Mansoura Journal of Chemistry Vol. 38 (1), June, 2011.

RECOVERY OF LANTHANIDES AND NICKEL FROM SCRAP NICKEL-METAL HYDRIDE RECHARGEABL BATTREIES

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(Received:3/ 7/ 2010)

ABSTRACT

An attempt has been developed to recover the metal values such as: nickel and lanthanides from the scrap nickel-metal hydride (Ni-MH) rechargeable batteries. The chemical analysis of scrap Ni-MH batteries revealed the presence of 65% Ni, 10% Co and 15% lanthanides, beside considerable concentrations of Mn, Al, and Zn. On the other hand, the internal paste of Ni-MH scrap batteries was easily leached. The optimum leaching conditions were 3M H_2SO_4, solid/liquid (S/L) ratio 1/3 and leaching time 2hours at 90°C. The chemical analysis of the prepared sulfate leach liquor revealed the presence of 9.36g/l Ni and 2.09g/l lanthanides with leaching efficiencies 96% and 93.5%, respectively.

Direct precipitation technique was performed to separate lanthanides and Ni from the prepared sulfate leach liquor using 20% oxalic acid at pH 3 and 10% NaOH at pH 6.5, respectively. The recovery of lanthanides and Ni achieved 97% and 85% with purity 98% and 97%, respectively.

INTRODUCTION

The importance of lanthanides in the nuclear field that, they are characterized by their ability to absorb thermal neutrons during the chain reactions inside nuclear reactors. Thus, they are utilized in the manufacturing of control rods used for controlling the continuous chain reactions, **El Hazek, (1991)**. Thus, it was necessary to find out new lanthanide resources or try to recycle them from their enriched wastes especially from the waste batteries. In the last decades, the production of electronic equipments such as computers, cell phones and consequently batteries has increased dramatically. Rapid technological development has reduced the useful life of the electronic equipment in each new generation. Concerning batteries consumption, it was estimated that 3 billion batteries are commercialized per year only in the USA. This represents an amount of US $2.5 billions. In Europe 5 billion batteries were produced in the 2000 only, **Bernardes *et al*., (2004)**. Moreover, **Zhang *et al*., (1999)** has been reported that, the production rate of Ni-MH batteries has been increased from 200 million in 1994 to 650 million in 1997.

According to, **[Rydh *et al.,* (2003)]** another important factor in relation to the amount of spent batteries is that the consumers change their cell phones often before finishing their useful life. This happens due to the continued introduction of new technologies. Each new cell phone generation presents advantages in weight and size reduction, with different accessories as radios, cameras, etc. Thus, very large numbers of batteries are discharged before ending their useful life. In 1992 Ni-Cd batteries were responsible for almost 100% of the world market of portable rechargeable batteries, but in 1999 they represented only 49%. In this same period Ni-MH batteries, which had an insignificant participation in the market in the year 1992, already represented around 43% of the world market. The Ni-Cd batteries substitution happened because the Ni-MH batteries present a better performance, e.g., larger energy density and an absence of memory effect. Another important factor for the substitution of the Ni-Cd batteries is due to Cd toxicity,

In addition, the growing concern about the environment, associated with the continuous increase in the production of electronic equipment, such as computers, cell phones, mobile devices and consequently batteries, has induced research to develop new technologies to recycle the huge numbers of spent batteries generated in the last few years. The amount of spent Ni-MH batteries will tend to grow continually over the next few years. These batteries have in their chemical composition, valuable metals such as Ni, Co and rare earths,[**Bertuol *et al.,* (2006)**.]

[Zhang *et al.,* (1998)] reported that, Ni-MH batteries have sealed to prevent the leakage of electrolytic solution and the generated gas during charging. The positive electrodes are constructed of a porous Ni plate with $Ni(OH)_2$ as activating agent. While the negative electrodes are constructed mainly of hydrogen storage metals such as Ni, Co and some light lanthanides e.g. La, Nd, Pr, Eu and Sm. Thus, the recycling of spent Ni-Cd and Ni-MH batteries has become an urgent matter from the viewpoint of environmental protection and resource conservation. The chemical reactions of the two electrodes can be expressed by the following equations.

The cathodic reaction:

$$M + H_2O + e \longrightarrow MH + (OH)^- \qquad (1)$$

The anodic reaction:

$$Ni(OH)_2 + (OH)^- \longrightarrow Ni(OH)_2 + H_2O + e \qquad (2)$$

The overall reaction:

$$Ni(OH)_2 + M \rightleftarrows Ni(OH)_2 + MH \qquad (3)$$

Where the forward direction is the charge reaction and the reverse is the discharge reaction. M represents the alloy to be hydrided.

Moreover, **[Zhang *et al.,* (1999** used 2M H_2SO_4 at 95 °C to dissolve (g l^{-}), 10.6 Ni, 0.85 Co, 1.70 Fe, 0.36 Zn, 0.21 Al, 0.54 Mn,1.73 La, 0.10 Ce, 0.33 Pr, 1.10 Nd and 0.032 Sm from Ni–MH batteries. The rare earths are recovered from the liquor by means of a solvent extraction circuit with 25% D2EHPA in kerosene, followed by precipitation with oxalic acid. A mixed rare earth oxide of about 99.8% purity is obtained after calcinations of the precipitate. The total yield of rare earths approaches 93.6%. The cobalt and nickel in the raffinate are effectively separated by solvent extraction with 20% bis_2,4,4-tri-methyl-penthylphosphinic acid Cyanex 272 in kerosene. The individual cobalt and nickel are then recovered as oxalates by the addition of oxalic acid. Cobalt and nickel oxalates with purities close to 99.6% and 99.8%, respectively, are obtained.

[Nan *et al.*, (2006)] recovered exceeded 94% for all metal values such as Ni, Co and total REEs from sulfate leach liquor of Ni-MH batteries. Lanthanides were precipitated as Na-double sulfate; Cu was extracted as $CuSO_4$ with 10 % aqua regia M5640 at pH 1.5–1.7, Co and Ni were extracted as their sulfates with 1 M Cyanex 272 at pH 5.1. Also, **[El-Sheikh and Abd El Wahab, (2009)]** recovered 99% of Cd and 96% of Ni from Ni-Cd batteries by precipitation from sulfate leach liquor.

Finally, this work plays a vital role in the protection of the environment and finding out new industrial resources of lanthanides, Co and Ni.

EXPERIMENTAL

1. Materials:

In the present work, a scrap Ni-MH battery (VARTA, GERMANY) weighted 36.5g was used. After mechanical removing of the outer and inner steel covers, the net weight of the internal paste was 17.22g. The net weight of the positive electrode was 8.52g, while that of the negative electrode was 8.7g. A weight 1g of each electrode and also equal mixed electrodes were completely dissolved in 25ml aqua regia at room temperature for 15min and subjected to the complete chemical analysis.

2. Analysis:

The concentrations of various metal ions namely, Ni, Co, Zn, Al, Mn and Fe in the aqueous solutions were analyzed by using the flame atomic absorption spectroscopy (FAAS), Unicam 969, England at the portable wavelengths. While lanthanides were estimated using visible-ultra violet spectrophotometer (Shimadzu UV-160) using 0.015% Arsenazo III at λ 654nm using Ce as reference **[Marczenko, (1986)]**. The pH values of the aqueous solutions were adjusted with a pH meter (Digimed DM-21). On the other side, the final products were identified using SEM and XRD, PHLIPS.

3. Leaching and separation of lanthanides and Ni. :

The internal paste of Ni-MH batteries leached with 3M H_2SO_4 and lanthanides were directly precipitated from the sulfate leach liquor using $H_2C_2O_4$. While Ni was separated from the sulfate leach liquor free of lanthanides by precipitation using NaOH.

RESULTS AND DISCUSSIONS

1. Characterization of scrap Ni-MH battery:

The complete analyses of the internal paste of scrap Ni–MH batteries emphasized the presence of several metal values. These metal values were irregularly distributed between the two electrodes as given in **Table (1)**. On the other side, **[Pietrelli *et al.*, (2002)]** has published a study for the X-ray diffraction obtained from both the positive and the negative electrodes of internal paste of scrap Ni–MH as shown in **Figures (2)**, **(3)**. This study proved the presence of lanthanides on the negative electrode of these batteries.

Table (1): Chemical composition of internal paste of scrap Ni-MH batteries.

Element	**(-)electrode Wt., %**	**(+)electrode Wt., %**	**Mixed Wt., %**
Ni	48	82	65
Co	16.1	3.9	10
Mn	0.1	3.26	1.7
Al	1.6	0.17	0.85
Zn	0.85	0.45	0.65
lanthanides	15	nil	15
Fe	0.01	0.009	0.01

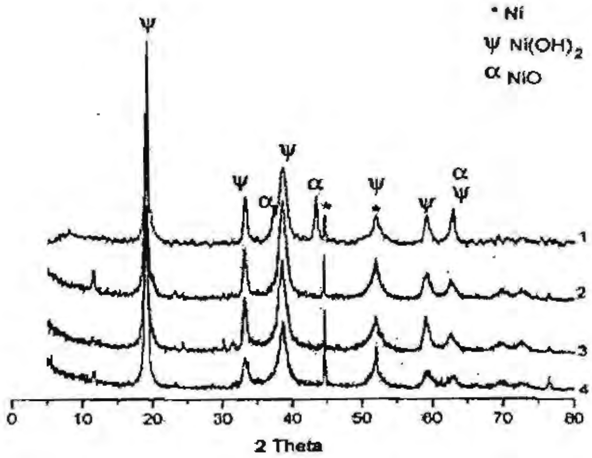

Fig. (2): X-ray pattern obtained from the positive electrode of scrap Ni-MH batteries, [(**Pietrelli *et al.*, 2002**)].

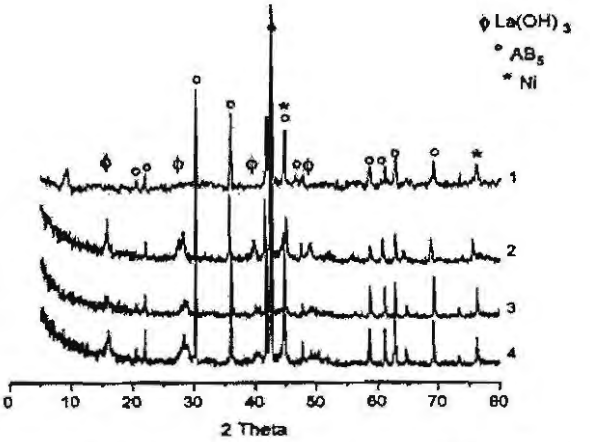

Fig. (3): X- ray pattern obtained from the negative electrode of scrap Ni-MH batteries, [**Pietrelli** ***et al.*****, 2002)**].

2. Leaching:

It was possible to leach a weight 15g of the internal paste of scrap Ni–MH battery with 45ml of $3MH_2SO_4$ at solid/liquid (S/L) ratio of 1/3, by stirring for 2h at 95°C. After washing with distilled H_2O and filtration, the total volume of the prepared sulfate leach liquor became 500ml. The maximum of metal values leached and brought out to the sulfate leach liquor. The resulted leach liquor was a dark blue solution of pH 0.8 and its chemical composition revealed the presence of the metals of interest as shown in Table (2). It is worthy to mention that, [**Bellomo, (2000)** and **Pietrelli** ***et al.*****, (2002)**] have leached the same type of these batteries at conditions closed to these conditions. Also, [**El-Sheikh, and Abdel Wahab, (2009)**] leached Ni-Cd scrap batteries which are the same as Ni-MH batteries at the previous conditions.

Table (2): Chemical composition of sulfate leach liquor of the scrap Ni-MH batteries.

Element	**Conc., g/l**	**Leaching efficiency, %**
Ni	9.36	96
Co	1.45	95
lanthanides	2.09	93
Mn	0.26	100
Al	0.13	100
Zn	0.12	100
Fe	0.005	55

2. Direct precipitation of lanthanides:

The prepared sulfate leach liquor was subjected to the precipitation of lanthanides as oxalates. For this purpose, the pH value of the leach liquor was adjusted up to pH 3 by using drops of 10% NaOH solution. After then the solution of 20% oxalic acid was added with continuous stirring at room temperature until the pH value was adjusted to 1.78 at which more than 97% of lanthanides were precipitated, [**Abd Ella, (2010)**]. It should be vastly filtrated the lanthanides cake to avoid the precipitation of both Ni and Co oxalates. After filtration and washing, the lanthanide oxalates calcinated at 900°C for 1h. The produced lanthanide oxides were washed with suitable amount of distilled H_2O before directed to identify using SEM as shown in **Figure (4).** The produced oxides have a purity reached 97% with traces of Ni, Ca and S includes maximum 3%.

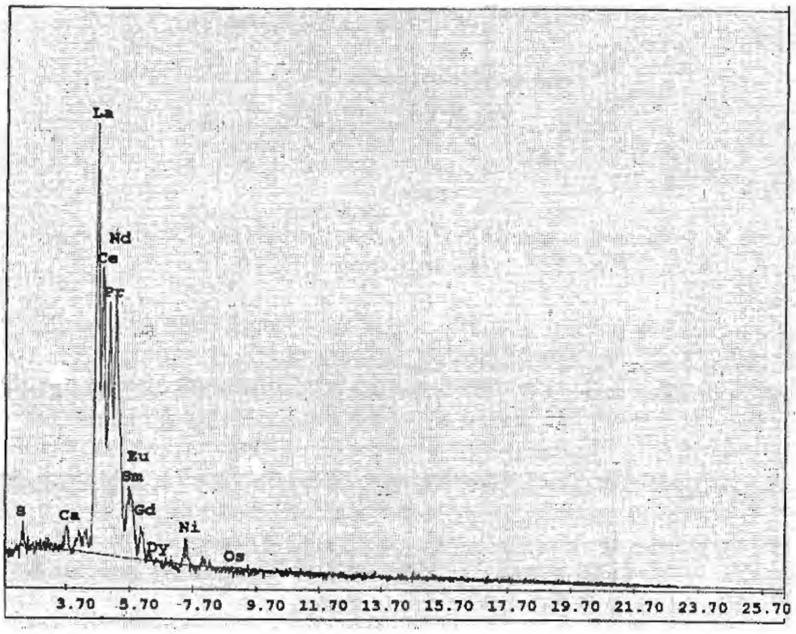

Fig. (4): SEM chart for the identification of lanthanides cake precipitated from sulfate leach of scrap Ni-MH batteries.

4. Direct precipitation of Ni:

Ni was directly precipitated from the sulfate leach liquor (600ml filtrate of pH1.74, free of lanthanides) and concentrated with 9.6 g/l Ni by the addition of 10% NaOH solution at room temperature. However, the precipitation of 85% Ni with low concentration of Co was achieved at pH 6.5 due to the high difference between their concentrations in the sulfate solution. After filtration, the precipitate $Ni(OH)_2$ was washed with distilled H_2O to get rid of any impurities and ignited at 850°C for 1h. A weight 10.4g of NiO was produced with recovery of Ni achieved 85% and purity reached 93.5% with other impurities such as: 3% Al, 0.25% Zn and 2.5% Co.

Purification of NiO:

The prepared NiO was purified by boiling with 4% NaOH solution; however both Zn and Al impurities were librated and brought out to the alkaline solution. The purity of NiO was raised up to 97%. In fact, the interfering problems of Co were overcome by the high dilution of solution. The produced NiO was identified by using XRD as shown in **Figure (5).**

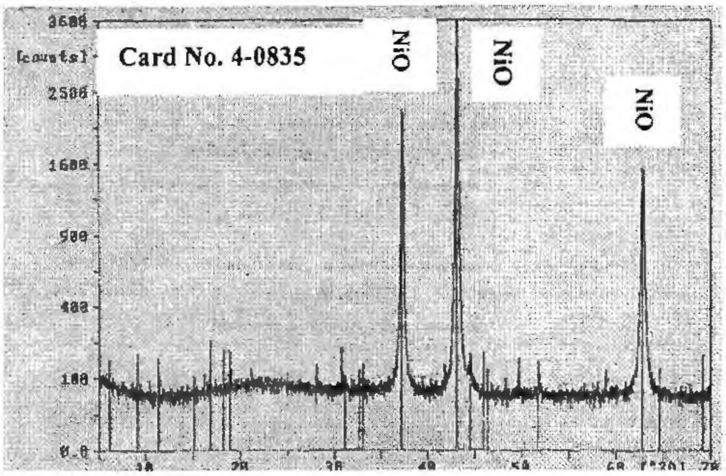

Fig. (5): XRD pattern for the identification of pure NiO precipitated from sulfate leach of scrap Ni-MH batteries.

CONCLUSIONS

1- Chemical analysis of the internal paste of the scarp Ni-MH batteries reveals the presence of 65% Ni, 15% REEs, and 10% Co as the metal values beside considerable concentrations of Al, Mn and Zn as well as traces of Fe.

2- Agitation leaching of Ni-MH scrap batteries with sulfuric acid was effective to dissolve Ni, REEs and Co with efficiencies 96, 93 and 95%, respectively. The performed optimum conditions were 3M H_2SO_4, S/L ratio 1/3, pH 0.8 and 2h leaching time at 95°C.

3- Separation of REEs was carried out from the sulfate leach liquor of scrap batteries by precipitation using 20% solution of $H_2C_2O_4$ at pH 3 to achieve REEs recovery of 93%.

4- The recovery of Ni as NiO achieved 85% with purity 97% using 10% NaOH solution at pH 6.5. The interference caused by Co in the precipitation of Ni was overcome by dilution of the sulfate solution due to its lower concentration compared to Ni.

5- Finally a tentative flowsheet for separating pure NiO and RE_2O_3 from the sulfate leach liquor of scrap Ni-MH batteries was designed.

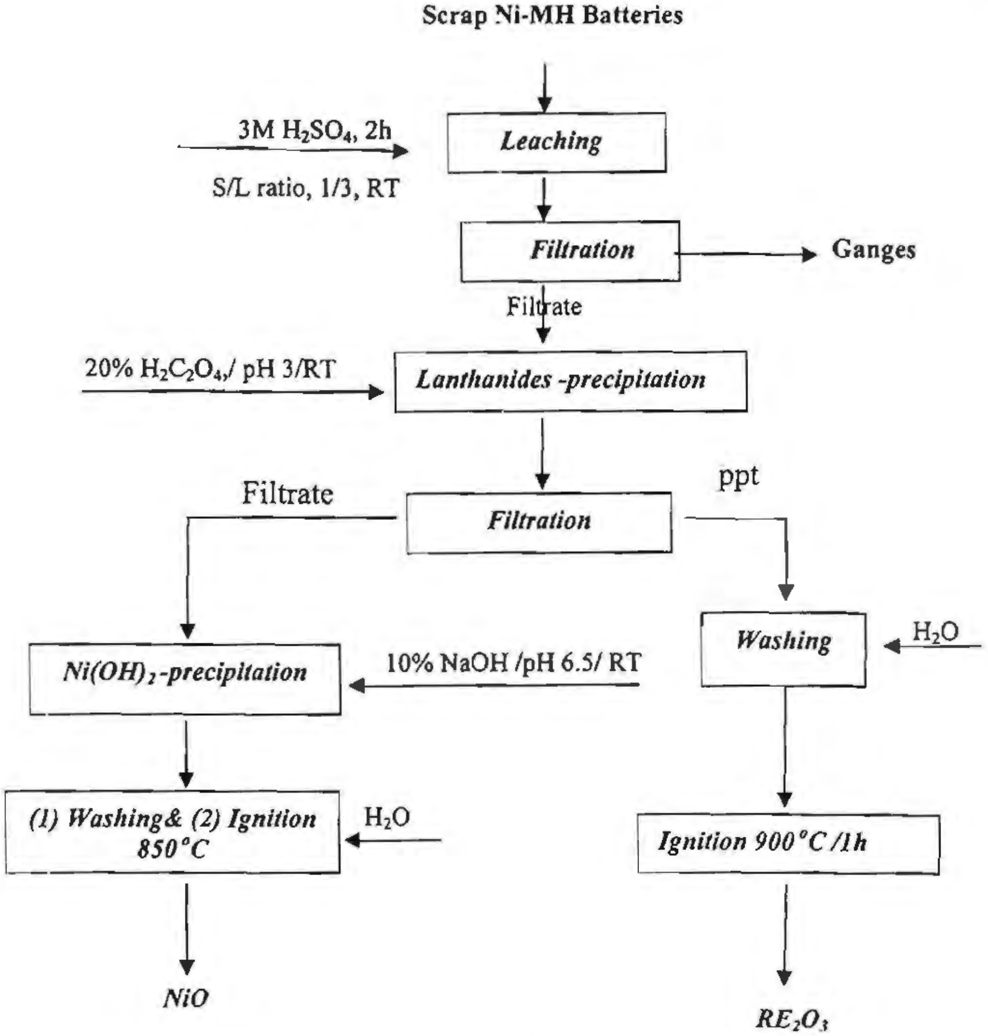

Fig. (6): A tentative flowsheet for separating pure RE_2O_3 and NiO from scarp Ni-MH batteries.

REFERENCES

Abd Ella, W. M. (2010), Master Thesis Faculty of Science, Chem., Depa., Ain Shams, Uni., Cairo, Egypt.

Bellomo, B. and Pietrelli. L. (2000). Graduation Thesis. Tutor Rome University.Frohlich, S., Sewing, D., 1995. The Batenus process for recy-cling mixed battery waste. Power Sources 57, 27– 30.

Bernardes, A.M. Espinosa, D.C.R. and Ten'orio J.A.S. (2004), J. Power Sources 130 pp. 291–298.

Bertuol , D. A., Bernardes A. M. and Ten'orio J. A. S. (2006) J., Power Sources, 160, pp 1465–1470.

El Hazek, N.T., (1991), "Internal Report", Nuclear Materials Authority, pp.61–63 .

El-Sheikh, E. M., and Abd El Wahab, G. M., (2009) 3rd int. conf. of Inorganic Chemical industries and mineral recourses research division, 1-2 Feb., 2009.

Marzenko, Z. (1986), Separation and Spectrophotometric Determination of Elements. Ellis Horwood, Chichester, England.

Nan, J. D. Han, Yang, M. Cui, M. and Hou, X. (2006), Hydrometallurgy, 84, pp.75–80.

Pietrelli, L. Bellomo, B., Fontana, D. and Montereali, M.R. (2002), Hydrometallurgy, 66, pp.135–139.

Rydh, C.J. and Sv¨ard, B. (2003) Sci. Total Environ., 302, pp.167–184.

Zhang, P. Yokoyama, T. Itabashi, O. Wakui Y. and Suzuki, M., (1998), Hydrometallurgy, 50, pp. 61–75.

Zhang, P. Yokoyama, T. Itabashi, O. Wakui Y. and Suzuki, M., (1999), Hydrometallurgy, 77, pp. 116–122.

الملخص العربى

استخلاص اللانثانيدات والنيكل من خردة بطاريات النيكل- هيدريد المعدن القابلة للشحن

جلال محمود عبدالوهاب - هيئة المواد النووية – القاهرة

هذه محاولة استخلاص المعادن ذات القيمة مثلااللانثانيدات والنيكل من خردة بطاريات النيكل- هيدروجين المعدن القابلة للشحن حيث اثبت التحليل الكيميائى ان هذة البطاريات تحتوى على ٦٥% نيكل و ١٠% كوبلت و ١٥% اللانثانيدات بجانب تركيزات محسوسة من المنجنيز و الالومنيوم و الزنك٠ من ناحية اخرى فان هذة البطاريات يسهل اذابتها باستخدام ٣مول من حامض الكبريتيك بنسبة خلط ١/٣ مع الخامة مع التقليب لمدة ساعتين عند درجة حرارة ٩٠منوية اثبت التحليل الكيميائى ان محلول الاذابة يحتوى على٩,٣٦ جم/ل من نيكل و٢,٠٩جم/ل من اللنثيدات بنسنة اذابة ٩٦% و ٩٣,٥% على الترتيب .٠

لقد استخدامنا تقنية الترسيب المباشر لترسيب كلا من النيكل واللانثانيدات باستخدام الصودا الكوية بتزكيز ١٠% عند الاس الهيدروجينى ٦,٥و حامض الاوكساليك بتزكيز ٢٠% عند الاس الهيدروجينى٢ و كان المردود لكل من النيكل واللانثانيدات ٨٥% و٩٧% بنقاوة ٩٧% و ٩٨% على الترتيب٠