Influences of a Wetter and Other Plating Metals On Removal of Dissolved Nickel Metal

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The effect of a wetting agent, plus other plating metals, on nickel metal treatment in wastewater was studied. The nickel removal efficiency was decreased by the wetter in all cases. Zeta potential, ionic strength, and coprecipitation were studied to correlate the results of nickel hydroxide precipitation.

recipitation with sodium hydroxide is the conventional method of removing heavy metals from wastewater of plating shops. The discharge standard for nickel metal in Taiwan is 1.0 mg/L, and this stringent regulation cannot always be met with hydroxide precipitation method because of the ineffectiveness of some organic additives present in the wastewater streams.'It is necessary, therefore, to investigate the influence of organic impurities on the efficiency of removal of dissolved nickel metal.

Besides organic impurities, copper and zinc metals are always present in wastewater from plating shops and were also treated by sodium hydroxide. Therefore, the effect of these major plating metals on the removal of dissolved nickel metal must be simultaneously considered. As a result, the influences of a wetting agent and these two metals were studied individually and in various combinations.

Although considerable research is being devoted to treatment processes for removal of heavy metals from wastewater, the mechanisms that limit removal efficiencies in metal hydroxide precipitation have not been fully studied. Besides the soluble metal ions, the clear layer of the settling solution also contains very finely divided metal hydroxide particles. To induce these ions and fine particles to aggregate for settlement, at least five factors must be considered: (1) incomplete reaction, (2) soluble metal complex formation, (3) poor separation of colloidal particles, (4) ionic strength of solution, and (5) coprecipitation of hydroxides. The latter three of these factors were studied in this work. Results indicated that for removal efficiency of dissolved nickel metal, coprecipitation could most easily explain the influence of the other two plating metals. The zeta potential (Zp) was the basis for explanation of the influence of the wetting agent.²Further study is desirable for the case when a coagulant or flocculent is added to the treated system.

Experimental Procedure

Nickel, copper and zinc sulfates were used to prepare synthetic wastewater. Sodium lauryl sulfate (SLS) was selected as a wetting agent. Precipitation of hydroxides of heavy metals was carried out with 1.0 N sodium hydroxide solution to increase the pH of the wastewater to about 11 or 12, higher than the ordinary pH setpoint of plating shop wastewater. After five min agitation, these neutralized solutions were transferred into Nessler tubes for settling. After two hr, the level of residual metals in the clear layer of the settling tubes was tested by atomic absorption spectroscopy. The optimum pH range of treatment was defined when the test showed residual metal in the clear layer was less than 1.0 mg/L. In actuality, the optimum pH range appeared as wavy lines.

In the optimum pH range, zeta potential (Zp) values and size of colloidal hydroxide particles in solution were measured by an electrophoretic light scattering spectrophotometer (ELS),³ in which zeta potential values were calculated from mobility values, using the Smoluchowski equation.³ The size of precipitated hydroxide particles was examined by a scanning electron microscope (SEM).³

Results and Discussion

Titration Curves for Wastewater

Hydroxide precipitation is a typical neutralization process; at fixed titration rate and agitation speed, various compositions of wastewater result in various titration curves. For example, as shown in Fig. 1, the titration curves for 1000 mg/L nickel wastewater were changed, even though only the concentrations of SLS were changed. As indicated by these curves, precipitation of dissolved nickel metal in wastewater should be affected by a wetter or other components. Later results indicated that when the titration curve of wastewater in Fig. 1 was shifted to a higher pH, then its corresponding precipitation edge also shifted to a higher PH.

Metal Hydroxide Precipitation

The optimum pH value and the associated minimum volubility of hydroxide precipitation can be determined from volubility calculations. Unfortunately, because of the factors of incomplete reaction, soluble metal complex formation, poor separation of colloidal particles, ionic strength of solution, and coprecipitation of hydroxides, the optimum pH value and actual volubility for hydroxide precipitation are seldom the same as indicated by their respective volubility curves. In this study, reaction time of precipitation was fixed at five min agitation and two hr settling. Also, no other important ligand except hydroxide ion exists to form soluble metal complexes. During precipitation, therefore, the most important considerations of nickel volubility were stabilization of colloidal particles, ionic strength of treated solution, and coprecipitation of hydroxides.

[°]Topcon ABT-32, Akashi Beam Technology Corp., Tokyo, Japan.

Table 1Zeta Potential Values of Colloidal NickelHydroxide Particles as a Function of pH*

SLS concentration	Zp values, mV			
none 10 mg/L 250 mg/L	-5.50 (9.42)** -7.49 (9.50) 	-6.35 (1 -8.30 -17.61	0.50) -6.7 (10.52) (10.67)	3(1 1.42)

*Initial concentration of nickel metal is 1000 mg/L.

**Numbers in parentheses are pH values of treated wastewater.

^aELS-800, Otsuka Electronics Co., Ltd., Osaka, Japan.



Fig. 1—Titration curves of 50 mL of 1000 mg/L nickel wastewater with 1 N NaOH for two hr. SLS concentrations: (1) 100 mg/L; (2) 150 mg/L; (3) 250 mg/L.



Fig. 3-Observed solubilities of copper hydroxides as a function of pH. Metal concentrations: (1) 1000 mg/L Cu; (2)2000 mg/L Cu; (3) 1000 mg/L each of Ni and Cu; (4) 1000 mg/L each of Cu and Zn; (5) 1000 mg/L each of Ni, Cu and Zn.



Fig. 4-Observed solubilities of zinc hydroxides as a function of pH. Metal concentrations: (1) 1000 mg/L Zn; (2) 2000 mg/L Zn; (3) 1000 mg/L each of Ni and Zn; (4) 1000 mg/L each of Cu and Zn; (5) 1000 mg/L each of Ni, Cu and Zn.



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Fig. 2-Observed solubilities of nickel hydroxides as a function of PH. Metal concentrations: (1) 1000 mg/L Ni; (2) 2000 mg/L Ni; (3) 1000 mg/L each of Ni and Cu; (4) 1000 mg/L each of Ni and Zn; (5) 1000 mg/L each of Ni, Cu and Zn.

The overall stability of a colloidal particle in solution is controlled by van der Waals force of attraction and Nernst potential of repulsion. Nernst potential is the electrical potential at the surface of the particle. Both van der Waals force and Nernst potential are difficult to measure, whereas Zp value is relative to Nernst potential and can be determined experimentally. For simplification, Zp values of double metal hydroxide layers were considered,' with higher absolute values of Zp resulting in greater stability and volubility of colloidal particles in solution. The Zp values, as shown in Table 1, indicated that the nickel hydroxide particles have small absolute Zp values in wetter-free solution and that coagulation occurred easily in the optimum pH range.⁵Also, the Zp values of colloidal particles were affected to some extent by the pH of the solution. For the



Fig. 5-SEM photograph of precipitated particles from 1000 mg/L metal wastewater: (a) $Cu(OH)_2at pH 9.90$; (b) $Zn(OH)_2at pH 9.92$; (c) $Ni(OH)_2at pH 9.42$; (d) $Ni(OH)_2at pH 10.42$, SLS 10 mg/L added; (e) $Ni(OH)_2at pH 10.47$, SLS 100 mg/L added.

wetter-free solution, the particles formed in the presence of an excess of hydroxide ions. With greater affinity for the colloidal particle surface, the hydroxide ions are potentential-determining ions, with higher concentrations resulting in more negative Zp values.

Higher concentration of electrolyte will increase the ionic strength 'of the nickel wastewater, decreasing the value of the activity coefficient and increasing the volubility of nickel metal. Consequently, residual nickel volubility in the treated wastewater was found to depend on the initial nickel concentration. As shown in Fig. 2, when the initial concentration of nickel was increased from 1000 to 2000 mg/L, the minimum volubility of nickel increased. In addition, when the metal content of the 1000 mg/L nickel solution was increased to 2000 mg/L by addition of 1000 mg/L of copper or zinc individually, the volubility minimum of nickel was decreased significantly more than that of 2000 mg/L nickel wastewater, though these three solutions had the same ionic strength. This result suggested the strong possibility of coprecipitation of nickel hydroxide by copper or zinc hydroxide. In addition, when 1000 mg/L copper, along with 1000 mg/L zinc, were added to the 1000 mg/L nickel wastewater, though the ionic strength was higher than that of 2000 mg/L nickel solution, and which may be because of the coprecipitation effect, the minimum volubility of nickel was also lower than that of the 2000 mg/L nickel solution. As a result, the effect of ionic strength was overcome by the coprecipitation of the other two metal hydroxides. Greater removal efficiency of nickel metal from wastewater was found when copper metal, zinc metal, or both, were added to the nickel wastewater.

Similarly, as shown in Figs. 3 and 4, during the treatment of copper or zinc wastewater, the effect of ionic strength was also overcome by coprecipitation of the other two metal hydroxides. Consequently, the removal efficiency of metal in wastewater may be improved by the presence of other metals.

It should be kept in mind that no two wastewaters have identical titration curves and that pH change is required for different compositions of nickel wastewater. Therefore, as shown in Figs. 2, 3, and 4, the optimum pH value of metal hydroxide precipitation varied with the composition of the wastewater. For example, the volubility minimum of nickel metal was shifted to a lower pH value when copper was present.

Wetting Agent

Besides the effect of other plating metals, as predicted by the results shown in Fig. 1, SLS should affect the volubility of nickel hydroxide. In general, a wetting agent is always present in the plating process and in the wastewater of plating shops. SLS is a typical anionic soluble wetter. Its critical micelle concentration was about 10 mg/L in the solutions studied. Therefore, concentrations of 5, 10, and 20 mg/L of SLS were added to the untreated nickel wastewater to study its influence on the volubility of nickel hydroxide.

Although the ratio of increased ionic strength by 5 to 20 mg/ L of SLS in 1000 mg/L nickel wastewater was small, comparison of Figs. 2 and 5 show clearly that SLS decreased the removal efficiency of dissolved nickel metal. This effect maybe the result of a more stable colloidal nickel hydroxide particle system established by the presence of SLS. The data of Table 1 show the same prediction. Nernst potential was determined by both double layer length and Zp value. Higher absolute Zp values of the wetted colloidal nickel hydroxide particles in Table 1 indicated that SLS provided greater stability than for wetterfree particles. This result may be explained by the mutual attraction between the finely divided colloidal nickel hydroxide particles and adsorbed dipole wetter molecules.[®] leading to more soluble colloidal particles in solution. Therefore, SLS prevents the fine colloidal particles from forming a large particle having a more significant mass that will settle more efficiently. The effectiveness of SLS was more obvious when its concentration was increased. At pH values below 11, as shown in Fig. 5, the removal efficiency for dissolved nickel metal was very low



Fig. 6-Observed solubilities of nickel hydroxides as a function of pH. SLS concentrations in 1000 mg/L nickel wastewater: (1) 5 mg/L; (2) 10 mg/L; (3) 20 mg/L; (4) 100 mg/L.

when the SLS concentration increased to 100 mg/L. Further, when the SLS concentration was increased to 250 mg/L, the precipitation edge of nickel hydroxide was more than pH 12 and could not be precipitated at the ordinary pH setpoint of wastewater. Consequently, the removal efficiency of nickel metal was decreased in direct proportion to the concentration of SLS.

Particle size of the colloidal nickel hydroxide was also studied and correlated with Zp to investigate the effect of SLS on nickel removal efficiency. By spectrophotometer measurement, the Stokes diameter (d) of the colloidal particle was determined as

$$d = kT/3\pi vD$$

where v is the viscosity, T is the absolute temperature, k is Boltzmann's constant, and D is the diffusion coefficient. Higher absolute Zp values means greater repulsion between colloidal particles, resulting in small colloidal particles in solution. Therefore, with higher absolute Zp values, SLS should decrease the d values of colloidal nickel hydroxide particles. This prediction is supported by the d values shown in Table 2. Greater concentration of SLS results in small d value. Although these d values for colloidal nickel hydroxide particles were very large, the dispersed particles did not impart turbidity to the solution.

During precipitation, numbers of fine particles were merged to forma large particle having a more significant mass, which then settled to form a precipitated particle. The SEM photographs of Fig. 6 show the aggregates. Figures 6a, b and c show the three hydroxides as precipitated separately, without addition of the wetter.

The precipitated particle contracts on drying, resulting in a smaller diameter. In the optimum range, the size of precipitated nickel hydroxide particles in the SLS-added systems was always less than that of SLS-free systems. The diameter of a precipitated particle is less than 0.2 µm in the SLS-added nickel wastewater, except at the pH of volubility minimum. For example, curve 2 of Fig. 6 shows a solubility minimum at pH 10.42,



wastewater	additive	d valu	ues, µm
1000 mg/L Ni metal	none	19.5 (9.42)*	19.2 (10.50)
	10 mg/L SLS	15.2 (9.50)	15.0 (10.52)
	250 mg/L SI	LS —	3.5 (10.67)

*Numbers in parentheses are the pH values of treated wastewater.

therefore the diameter of precipitated nickel hydroxide particles was increased to more than 0.2 μ m at that pH when 10 mg/L SLS was added (Fig. 5d). But pH 10.47 is not the volubility minimum of 100 mg/L SLS-added nickel wastewater, so the diameter of precipitated particles was only 0.1 μ m or less at that pH (Fig. 5e). As a result, most of the diameters of precipitated nickel hydroxide particles were also decreased by the presence of SLS in nickel wastewater.

Compare Figs. 2 and 7. The influence of divalent metal in the SLS-added nickel wastewater is similar to that of a SLS-free system. As shown in Fig. 7, although solutions 2 to 4 did not have lower ionic strength than that of solution 1, the removal efficiency of nickel metal was higher in the bi- or tri-metal systems. Consequently, the effect of ionic strength was overcome by coprecipitation in the SLS-added solution. On the other hand, compare Figs. 2 and 8, where nickel wastewater contained two other divalent metals. The influence on the volubility of nickel hydroxide was also dependent on the concentration of added SLS. As shown in Fig. 8, both the volubility minimum and precipitation increased to 100 ma/L in the treated system.



Fig. 7-Observed solubilities of nickel hydroxides as a function of pH, Metal concentrations with 10 mg/L SLS: (1) 2000 mg/L Ni; (2) 1000 mg/L each of Ni and Cu; (3) 1000 mg/L each of Ni and Zn; (4) 1000 mg/L each of Ni, Cu and Zn.



Fig. 8—Observed solubilities of nickel hydroxides as a function of pH. SLt concentrations in 1000 mg/L each of Ni, Cu and Zn: (1) 5 mg/L; (2) 10 mg/L; (3) 15 mg/L; (4) 100 mg/L.

Conclusions

When nickel wastewater has the same ionic strength, then because of the effect of coprecipitation, the removal efficiency for dissolved nickel by hydroxide precipitation will be better than for nickel alone when copper, zinc, or both are present. On the other hand, because SLS decreases the diameter and increases both the double layer length and the absolute value of zeta potential of colloidal nickel hydroxide particles, the removal efficiency for nickel metal in the systems studied was decreased by the presence of SLS. The higher the concentration of SLS, the lower the removal efficiency for dissolved nickel in hydroxide precipitation.

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