

A Study on Nickel Hydroxide Crystallization Characteristics

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Abstract—The precipitation characteristics of nickel hydroxide as well as carbonate and sulfide were studied to determine the proper treatment condition of the wastewater induced from nickel-plating industry. When the pH value was maintained higher than 10, the nickel concentrations in the effluent could be kept lower than 5 mg/l. The precipitation of nickel salts in the model wastewater was conducted by alkaline addition, such as the uses of sodium hydroxide, sodium carbonate, sodium bicarbonate and sodium sulfide. In case of sulfide treatment, the nickel concentration of treated wastewater showed the lowest value after the removal of precipitates. The change of particle size of the crystal precipitates by the precipitation conditions and precipitants was also investigated. In spite of the various precipitation conditions that were adopted, the change of particle size of the crystal precipitates showed no great differences. The settling rates of the precipitated particles were observed and the free settling period was terminated within 20 minutes. Although the hindered settling as well as bed compaction progressed subsequently, the bed heights were maintained almost the same level after few hours later.

Key words: Nickel, Electroplating, Wastewater, Treatment, Precipitation

INTRODUCTION

The clean water act stipulates that industry must apply the “Best Available Technology” for toxic pollutant removal. The effluent guidelines for the metal finishing category were developed from previous EPA studies, plant surveys and evaluations. These guidelines apply to plating processes that include copper, nickel, chromium, brass, bronze, zinc, tin, lead, cadmium, iron and aluminum.

Some of the techniques include chemical precipitation, complexation, cementation, electrolysis, reverse osmosis, carbon adsorption, ion exchange, evaporation or some combination of these processes. The most common and successful method of reducing heavy metal concentration in solution is chemical precipitation [Stephen et al., 1984; Daniels, 1975]. And the conventional method for heavy metal removal from industrial wastewater generally involves a chemical precipitation process [Kim, 1981].

Although the regulation about the nickel discharge from rinse water of the nickel plating processes is rather mild compared to other substances such as chromium, lead, copper and so on, the increasing interest in the water pollutants induced from the electroplating industry will come to nickel.

The conventional treatment method of electroplating wastewater, chemical precipitation method, required longer than 23 hours prior to treating effluent discharge and more than half of this time is used on the precipitation and settling even though some sort of artificial coagulating agents are applied.

Environmental crystallization has been for wastewater treatment. There is a need for treating contaminations in wastewater efficiently and economically, and for designing a new environmental restoration process. One of the valuable processes is to remove and recover ions from plating wastewater as a form of stable solids, such

as crystal [Horikawa et al., 2000].

The optimization of precipitation has been carried by the operational conditions, and the optimized reaction has been undertaken without a full understanding of the real precipitation mechanism.

The goal of this study was the optimization of precipitation processing of nickel wastewater to reduce processing time and energy. This study was conducted to determine an efficient and economic approach for treatment of industrial wastewater which contained nickel constituent and to provide a more in-depth investigation on the effect of pH, total hydroxide, total carbonate and total sulfide contents in the nickel precipitation reaction.

EXPERIMENTAL

Precipitation experiments were carried out in a stirred vessel as crystallizer. The experimental apparatus is shown in Fig. 1. The cylin-

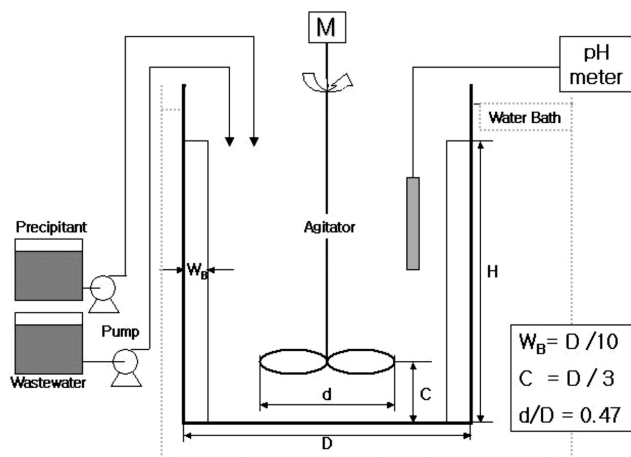


Fig. 1. Experimental apparatus.

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drical vessel was 90 mm in diameter, the width of each baffle was 1/10th of the diameter of vessel. This crystallizer was equipped with 4 baffle-plates and a draft tube. The draft tube was located in center of vessel. The propeller was inserted to the draft tube. The diameter of draft tube was 34 mm, and its height was 40 mm. The 3-blade propeller stirred the reactants and the flow of reactants was downward or upward depending direction of rotation of propeller. The temperature of the vessel in the circulating constant-temperature bath was maintained at 25 °C.

Two types of experiments were investigated: the first was a batch experiment and the other was semi-batch. In the batch experiment, the crystallizer was filled up 800 ml with the model wastewater. The precipitant was injected to the crystallizer by a syringe. For the semi-batch experiments, 200 ml of model wastewater was contained in the crystallizer. The proper volume of precipitant for controlling of pH condition and the 600 ml of model wastewater were fed to the crystallizer by the peristaltic pump. Batch and semi-batchwise experiments were carried out with the model wastewater and various precipitants, such as sodium hydroxide, sodium carbonate and sodium sulfide solution. The solutions were rapidly mixed at approximately 160 or 360 rpm for 1 hour by impeller. The 3-blade propeller stirred the crystallizer for 20 minutes. The model wastewater was injected to the stirred vessel at the rate of 10 ml/min for 1 hour. The settling rates were determined in long cylindrical glass tubes of 400 ml.

To separate precipitates from the mother liquid, the reacted solutions were filtered through 0.45 µm membrane filters and the filtered precipitates were rinsed several times with distilled water. The filtrates were used to analyze the concentrations of ions by Ion chromatography (Metrohm) and inductively coupled plasma optical emission spectrometer (Optima 2000DV, PerkinElmer). The distribution of precipitate sizes was measured by dynamic laser diffraction method using Laser Particle Size Analyzer (PHOTAL, PAR III).

To observe the size and morphology of nickel salts crystal with scanning electronic microscope (JSM-6335F, JEOL), the filtered precipitates were dried at 115 °C in a drying oven during 24 hours. The model wastewater, which contains 300 to 3,000 mg/l of nickel, was prepared by dissolving a nickel sulfate six hydrates in the distilled water.

RESULTS AND DISCUSSION

As the clear water is to be discharged into the natural environment after pH adjustment, the nickel concentration is better to be kept as low as possible. Although the domestic environmental regulations about hazardous or toxic waste do not yet regulate the nickel compound, the growing interest in environmental problems will lead to concerns about the nickel compound in near future. The concentrations of nickel in the effluent that the precipitates were removed show a drastic change with pH as shown in Fig. 2. The starting pH of precipitation for nickel hydroxide was about 8.0. As a result, if the pH condition is higher than 9.0, the concentration of nickel in treated wastewater could be maintained lower than 5 mg/l.

Consequently, we tried to find the precipitation conditions by which the nickel concentration in the effluent could be maintained lower than 5 mg/l, which is the environmentally regulated value for the hazardous metals such as copper and total chromium. As can

be seen in Fig. 2, the value of pH was required to be maintained higher than 10.0 until the precipitates were removed for all treatment methods. Among these treatment methods, sulfide treatment was better to lower the nickel concentration compared to the conventional hydroxide treatment. This is mainly because the solubility of nickel sulfide in water is lower than that of nickel hydroxide. For example, the solubility of nickel sulfide in water at pH of 8 is 0.14

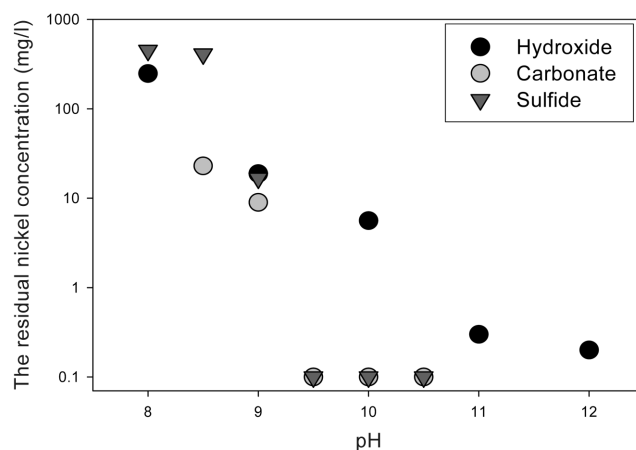


Fig. 2. The residual nickel concentration of wastewater after removing the precipitates.

Table 1. The average size and standard deviation (S.D.) of nickel hydroxide

pH	Size (µm)	Average size	Average size	Average size	Average size
		S. D.	S. D.	S. D.	S. D.
9.0		1.8	2.1	1.8	2.5
		(0.7)	(0.9)	(1.0)	(1.3)
11.0		2.2	1.7	1.7	1.6
		(0.8)	(0.6)	(0.6)	(0.6)
Flow	Draft tube	Upward	Down	Upward	Down
		No	No	Yes	Yes

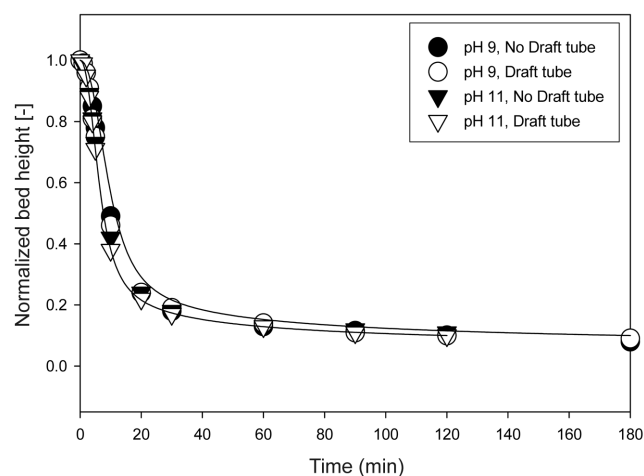


Fig. 3. The settling rate of nickel hydroxide precipitates for various pH.

ppb and nickel hydroxide is 120 ppm, respectively.

The average size of nickel hydroxide precipitates measured by PSA is shown in Table 1. The average size of the nickel hydroxide particles was distributed between 1.6 μm and 2.5 μm . Table 1 shows that the various changes in the precipitation conditions, such as pH, the draft tube, and flow direction, did not affect the mean particle

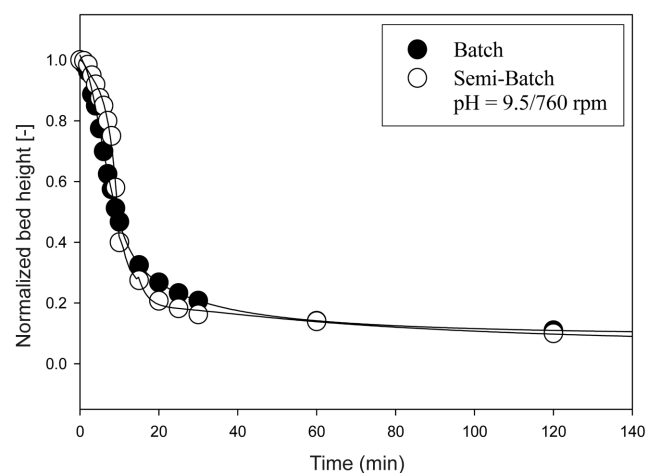


Fig. 4. Effect of operation mode on the settling rate of nickel hydroxide precipitates.

size of the precipitates.

These results might due to reaction speed. The precipitation reac-

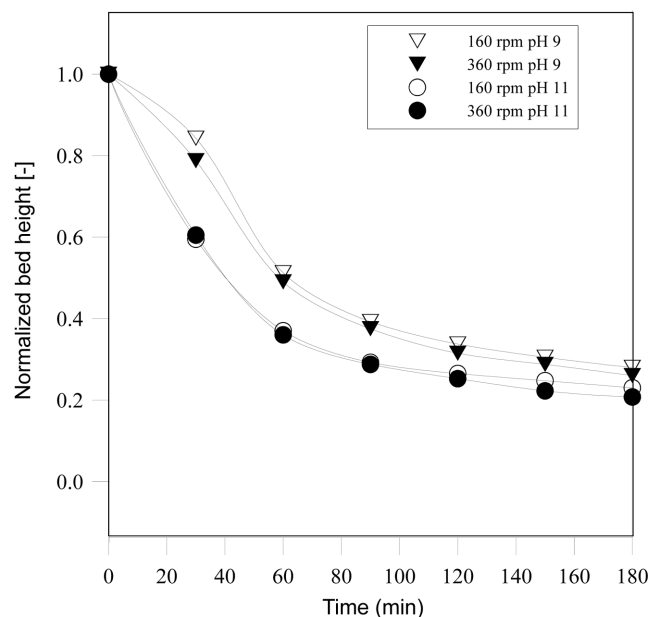


Fig. 5. Effect of the velocity of impeller on the settling rate of nickel hydroxide precipitates.

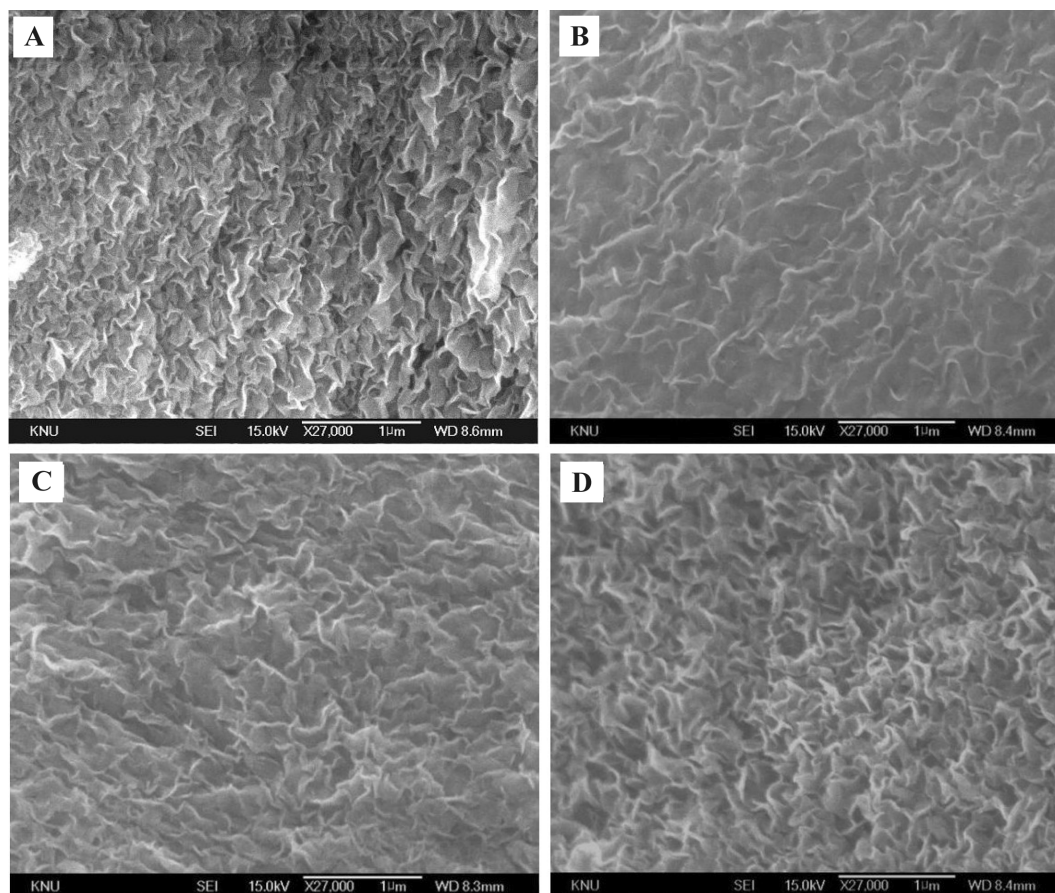


Fig. 6. SEM photographs of nickel hydroxide. (A) pH : 9.0/Upward flow/No draft tube, (B) pH : 9.0/Upward flow/Draft tube, (C) pH : 11.0/Downward flow/No draft tube, (D) pH : 11.0/Downward flow/Draft tube.

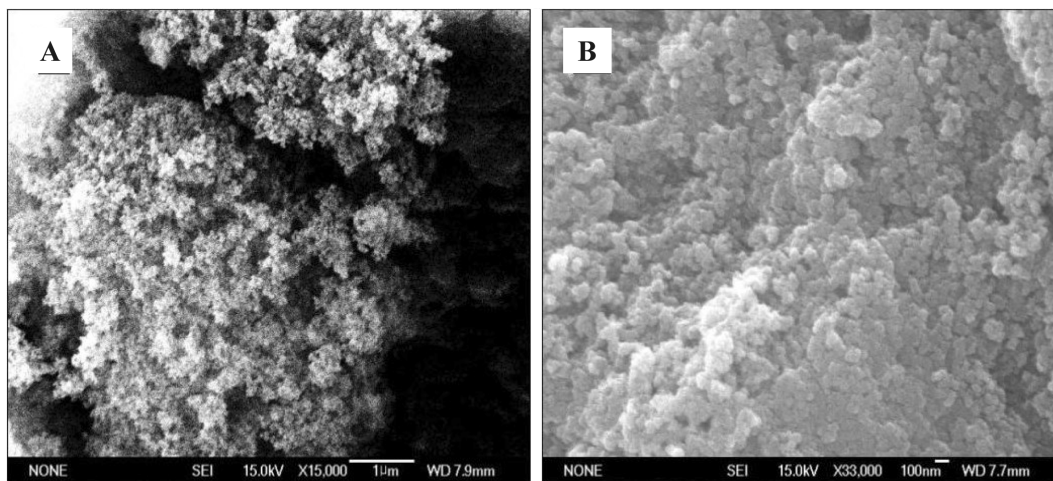


Fig. 7. SEM images of (A) Nickel Sulfide and (B) Nickel Carbonate.

tion was very fast and the level of solubility was very low. This reaction did not give any chance of growing the nickel hydroxide crystals during the reaction. Moreover, the measured data were lacking in consistency because an agglomeration among hydroxide particles occurred actively. The standard deviation values of particle size analysis results showed a rather higher value. It may be due to fact that the agglomeration of the precipitates occurred actively during analysis.

Crystal agglomeration is largely responsible for properties of the final product, such as size distribution, surface area and filterability. For understanding the precipitation processes in general and for their design and control, reliable agglomeration models are required [Hostomsky et al., 1993].

To enhance the settling rate and reduce the wastewater treatment period, the precipitates have to be coagulated by fluidization with foreign particles. The settling rates of nickel salt precipitates were measured by the sediment bed test as shown in Fig. 3. Although various changes of precipitation conditions were carried out, the settling rates did not show significant differences. Therefore, the various changes in the precipitation conditions, such as pH of higher than 9 and existence of a draft tube, do not affect the size of precipitates.

In case of the semi batch test, a part of precipitates were formed with an excess amount of sodium hydroxide and the remainder of the nickel sulfate solution was pumped into the precipitation vessel slowly. The semi batch test was performed to reduce the effect of agglomeration and to enhance the growth of the nickel hydroxide precipitates. Nevertheless, the experimental results of the settling rate for the two tests showed no great difference as shown in Fig. 4.

Fig. 5 shows settling rates of nickel hydroxide precipitates that were prepared in the different pH and stirring speed. As seen in Fig. 5, increasing the stirring speed and the pH value slightly increased the settling rate. But the influences of the changes in the precipitation condition were not so predominant and the difference in the settling rates with pH may be due to the change in the total volume of precipitates.

Fig. 6 shows some SEM images of nickel hydroxide precipitates. The morphologies of precipitates through SEM image were difficult to determine because the tendency to agglomeration of the pre-

cipitates was high and the precipitates were hard to grow to be typical crystals. The precipitate size was distributed between 0.1 µm and 0.2 µm. And Fig. 6 shows no influence on the morphology and shape of precipitates with the conditions of pH, existence of the draft tube and flow direction.

The SEM images of nickel sulfide and carbonate precipitates are shown in Fig. 7. The precipitate sizes of the carbonate and sulfide were distributed between 0.1 µm and 0.2 µm. This was almost equal to that of hydroxide precipitates. The morphologies of carbonate and sulfide were hard to identify, possibly because the tendency to agglomeration of the precipitated was high and the precipitates were hard to grow to be typical crystals.

CONCLUSION

To maintain the nickel concentration in the effluent of wastewater treatment facility lower than 5 ppm, the pH of the treated water has to be kept higher than 10. It means that the effluent from the wastewater treatment facility has to neutralize prior to discharge to the sewer line after the nickel salt precipitates are removed. The nickel concentration by the sulfide treatment method was lower than the conventional hydroxide treatment method. The size of precipitates itself was hard to enlarge only by changing the precipitation condition; therefore, to enhance the settling rate and reduce the size of the wastewater treatment facilities, the precipitates had to be coagulated by fluidization with foreign particles. We recommend adopting an inclined surface at the bottom of clarifier.

ACKNOWLEDGMENT

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