

## A study on Nickel Hydroxide Crystallization for Plating waste Treatment

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A Study on the precipitation characteristics of nickel hydroxide as well as carbonate and sulfide is carried out to determine the proper treatment condition of the wastewater induced from nickel-plating industry. The nickel concentrations in the effluent could be kept lower than 5ppm when the value of pH was maintained higher than 10. The precipitation of nickel salts by alkaline addition to the nickel containing model wastewater was conducted by using proper amount of sodium hydroxide, sodium carbonate, sodium bicarbonate and sodium sulfide. In case of the sulfide treatment, the residual nickel concentration in the clear water after precipitates removed showed the lowest value. The influences of the precipitation condition upon the particle size of the crystals precipitated were also investigated. In spite of the various precipitation conditions were adopted, the particle size of the precipitated crystals showed no great differences. The sedimentation rates of the precipitated particle bed were observed and the free sedimentation period was terminated within 20 minutes. Although the hindered sedimentation as well as bed compaction progressed subsequently, the bed heights were maintained almost the same level after two hours of sedimentation.

Keywords: Nickel, Electroplating, Wastewater, and Treatment

### Introduction

The Clean Water Act stipulates that industry must apply "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 [1]. Some of these techniques are: 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 [2-6].

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

The conventional treatment method of electroplating wastewater, known as chemical precipitation method, requires longer than 23 hours prior to treated effluent discharge and more than half of this time is caused on the precipitation and sedimentation even though some sort of artificial coagulating agents are applied.

This study is conducted to determine the efficient and economic approach to treat an industrial wastewater which contains 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.

Environmental crystallization has been proposed from the standpoint of such as wastewater treatment. There is a

need for treating contaminations in wastewater efficiently and economically, and for designing a new environmental restoration process. One variable process is to remove and recover ions as a form of stable solids, such as crystal[7]. The objectives of this study are lowering the nickel concentration in the effluent stream and shortening the time required to treat the wastewater from electroplating industry.

### Experiment

Precipitation experiments were carried out in a stirred vessel made by Pyrex glass of 1l equipped with baffles and draft tube. This vessel was immersed in a constant temperature bath that was maintained at 25 °C. Batch and semi batch wise experiments were carried out with model wastewater and 1 to 10N of sodium hydroxide, sodium carbonate and sodium sulfide solution. The solutions were rapidly mixed at approximately 160 or 360rpm for 1 hour. For the semi batch experiments, the 200ml of model wastewater was injected in the vessel and precipitated by an excess amount of 1N sodium hydroxide solution. After 20 minutes, the model wastewater was injected to the vessel at the rate of 10ml/min for 1 hour. The sedimentation rates were determined in long cylindrical glass tubes of 400ml. To separate precipitates from the mother liquid, 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 analysis the nickel concentration by Ion chromatography and Inductively coupled plasma Emission spectrometer. The precipitate size distribution

was measured by dynamic laser diffraction method using PHOTAL PAR III Laser Particle Size Analyzer.

To observe the size and morphology of nickel salts crystal with Scanning Electronic Microscope, filtered precipitates were dried at 115°C in a drying oven during 24 hours. The model wastewater, which containing 300 to 3,000 mg/l of nickel, was prepared by dissolving a nickel sulfate six hydrates in the distilled water.

## Results and Discussion

The nickel concentrations in the clear water after removing the precipitates show a drastic change with pH as shown in Figure 1. As this clear water will be discharged into the natural environment after pH adjustment, the nickel concentration is better to be kept as low level. Although the domestic environmental regulations about the hazardous or toxic waste from electroplating industry do not regulate the nickel compounds yet, the glowing interest in the environmental problems will come to concern the nickel compound in near future. Although the nickel hydroxide particles are known to precipitate above the pH of about 7.8, the quantitative amount of precipitation is expected above the pH of 9.3. And if one wanted to remove the more of nickel ions in the solution as nickel hydroxide particles, he had to increase the pH of such solution. Upon this sense, we tried to find out the precipitation conditions by which the nickel concentration in the effluent could maintain lower than 5mg/l, which is the environmentally regulated value for the hazardous metals such as copper and total chromium. As can be seen in Figure 1, the value of pH is required to maintain higher than 10 until the precipitates are removed for all treatment methods. In between these three treatment methods, sulfide treatment will be better to lower the nickel concentration compared to the conventional hydroxide treatment. This is mainly due to the solubility of nickel sulfide is lower than that of nickel hydroxide. For example, the solubility of nickel sulfide and nickel hydroxide at pH of 8 is 0.14 ppb and 120 ppm, respectively.

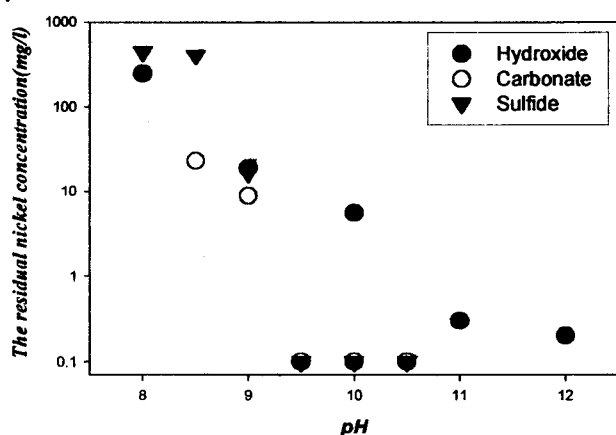


Figure 1. The residual nickel concentration of water after removing the precipitates.

Table 1 shows the average size of nickel hydroxide precipitates measured by PSA. The average size of the nickel hydroxide particles was distributed in between 1.6  $\mu\text{m}$  and 2.5  $\mu\text{m}$ . It can be seen from the Table 1 that the various change in the precipitation conditions such as pH, draft tube and flow direction does not affect the mean particle size of the precipitates.

This may due to the precipitation reaction is so fast and the level of solubility is so low to give any chance to growing the nickel hydroxide crystals. Moreover, the measured data were lacking in consistency, because an agglomeration among hydroxide particles occurred actively. And the standard deviations of particle size analysis results show rather higher value. This may due to the agglomeration in between the precipitates occurred actively during analysis

Crystal agglomeration is largely responsible for the final product properties, such as size distribution, surface area and filterability. For understanding these processes in general and for their design and control, reliable agglomeration models are required [7].

From these observations, to enhance the settling rate and reduce the wastewater treatment period, incite the precipitates to coagulate by fluidization with foreign particles.

pH \ Size( $\mu\text{m}$ )	Average Size	Average Size	Average Size	Average Size
	SD	SD	SD	SD
9.0	1.8	2.1	1.8	2.5
	0.7	0.9	1.0	1.3
10.0	2.2	1.7	1.7	1.6
	0.8	0.6	0.6	0.6
Flow	Upward	Down	Upward	Down
Draft Tube	No	No	Yes	Yes

Table 1. The average size and standard deviation of nickel hydroxide precipitates measured by PSA.

The sedimentation rates of nickel salts precipitates were measured by the sediment bed test as shown in Figure 2. Although various changes of precipitation conditions were carried out, they have no significant differences in between. Therefore the various changes in the precipitation conditions such as pH of higher than 9, draft tube existence and flow direction do not affect the size of precipitates.

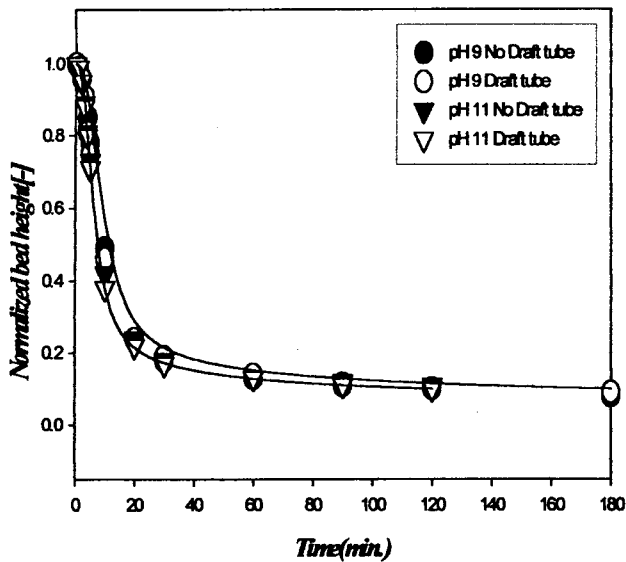


Figure 2. The sedimentation rate of nickel hydroxide precipitates with various pH and draft tube.

The semi batch type test, in which a part of precipitates were formed with the excess amount of sodium hydroxide and remainder of the nickel sulfate solution was pumped into the precipitation vessel slowly, is performed to reduce the effect of agglomeration and to enhance the growth of the nickel hydroxide precipitates. Nevertheless, the experimental results about the sedimentation rate of these two tests show no great difference as shown in Figure 3.

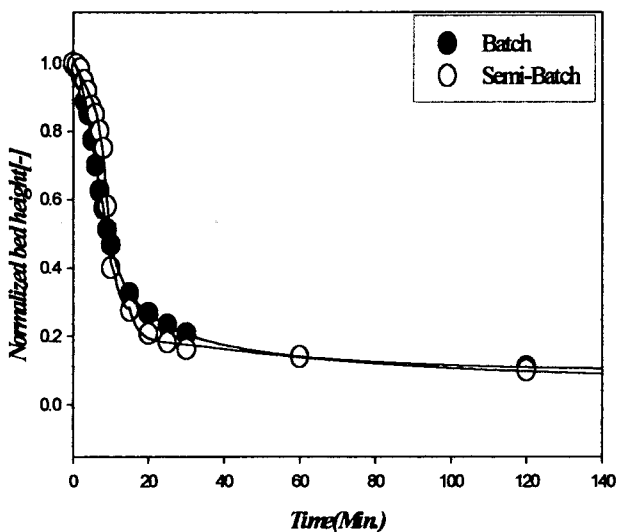


Figure 3. The sedimentation rate of nickel hydroxide precipitates by Batch and Semi batch test.

Figure 4 shows sedimentation rates of nickel hydroxide precipitates, which were prepared in the different pH and stirring speed. This figure shows that an increase in the stirring speed and the pH value slightly increase the sedimentation rate. But the influences of these changes in the precipitation condition are not so predominant and

the difference in the sedimentation rates with pH may due to the change in the total volume of precipitates.

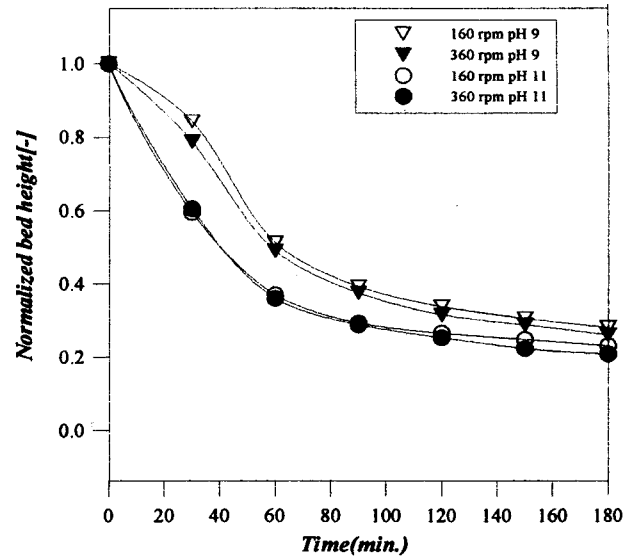


Figure 4. The sedimentation rate of nickel hydroxide precipitates with velocity of impeller.

Figure 5 shows some SEM images of nickel hydroxide precipitates. The morphologies of precipitates through SEM image are difficult to determine because the tendency toward the precipitates agglomeration is high and the precipitates are hard to grow to be a typical crystals. From these images, the precipitate size shows to distribute in between  $0.1\mu\text{m}$  to  $0.2\mu\text{m}$ . And they show no influence on the morphology and shape of precipitates with the conditions of pH, existence of the draft tube and flow direction.

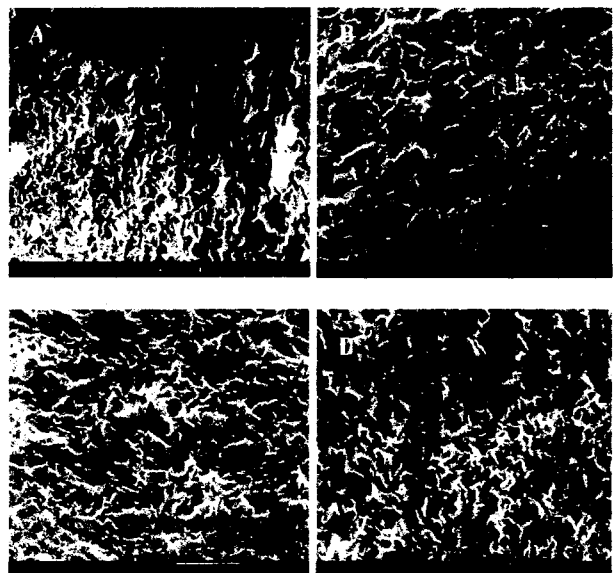


Figure 5. The images of nickel hydroxide by SEM. (A: 9.0/U/N, B: 9.0/U/D, C: 10.0/D/D, D: 10.0/D/N) U: Upward flow, D: Downward Flow, D: Draft tube N: No Draft tube

The SEM images of nickel sulfide and carbonate precipitates are showed in Figure 6. The precipitate size of the carbonate and sulfide distributes in between 0.1 $\mu$ m to 0.2 $\mu$ m. It is almost the same size as that of hydroxide precipitates. The morphologies of carbonate and sulfide are hard to identify. This may be due to the tendency toward the precipitates agglomeration is high and the precipitates are hard to grow to be a typical crystals.

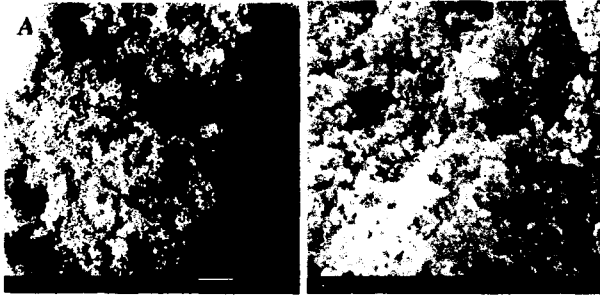


Figure 6. The images of (A) Nickel Sulfide and (B) carbonate by SEM.

### Conclusion

To maintain the nickel concentration in the effluent of wastewater treatment facility lower than 5ppm, the pH of the treated water is better to keep higher than 10. It means that the effluent from the wastewater treatment facility have to neutralize prior to discharge to the sewer line after removing the nickel salt precipitates. The sulfide treatment method will give lower nickel concentration than the conventional hydroxide treatment method. The size of precipitates itself is hard to enlarge only by changing the precipitation condition and so to enhance the settling rate and reduce the size of the wastewater treatment facilities, incite the precipitates to coagulate by fluidization with foreign particles and adopt an inclined surface at the bottom of clarifier.

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