Recycling of NiCd Batteries by Hydrometallurgical Process on Small Scale

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Summary: High recovery of cadmium metal from household spent nickel cadmium batteries through hydrometallurgical process on small scale was conducted. Recovery of metal through separation of leached metal ions using ion exchange resin was examined. Hydrochloric acid (4.0 M) solution showed relatively better leaching potential than other acids, however, considering overall efficiency of the process, sulphruic acid was suggested to be employed as leaching and regeneration reagent in this study. Variations in solid/liquid ratio did not show a significant difference in the amount of heavy metal ions leached out; however, leaching temperature greatly affected the leaching efficiency. Changes in bed volume of the resin greatly influenced the sorption of cadmium metal ions while concentration and flow rate of the regeneration reagent were found important parameters affecting regeneration capacity of the resin.

Introduction

The nickel cadmium battery (NiCd) is a type of rechargeable battery using nickel oxide hydroxide and cadmium as electrodes. NiCd batteries are generally used in laptop, cordless and wireless telephones, emergency lighting and other electronics applications [1-3].

NiCd batteries along with other materials use cadmium that acts as cumulative poison and is listed among the 25 hazardous substances that pose the most significant potential threat to the human health [4]. US Environmental Protection Agency in a report stated that although NiCd batteries represented only 0.1% of the urban waste in weight, about 75% of cadmium in urban waste incineration, however, came from NiCd batteries [5]. Recycling of NiCd batteries, therefore, is essential, both from environmental and economical point of view as well.

Generally, there are some alternatives for the disposal of spent batteries; landfilling, stabilization, incineration and recycling [6]. Problem associated with the landfilling is the potential release of toxic metal ions with subsequent contamination of soil and groundwater. Incineration is linked with the emission of metallic ions into the ambient air due to burning of waste at high temperature and also concentration of metals in the ashes that must be landfilled or disposed in a plant specifically designed for the disposal of hazardous waste. Stabilization still offers a costly solution of spent battery management. Recycling of spent batteries, however, could be a promising option since it recovers valuable metals and supports healthy environmental activity.

Hydrometallurgical process can be a recycling alternative that offers high recovery of metal following low energy routes with minimum generation of wastewater for the treatment of spent batteries [7, 8]. Hydrometallurgical process uses an aqueous solution to extract metals from its source. The process includes leaching, ionic separation, solution concentration with subsequent metal recovery. Several hydrometallurgical processes with some modifications have been developed and practiced for the treatment of spent batteries. Bartolozzi *et al*., [9] developed a method for recovery of metals from NiCd batteries using sulfuric acid leaching, followed by cadmium recovery by selective electrodepositon. For improved efficiency of cadmium recovery, the process required a pressure autoclave at 400 PSIG and 110 °C under oxygen sufficient environment. Tzanetakis *et al.,* [10] investigated another process for NiCd batteries using hydrochloric acid leaching followed by the separation of cadmium chloride complexes by solvent extraction with TBP and selective nickel and cadmium electrowinning. Nogueira *et al.,* [11] proposed a process for the recovery of cadmium, cobalt and nickel from spent NiCd batteries by sulfuric acid leaching and separation of metal ions by solvent extraction with D2EHPA and Cyanex 272. Zang *et al.,* [12] presented hydrometallurgical treatment methods for the metal recovery form nickel-metal hydride and lithium ions spent batteries.

High recovery of valuable metallic components from NiCd rechargeable batteries was also investigated by many researchers [13]. Stefanut *et al.,* [14] while working on electrochemical recovery of nickel and cadmium from spent NiCd batteries investigated that relatively larger and more uniform deposits of recovered metals were observed

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on the working electrodes at potential between 1000-1300 mV and scan rate of 10 mV/s. Lyman *et al*., [15] found that 4 mol dm^{-3} HCl was the best suited acid medium to get the highest leaching efficiency of metals in recovery process. Pietrelli *et al.*, [16] recovered 80% of the rear earth elements contained in spent batteries through precipitation as insoluble double sulfate salts. Tenorio *et al.,* [17] suggested mineral processing techniques, which involved hammer and knife milling, magnetic and size separation for the recovery of nickel-based alloys from spent batteries.

Present study focused on the recovery of cadmium metal from spent NiCd batteries by hydrometallurgical process designed on small scale. The study was applied on used household/domestic batteries since spent batteries of industrial type do have a well collection and recycling process. Separation of cadmium from leaching solution by ion exchange resin is examined. Optimum conditions for high recovery of cadmium through resource recycling are reported in this paper.

Results and Discussion

Leaching of Metal Ions

Leaching tests were performed using three different acids of varying concentrations. The type and strength of acids strongly affected leaching capabilities of metal ions. HCl (4.0 M) solution showed relatively better potential of leaching than other acid solution at the similar conditions of leaching process (Table-1). Variations in solid/liquid ratio did not show a significant difference in the amount of heavy metal ions leached out. HCl was employed as a leaching medium due to its relatively low cost and good suitability of extracting nickel ions from chloride solutions.

Table-1: Chemical composition of leachate at varying concentrations of acids.

Acid	+ive mass (g)	-ive mass (g)	Cell mass (g)	Cd^{+2} (ppm)	Ni^{+2} (ppm)
HCl (2M)	7.29	8.39	23.21	22300	26800
HCl (4M)	7.33	8.42	23.40	24500	29000
HCl (6M)	7.21	8.33	23.51	23500	28500
HNO_3 (2M)	7.19	8.11	22.91	19200	27100
HNO_3 (4M)	7.37	8.34	23.27	20500	27250
HNO_3 (6M)	7.42	8.73	23.56	19800	25120
H_2SO_4 (2M)	7.25	8.33	23.37	21000	26500
H_2SO_4 (4M)	7.35	8.28	23.84	21300	26900
H_2SO_4 (6M)	7.40	8.55	23.78	21210	26600

Although HCl solution showed relatively better leaching potential than H_2SO_4 and HNO_3 solution (Table-1), however, considering efficiency of the whole recovery process, H_2SO_4 was suggested to be employed as leaching and regenerating reagent in this study. The metal constituents in the form of their oxides and hydroxides as electrode materials react with sulphuric acid to give sulphate salts. High initial slope during the first hour is due to rapid reaction of the metal particle with the acid. The results indicated that at a solid to liquid ratio 4.0, cadmium and nickel metals were almost completely leached out in 2.0 M sulfuric acid solution within the period of 2.0 hrs at operating temperature 80 °C (Fig. 1, 2). At solid to liquid ratio 2, sulphuric acid 2.0 M solution took relatively double time, around 4.0 hrs to show the highest efficiency of leaching of cadmium and nickel metal ions (Fig. 3, 4). At completion, the leaching solution had a clear green clour due to the presence of nickel ion and pH of the leached solution was closed to the range 0.3-0.7.

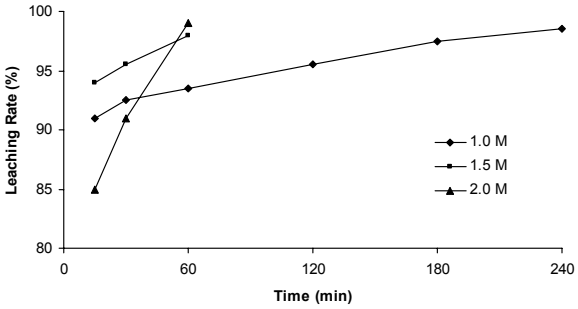

Fig. 1: Profile of leaching efficiency of Cd versus time at various concentration of sulphuric acid solution (T= 80 ºC, S/L ratio: 4).

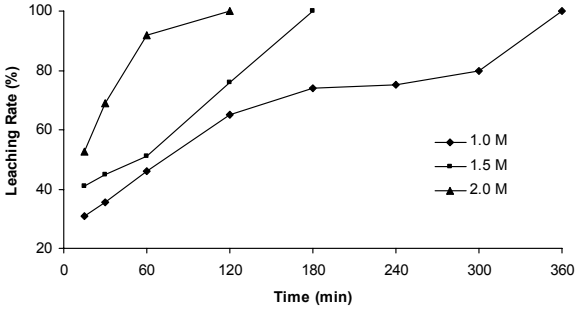

Fig. 2: Profile of leaching efficiency of Ni versus time at various concentration of sulphuric acid solution (T= 80 ºC, S/L ratio: 4).

Leaching experiments were conducted at a temperature range 60 – 110 ºC. However, 80 ºC showed an optimum temperature to get highest efficiency of leaching metal ions. Leaching of metals

was found to depend significantly on leaching temperature. Study revealed that temperature higher than 80 ºC generally improved kinetics of leaching metal ions. The leaching process, however, became difficult at high temperature. This might be due to loss of a large amount of water that helped facilitate leaching reactions.

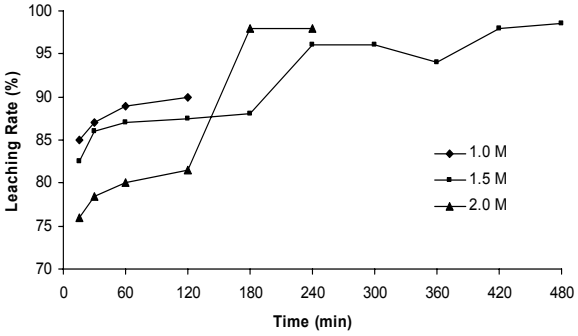

Fig. 3: Profile of leaching efficiency of Cd versus time at various concentration of sulphuric acid solution (T= 80 ºC, S/L ratio: 2).

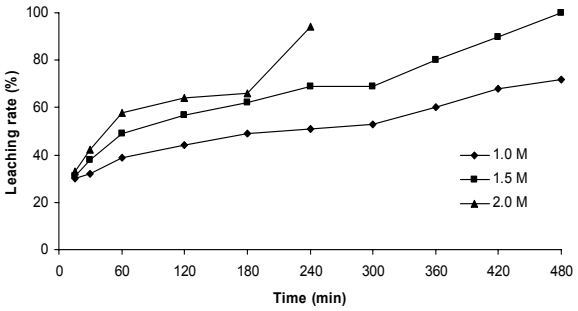

Fig. 4: Profile of leaching efficiency of Ni versus time at various concentration of sulphuric acid solution (T= 80 ºC, S/L ratio: 2).

Reduction of Ni^{+3} to Ni^{+2}

After leaching experiments, metal ions recovery process was started. Nickel was recovered through reduction of Ni^{+3} to Ni^{+2} process since the salt of Ni^{+3} is not stable and prone to be hydrolyzed easily ultimately affecting purity of the recycled products. Therefore, to get the high purity of recovered metal, Ni^{+3} ions were reduced to Ni^{+2} so that stable salt ($NiSO_4$) of bivalent nickel metal ions could be achieved. Reduction of nickel ions was studied within temperature range 120-200 ºC in oxygen deficient environment. It was observed that increase in temperature increased reduction efficiency of nickel. Highest reduction efficiency was achieved at 160 ºC in 3.0 hrs (Table-2).

Table-2: Reduction efficiency of nickel on varying conditions of temperature and time.

Time (hr)	Efficiency (%)	Temperature (ºC)	Efficiency (%)
2.0	**84.3**	**120**	**77.5**
2.5	**91.6**	**130**	**80.7**
3.0	**98.2**	**140**	**85.3**
3.5	**96.4**	**150**	**91.1**
4.0	**95.1**	**160**	**98.4**
4.5	**90.7**	**200**	**89.0**

Ion Exchange Separation of Cd^{+2}

Separation of cadmium ions from nickel was performed by selective ion exchange process using laboratory designed resin column. Adsorption performance of the resin was evaluated by drawing adsorption or loading curve. The breakthrough curves were obtained by plotting C/Co versus bed volume as described in the experimental part of the study (Fig. 5). These curves described breakthrough profile of cadmium at different flow rates. Relatively lower flow rate with increased contact time between metal ions and resin favored the metal sorption rate. Data presented a sharp increase in the sorption of metal ions that indicated a high affinity of the resin with metal ions (Fig. 5). About 99% of cadmium was trapped by the resin at flow rate of 2.0 mL/min and 3.0 BV.

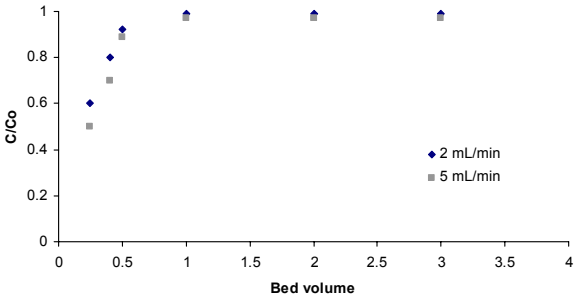

Fig 5: Breakthrough curve of Cd^{+2} sorption at different flow rate.

After sorption of Cd^{+2} metal is achieved, rest of the leaching solution contained nickel sulfate was concentrated by heating around 100 ºC until appearance of nuclei crystals of nickel sulfate. Finally the mixture was cool down until 30 ºC to get green crystals of $NiSO_4.7H_2O$.

Regeneration of Resin

As sorption experiments were completed, regeneration of the resin was conducted to get cadmium metal. Two parameters were taken into consideration while doing regeneration of the resin; one was the concentration of the reagent used for regeneration and second was flow rate of the

regeneration solution through the column. Sulfuric acid of 2.0 M strength was pumped to the bottom of the column at flow rate of 0.5 mL/min that would be in accordance with the volume of resin. It was found that the regeneration rate reached 90% at the bed volume equal to 2.0 (Fig. 6). Also after 3.0 BV, almost all of the cadmium in the form of cadmium sulfate was regenerated from the resin. Solution of cadmium sulfate was concentrated and crystallized at the temperature below 45 ºC to get crystals of $CdSO_4$. $8/3H_2O$.

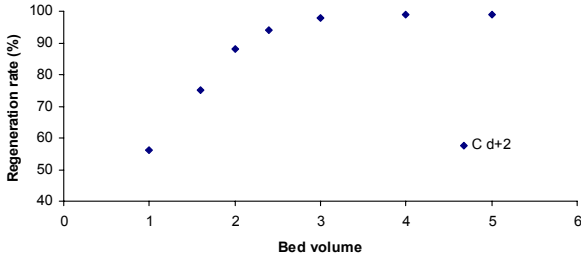

Fig. 6: Breakthrough curve of Cd^{+2} regeneration.

Experimental

Primary Treatment

Spent NiCd batteries of mean weight 25 g (AA-size) supplied by Panasonic were chosen for this study (Table-3). The batteries were first milled in a shredder and iron contents were removed by magnetic separator. Paper, plastics and other non-ferrous metals were screened out and the dismantled materials were washed thoroughly with distilled water and then dried overnight around 100 ºC**.** The material was next ground to particle size 100-200 µm. A schematic diagram showing recovery of metal right from primary treatment of batteries until regeneration of the resin is given in Fig. 7.

Table-3: Component analysis of AA-size NiCd battery.

Component	Mass (g)	Weight (%)
Positive $NiOH_2$	7.33	31.36
Negative $CdOH_2$	8.42	35.97
Separator (PE/PP)*	1.25	5.36
Can (Stainless steel)	4.66	19.91
Cap	0.98	4.22
Residue	0.75	3.19
Total	23.40	100

*Poly ethylene/Poly propylene

Ion Exchange Resin

Commercially available chelating ion-exchange resins with aminophosphonate functional groups Purolite S 950 was used in this study. It has been found that aminophosphonate resin is highly selective for Cd^{+2} where as Ni^{+2} sorption is negligible. Physical and chemical properties of the resin are listed in Table-4. The following series of selectivity can be deduced:

S 950: $H^+ > Cu^{2+} > Zn^{2+} > Cd^{2+} > Ca^{2+} > Co^{2+} > Ni^{2+} > Na^+$



Fig. 7: Schematic diagram of recovery of metal ions.

Table-4: Physical and chemical characteristics of Purolite S 950 resin.

Characteristics	Description
Matrix	Polystyrene/DVB, macro porous
Particle density, g/cm^3	1.11
Functional group	aminothiophosphonate
Bed density, g/L	710-745
Exchange capacity, eq./kg of wet resin	2.4
Moisture contents, %	61
Particle size, mm	0.42-1.2
pH range	2.0-11

Adsorption of cadmium was done in a laboratory designed ion exchange column. Prior to its use, the resin was washed with NaOH 1.0 M, HCl 1.0 M, and n-hexane in sequence to remove possible organic and inorganic impurities. The resin was then washed with deionized water (Millipor Milli-Q) three times and dried in an oven at 50 ºC overnight. The operation was performed at down stream flow using a peristaltic pump. The resin of volume 70 cm^3 (10 cm height) was packed into a fiberglass cylindrical column having dimensions 15×3 cm. Feeding flow rate varied at 2-5 mL/min and the process was operated at room temperature and pH~4. The empty bed contact time can be calculated as:

$$EBCT = VR/QF$$

where VR is the resin volume while QF denoted the flow rate at the bed.

Since resin volume and flow rate were measured at 70 cm^3 and 2-5 mL/min, EBCT was calculated as 35 and 14 minutes, respectively. The bed volume is defined as;

$$BV= VF/VR$$

whereas VF is the total feeding flow volume passed in the column during the adsorption process. Bed volume refers to the volume of the solution equivalent to the resin volume in space. Samples were taken at varying BV.

Leaching Experiments

Leaching experiments were carried out in a 1.0 dm^3 spherical flask, fitted with a water condenser to avoid evaporation when elevated temperatures were used. Flask was heated with digital temperature controlled heating mantle. Leaching tests were performed at varying solid/liquid ratio and a temperature ranges 60-110 ºC. Crushed waste material of the batteries was first cleaned thoroughly using distilled water and then dried. The material was next pulverized to particle size 100-200 µm ready for further leaching procedures. The ground particles of the materials were shaken with varying concentration of acid for 6.0 hours while heating. The leachate and insoluble materials were separated by filtration using 0.45 µm filter paper. Metal contents in the leacahate were determined by using atomic absorption spectrophotometer (Varian Specter AA-800, Japan).

Conclusions

Hydrometallurgical process designed on small scale can successfully be utilized for high recovery of metal ions from spent NiCd batteries recycling operations. Considering efficiency of the whole recovery process, H_2SO_4 2.0 M solution was suggested to be employed as leaching and regenerating reagent in the study. High temperature generally improved kinetics of leaching of metal ions, however, it made leaching process complicated affecting leaching efficiency of the system. Sorption of Cd^{+2} was optimized at a flow rate 2.0 mL/L and 3.0 BV. Concentration and flow rate of the regeneration reagent were found important parameters affecting regeneration capacity of the resin.

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