pH of solution was maintained at predetermined value (Cu: pH=1.5, Zn: pH=4.5, Ni: pH=6.5-7.0) using NaOH aqueous solution[1, 2]. H₂S gas concentration was varied in the range of 2500-5000 ppm (N₂ was used as a carrier gas) and N₂/H₂S flow rate was changed from 150 to 350 ml/min. Bubble diameter of N₂/H₂S mixed gas was also varied using bubble generators with different mesh size and the bubble size was determined using a video camera. In the experiments, the samples were withdrawn at the bottom of reactor using sampling tap and then analyzed by means of inductively coupled plasma (ICP-OES, VISTA-MPX, Varian). Moreover, chemical composition of the precipitated metal compounds was analyzed by using X-ray diffractometer (XRD, Rint-2500, Rigaku).

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first, in accordance with Higbie’s penetration theory, sulfidation rate equation was written in its differential form (Eq. (1)) and the solution is given in Eq. (2). In these equations, $C_{H,2S}$ is the interfacial concentration of hydrogen sulfide in aqueous phase, $C_{Me^{2+}}$ is the initial concentration of Me $^{2+}$ in the bulk aqueous phase, $C_{Me^{2+}}$ is the concentration at time $t$ of Me $^{2+}$ in the bulk aqueous phase, $A_b$ is the gas-liquid interfacial area, $k_b$ is the mass-transfer coefficient and $V$ is the volume of aqueous phase. The gas-liquid interfacial area was determined using Eq. (3), where $n$ is the number of bubbles per second, $h$ is the height of aqueous phase, $U$ is the rising velocity of bubbles, and $d^*$ is the equivalent bubble diameter. Then, the mass-transfer coefficient was calculated using Eq. (4), where $K$ is reaction rate constant.

$$\frac{dC_{Me^{2+}}}{dt} = -\frac{A_b}{V}k_b\left(C_{Me^{2+}} - C_{H,2S}\right) \tag{1}$$

$$\ln\left(\frac{C_{H,2S} + C_{Me^{2+}}}{C_{H,2S} + C_{Me^{2+}}^{0}}\right) = -\frac{A_b}{V}k_b t \tag{2}$$

$$A_b = n\left(\frac{d}{2}\right)^2 h/U \tag{3}$$

$$K = \frac{A_b}{V}k_b \tag{4}$$

Fig. 2 Determination of mass-transfer coefficient

3. RESULTS AND DISCUSSION

3.1 Sulfidation of single metal model wastewater

The sulfidation experiments were conducted by introducing H$_2$S to Cu-containing model wastewater. In the experiment, Cu initial concentration in filtrate was set at 100 mg/dm$^3$, value of the sample solution pH was 1.5, H$_2$S concentration was 5000 ppm. The flow rate of H$_2$S gas was changed in the range of 150-350 ml/min.

Fig. 3 Relation between time and C/C$_0$ for different H$_2$S flow rates

Fig. 4 ln[(7.6 × 10$^{-3}$+C$_{Cu^{2+}}$)/(7.6 × 10$^{-3}$+C$_{H,2S}^{0}$)] vs. time plots for different gas flow rate

3.2 Kinetic study of sulfidation of heavy metals with H$_2$S

In this experimental condition, it is reported that the reaction of metal sulfidation with H$_2$S will progress through the following several steps. The first step is the absorption of hydrogen sulfide at the gas-solution interface, the second step is diffusion of hydrogen sulfide to the reaction zone, the third step is chemical reaction at the reaction zone, and the last step is diffusion and precipitation of reaction products away from the reaction zone [3, 4]. In addition, it is generally reported that chemical reaction and adsorption steps were much faster than diffusion steps.

Then in this section, reaction kinetics of sulfidation of heavy metals with H$_2$S was studied in accordance with Higbie’s penetration theory to determine reaction rates and mass-transfer coefficients. As a sample, CuSO$_4$ aqueous solution (Cu initial concentration of 100 mg/dm$^3$) was used. Then, the effects of experimental parameters of N$_2$/H$_2$S gas flow rate, H$_2$S concentration and bubble diameter on the sulfidation treatment were investigated at a pH value of 1.5. After the experiments, the left side of Eq. (2) was plotted against time for each experimental parameter as shown in Figs. 4-6. Subsequently, corresponding reaction rate constants and mass-transfer coefficients were determined and the results are indicated in Tables 1-3.

From the results, precipitation occurred by sulfidation treatment with H$_2$S, and Cu$^{2+}$ in the sample solution was removed to 1 mg/dm$^3$ or less by supplying H$_2$S at an amount equimolar to Cu$^{2+}$, in all H$_2$S gas flow rate. Moreover, unreacted H$_2$S gas was not detected at the outlet of the reactor, and hence it was considered that all H$_2$S was consumed to react with Cu$^{2+}$. Further, based on the XRD analysis of reaction precipitates, it was confirmed that Cu$^{2+}$ ions were precipitated as CuS. The results similar to Cu sample solution were also obtained with Zn and Ni sample solutions. Consequently, in this experimental conditions, it is concluded that H$_2$S gas reacts with dissolved metal ions according to Eq. (5), resulting in the formation of insoluble metal sulfides.

$$Me^{2+} + H_2S \rightarrow MeS + 2H^+ \tag{5}$$
found to be virtually constant. While, in the case of bubble diameter reaction rate was increased. Mean-
4. CONCLUSIONS

An attempt was made to selectively recover copper, zinc and nickel from simulated plating wastewater with \( \text{H}_2\text{S} \) gas, in single-metal and multi-metal systems. As a result, it was found that an amount of \( \text{H}_2\text{S} \) equimolar to a given metal was sufficient to achieve almost complete precipitation of this metal. Further, the selectivity of the precipitation was determined to be higher than 95 % for all three metals used in this study.

In addition, it was confirmed that the sulfidation reaction proceeded in accordance with Higbie’s penetration theory. Finally, reaction rate constants and mass-transfer coefficients were determined for various experimental conditions.

**Table 4** Comparison between reaction rate constant of single component and multi component

<table>
<thead>
<tr>
<th></th>
<th>( k \times 10^4 ) [s(^{-1})]</th>
<th>Cu</th>
<th>Zn</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single-metal system</td>
<td>7.43</td>
<td>8.52</td>
<td>6.71</td>
<td></td>
</tr>
<tr>
<td>Multi-metal system</td>
<td>7.77</td>
<td>9.00</td>
<td>6.10</td>
<td></td>
</tr>
</tbody>
</table>

As seen in Table 4, almost the same reaction rate constants were obtained for single-metal and multi-metal system. Given this, it was concluded that the precipitation of a particular metal was not significantly affected by the presence of other components.

Finally, the selectivity of the precipitation of each metal was determined by an analysis of filter cakes after the precipitation and the results are shown in Table 5. It can be seen that, by controlling precisely the pH value, the selectivities higher than 95 % can be obtained for metals used in this study.

**Table 5** Selectivity of each metal by filtrate separation

<table>
<thead>
<tr>
<th>Selectivity [%]</th>
<th>pH 1.5</th>
<th>pH 4.5</th>
<th>pH 6.5-7.0</th>
</tr>
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<tbody>
<tr>
<td>Cu</td>
<td>96.6</td>
<td>2.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Zn</td>
<td>2.5</td>
<td>96.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Ni</td>
<td>0.9</td>
<td>1.4</td>
<td>99.4</td>
</tr>
</tbody>
</table>

REFERENCES