

*CHAPTER – 5*  
**CONCLUSIONS**

With the significant use of critical metals in rechargeable batteries, the recycling of the spent batteries is important to address the stringent environmental regulations as well as exploitation of such resources for secured supplies of metals such as Li, Ni, Co, Mn, Zn, and the rare earths. The processes in vogue so far address the problem only partially as they hardly ensure the extraction and separation of all the major metals under the moderate operating conditions thereby impacting the process economics, besides producing other secondary wastes. In this context the present work has been carried out to recover valuable metals apart from cobalt, from the two types of spent batteries viz., the *lithium ion batteries (LIBs) and nickel metal hydride (NiMH) batteries*. The study gains further importance in view of the scanty resources of metals of interest in LIBs and NiMH batteries and the environmental problems associated with the post usage.

The thesis reports and discusses the results of an elaborative study on the hydrometallurgical processing of above resources for the extraction of the metallic values.

Out of the **five chapters** starting from introduction to the conclusions presented in the thesis, the introduction part details the resources of metals for the modern battery applications and the literature review for the recycling of secondary resources / spent batteries. The kinetic models used in leaching of metals, and objectives and scope of the present work are also described.

As regards the objectives of the present research, the dissolution of valuable metals from the spent rechargeable batteries including the kinetics and mechanism of the leaching is stressed upon. In particular the recovery of metals such as Li, Co, Ni and Mn from the spent LIBs as much as possible is aimed at, while the extraction of both base metals (Ni, Co, Zn, Mn, Fe) and the rare earth metals (La, Ce, Pr, Nd, Sm) from the spent NiMH batteries is targeted. Using a process intensification step by acid baking, selective leaching of some of the metals over others is examined.

In the materials and method section, dismantling of both the batteries and separation of useful electrode powders with other components are discussed and the powder

materials are characterized by various techniques. The major phases identified by the XRD analysis of cathode material from the spent LIBs are  $\text{LiCoO}_2$ ,  $\text{Li}_2\text{CoMn}_3\text{O}_8$  and  $(\text{Li}_{0.85}\text{Ni}_{0.05})(\text{NiO}_2)$ , whereas  $\text{Ni}(\text{OH})_2$ ,  $\text{Ni}$ ,  $\text{Nd}_2\text{Ni}_7$  and  $\text{Ni}_5\text{La}$  being the major phases in the electrode powder of NiMH batteries. The minor phases are also determined in both materials.

The cathode active material of spent LIBs can be leached in sulfuric acid in the absence / presence of a reductant ( $\text{NaHSO}_3$  and  $\text{H}_2\text{O}_2$ ), while the electrode powder of spent NiMH batteries is treated by sulfuric acid only. The acid baking-water leaching is also investigated to treat both battery materials.

The parameters for the leaching of metals from the cathode active powder of spent LIBs containing 35.8% Co, 6.5% Li, 11.6% Mn and 10.06% Ni, are optimized. The kinetics and mechanism of the leaching are particularly examined, and the results are summarized below:

- ❖ The cathode material leached in 1 M  $\text{H}_2\text{SO}_4$  at 368 K and 50 g/L pulp density (PD) for 240 min, yields the leach recovery of 93.4% Li, 66.2% Co, 96.3% Ni and 50.2% Mn. Kinetically the leaching of Li, Co and Ni is best represented by the logarithmic rate law with the activation energy values of 16.4, 7.4 and 18.5 kJ/mol respectively, in the temperature range 308-368 K.
- ❖ Improvement in the leaching of metals could be noticed in presence of a reductant-  $\text{NaHSO}_3$  and  $\text{H}_2\text{O}_2$ . In the presence of 5% (v/v)  $\text{H}_2\text{O}_2$  with 1 M  $\text{H}_2\text{SO}_4$  at 368 K and 50 g/L pulp density, the leaching efficiency of Co and Mn increases significantly to 79.2 and 84.6% respectively, along with the dissolution of 94.5% Li and 96.4% Ni in 240 min. Addition of 0.075M  $\text{NaHSO}_3$  as a reducing agent in 1 M sulfuric acid leads to the dissolution of ~96.7% Li, 91.6% Co, 96.4% Ni and 87.9% Mn at 368 K and 20 g/L pulp density in 240 min.
- ❖ Sodium bisulfite addition thus gives better recovery of cobalt and manganese compared to that of hydrogen peroxide by reducing them to their lower oxidation states. The thermodynamic feasibility of the leaching reactions with hydrogen peroxide and sodium bisulfite is also predicted.

- ❖ Kinetics of leaching follow the logarithmic rate law controlled by surface diffusion of the lixiviant on the particles. The activation energy values acquired during the dissolution of Li, Co and Ni in the presence of sodium bisulfite are found to be 20.4, 26.8 and 21.7 kJ /mol in the temperature range 308-368 K; the corresponding values being higher at 30.7, 29.6, 42.6 and 43.9 kJ /mol with H<sub>2</sub>O<sub>2</sub> as the reductant. The mechanism is further corroborated by the XRD phase analyses and SEM-EDAX of the untreated sample and the leach residues generated in the process.
- ❖ The cathodic material baked at 300 °C with 2 mL H<sub>2</sub>SO<sub>4</sub> /5g powder for 30 min followed by water leaching (leach-I) results in the selective recovery of metals like Li (78.6%) and Co (80.4%) over Ni and Mn with low (<15%) dissolution in 60 min at 25% pulp density and 348 K. While the leaching of 67% Ni and 64.8% Mn is achieved using an acid mix of 1 M H<sub>2</sub>SO<sub>4</sub> and 0.5 M HNO<sub>3</sub> in the presence of glucose (2% w/v) at 323 K in 45 min (leach-II), the overall leaching efficiency is found to be 93.2% Li, 90.52% Co, 82.8% Ni and 77.7% Mn in a two-step process. Selectivity of Li and Ni in acid baking-water leach (stage-I) and subsequent dissolution of Co and Mn in leach-II, are predicted by the thermodynamic analysis ( $\Delta G^\circ$  values) of various reactions.
- ❖ As a typical case the leach liquor produced during the sulfuric acid leaching with NaHSO<sub>3</sub> is processed to recover the individual metal by precipitation method. Almost >98% Co as oxalate (CoC<sub>2</sub>O<sub>4</sub>.2H<sub>2</sub>O) can be precipitated with oxalic acid. MnCO<sub>3</sub>, NiCO<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub> are then precipitated from the cobalt depleted solution, and suitably characterized. Thus high recovery of Co, Li, Mn and Ni can be achieved from the leach solutions. The materials so obtained can be further purified and converted to the desired products.

As regards the leaching of metals from the electrode material of NiMH batteries, the following conclusions are drawn:

- ❖ Most suitable conditions for the leaching of different metals present in the battery material are optimized as: 2 M H<sub>2</sub>SO<sub>4</sub>, 100 g/L pulp density, 348 K, and 120 min. Under the optimised conditions the leaching efficiency of base

metals is obtained as 91.6% Ni, 97.8% Co, 65.5% Fe, 93.5% Mn & 99.2% Zn. The leaching of rare earths is found to be 98.1% Nd, 98.4% Sm, 95.5% Pr and 89.4% Ce under the above conditions.

- ❖ The leaching kinetics follow the chemical control shrinking core model for all the individual base and rare earth metals including the REs together as group. Regarding the mechanism of leaching, it is governed by the chemical reaction of the lixiviant on the particle surface of the electrode powder which is corroborated by the XRD and SEM-EDAX studies. The leaching of Ni, Co, Fe, Mn and Zn acquired activation energy values of 8.7, 6.8, 7.12, 6.7 and 7.9 kJ /mol respectively, in the temperature range 305-348 K. The activation energy values for the leaching of rare earths viz., Nd, Sm, Pr and Ce are found to be 7.6, 6.3, 11.3 and 13.5 kJ /mol, respectively
- ❖ In a two-stage leaching approach the effect of process intensification is attempted through the baking of the electrode material [at 300 °C, 1.5 mL sulfuric acid /2 g material, 90 min] and water leaching (leach-I) at 75 °C and 50 g/L PD for 60 min, followed by the second stage leaching (leach-II) using NaHSO<sub>3</sub> in H<sub>2</sub>SO<sub>4</sub> at 95 °C and 20 g/L PD for the same duration. The acid baking-water leach sequence appears to be an alternate process which could result in selective dissolution of Ni, Zn and REs over other metals (Co and Mn), besides lower acid consumption compared to the direct sulfuric acid leaching. The overall recovery in the two-stage leaching of the baked material is worked out to be 98.2% Ni, 91.39% Co, 98% Z), 97.8% Mn and 96% REs. The leaching of the constituent REs is found to be 80.35% La, 98.8% Ce, 98.2% Nd, 98.5% Pr and 99.2% Sm.

The thesis is appended with the suggestions for further work in brief. The references cited in the thesis are given at the end.