

# Recovery of Nickel Oxide from Primary-type Portable Spent Battery: an Experimental Strategy

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## Abstract

In the present work three methods were chosen for the recovery of NiO from primary-type spent battery. In first method, Ni(OH)<sub>2</sub> rich fraction of the precipitate was obtained at 7.4 pH after removing the precipitate obtained at pH 4. Second method followed the path of acid (HCl) leached solution treated with sodium hydroxide and thus obtained metal hydroxides which were treated with ammonia solution. Ni(OH)<sub>2</sub> solid obtained after evaporation of [Ni(NH<sub>3</sub>)](OH)<sub>2</sub> complex solution was calcinated at 1000°C to get NiO. The method followed the path of acid (HCl) leached solution treated with ammonia solution. Thus obtained [Ni(NH<sub>3</sub>)](OH)<sub>2</sub> complex solution was evaporated till the blue color vanished and then treated with NaOH up to pH 12. The Ni(OH)<sub>2</sub> solid after filtration and some more Ni(OH)<sub>2</sub> after further heating of liquid solution were dried in oven and then calcinated at 1000°C. Variations of initial amount of battery waste and NH<sub>3</sub> concentration were made in order to confirm the degree of efficiency. Third method was found superior in terms of recovery efficiency while second method was better in term of finer and smaller NiO particles.

**Key words:** efficiency; NiO recovery; pH controlled precipitation; spent battery

## Introduction

Batteries are essential parts of human life as these supply energy to many kinds of portable electric and electronic devices such as telephones, radios, compact disk players, computers, cordless tools, flashlights and even electric and hybrid cars. The wide range of applications of batteries results the production of several billions of batteries each and every year which is increasing day by day. This brings a new problem: what to do with billions of used batteries worldwide containing millions of tons of toxic and hazardous compounds.

In general, the batteries are of two categories: primary-for replacement after discharge and secondary- lasting for often many hundreds of charging–discharging cycles. From an environmental preservation point of view, secondary batteries are preferable over primary as it is connected with the possibility of long time use

of the same electrode materials in contrast with primary cells, where after discharge electrode materials are irreversibly converted into products. Other batteries classification splits them according to their four major markets: primary, starting lightning and ignition (SLI), industrial rechargeable and portable rechargeable.

Regardless of classification, the most popular types of batteries (zinc–manganese dioxide, nickel–cadmium, lead–acid) contain hazardous elements such as Hg, Cd, Pb, Ni, *etc.*, which can leach out from the waste to the landfill base if improperly disposed (Pistoia *et al.* 2001, Linden & Reddy 2002). Now-a-days, only automotive-sized lead–acid and industrial lead–acid and nickel–cadmium types are systematically collected for recycling (Rogulski & Czerwiński 2006). Smaller, portable batteries are disposed in municipal solid waste (MSW). The same happens also in the developing

countries, where regulations for production, collection, utilization and recycling of batteries were often introduced but are not kept in function. A small environmental education level of the societies and resulting insufficient budget spending on environmental protection can explain this situation.

Several methods have been reported for the recovery of valuable metal from spent battery. Ni and Cadmium had recovered from spent Ni-Cd portable battery hydrometallurgically (Rudnik & Nikiel 2007). In their original experiment, sulphate solution of electrode material was subjected to electrolysis. Cd and Fe ions were separated using NaOH solutions at pH 1 and 3 respectively. Finally with the use of  $\text{NH}_3$  solution at pH 9, Ni component was recovered. The recovery of Ni component from spent Ni-metal hydride (hereafter, Ni-MH) battery was reported by leaching the electrode material in sulphuric acid followed by ammonia solution and thereby the use of dimethylglyoxime to precipitate Ni component as nickel dioxime (Rabah *et al.* 2008). This precipitate was then either calcinated to get NiO or acid treated and crystallized to get pure Ni salt. The recovery of Ni component from spent Ni-MH battery by applying solvent extraction technique using phosphorus based extractants such as TOPS 99, Cyanex 923, Cyanex 272, Cyanex 302 and Cyanex 301 diluted in kerosene from sulphate leached solution of electrode material was also reported (Reddy *et al.* 2006).

The recovery of Ni component from secondary-type spent Ni-MH battery using HCl leaching of the electrode material and precipitation of metal hydroxide by NaOH solution at pH 12 was reported (Kanamori *et al.* 2006). Those solid dry metal hydroxides were then treated with ammonia solution to get hexa-ammonia nickel complex. Finally, NiO was obtained with heat treatment of liquid solution followed by calcinations of nickel hydroxide. A little modification on above experimental procedure was reported where after acid leaching of electrode materials, the ammonia treatment was performed instead of NaOH treatment for better efficiency (Hayashi *et al.* 2007).

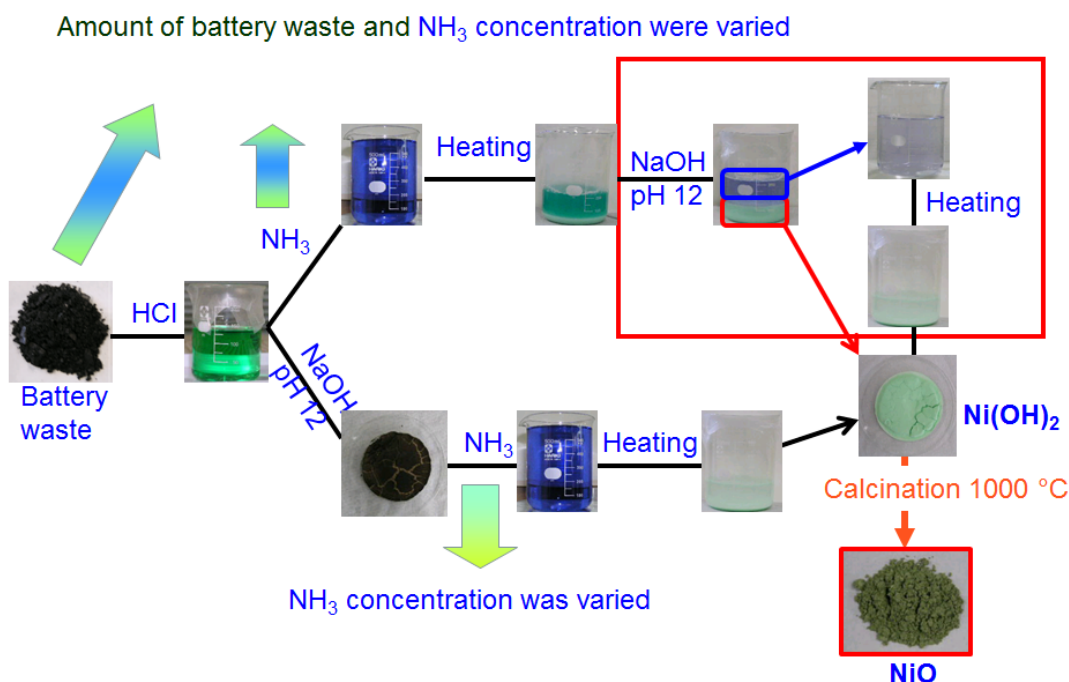
There may be several other experimental procedures for the recovery of nickel components from spent battery but our present target is not to go for the overview study of metal recovery processes.

Recovery of valuable materials from any product after it served its purpose is highly desirable at present time due to the environmental concern and productivity. But we can see several used products in our vicinity as waste though it can be further utilized. There are several reasons for such non-utilization. In this report, we have focused our attention on four major facts regarding the recovery of valuable metals from small portable spent-batteries, *namely*, procedure, efficiency, cost and purity of the recovered output.

### Methodology

Panasonic brand (ZR6, XJ) primary-type spent Zn-Mn/Ni oxide AA-size batteries (with 51 mm in length, 14 mm in diameter and a mean weight of 23 g) were used in the experiments. The batteries were dismantled into the separate components of the cell. The zinc case was opened manually and the rolled electrodes with the polymeric separators and the active cell material were extracted carefully. Finally the anode materials (hereafter battery waste, BW) were collected for the recovery of nickel component. An average of 11.5 g BW was recovered from a spent battery. The schematic diagram of the experimentation is shown in Fig. 1. Three separate processes were adopted for the recovery of NiO from BW and are as follows:

- a. In first method, the BW was leached with HCl solution using 10 g BW in 200 ml 2 M aqueous solution stirred for 24 h at room temperature. The solution was finally filtered. The acidic filtered solution was titrated with NaOH solution and the change of pH was monitored. The precipitates were separated at various pH values and dried at 50°C overnight and then collected for characterization with XRD patterns. With varying pH during the titration, precipitate with the majority of  $\text{Ni}(\text{OH})_2$  component observed in XRD pattern was kept in oven at 110°C for whole night and then subjected to calcinations at 1000°C for conversion of  $\text{Ni}(\text{OH})_2$  to NiO. Thus obtained sample was analyzed further.
- b. In second method (hereafter, BW-HCl-NaOH- $\text{NH}_3$ ), the acid leached BW solution was titrated with 2 M NaOH solution until the pH of the solution reached to 12. The precipitate was separated out by filtration. Finally, Ni component was extracted from this precipitate using  $\text{NH}_3$  solution with air bubbling. During this method, two parameters were varied: the amount of BW was varied in between 2.5 to 10.0 g per 200 ml 2 M



**Fig. 1.** Experimental diagram of recovery of NiO from primary-type spent battery waste.

HCl solution while the concentration of  $\text{NH}_3$  solution was set fixed at 5 M and 450 ml. In the second step, the concentration of  $\text{NH}_3$  solution was varied in between 2 to 10 M (the volume was as before 450 ml) while the amount of BW was set fixed at 10.0 g. The filtered liquid solution was heated around  $80^\circ\text{C}$  to decompose the Ni-ammonium complex into  $\text{Ni}(\text{OH})_2$ . The NiO was obtained by calcination of the resulting  $\text{Ni}(\text{OH})_2$  at  $1000^\circ\text{C}$ .

- c. In third method (hereafter,  $\text{BW}_{\text{HCl-NH}_3\text{-NaOH}}$ ), BW was leached using HCl solution (as in the case of a) followed by treatment with  $\text{NH}_3$  solution with air bubbling. The Ni component of BW was converted to Ni-ammonium complex in liquid phase while rest parts were precipitated as metal hydroxides. The filtered liquid solution was heated at around  $80^\circ\text{C}$  for 6 hours. A whitish-green precipitate ( $\text{Ni}(\text{OH})_2$ ) along with green solution was obtained. The precipitate was collected after filtration and washing with distilled water. The liquid solution was treated with 2 M NaOH solution until the pH value reached to 12. The liquid sample was again heated at around  $80^\circ\text{C}$  and the solid sample ( $\text{Ni}(\text{OH})_2$ ) was collected as

above procedure. In this method also, two parameters *namely*, amount of BW and concentration of  $\text{NH}_3$  solution with fixed volume of 450 ml, were varied (as in b). The NiO was obtained by calcination of the resulting  $\text{Ni}(\text{OH})_2$  at  $1000^\circ\text{C}$ .

The phase characterization studies of obtained samples were carried out using a X-ray diffractometer (RINT2100/PC, Rigaku Japan) with monochromated  $\text{CuK}\alpha$  radiation and the chemical compositions of some selected samples were analyzed by X-ray fluorescence (ZSX-100s, Rigaku Japan).

## Results and Discussion

### Chemical Compositions of BW and acid leached residue

The chemical composition of BW and the residue left after acid treatment were obtained from XRF measurement and shown in Table 1. An average of 7.7% moisture and other water content were evaluated with the loss of mass after drying at  $150^\circ\text{C}$  for 24 h in oven. The presence of carbon/graphite was confirmed from the XRD pattern of the acid leached residue and its composition was evaluated from loss of ignition (LOI) of BW at  $700^\circ\text{C}$  in air. 32 % of the BW was found

unleached during HCl treatment and the unleached solid residue was rich in MnO with almost absence of NiO, ZnO and K<sub>2</sub>O indicating 2M HCl concentration and 24 h stirring time at room temperature are sufficient for leaching of target Ni ion in solution phase.

**Table 1.** Chemical composition (mass%) of battery waste (BW) and acid leached residue

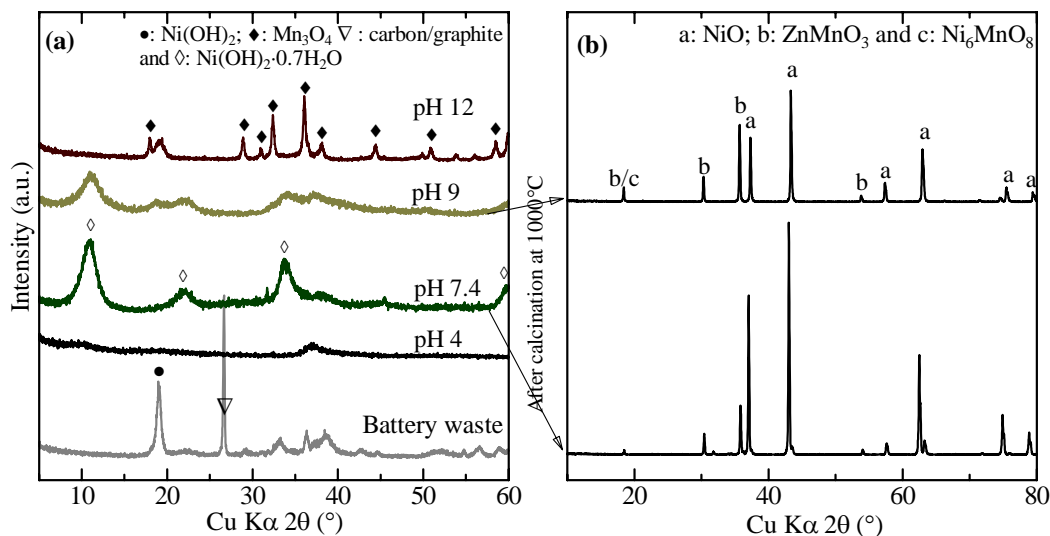
Component	Battery Waste	HCl-leached residue
MnO	32.6	67.2
NiO	35.3	0.14
ZnO	7.1	0.10
K <sub>2</sub> O	3.6	0.06
Others	0.8	—
LOM (moisture)	7.7	2.7
LOI (≅ Carbon)	12.9	29.3

**The pH controlled precipitation**

Metal hydroxides are ‘water-loving’ and amphoteric, *i.e.*, they are increasingly soluble at both low and high pH the optimum pH for precipitation occurs at a different pH value for different metal. The common and simple method to remove soluble metal ions from acidic solution is to precipitate the ion as a metal hydroxide. The process is readily controlled by pH. By raising the pH value of a solution with a common alkali solution, such as sodium, potassium or calcium hydroxide, the corresponding metallic hydroxide compounds become insoluble and precipitate from solution. Hence, it is clear from the above facts that

the solid metal hydroxide (rich in Ni(OH)<sub>2</sub>) recovered from BW with controlled pH precipitation cannot be evaluated in terms of quantitative efficiency and purity but the major target of the work at this point was to find the optimum condition of pH adjustment with sodium hydroxide solution to get Ni rich metal hydroxide from BW.

The precipitates from acidic solution of BW were obtained at various pH values such as 2, 4, 5, 6, 7, 7.4, 8, 9, 10 and 12. The oven dried precipitates were then subjected to XRD analysis. The XRD patterns of the oven dried precipitates obtained at pH values of 4, 7.4, 9 and 12 along with the calcined products of precipitates of pH values 7.4 and 9 are shown in Fig. 1. It was observed that there was almost absence of Ni(OH)<sub>2</sub> in precipitates obtained at pH below 4 and above 10. The calcined samples of the precipitates obtained at pH values of 7.4 and 9 have shown the presence of three phases like NiO, ZnMnO<sub>3</sub> and Ni<sub>6</sub>MnO<sub>8</sub>. Furthermore, the NiO peaks of the XRD patterns observed for the sample obtained from the calcination of the precipitate of pH 7.4 are stronger than those of the sample obtained from the calcination of the precipitate of pH 9 while ZnMnO<sub>3</sub> peaks are stronger in later case. Hence, at this point it can be said that Ni(OH)<sub>2</sub> rich fraction of the precipitate can be obtained at 7.4 pH after removing the precipitate obtained at pH 4 but due to the amphoteric nature of the metal hydroxides it is impossible to obtain pure Ni(OH)<sub>2</sub> just by controlling the pH for precipitation.



**Fig. 2.** The XRD patterns of (a) the oven dried precipitates obtained at pH values of 4, 7.4, 9 and 12 (b) the calcined products of precipitates of pHs 7.4 and 9.

**NiO recovery from metal hydroxides precipitate**

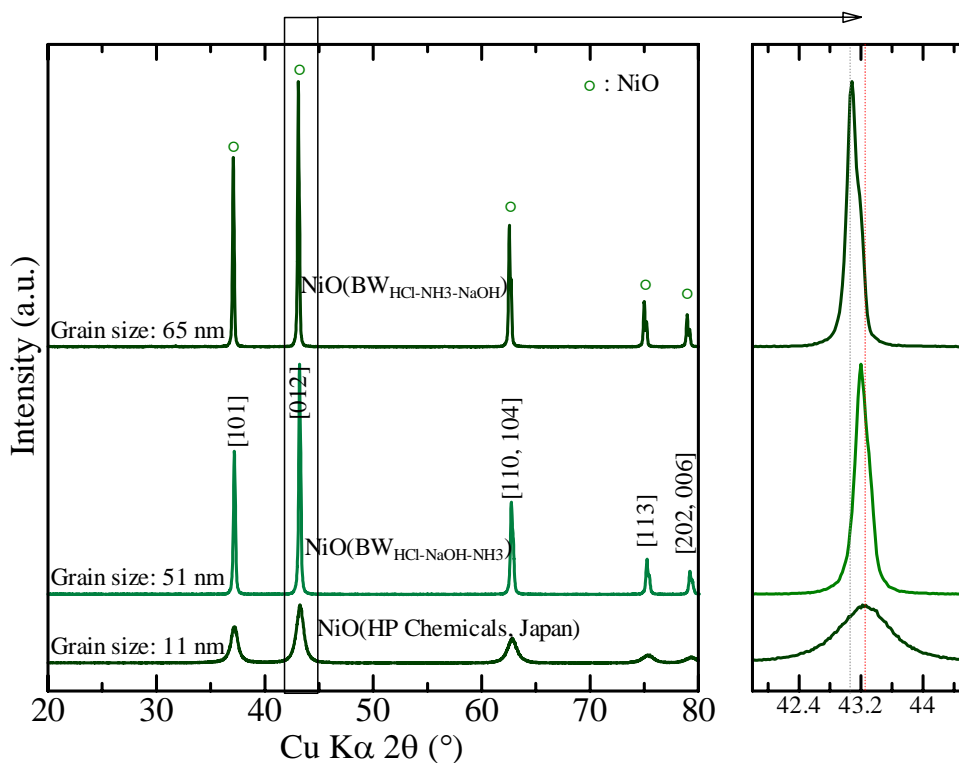
All metals form complexes, although the extent of formation and nature of these depend very largely on the electronic structure of the metal. The concept of a metal complex originated in the work of Alfred Werner (awarded the first Nobel Prize in Inorganic Chemistry in 1913).

The major metal ions of BW are  $Mn^{2+}$ ,  $Ni^{2+}$ ,  $Zn^{2+}$  together with  $K_2O$  and graphite (can be separated as unleached fraction by acid leaching of BW). Most of the  $Zn^{2+}$  contents in BW came from positive terminal, outer metal casing and metal grid of the battery which were manually separated. The reaction between metal ion solution and the alkali metal hydroxide results in the precipitation of the metal hydroxide. The  $Ni(OH)_2$  is readily soluble in aqueous solution of ammonia by forming hexa-ammonium nickel hydroxide complex while such a reaction does not occur with manganese hydroxide and thus remains in solution as solid

precipitate. When the nickel-ammonium complex reacts with the alkali metal hydroxide, nickel hydroxide precipitate is grown.

**Selection of appropriate procedure**

NiO obtained in the present work with two different approaches, namely,  $BW_{HCl-NaOH-NH_3}$  and  $BW_{HCl-NH_3-NaOH}$ . NiO of 0.09 and 0.293 g/g BW were obtained in these two different methods respectively when same initial amount of BW and  $NH_3$  concentration were used. This clearly indicates the superiority of third method in terms of NiO recovery efficiency. The XRD patterns of these two types of NiO along with supplied fine NiO particles (HP Chemicals, Japan) are shown in Fig. 3. The primary information we get from the XRD pattern is the size of NiO particles (by using Scherrer's equation). The NiO obtained from second method was found smaller than that of third method. This was even observed by physical nature in terms of smoothness and volume occupied.

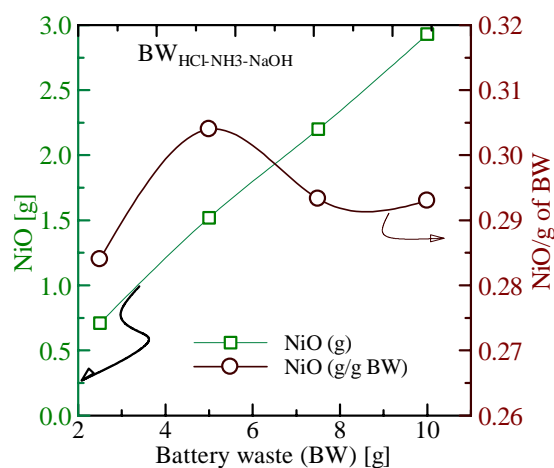


**Fig. 3.** XRD patterns of two types of NiO recovered from present work together with commercial fine NiO particles (HP Chemicals, Japan)

The efficiency and particle size phenomena can be explained on the basis that in the second method basic sample (metal hydroxide) is reacted with basic solution while in third method a strong acidic solution is reacted with basic solution. The reaction of basic sample with basic solution cannot be as fast and efficient as that of acid-base reaction. The possibility of the existence of equilibrium between  $\text{Ni}(\text{OH})_2$  and  $[\text{Ni}(\text{NH}_3)_6](\text{OH})_2$  may be the reason for not converting all the  $\text{Ni}(\text{OH})_2$  to  $[\text{Ni}(\text{NH}_3)_6](\text{OH})_2$  complex and thereby the efficiency is lowered. Furthermore, the slow reaction may be the reason for smaller size of particles in the case of first method (*slower the reaction, finer the particles*).

### Amount of NiO recovery

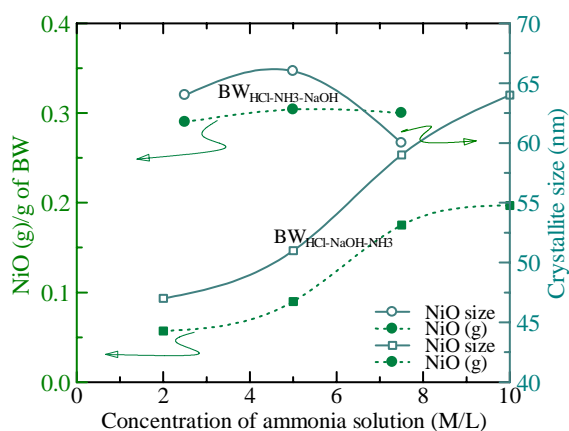
After confirming the superiority in percentage efficiency of NiO recovery in third experimental setup ( $\text{BW}_{\text{HCl-NH}_3\text{-NaOH}}$  method), the initial amount of BW was varied in order to obtain final NiO product while other parameters (concentration of  $\text{NH}_3$ , time and temperature) were made constant. The plots of the recovered NiO in grams as well as per gram of BW as a function of initial amount of BW are shown in Fig. 4. The recovery of NiO was found linearly increasing with the initial amount of BW, which is the normal trend of recovery progress, but the important point to be focused is the efficiency in terms of per gram of BW. The maximum recovery of NiO per gram of BW (0.304 g) was obtained with 5.0 g of BW. Hence, this amount of BW was taken as suitable amount to process for another experimental setup.



**Fig. 4.** NiO recovery as a function of initial amount of battery waste

### The role of $\text{NH}_3$ concentration

The plots of NiO obtained per gram of BW and crystallite size as a function of  $\text{NH}_3$  concentration for NiO recovered from  $\text{BW}_{\text{HCl-NaOH-NH}_3}$  and  $\text{BW}_{\text{HCl-NH}_3\text{-NaOH}}$  methods are shown in Fig. 5. In case of  $\text{BW}_{\text{HCl-NaOH-NH}_3}$  method, NiO recovered amount was found increasing with increasing  $\text{NH}_3$  concentration while in case of  $\text{BW}_{\text{HCl-NH}_3\text{-NaOH}}$  method it was initially increased in going from 2.5 M to 5.0 M  $\text{NH}_3$  concentration. With further increase of  $\text{NH}_3$  concentration the amount of recovered NiO became almost constant.



**Fig. 5.** NiO recovery per g of BW and crystallite size as a function of  $\text{NH}_3$  concentration

This behavior can again be explained on the basis of equilibrium between  $\text{Ni}(\text{OH})_2$  and  $[\text{Ni}(\text{NH}_3)_6](\text{OH})_2$ . The increase of  $\text{NH}_3$  concentration makes the shifting of the equilibrium towards  $[\text{Ni}(\text{NH}_3)_6](\text{OH})_2$  complex and NiO recovery increases. By contrast, there is no such existence of equilibrium in  $\text{BW}_{\text{HCl-NH}_3\text{-NaOH}}$  method and hence NiO recovery is almost constant with increasing  $\text{NH}_3$  concentration higher than 5.0 M. Furthermore, the crystallite size of NiO obtained from  $\text{BW}_{\text{HCl-NaOH-NH}_3}$  method was found increasing with the increase of  $\text{NH}_3$  concentration.

### Modification on existing procedure

In process of Ni component recovery from spent battery, initially the method of acid leached solution treated with sodium hydroxide followed by  $\text{NH}_3$  solution and finally on evaporating and calcinations of  $\text{Ni}(\text{OH})_2$  was undertaken. In course of time, a modification was done by removing sodium hydroxide treatment step for better efficiency. But in that modified step the formation of hexaaquanickel chloride was ignored. A slight modification in between the

evaporation of  $[\text{Ni}(\text{NH}_3)_6](\text{OH})_2$  complex and  $\text{Ni}(\text{OH})_2$  precipitation can enhance the efficiency of NiO recovery. The proposed modification is shown under the rectangle of Fig. 1 and the mechanisms of reactions are shown in following equations:

In this work, electrodes from spent Zn-Mn/Ni oxide AA-size batteries were leached in 2M hydrochloric acid solution. Selective precipitation tests were done aiming at recovering of nickel oxide as well as to get rid of the impurities present in the leached solution. The results demonstrated the technical feasibility for nickel oxide recovery by precipitation in 7.4 pH after removing the precipitate obtained at pH 4.

The third method of NiO recovery process was found more appropriate in term of NiO recovery efficiency while the second method was appropriate in term of qualitative output. These results are compatible with the results found in the literature if solvent extraction was employed. Furthermore, the proposed process, besides of being easier to handle, is more economical and does not present the environmental risks like the solvent extraction.

### Acknowledgements

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