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Separation and Recovery of Nickel and Cadmium from Spent Cd–Ni Storage Batteries and Their Process Wastes

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Abstract

Several typical methods for the recovery and separation of cadmium and nickel from Ni- and Cd-bearing wastes are briefly described. Laboratory- and large-scale experiments were respectively developed to improve the processes for the recovery and treatment of cadmium and nickel. A high degree of purity of recovered cadmium was obtained. Yields of >95% for nickel and >99.66% for cadmium were obtained. The large-scale experimental process involves no secondary pollution, and it decreases and sometimes eliminates the disposal of spent process streams. A plant in China has established a production line based on the large-scale process, and a large number of benefits in cadmium recovery from spent alkaline Ni–Cd storage batteries and their process wastes have resulted.

INTRODUCTION

A large number of spent alkaline storage batteries are produced every day. In addition, large quantities of process wastes are generated from the manufacture of alkaline storage batteries. Both spent alkaline storage batteries and process wastes contain nickel and cadmium. Nickel is a very useful metal, while cadmium is a toxic element. If the spent batteries and

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process wastes are discarded directly into the environment, soil and water are potentially polluted. At the same time, large quantities of useful substances are disposed of without recycling. Therefore, great concern over the recovery and treatment of nickel and cadmium from spent alkaline Ni–Cd storage batteries and its process wastes has been shown by many researchers.

The anode substances in an alkaline Ni–Cd storage battery contain $Ni(OH)_2$, $Ba(OH)_2$, KOH, and powdered graphite, while the cathode substances contain CdO, Fe_3O_4, $NiSO_4$, transformer oil, and powdered graphite. The depleted electrolyte consists of potassium hydroxide, lithium hydroxide, and distilled water. So a key technology for the recovery and treatment of spent alkaline batteries is to separate cadmium or nickel from the mixture wastes (*1*).

A dry treatment method (*2*), such as the pyrometallurgical method, may be used to remove cadmium or nickel from the wastes by means of high-temperature extraction. This process requires that all substances be in the solid state. Some traditional wet treatment methods (*3*) for separating cadmium or nickel from industrial wastewater containing Cd(II) and Ni(II) are as follows.

1. Electrochemical Deposition. This method depends upon the electrical potential difference for separating cadmium or nickel from the wastewater. Because the electrical potentials of cadmium and nickel are very low and close, only lower current density under careful supervision can be employed to remove cadmium by electrodeposition from the wastewater containing nickel. Current removal efficiencies are very low, while operating costs are high.

2. Sulfide Precipitation. Under certain conditions, cadmium sulfide can be precipitated when hydrogen sulfide is added to these wastewater. The simultaneous precipitation of nickel sulfide does not occur. Very high rates of cadmium removal can be obtained by this method. A disadvantage is the toxicity of hydrogen sulfide gas. Recovered cadmium sulfide, however, cannot be directly recycled into the production of alkaline storage batteries.

3. Solvent Extraction. Many kinds of solvents can be used to extract nickel and cadmium from battery wastes under certain conditions. Solvent extraction is widely employed in laboratories to separate cadmium from scrap alkaline Ni–Cd storage battery waste. This method, however, is costly and limited to large-scale applications.

The experimental programs of this research were intended to develop economical and effective methods for the recovery and treatment of cadmium and nickel from scrap alkaline Ni–Cd storage battery waste.

REVIEW OF METHODS FOR SEPARATION AND RECOVERY Ni AND Cd FROM Ni–Cd BATTERY WASTES

Many researchers and inventors have focused upon the recovery and separation of nickel and cadmium from nickel–cadmium battery waste during the past two decades. Brief descriptions of typical methods follow.

1. A method developed by T. Furuse (*4*), Yuasa Battery Co., Ltd., Japan, in 1976 involves several steps. Spent Ni–Cd storage batteries were crushed and screened to separate active materials. The active materials were dissolved in H_2SO_4. The solution, which contained 40 g/L Cd, 70 g/L Ni, 7 g/L Fe, and 120 g/L H_2SO_4, was electrolyzed to recover Cd at the cathodes. The degree of purity of the recovered Cd was as high as 99.95%. The remaining electrolyte, which contained 3 g/L Cd, 70 g/L Fe, and 152 g/L H_2SO_4, was also concentrated. The concentrated residue, which contained mainly $NiSO_4$ and small quantities of the other materials, was then dissolved in water. The solution was oxidized with air or an oxidizing agent, neutralized with lime at pH 6, and filtered to remove H_2SO_4 and Fe. The remaining solution was mixed with gypsum seed crystal and filtered to remove suspended gypsum. $NiSO_4$ crystals were obtained when the solution was cooled to room temperature. This method requires careful supervision because very low current density (7 mA/cm^2) is used and the consumption of heat energy is high.

2. D. A. Wilson and B. J. Wiegard (*5*), U.S. Bureau of Mines, developed another method for selectively leaching and recovering cadmium from Ni–Cd scrap battery waste in 1971. The waste was initially washed to remove KOH electrolyte, roasted at 550–600°C for 1 h to oxidize metallic cadmium and decompose cadmium and nickel salts, and then leached at 25°C with 4*M* NH_4NO_3 solution without dissolving nickel and iron. The leached cadmium from the solution was then precipitated as $CdCO_3$ by using CO_2 gas at 8–12 psi for 30 min. The excess CO_2 was expelled from the leaching solution by adjusting the pH to 4.5, heating at 40–60°C, and evacuating the system at 500 mmHg for 30 min. Small amounts of leached nickel were extracted from the lixiviator by adding HNO_3 solvent. The regenerated lixiviator was then reused to leach new plates or waste. Although the cadmium carbonate product contained 0.14% Ni and 0.12% Co impurity, only about 94% of the cadmium was leached out of the waste, and the iron and nickel were not separated from one another. Other disadvantages of the method are costly furnace apparatus, loss of CO_2 gas, and the expense of the process.

3. An improved method was invented by H. Reinhardt, et al. (*6*), Nife Jungner AB, Sweden, in 1975. The main steps in the process are: 1) washing the waste to remove KOH electrolyte, 2) leaching the waste with an am-

moniacal carbonate solution (NH_4HCO_3 + $NH_3 \cdot H_2O$). The amounts of NH_3, NH_4^+, HCO_3^-, and CO_3^{2-} can be controlled by adding NH_3 and CO_2 gas. The aqueous ammoniacal carbonate solution contained cadmium, nickel, and cobalt(II) ammine complexes and a leaching residue. The leaching solution contained 6 g/L Ni, 5 g/L Cd, and <0.005 g/L Fe. 3) Adding air for 60 h to the leaching solution to oxidize the cobalt(II) ammine complex to a cobalt(III) ammine complex. 4) Extracting nickel from the resulting aqueous ammoniacal carbonate solution by using a chelating agent such as an hydroxyoxime or hydroxyquinoline (Lix 64 N or Kelex 120). Cadmium and cobalt(III) were not affected by the solvent. The chelating agent was recovered by reacting the chelate with H_2SO_4. 5) Precipitating the cadmium carbonate by driving off ammonia from the above solution. Cadmium was thereby removed. 6) Precipitating the cobalt as a hydroxide by removal of ammonia at 100°C for 1 h from the preceding step after precipitation of Cd. 7) Returning the ammonia to the Cd-free filtrate and adding gaseous CO_2 to replace lost carbonate ions. This solution can be used to alkalize more Cd-containing wastes.

Under optimal conditions, yields of >95% for nickel and >99% for cadmium were obtained, and a higher degree of purity of recovered Cd and Ni was also produced. However, the expensive chelating agent and high investment of equipment for continuous operation are disadvantages of this process.

4. A 2-stage cementation method was developed for the selective separation of Cd and Ni from a Cd- and Ni-bearing solution by L. Kaufmann et al. (*7*) in 1979. Mother liquors containing 10–80 g/L Ni and 120–150 g/L Cd from the H_2SO_4 leaching of spent Ni–Cd batteries and other waste materials were first made. Then, 40–100 g/L NaCl was added to the liquors at 25–30°C and pH 2.1–2.5. The cementation of Cd took place in the first stage with aluminum powder. The cementation of Ni with aluminum powder took place in the second stage at 55–60°C at pH 2.4–2.5 in the presence of 120–150 g/L NaCl. A high degree of purity of recovered Cd and Ni was difficult to obtain by this method. The recovered Cd and Ni could not be directly reused in the production of alkaline Ni–Cd storage batteries.

5. A process for the recovery of Cd and Ni from a Cd- and Ni-containing solution was also proposed by H. Hamamatsa and H. Matsumoto (*8*), Mitsui Mining and Smelting Co., Ltd., Japan, in 1973. A Ni- and Cd-containing H_2SO_4 solution at pH 4.5–5 was obtained by means of the extraction process of Ni–Cd battery materials with H_2SO_4 under heating. Excess NH_4HCO_3 was added to the solution to selectively precipitate cadmium carbonate. Then NaOH and Na_2CO_3 were added to the remaining solution to recover Ni as nickel hydroxide. This proved to be a good method to separate Cd and Ni from Cd- and Ni-bearing solutions. NH_4HCO_3 was,

however, very easy to decompose automatically. Careful supervision of the NH_4HCO_3 materials was required for this process.

EXPERIMENTAL PROGRAMS

Laboratory-Scale Experiment

Pretreatment of Ni- and Cd-Bearing Sludges. Insoluble solid wastes were screened from nickel- and cadmium-bearing sludges. The sludges were then heated to 600–700°C for 1 h in a roaster to decompose and carbonize organic matter in the sludges.

Leaching. Roasted sludges were soaked in sulfuric acid solution for more than 24 h. Heating and stirring were used to speed the soaking time. An aqueous solution containing $CdSO_4$, $NiSO_4$, and $FeSO_4$ was obtained. Some sulfate precipitations, such as $CaSO_4$, $BaSO_4$, and $PbSO_4$, occurred.

Complex Reaction. Ammonia was added to the leaching solution at pH 10–11 to form cadmium and nickel ammonia complexes. The complex reactions were as follows:

$$H_2SO_4 + 2NH_4OH \rightarrow (NH_4)_2SO_4 + 2H_2O$$

$$NiSO_4 + 6NH_3{\cdot}H_2O \rightarrow [Ni(NH_3)_6]SO_4 + 6H_2O$$

$$CdSO_4 + 4NH_4OH \rightarrow [Cd(NH_3)_4]SO_4 + 4H_2O$$

A solution containing $[Cd(NH_3)_4]SO_4$, $[Ni(NH_3)_6]SO_4$, K_2SO_4 (or Na_2SO_4), Li_2SO_4, $(NH_4)_2SO_4$, and small quantities of Mn^{2+} and Fe^{2+} was obtained. The other ions, such as Fe^{3+}, Mn^{4+}, and Al^{3+}, remained in the residues.

Fine Leaching. H_2SO_4 was added to the above solution to adjust the pH to 5–6. Then Fe^{2+} and Mn^{2+} were removed as the precipitates $Fe(OH)_3$ and $MnO(OH)_2$ by means of introducing oxygen and heating the solution. A fine leaching solution was obtained by filtration.

Crystallization. Large quantities of $(NH_4)_2{\cdot}Ni(SO_4)_2{\cdot}6H_2O$ crystal were created when $(NH_4)_2SO_4$ was added to the fine leaching solution at room temperature:

$$(NH_4)_2SO_4 + NiSO_4 + 6H_2O \rightarrow (NH_4)_2{\cdot}Ni(SO_4)_2{\cdot}6H_2O$$

After filtration of the crystal, the remaining solution contained a very small quantity of nickel.

Precipitation. Cadmium carbonate was precipitated by adding NH_4HCO_3 at 70°C and pH 6–6.5 to the above solution. The precipitate contained only 0.3% $NiCO_3$ and was heated to decompose to CdO which could be reused in the production of Ni–Cd storage batteries.

Further Treatment. The mixture compound containing small quantities of Cd and Ni in solution was precipitated by adding sodium hydroxide and recycled to the H_2SO_4 leaching process.

$(NH_4)_2 \cdot Ni(SO_4)_2 \cdot 6H_2O$ crystals were dissolved in heating water. Sodium hydroxide was introduced into the solution. Then $Ni(OH)_2$ precipitation took place, and the precipitate was directly recycled into battery production.

A process flow sheet of the laboratory-scale experiment is presented in Fig. 1. Recovered yields of >95% for nickel and >99.66% for cadmium were obtained by using this process.

Large-Scale Experiment

Based on the properties of actual spent alkaline Ni–Cd storage battery wastes which usually consist of 50–85% Cd, 3% Ni, and 12–47% Fe (assuming that the amounts of Cd, Ni, and Fe total 100%), a large-scale experiment based on the laboratory-scale experiment was proposed. The process flow sheet of the large-scale experiment is illustrated in Fig. 2.

Roasting and Leaching. Waste containing cadmium and nickel was roasted at 700°C for 1 h. The roasted sludges were allowed to cool and soaked in a 10% H_2SO_4 solution at pH 2–3.

Removal of Fe. MnO_2 was added to the solution under heating at 60–70°C. The solution was stirred for 1 h with $CdCO_3$ or NaOH added to adjust the pH to the 5–6 range. Stirring was continued for another hour, and Fe was then removed by filtration.

Electrolysis. The remaining solution was made to contain 10 g/L H_2SO_4 by adding H_2SO_4. Electrolysis of the fine leaching solution took place at 25–35°C with a current density of 300–350 A/m^2. The cadmium cathode was stripped every 24 h. Electrolysis was not stopped until 20 g/L Cd^{2+} was obtained in the fine leaching solution. The depleted electrolyte together with the anode mixture was returned to the H_2SO_4 leaching process repeatedly (approximately 10 times) until the concentration of nickel in the depleted electrolyte equaled 20 g/L. The concentrated spent electrolyte was then ready to be treated for the separation of Ni and Cd.

Separation of Cd. NH_4HCO_3 was added to the concentrated spent electrolyte at 50–60°C and the pH value was adjusted to 6–6.5 with H_2SO_4. The solution was stirred for 1 h with cadmium carbonate obtained by filtering the precipitate.

Recovery of $(NH_4)_2SO_4$. The above leaching solution was adjusted to pH 5–6 by adding H_2SO_4 or NH_4HCO_3 and pumped into 2-stage electrolysis cells. The electrolyte containing $(NH_4)_2SO_4$ was reused in Ni–Cd battery production when the concentrations of both Ni^{2+} and Cd^{2+} in the electrolyte were <10 mg/L.

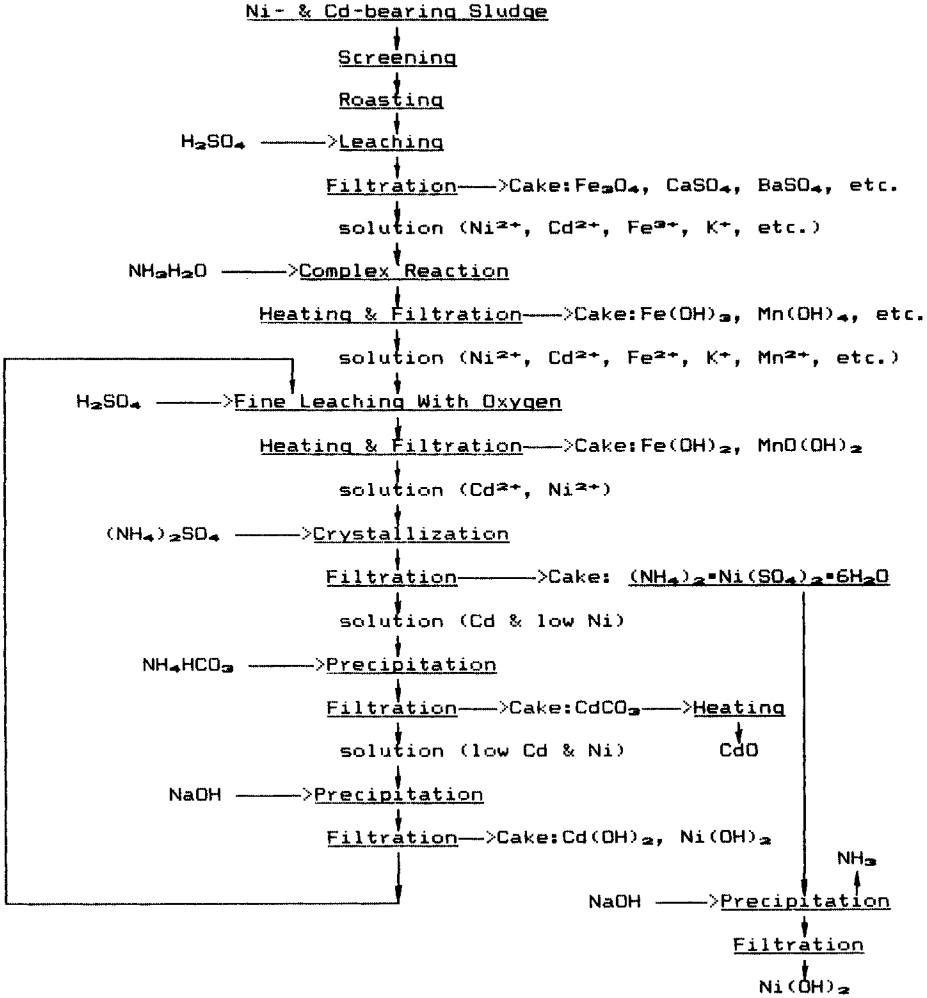

FIG. 1. Process flow sheet of laboratory-scale experiment for separation and recovery of Ni and Cd.

RESULTS AND APPLICATION

In our laboratory-scale experiment, a high degree of purity of cadmium carbonate powder was obtained. The concentration of $CdCO_3$ in the powder was >97.2% and the powder contained <0.14% Ni. Adding $(NH_4)_2SO_4$ to the fine leaching solution was a key step in the process. According to the results of several experiments that compared the effects of $(NH_4)_2SO_4$,

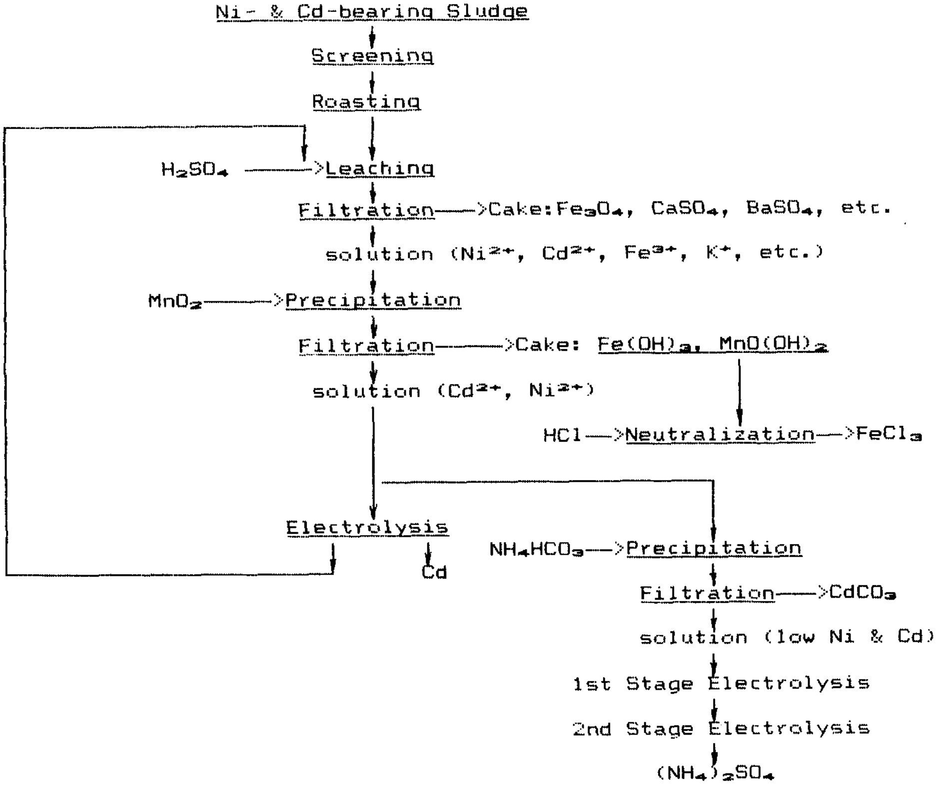

FIG. 2. Process flow sheet of large-scale experiment for separation and recovery of Ni and Cd.

the degree of purity of $CdCO_3$ powder increased when $(NH_4)_2SO_4$ was added to the fine leaching solution.

The laboratory-scale process for the recovery of nickel and cadmium from scrap Ni–Cd storage battery wastes was successful. The recovery rate was more than 95% for nickel and 99.66% for cadmium. Cadmium could be completely separated from the solution containing nickel salts in the laboratory-scale process.

In our large-scale experiment, the degree of purity of the recovered cadmium was more than 99.82%, and the recovered cadmium could be used directly in all types of Ni–Cd storage battery productions without further purification. This cyclic process had no secondary environmental pollution. The consumption of chemical reagents in the large-scale process was reduced to 10% of that in the laboratory-scale process. The large-scale process decreased and sometimes eliminated the disposal of spent process streams. The advantage of the large-scale process, apart from the low investment in equipment, is that more than 99.90% of the cadmium is leached out of the wastes.

Fengyun Electronic Equipment Plant, Henan, China, established a production line for the recovery and treatment of cadmium from scrap alkaline Ni–Cd storage batteries and their process wastes in 1988. The production line consists of equipment stages and can recover 5 tons of metallic cadmium per year. The production line processes are based on the large-scale experimental process.

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REFERENCES

1. W. Ying and R. R. Bonk, "Removal of Nickel and Phosphorus from Electroless Nickel Plating Baths," *Met. Finish.*, *85*(12), 23 (1987).
2. M. Shamsuddin, "Metal Recovery from Scrap and Waste," *J. Met.*, *38*(2), 24 (1986).
3. C. S. Brooks, "Metal Recovery from Industrial Wastes," *Ibid.*, *38*(7), 50 (1986).
4. T. Furuse (to Yuasa Battery Co., Ltd.), Japanese Patent 53/19,102 (February 22, 1978).
5. M. Sittig, *Metal and Inorganic Waste Reclaiming Encyclopedia—Pollution Technology Review No. 70,* Noyes Data Corporation, Park Ridge, New Jersey, 1980, pp. 89–92, 386–389.
6. H. Reinhardt, V. Frolunda, H. D. Ottertun, et al. (to Nife Jungner AB), U.S. Patent 4,053,553 (October 11, 1977).
7. L. Kaufmann, K. D. Hellwig, and P. Tilp (to Degussa AG), West Germany Patent 2,913,893 (October 16, 1980).
8. H. Hamamatsu and H. Matsumoto (to Mitsui Mining and Smelting Co., Ltd.), Japanese Patent 49/93,212 (September 5, 1974).

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