

*CHAPTER-1*  
**INTRODUCTION**

## **Metals in the Modern Battery Applications and the Present Work**

The production and use of metals play a crucial role in developing the society and creating the future economy. Because of the economic worth of important strategic metals globally as well as in the Indian context, development of an efficient recycling process is the need of the hour to achieve the goals of ‘waste minimization and sustainable resource recovery’. The recycling at a certain scale may thus supplement the current supply of the metals, turning it profitable eventually while addressing the environmental concerns simultaneously. Due to the increase in mobility and transportation system, communication and information technology / internet as well as electricity generation from renewable energy sources, the technological development of batteries experienced over the latter half of the last century has been significant (Vincent, 2000). Practically all technologies run on electricity and therefore, the share of electricity is increasing rapidly. The growing energy demand leads to increased demand of efficient and renewable energy resources. The renewable sources such as solar and wind energy, are the “green” sources but are intermittent in nature. For a continuous use, storage of energy is necessary. Batteries are electrochemical storage devices which can store energy in the form of chemical potential difference which can be used whenever and wherever it is needed.

The increasing usage of all kinds of electronic devices over the recent decades is due to a variety of factors which include the increasing population and electronic product ownership, besides decreasing lifespan of the products due to the faster replacement by better ones. The accelerated demand for some metals /elements is also governed by the use in new energy technologies (e.g. solar cells, batteries, etc.) and the production of complex electronic devices and networks enabling sustainability. For example, battery technology is extremely important today. The consumption of batteries in the coming years is expected to increase with that of electronic devices (Chagnes and Pospiech, 2013). Recycling of these batteries after use is thus an important issue to address the stringent environmental regulations and resource conservation. If successful, recycling may also address adverse effects of mining/ brine extractions for virgin metals, raw material transportation, energy consumption, etc. In addition it can

balance fluctuating cost dynamics and ensure a steady supply of raw material. Physical and metallurgical recycling processes have made some progress for the separation of a few metals, but each process flowsheet differs significantly with metal mixes. When such metals and their compounds have compatible thermodynamic and physical properties, the processing technology used is likely to succeed in economically separating them. If not, mixed alloys, sludges, slimes and slags produced become waste containing resources adding further to the dumping or storage cost.

As a result, there is a great interest in secured supplies of the metals and compounds used in batteries, including rare earth elements (REs, specifically La), nickel, cobalt, manganese and lithium and their compounds. Recycling processes are needed that may:

- recover all recyclables to extend material supply and moderate prices,
- process all likely chemistries, and
- minimize energy and environmental impacts.

## **1.1. PRIMARY RESERVES, PRODUCTION SCENARIO AND SECONDARY RESOURCES**

This section highlights the primary ore reserves of metals viz., lithium, nickel, cobalt, manganese, zinc and rare earth elements which are often used in the batteries such as lithium ion (LIBs) and nickel metal hydride (NiMH) batteries, and are relevant to the present thesis. Also described are the availability of minerals at the global and national level, the mine production and location of large deposits (Table 1.1), besides a brief on the secondary resources.

### ***1.1.1. Lithium***

Lithium is produced from a variety of natural sources, e.g., minerals such as spodumene, clays such as hectorite, salt lakes, and underground brine reservoirs, *etc.* Lithium is a minor component of igneous rocks, primarily granite. The most abundant

lithium containing rocks/minerals are pegmatites, spodumene and petalite. Other minerals are lepidolite, amblygonite, zinnwaldite and eucryptite (Ferrell, 1985). Zinnwaldite is the impure form of lepidolite with higher FeO content (up to 11.5% Fe as FeO) and MnO (3.2%) (Paukov et al., 2010). Pegmatites contain recoverable amounts of lithium, tin, tantalum, niobium, beryllium and other elements. The theoretical lithium content in these minerals is 3% to 5.53%, but most mineral deposits have around 0.5%–2% Li and the pegmatite-bearing ores that are often exploited have <1% Li (Mohr et al., 2010). Spodumene is the primary lithium mineral being mined.

Almost 70% of the global lithium deposits are concentrated in South America's ABC (Argentina, Bolivia and Chile) region. The lithium concentrations in the salars of Chile, Argentina, and Bolivia are in the range 0.04-0.16%. The resource of lithium is estimated (Yaksic and Tilton, 2009) to be 64 million tons (M t). Chile has the world's largest resource of brine (7.5 million tons, 1500-2700 mg/L Li) containing lithium, followed by Bolivia (9.0 M t with 532 mg/L Li) and Argentina (2.6 M t, 400-700 mg/L Li) and these three countries account for almost 80% of the world's brine reserves (Mohr et al., 2012). Currently 8% of lithium is obtained from salt lake brines and sea by sedimentation. Seawater contains about 0.1-0.2 mg/L Li (Bach and Wasson, 1981) with a total amount of ~230 billion tons of metallic lithium (globally). Brine sources include lithium found in salt water deposits - lakes, salars, oilfield brines, and geothermal brines. Oilfield brines are underground brine reservoirs that are located with oil. Brines containing lithium make up 66% of the world's lithium resources; pegmatites make up 26% and sedimentary rocks make up 8% (Gruber, 2010; Kesler et al., 2012).

Lithium extraction from ores /minerals utilises roasting and leaching, while its extraction from brines includes evaporation, precipitation, adsorption and ion exchange (Garrett, 2004). Lithium concentrate obtained by the flotation of pegmatites, is pulverized, leached in hot acid and precipitated as  $\text{Li}_2\text{CO}_3$  (Tahil, 2010). The processing of pegmatites is expensive as compared to that of brines due to heating and dissolution steps involved, but higher metal concentration in pegmatites

## HYDROMETALLURGICAL PROCESSING OF SPENT BATTERIES FOR THE RECOVERY OF METALLIC VALUES

**Table 1.1:** Compilation of the mine production and reserves for Li, Co, Ni, Mn, Zn and REs in 2015 (values in '000 metric ton) (USGS 2016)

Country	Lithium		Nickel		Cobalt		Manganese		Zinc		Rare Earth Elements	
	Production	Reserves	Production	Reserves	Production	Reserves	Production	Reserves	Production	Reserves	Production	Reserves
<b>United States</b>	W	38	26.5	160	0.7	23	-	-	0.85	11	4.1	1800
<b>Argentina</b>	3.8	2000	-	-	-	-	-	-	-	-	-	-
<b>Australia</b>	13.4	1500	234	19000	6	1100	2.9	91	1.58	63	10	3200
<b>Brazil</b>	0.16	48	110	10000	2.6	78	1	50	-	-	-	22000
<b>Canada</b>	-	-	240	2900	6.3	240	-	-	0.3	6.2	-	-
<b>Chile</b>	11.7	7500	-	-	-	-	-	-	-	-	-	-
<b>China</b>	2.2	3200	102	3000	7.2	80	3	44	4.9	38	105	55000
<b>Colombia</b>	-	-	73	1100	-	-	-	-	-	-	-	-
<b>Cuba</b>	-	-	57	5500	4.2	500	-	-	-	-	-	-
<b>Guatemala</b>	-	-	50	1800	-	-	-	-	-	-	-	-
<b>Indonesia</b>	-	-	170	4500	-	-	-	-	-	-	-	-
<b>Madagascar</b>	-	-	49	1600	3.6	130	-	-	-	-	-	-
<b>New Caledonia</b>	-	-	190	8400	3.3	200	-	-	-	-	-	-
<b>Philippines</b>	-	-	530	3100	4.6	250	-	-	-	-	-	-
<b>Russia</b>	-	-	240	7900	6.3	250	-	-	-	-	2.5	-
<b>South Africa</b>	-	-	53	3700	2.8	31	6.2	200	-	-	-	-
<b>Congo</b>	-	-	-	-	63	3400	-	-	-	-	-	-
<b>Zimbabwe</b>	0.9	23	-	-	-	-	-	-	-	-	-	-
<b>Zambia</b>	-	-	-	-	5.5	270	-	-	-	-	-	-
<b>Gabon</b>	-	-	-	-	-	-	1.8	22	-	-	-	-
<b>India</b>	-	-	-	-	-	-	0.95	52	0.83	10	-	3100
<b>Ireland</b>	-	-	-	-	-	-	-	-	0.23	1.1	-	-
<b>Kazakhstan</b>	-	-	-	-	-	-	0.39	5	0.34	4	-	-
<b>Mexico</b>	-	-	-	-	-	-	0.24	5	0.66	15	-	-
<b>Bolivia</b>	-	-	-	-	-	-	-	-	0.43	4.6	-	-
<b>Ukraine</b>	-	-	-	-	-	-	0.39	140	-	-	-	-
<b>Other Countries</b>	0.3	60	410	6500	7.7	610	1.24	scanty	1.87	26	2.3	41030
<b>World Total</b>	<b>37</b>	<b>13000</b>	<b>2530</b>	<b>79000</b>	<b>124</b>	<b>7100</b>	<b>18</b>	<b>620</b>	<b>14.77</b>	<b>225</b>	<b>110</b>	<b>140000</b>

partly compensates for the cost. Cost factor in the lithium extraction from brines compared to the ores, discourages exploitation of many deposits of spodumene. As regards lithium metal, it can be produced by both carbothermic reduction and metallothermic reduction of oxide / hydroxide and also by electrolysis of LiCl (Kipouros and Sadoway, 1998).

*Lithium reserves (Indian scenario):* In India small pocket deposits mostly comprising of lepidolite in pegmatites of mica fields are located. The maximum lithium content (lepidolite: 2-6% Li<sub>2</sub>O) is found in Jharkhand followed by that of Chhattisgarh (2.56% Li<sub>2</sub>O) and Rajasthan (2.25% Li<sub>2</sub>O as pegmatites in Udaipur, Bhilwara, Jodhpur and Ajmer, and zinnwaldite in Dagana). Others include spodumene in Raichur, Karnataka (Banerjee et al., 1994), amblygonite in granitic rocks of Paddar (Kashmir) and lepidolite at Dhir-Bil (Goalpara), Assam. Lithium bearing bauxite has also been identified in Salal area, Jammu (Roonwal et al., 2005; Krishnaswamy, 1979; Brown and Dey, 1955).

*Secondary resource for lithium:* Several categories of lithium uses are of dispersive in nature, with too low metal in the final product to make recycling attractive and /or to materials from which recycling is not feasible. Only lithium in batteries and Al-Li alloys can be recycled with current technologies. Lithium usage in the aeronautics could make a breakthrough in the coming years, impacting on the overall demands for lithium. According to a producer of this alloy (Constellium Airware), it is 100% recyclable with the average life span of 30-40 yrs for jet aircraft made with the highly corrosion-resistant Al-Li alloy.

The growing market for lithium-ion batteries (LIBs) raises concerns about sustainable management of these batteries at the end-of-life. Current recycling efforts of LIBs focus mainly on the cathode materials viz. cobalt and nickel, but largely neglect manganese and lithium even where sophisticated recycling systems are in place (Dewulf et al., 2010). Lithium is generally not considered for recycling because it is cheap enough to dump old batteries and mine the virgin material. Recycling of LIBs is further detailed in Section 1.3.1.1.

### *1.1.2. Nickel*

Nickel is the Earth's 16<sup>th</sup> most abundant metal, and its average crustal abundance by weight is about 0.008% (Smith and Huyck, 1999). Nickel performs well under conditions of high temperature and high stress therefore, nickel-containing alloys are essential in such applications (turbines, jet engines). Nickel alloys are resistant to corrosion, facilitate chemical reactions through catalysis, and find applications in battery manufacturing, electroplating, and hydrogenation of fats and in pigmentation. Nickel can be fabricated into desired forms and shapes by different metalworking techniques viz. casting, drawing, extrusion, forging, machining, or rolling.

The world's nickel resources are currently estimated at almost 300 million tons. Australia, Indonesia, South Africa, Russia and Canada account for more than 50% of the global nickel resources. Laterite-type (oxide) resources are found in Indonesia, the Philippines, Brazil, Cuba and New Caledonia. Sulfide type deposits are found in South Africa, Russia and Canada. Australia has the biggest nickel resources with both sulfide- and laterite type ore deposits. World primary nickel production was 1.989 M t in 2014, and decreased to 1.983 M t in 2015. INSG projects a decrease in production which could reach around 1.913 M t in 2016. The bulk of the nickel is believed to be concentrated in the Earth's core. Geological studies indicate that most nickel deposits are hosted in ultramafic rocks, such as peridotite and serpentinite. These are igneous rocks that are low in quartz and feldspar but high in ferromagnesian silicates. The average nickel content (by wt.) in ultramafic rocks is ~ 0.20% (Turekian and Wedepohl, 1961), which is revised to 0.15% (Goles, 1967). Improved technologies in mining, smelting and refining, as well as increased capacities, allow for lower-grade nickel ore to be processed. Manganese nodules, which are found on the deep-sea floor, contain significant amounts of various metals, including nickel. Recent estimates show the presence of more than 290 million tons of nickel contained in such deposits. Economic concentrations of nickel occur in two principal types of ores: (1) sulfide deposits consisting mainly pyrrhotite and pentlandite, with or without accompanying chalcopyrite, and closely associated with norite and peridotite, and (2)

nickeliferous laterite deposits, occurring as weathering mantles that overlie peridotite (the nickel silicate variety) and serpentinite (the nickeliferous iron variety).

*Secondary resources for nickel:* Different types of available secondary resources of nickel can be economically processed to recover the metals which will also minimize the environmental pollution. Most recycled nickel is in the form of stainless steel scrap or alloy steel scrap. Other secondary resources are batteries, bronzes, catalysts, chemical leachates /metal-rich solutions /pickle liquors, coinage and dusts, besides drosses, filter cakes, grindings /turnings, electrodes, sludges, etc. (Goonan, 2009).

*Stainless steel scraps / alloy scrap:* Nickel (in alloys and superalloys) is recycled through mixed-scrap processing. Stainless-steel (SS) scrap, being more valuable than iron and steel scrap, contains nickel which is highly recyclable and typically comprises of ~60% of a new batch of SS. The scrap is recycled by melting with the ferronickel while correcting the composition. Alloy scrap, yet another secondary source is investigated for nickel recovery. While Alex et al. (2001) used cupric chloride leaching followed by solvent extraction and precipitation to obtain the pure Ni and Co-salts (overall recovery ~99%), HCl leaching at 95 °C followed by crystallization of nickel as chloride (overall recovery ~ 95%) was reported by Shen et al. (2008).

*Nickel based catalysts:* Nickel alloys are also used in industrial processes requiring catalytic assistance, for example, in petrochemical processing (cracking) and for food processing (fat hydrogenation). Raney nickel is an example of a hydrogenation catalyst (developed in 1926), containing (by mass) ~90% Ni and 10% Al (Marafi and Stanislaus, 2008). The nickel spent catalysts have metallic nickel and nickel oxide, although nickel aluminate, spinel-like compounds and nickel sulfides may occasionally occur, besides admixtures of coke, hydrocarbons or fat. Hydro- and pyro-metallurgy are frequently used for metal recovery from the spent catalysts (Marafi and Stanislaus, 2008; Singh, 2009). Leaching of nickel from the spent catalysts in sulfuric acid, and separation as NiSO<sub>4</sub> are most often practiced (Ivascan and Roman, 1975; Al-Mansi and Monem, 2002; Miazga and Mulak, 2008; Lee et al., 2010).



Electroplating effluents: Nickel based solutions for plating become unusable due to inadequate concentrations of nickel and acid and increased level of impurities with time. The effluent generally contains 30-100 g/L Ni, is a hazardous waste which is often converted to the category of non-hazardous and then returned to the electroplating process again. Ni can be recovered from the electroplating effluents employing the methods such as electro-dialysis (Li et al., 1999), electro-winning (Vegliò et al., 2003) and continuous solvent extraction (Tanaka et al., 2008).

Ni-based batteries: Used NiMH and NiCd batteries are also good source of nickel. As batteries break down in landfill particularly in an acidic environment, heavy metals can leach into surface and groundwater. Nickel is used as the anode material in both batteries (Shukla et al., 2001) with ~16.4% Ni in Ni–Cd (Huang et al., 2009) and 25-49% Ni in Ni-MH batteries (Scott, 2009). These batteries are rechargeable and are categorized as the aqueous electrolytes type (Beck and Rüetschi, 2000). The Ni active material used is in fact Ni(III) oxide hydroxide (NiOOH), which is converted into Ni(OH)<sub>2</sub> during the battery discharge and reformed during recharge. Cadmium, a highly toxic metal can be replaced with a hydrogen-absorbing alloy in Ni-MH batteries which is less environmentally benign and increases the performance of such batteries (Beck and Rüetschi, 2000; Fetcenko et al., 2007; Shukla et al., 2001). The current recycling approaches include separation of battery components followed by pyrometallurgical and/or hydrometallurgical technologies (Bernardes et al., 2004; Espinosa et al., 2004a; 2004b). The first separation step has limited applications but can lower the total cost of the process. The pyrometallurgical processes used industrially recover metals at elevated temperatures, whereas the hydrometallurgy uses acids or bases for leaching followed by metal recovery by different techniques. Metal recovery from NiMH batteries is detailed in Section 1.3.2.

### ***1.1.3. Cobalt***

Cobalt is the 33<sup>rd</sup> most abundant element and is primarily used in rechargeable battery as cathode (as LiCoO<sub>2</sub>) in LIBs. Cobalt also finds use in carbide and diamond tools, corrosion- and wear-resistant high-strength alloys, high-speed steels, catalysts for petroleum and chemicals, biofuel production (Fischer-Tropsch process), carbon

dioxide reduction as well as in fuel cells, drying agents in chemistry, pigments, ground coats for porcelain enamels, permanent magnets (Alnico and SamCo alloys) and magnetic recording media, steel-belted radial tires, etc. Cobalt-60 is a commercially important radioisotope used as a radioactive tracer and for the production of high intensity gamma rays. Cobalt, being a part of vitamin B12, is essential to maintain human health.

Identified land-based resources of cobalt exceed 10 M t with additional ~600 M t of cobalt believed to be contained in oceanic crusts and nodules (sea bed manganese nodule). The present world cobalt reserves are estimated at 7.1 M t (as metal). Main cobalt reserves are found in the Democratic Republic of Congo (DRC) accounting for 47% of the world total. Besides, major reserves are located in Australia, Cuba, Zambia, Canada, Russia and New Caledonia as nickel-bearing laterites and rest as Ni-Cu sulfide deposits hosted in mafic and ultramafic rocks in Australia, Canada and Russia, and in sedimentary copper deposits of Congo and Zambia.

The common cobalt-bearing minerals found in economic deposits include erythrite, skutterudite, cobaltite, linnaeite, carrollite and asbolite (asbolane). Cobalt is found in chemical compounds often associated with sulfur and arsenic. Though some cobalt is produced from metallic-lustered ores like cobaltite ( $\text{CoAsS}$ ) and linnaeite ( $\text{Co}_3\text{S}_4$ ), it is industrially produced as a by-product of copper, nickel and lead. While nickel laterites are mostly processed directly, other Co-bearing ores are beneficiated (by flotation or gravity methods) to produce the concentrates, which are hydrometallurgically processed to extract cobalt (Shedd, 2004). Cobalt present as a by-product of copper, is concentrated (sulfides) and converted to oxides by roasting. The oxide is leached in sulfuric acid dissolving metals more reactive than copper, particularly Fe, Co and Ni as sulfates. After removing iron as iron oxide, cobalt is precipitated as  $\text{Co}(\text{OH})_3$  which is roasted and then reduced to cobalt metal with charcoal or hydrogen gas (Panayotova and Panayotov, 2014).

*Secondary resources for cobalt:* Cobalt can be recovered from a variety of scrap materials, including alloys, spent Li-ion and NiMH batteries and battery

manufacturing scrap, spent catalysts from the petroleum and polyester fiber manufacturing industries, residues, and other cobalt-bearing materials. These scraps are generally processed by leaching, purification, solvent extraction, precipitation of cobalt carbonate, and drying the carbonate or calcining it to oxide. The current processes for a few wastes are discussed below.

**Battery and battery manufacturing scrap:** Spent battery scrap is shredded, screened and then magnetically separated before processing to recover products in desired forms. A wide range of nickel, chromium and iron-bearing wastes including spent batteries /catalysts, and wastes from specialty steel, superalloy, plating /surface-finishing industries (cakes, dusts, filters, grindings, mill scale, sludges, solutions) and swarf, are treated at high temperature by the International Metals Reclamation Company Inc. (INMETCO) in US (Bernardes et al., 2004). Cobalt-bearing batteries treated include LIBs, NiCd and NiMH type, and the solid wastes with < 2% Co (dry-weight basis) and liquid wastes with < 1,800 mg/L Co. Spent Ni-Cd batteries are initially treated in Cd-recovery furnace to separate it from the metals viz., Ni and Fe. The solid wastes are blended with carbon and pelletized by using either liquid wastes or water. The pellets, spent catalysts and shredded Ni and Fe from the batteries are reduced in a rotary hearth furnace and smelted in a submerged electric arc furnace. The molten metals cast into pigs are used as remelt alloy by the stainless steel industry; the alloy is primarily iron with 9 -19% Cr, 8 -16% Ni and ~0.8% Co with a Co recovery of 97%.

**Spent catalysts:** Spent catalysts based on Co-Mo and Ni-Mo used in the hydro-processing are mainly processed to recover the metals. Gulf Chemical & Metallurgical Corporation, US, the world's largest recycler of spent hydro-processing catalysts, has been recovering molybdenum and vanadium for years (Llanos and Deering, 2000). In this process, the catalyst is calcined with sodium carbonate in a multiple-hearth roaster at 650- 900 °C followed by water quenching to dissolve the Mo and V salts. Ammonium vanadate precipitated from the leach liquor is calcined and fused to produce V<sub>2</sub>O<sub>5</sub>, and the solution heated to 80-85 °C, is acidified to precipitate molybdic acid and then converted to molybdic oxide; the recovery being

98% for each metal. An alloy of Co-Ni is recovered from the tailings by smelting in a plant at Belgium. The AMAX process however, uses two-caustic leaches for alumina-based catalyst at  $\sim 150$  °C or more and 300-500 psi. The leach-I with a weak NaOH extracts Mo and V from which  $\text{Mo}_2\text{S}_3$  is precipitated by adding sulfuric acid and  $\text{H}_2\text{S}$  gas under pressure, followed by recovery of  $\text{V}_2\text{O}_5$  by adding NaOH. In stage-II, stronger NaOH leaches alumina which is precipitated as alumina trihydrate at low temperature (140-190 °F). The residue with Co and Ni is sold for refining.

A 2-stage pressure-leaching process is also reported by CRI-MET, a partnership between CRI International, Inc., and Cyprus Amax Minerals Co. The pressure leaching of the milled catalyst in sodium aluminates and NaOH solution under oxidizing conditions dissolves Mo and V which are recovered from the liquid and converted to their oxides. The solid is pressure leached second time with a strong caustic to recover aluminum from alumina. The residue rich in cobalt and nickel is calcined and then exported to a Ni-Co refiner (Shedd, 2004).

**Cemented carbide scrap:** These scraps are generally processed by direct and indirect recycling. In direct recycling, the cemented carbides are disaggregated and the resulting powders of tungsten carbide and cobalt are almost ready to be used to make new parts. The direct recycling processes include bloating, the cold stream process, leach milling with partial cobalt removal, and the zinc process. The individual components can be recovered and purified using chemical methods (indirect recycling) viz., chlorination, leach milling with total cobalt removal, nitrate and/or nitrate-carbonate fusion, and oxidation-sodium hydroxide leaching. The advantage of chemical process is the ability to remove impurities, but has higher costs and energy consumption, lower yields and generation of more wastes than the direct methods. A balance between using indirect and direct recycling processes has allowed recycling of soft and hard, contaminated and clean cemented carbide scraps (Shedd, 2004).

A tungsten production plant in US uses the chemical process to recycle cemented carbide scrap along with the ore concentrates (Shedd, 2004). The leaching in NaOH produces sodium tungstate solution and a sludge containing cobalt and other metals. The sludge is treated chemically to separate the metals. The cobalt is converted to

cobaltic oxide and is reduced by hydrogen to Co-powder. The Osram's chemical process is able to treat cemented carbide scrap and other cobalt-bearing scraps, such as alloys and catalysts.

Some U.S. tungsten processors and cemented carbide producers use the Zn-process to recycle hard cemented carbide scrap. The sorted scrap is cleaned to remove any brazing or impurities and then immersed in molten zinc under argon gas, which reacts with the cobalt binder causing the scrap to expand. The vacuum distillation removes zinc leaving behind a tungsten carbide and cobalt material which is crushed, milled and blended to adjust compositions, and then used to make new parts.

#### ***1.1.4. Manganese***

Manganese is the 12<sup>th</sup> most abundant element in the earth's crust. Because manganese metal is typically brittle and unworkable, only a small amount is used as an alloy with manganese as the major component. Rather, manganese is used predominantly in alloys where it is a minor component, principally in steel and to a lesser extent, aluminum. Manganese is essential to steel production by virtue of its sulfur-fixing, deoxidizing and alloying properties. Metallurgical applications account for most domestic manganese consumption, of which 85-90% is used in steelmaking and ~8% in dry cell batteries as electrolytic manganese dioxide (EMD).

According to the recent data (USGS, 2016), global manganese reserves stand at ~ 620 M t (as metal) with land-based resources distributed irregularly (Table 1.1). Manganese is found in more than 100 minerals including various sulfides, oxides, carbonates, silicates, phosphates and borates. The major manganese minerals in nature occur as pyrolusite, braunite, psilomelane, rhodochrosite, etc. Because manganese ores typically contain iron as well, the result of smelting is an iron-bearing ferroalloy, which is used to add manganese to liquid metal during steelmaking. The principal manganese ferroalloys and their typical components are high-carbon ferromanganese (78% Mn, 7% C, balance mostly Fe) and silico-manganese (66% Mn, 17% Si, 2% C). An electrolytic process is used to obtain EMD and electrolytic manganese metal (EMM), the two other forms in which manganese is commercially

used. These materials are produced in similar steps, leaching of reduced manganese ore with sulfuric acid and electro-depositing EMD or EMM from the purified leach liquors (USGS, 2016).

*Secondary resources for manganese:* Iron and steel scraps, used aluminium beverage cans and Mn containing dry batteries can be used for recycling of manganese.

**Iron and steel scraps:** The lower recycling rate of manganese (37%) than that of iron and steel scraps (41%) reflects relatively large loss of manganese. The only significant metal form recovered specifically because of its manganese content is wear-resistant steel with ~12% Mn (Hadfield steel). Otherwise, it is recovered because of recycling of another metal, iron in the case of steel scrap / iron castings and aluminum in the case of used beverage cans.

**Batteries:** A small amount of manganese is recovered through recycling of dry cell batteries or manganese-bearing wastes generated in battery manufacture; this makes a small contribution to manganese recycling. One of the original motivations for battery recycling, preventing mercury loss to the environment, has been greatly diminished because deliberate additions of mercury to the battery mix are no longer made. If impurities in the battery can be removed at a reasonable cost, recycling may be a suitable alternative to use manganese ores. The removal of potassium is necessary as it prevents the manufacture of  $MnO_2$  of a suitable quality. Potassium is not used in zinc-carbon batteries but exists in large amounts in alkaline manganese batteries.

#### ***1.1.5. Zinc***

Zinc is the 23<sup>rd</sup> most abundant element in the earth's crust. The main application areas of zinc are in construction (45%), transport (25%), consumer goods and electrical appliances (23%), and general engineering (7%). Ability of zinc to protect iron from corrosion in galvanizing determines its most important use, and most of this product is used in the construction industry. Identified zinc resources of the world are about 1.9 billion metric tons (USGS, 2016). Total world reserves of zinc are 200 M t of which Australia holds 63 M t, China 38 M t and Peru 25 M t (USGS, 2016). At present, approximately 70% of the zinc produced worldwide is primary and 30% is

from recycled or secondary sources. The most common ore minerals are sphalerite (ZnS) or Zinc blende, and its variety marmatite [(Zn,Fe)S] from which over 95% of world's zinc is produced.

*Secondary sources for zinc:* Zinc products in the form of zinc metal or alloys which have been discarded because of wear, damage or obsolescence, can be used as secondary sources. Die castings, automobile shredder scrap, brass and bronze products, galvanizing residues, sludge from iron and steel industries as well as contaminated water solutions (mine waste, rinse effluents, waste plating solutions and contaminated surface waters) are mainly used for recycling of zinc. As most of zinc metal is used for corrosion protection of iron and steel, the recyclable zinc is mostly supplied by such industries either as galvanizing residues or as flue dust. Galvanizing residues contain 90-95% Zn and 5-10% other metals. Depending on the steel type and the galvanizing process, some 10-40% of the total Zn consumed ends up in residues. Zinc metallurgically combined with steel during galvanizing is usually recovered from flue dust generated in reprocessing of steel scrap. The dust contains ~20% Zn which is generally recovered as crude ZnO for zinc metal production. The common processing options for a few of these wastes are summarized below.

**Brass and bronze scrap:** The brass and bronze scraps are mainly recycled by brass and copper industries due to high value and high content of copper in these alloys. It can be recycled by heating in muffle furnace or retorts and evaporation of zinc. The zinc vapor can be purified in distillation column to produce refined zinc metal.

**Galvanized residues:** Galvanized residues viz., top and bottom drosses, skimmings and ashes are the second most commonly recycled scrap. Drosses are metallic alloys of iron and zinc and some unalloyed zinc and other metals mainly Al, Pb and Sn. The bottom dross consists mainly of iron and zinc whereas the top dross contains primarily zinc and aluminium with small amounts of Fe, Pb, and Sn. Both drosses can react with various fluxes to release the entrapped metallic zinc which is cast into slabs for subsequent use by secondary zinc smelters.

Skimmings and ashes are formed by oxidation on the surface of a galvanizing bath when no flux is used. The high grade skims are directly used by secondary producers. Medium and low grade skims are upgraded for the Zn content before treatment by an intermediate reduction-distillation-pyrometallurgical step, or leached with acid, alkali or ammoniacal solution to extract zinc.

EAF dust: Zinc content varies from 5-40% (average 20%) and contains small amounts of hazardous constituent viz., Cd, Cr and Pb. In the predominant technology using the Waelz kiln, the EAF dust mixed with coal and flux is fed to the kiln which rolls along the slope. The energy is provided by coal combustion supplemented by natural gas or oil combustion via a burner at the discharge end of kiln. The feed is reducing and oxidizing simultaneously in the kiln, thus generating two products -a mixed zinc/lead oxide and an inert iron-rich slag (de Araújo and Schalch, 2014).

As regards the processing of the galvanized steel scrap, the process consists of dissolving Zn coating in a hot caustic solution and recovering the zinc from the solution electrolytically. The recycling rate of zinc however, will not be that high because of many dissipative or non-recoverable uses of zinc. Examples are zinc used in fertilizers or animal feed, and zinc in paints or in rubber products which have, at best, only limited recoverability (Plachy, 2004).

#### ***1.1.6. Rare Earth Elements (REs)***

REs (a group of 17 elements, 15 lanthanides from La to Lu, and Sc and Y) are relatively large in the Earth's crust with an overall crustal abundance of 9.2 ppm (Rudnick et al., 2003). The abundance of individual REE varies widely, from cerium the most abundant at 43 ppm (exceeding important metals including Cu -27 ppm and Pb -11 ppm) to 0.28 ppm for thulium in earth's crust (Taylor and McLennan, 1985; Rudnick et al., 2003). Rare earths are used in computer memory, DVDs, rechargeable batteries, cell phones, catalytic converters, magnets, fluorescent lighting, catalysts, air pollution control, illuminated screens on electronic devices, and the polishing of optical-quality glass. Many of the applications provide sources of heavy rare earths which are scarce and are critical for development of new technologies.



World mine production, reserves as well as resources of REs are shown in Table 1.1. USGS data (2016) estimates total world reserves of RE-oxides at ~14 M t. China dominates world reserves with 48% followed the Commonwealth of Independent States (17%), USA (12%), India (3%) and Australia (1%). The remaining 19% of reserves is divided between Canada, Malaysia, Brazil, Greenland, South Africa, Namibia, Kenya, Tanzania, Angola, Mauritania, Burundi, Malawi, Vietnam, Thailand, Indonesia, Finland, Sweden and Turkey.

Rare earths occur naturally in a wide range of minerals including halides, carbonates, oxides, phosphates and silicates (Table 1.2). Higher concentrations of REs are required to form their own minerals (Möller, 1986). Around 200 minerals are known to contain REs, but a relatively small number may be commercially significant. These minerals generally contain most of the REs in varying concentrations, but are biased towards either the light or heavy rare earth elements (LREs or HREs). Bastnäsite, monazite and xenotime are the 3-major minerals of REs. In some minerals the LREs are particularly enriched, whilst in others the opposite is the case. Bastnäsite and monazite are the primary source of the LREs, mainly Ce, La and Nd. Monazite contains less La and more Nd, but often contains the radioactive thorium and at times uranium. Xenotime is dominated by the heavier REs viz., Y, Dy, Er, Yb and Ho (Harben, 2002). China has been the main source of REs at the global level with a supply of ~95% till 2009, but the restricted supply there after affected their availability.

*Secondary sources for rare earth elements:* The increasing use of rare earths coupled with the Chinese control of supply (post 2009), opportunities exist for the processing of used fluorescent lamps, magnets, batteries, spent catalysts, etc., to supplement the availability. Post-production wastes such as scraps of magnet manufacture and sludge from shaping and grinding (Haque et al., 2014), besides the industrial process residues viz. phosphogypsum, red mud, mine tailings, metallurgical slags, and ash from thermal power and incineration facilities, are also good source of REs (Binnemans et al., 2015). Processing of a few secondary sources is given in brief.

Fluorescent lamp: Phosphors in fluorescent / compact fluorescent lamps (Fls/CFLs) and cathode ray tubes (CRT) are rich source of the heavy rare earths, Eu, Tb and Y. With the phasing out of CRT, use of total phosphors in FLs / CFLs has risen to ~ 90% in 2011 (Tan et al., 2015). The RE content in phosphors is more than 23% (230,000 g/t) (Binnemans et al., 2013; Tan et al., 2015). The considerable quantities of Eu, Tb and Y are present in phosphors (85.2% Tb and 76.7% Y) with only 1.6% La and 2.0% Ce. Phosphors can be chemically attacked by acid (Verma et al, 2013) to reclaim the REs, as applied to process ores. In absence of any commercial-scale facilities in India these are mostly disposed off by landfill or storage.

Magnets and magnet wastes: Two major REs that can be recovered from spent RE-magnets include Nd from NdFeB and Sm from SmCo magnets. NdFeB magnets contain 30–40 % REMs, of which 15–30 % is Nd and 60–70 % of other elements (50–70 % Fe and ~1% B) (Onal et al., 2015). The wastes in magnet production are material left in furnace after vacuum melting, atomising or quenching; - rejected magnets; and – the residues from grinding. Hitachi developed a process to recover the NdFeB based magnets from HDDs and compressors of air conditioners using a combination of vibration, demagnetization and manual collection. Using hydrogen at atmospheric pressure separates sintered RE-magnets from computer HDDs, leading to hydrogenated NdFeB powder for making new magnets of nearly similar properties or into cheaper bonded magnets of a lower magnetic performance (Walton et al., 2015).

Batteries: Nickel metal hydride (NiMH) batteries contain lanthanum, cerium, praseodymium and neodymium; the details of processing options are given separately in the thesis (Section 1.3).

Catalyst: Fluid cracking is a process in petroleum refining that converts a heavy hydrocarbon input into lighter hydrocarbon fractions. The catalyst is based on zeolite, a molecular sieve that has a very large reactive area within its own mineral structure. The zeolite is dealuminized to increase the Si/Al ratio, which weakens the structure of the mineral. The former aluminium sites in the zeolite are repopulated with REOs

**Table 1.2:** Rare earth bearing minerals, content availability and deposits

Minerals	Formula	~ REO%	Deposits	References
Aeschynite-(Ce)	(Ce,Ca,Fe,Th)(Ti,Nb) <sub>2</sub> (O,OH) <sub>6</sub>	32	Inner Mongolia, China.	Alexandrov, 1962
Allanite-(Ce)	(Ce,Ca,Y)2(Al,Fe <sup>3+</sup> ) <sub>3</sub> (SiO <sub>4</sub> ) <sub>3</sub> OH	38	New Mexico, USA, Central China	Liu et al., 1999
Apatite	Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> (F,Cl,OH)	19	Morocco & Western Sahara (75%), China (6%), Syria (3%), South Africa (2%)	Indian Minerals Yearbook, 2013
Bastnasite-(Ce)	(Ce,La)(CO <sub>3</sub> )F	75	Sweden, France, Pakistan, China	Donnay and Donnay, 1953
Brannerite	(U,Ca,Y,Ce)(Ti,Fe) <sub>2</sub> O <sub>6</sub>	9	USA, South Africa	Szymanski and Scott, 1982
Britholite-(Ce)	(Ce,Ca) <sub>5</sub> (SiO <sub>4</sub> PO <sub>4</sub> ) <sub>3</sub> (OH,F)	32	South Greenland, USA, Italy, Norway	Noe et al., 1993
Eudialyte	Na <sub>4</sub> (Ca,Ce) <sub>2</sub> (Fe <sup>2+</sup> ,Mn,Y)ZrSi <sub>8</sub> O <sub>22</sub> (OH,Cl) <sub>2</sub>	9	South Greenland, Canada	Johnsen and Grice, 1999
Euxenite-(Y)	(Y,Ca,Ce,U,Th)(Nb,Ta,Ti) <sub>2</sub> O <sub>6</sub>	24	Norway, USA	Weitzel and Schrocke, 1980
Fergusonite-(Ce)	(Ce,La,Nd)NbO <sub>4</sub>	53	China, USA	Santoro et al., 1980
Gadolinite-(Ce)	(Ce,La,Nd,Y) <sub>2</sub> Fe <sup>2+</sup> Be <sub>2</sub> Si <sub>2</sub> O <sub>10</sub>	60	Norway	Segalstad and Larsen, 1978
Kainosite-(Y)	Ca <sub>2</sub> (Y,Ce) <sub>2</sub> Si <sub>4</sub> O <sub>12</sub> CO <sub>3</sub> .H <sub>2</sub> O	38	Norway, Austria, Italy, Russia, Canada, USA	Pouliot et al., 1964
Loparite	(Ce,La,Na,Ca,Sr)(Ti,Nb)O <sub>3</sub>	30	Northern Russia	Mitchell et al., 2000
Monazite-(Ce)	(Ce,La,Nd,Th)PO <sub>4</sub>	65	Russia, Norway, USA, Japan, China, Western Australia, Australia, Sri Lanka, India, Brazil	Ni et al., 1995
Parisite-(Ce)	Ca(Ce,La) <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> F <sub>2</sub>	61	Colombia, USA, Canada, Norway, France, Italy, Russia, Congo (Zaire), Japan, China, Vietnam.	Ni et al., 2000
Xenotime	YPO <sub>4</sub>	61	Norway, Sweden, Switzerland, Japan, Brazil, USA, Canada	Ni et al., 1995
Yttrocerite	(Ca,Ce,Y,La)F <sub>3</sub> .nH <sub>2</sub> O	53	USA, Sweden	Sverdrup, 1968
Huanghoite-(Ce)	BaCe(CO <sub>3</sub> ) <sub>2</sub> F	39	China, Russia, Canada, Greenland	Mercier and Leblanc, 1993
Cebaite-(Ce)	Ba <sub>3</sub> Ce <sub>2</sub> (CO <sub>3</sub> ) <sub>5</sub> F <sub>2</sub>	32	China, Russia, Slovakia	Zaitsev et al., 1998
Florencite-(Ce)	CeAl <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	32	Brazil, Canada, Belgium, Chile, Namibia, Malawi, Western Australia	Tomašić et al., 2010; Nichols, 2012
Synchysite-(Ce)	Ca(Ce,La)(CO <sub>3</sub> ) <sub>2</sub> F	51	Italy, Austria, Germany	
Samarskite-(Y)	(Y,Ce,U,Fe <sup>3+</sup> ) <sub>3</sub> (Nb,Ta,Ti) <sub>5</sub> O <sub>16</sub>	24	USA, Russia, Norway, Congo, Brazil	

through an ion exchange process. REO concentration in catalysts varies between 1.5 to 5 (wt.) % with average of ~3.5% (Du et al., 2009). The catalyst contaminated with carbon is continually created and separated from the stream of light hydrocarbon products. Fluid catalytic cracking (FCC) catalysts extensively used in the petrochemical industry, contain ~3.5% RE-oxides, mainly La, and smaller amounts of Ce, Pr and Nd (Yu and Chen, 1995).

Scraps /sludges in manufacturing of magnets/alloys: Typical recovery methods may include re-melting, reuse and re-blending of scraps or other selective extraction methods (e.g. using a molten salt agent ( $\text{MgCl}_2$ ),  $\text{Na}_2\text{SO}_4$  double-salt precipitation technique or oxalate precipitation approach to recover  $\text{Nd}_2\text{O}_3$  (Tang et al., 2009). Some metal recyclers have pilot programs using simplified hydrometallurgical routes to recover Nd and Dy.

Besides above, processing of the industrial process residues to recover REs is also included.

Phosphogypsum: The phosphogypsum is a waste generated in large quantities (100-280 M t /y) in the wet phosphoric acid process. Light and middle REs concentrated into this waste make it a potential secondary source. South Africa is one of the largest phosphoric acid producers in the world, whereas the apatite and carbonatite deposits in Finland have REs. Phosphate rock also contains trace amounts of other elements, including Th, U and rare earths; the Ce, La and Nd account for 80% of total RE-content of the rock. About 70-85% of the REs present in the rock is concentrated in the phosphogypsum, the remainder stays dissolved in the phosphoric acid. With ~0.4% REs in phosphogypsum (Habashi, 1985), it is a low value compared to ore minerals, but becomes a valuable resource of rare earths taking the global production (~224 M t in 2013) of phosphate rock (Jasinski, 2014).

Bauxite residue (red mud): Red mud is a solid waste produced in the Bayer's process of alumina production from bauxite. It is a complex material with varied chemical and mineralogical composition depending upon the source of bauxite and the technological process followed. Six major constituents,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,

Na<sub>2</sub>O and CaO, and numerous minor /trace elements (as oxides) such as V, Ga, Cr, P, Mn, Cu, Cd, Ni, Zn, Pb, Mg, Zr, Hf, Nb, U, Th, K, Ba, Sr, and rare earths (La, Ce, Pr, Nd, Sm, Eu, HREE including Sc, Y) in varied ratio, make it an interesting waste (Abhilash et al., 2014; Sinha et al., 2016). As red mud contains components of great use including iron to rare earths, recovering some of them would be quite important.

**Mine tailings:** Another potential source of already available materials lies in mine tailings after extracting the primary mineral(s). Though the REs are typically found in very low concentrations, but excessive exploitation of the mines produces a great deal of mine tailings which need proper treatment. In China, the rare earth elements are also recovered as a by-product of iron mining. The world's largest light rare earth deposit is located in Bayan Obo, Baotou, China, with 48 M t of RE-reserves (bastnasite). The ore concentrate is calcined to drive off CO<sub>2</sub> and fluorine. It is then treated by 2-stage digestion in HCl and then in NaOH to produce RE-hydroxides which on chlorination yields their chlorides. Individual rare earth is separated by multiple recrystallisation as double salts, and ultimately by solvent extraction. The rare earth industries generally pose significant environment risks affecting water discharge (radionuclides, Th and U; heavy metals; acids; fluorides), tailing management and air emissions (radio-nuclides, Th and U, heavy metals, HF, HCl, SO<sub>2</sub> and dust).

**Metallurgical slags:** Blast furnace slag is a waste of iron ore smelting in which the rare earths are concentrated. The sources of the rare earths are ores or coal used. The BF slag from TATA steel (India) and Jindal steel (India) as reported by CSTEP, Ministry of Mines, Govt. of India (CSTEP Report, 2012) contains ~500 ppm (or lesser amount) of REMs. The TATA STEEL slag has 0.016% Ce, 0.013% La, 0.033% Er, 0.013% Nd and 0.004% Y.

**Fly Ash:** The investigation into coal fly ash as a potential source of REs is considered a new research area (Binnemans et al., 2013). The RE-extraction from fly ash may be far less intensive than that of mining a raw product. The coal fly ash contains a full range of REs, whereas most mines have only a few of them, hence REs from fly ash could be an alternative to the traditional mining.

## 1.2. RECYCLING OF SECONDARY RESOURCES

Along with the low energy consumption, recycling also saves resources and supplements the supply from primary mining by tapping the metals locked in secondary materials and urban mines. The recycling is often driven by the values of the recovered metal / material assuming that it would pay for all activities viz., collection, dismantling, sorting and processing. Accordingly numerous secondary resources including the spent batteries (Table 1.3) found in considerable quantities would be worth investigating to recover the metallic values.

In this thesis two types of spent batteries, viz. lithium ion batteries (LIBs) and Ni-metal hydride (NiMH) batteries have been considered to extract nonferrous and strategic metals viz., Li, Ni, Co, Mn, Zn and REs. Physical separation methods may include mechanical dismantling of the components such that it can significantly reduce the manual labour manifold (Haque et al., 2014). Extraction of base metals and rare earths generally involves pyro-and hydro-metallurgical approaches (Caravaca et al., 1994; Jha et al., 2001, 2005; Lucheva et al., 2003; Agrawal et al., 2004; Gálvez et al., 2006; Takeda et al., 2009; Koyama et al., 2010; Jones, 2013; Evdokimov and Evdokimov, 2014). Pyrometallurgical routes are being exploited to recover metals (Cu, Ag, etc.) from electronic scraps (Chen et al., 2014b). However, the rare earths are lost in the process as they enter the slag phase due to the high affinity of the REs to oxygen. Hence hydrometallurgical approaches may be required to leach out not only the base metals but also the rare earths from such battery wastes (Vassura et al., 2009; Wu et al., 2010; Khaliq et al., 2014). Recycling of REs (La and Ce) from the spent catalysts is not yet technically and economically attractive (Biswas et al., 1986; Alexandre et al., 1991; Pradhan et al., 2013). Several reports are available in the literature (Valiente et al., 1991; Sinha et al., 2012, 2014; Souza et al., 2016) citing the options for extraction of valuables from various secondary materials which depict their under-utilization in sustained manner.

### 1.3. RECYCLING OF METALS FROM BATTERIES

Rechargeable batteries are present in numerous waste electrical and electronics equipment (WEEE). Because of significant use of critical metals in rechargeable batteries, their recycling is important. The dominant primary battery types are alkaline and zinc, while lead/acid dominate secondary batteries. Other secondary batteries include portable batteries – LIBs and NiMH, while HEV batteries (mostly NiMH) have a small but growing market share (3%). A representative elemental distribution in these batteries is given in Table 1.4. The world market for rechargeable battery is dominated by LIBs (51%) followed by NiMH (22%), NiCd (17%) and lithium polymer (10%). Lithium batteries reduce the weight by half and volume by 20-50% compared to the same capacity NiCd and NiMH batteries. LIBs also provide three times the voltage of NiCd and NiMH, thus help reduce the dimension of electronic devices, besides allowing partial charging. Despite the low volumes of spent batteries in short terms due to the low penetration of hybrid and electric vehicles and their long life (> 10 years), the recycling chain must begin with safe handling of small and large LIBs and NiMH batteries, as the remaining charges represent a great risk from short-circuiting.

The two main recycling routes available for Li-ion batteries are a combined mechanical and hydrometallurgical process, and a combined pyro-and hydrometallurgical process (Fig. 1.1). These options are compatible with NiMH battery compounds as well, in addition to pyrolysis. In the mechanical-hydrometallurgical process, batteries dismantled to cell size enter a shredder as the shredding is dangerous due to the risk of explosion and release of hazardous volatile organic compounds (VOCs). Toxco (Canada) applies an energy-intensive cryogenic process to freeze the VOCs, while Recupyl (France) uses inert gases (CO<sub>2</sub> and Ar) to flush the shredder and prevent fire (Saloojee and Lloyd, 2015). Shredding produces three fractions. The fluff (plastic and paper) goes for landfill, metals (Cu, Al, Fe) for sorting and re-melting, and the black mass [anode graphite and cathode (Co, Ni, Al, Mn, Li oxides) materials] for incineration to remove graphite and hydrometallurgical recovery of the metals.

**Table 1.3:** A descriptive list of metal component vis-à-vis secondary resources

Resource Category		Metal Content (%)						References	
		<i>Li</i>	<i>Co</i>	<i>Ni</i>	<i>Mn</i>	<i>Zn</i>	<i>REs</i>		
<b>Batteries</b>	<i>LIBs</i>	3-7	20-35	1-10	1-10	-	-	Chagnes and Pospiech, 2013	
	<i>Ni-MH</i>	--	--	30-50	1	1	10	Vassura et al., 2009	
	<i>Ni-Cd</i>	--	0.8-1	22-30	--	--	--	Shin et al., 2007a,b	
	<i>Alkaline</i>	-	-	1-1.5	20-30	15-20	-		
	<i>Zn-C</i>	--	--	--	18-20	20-35	--		
<b>WEEEs</b>	<i>PCBs</i>	--	200 ppm	0.25-3	--	0.1-2.2	--	Khaliq et al., 2014	
	<i>Magnets</i>	<i>Sm-Co</i>	--	45-65	--	--	--	30-35	Tanaka et al., 2013
		<i>Nd-Fe-B</i>	--	--	--	--	--	30	
	<i>Phosphors</i>	--	--	--	--	--	55	Verma et al., 2013	
<b>Process Wastes</b>	<b>Catalyst</b>	<i>Fluid Cracking</i>	--	--	--	--	--	0.5-2	Alexandre et al., 1991
		<i>Hydrogenation</i>	--	0.5-6	1-6	--	--	--	Biswas et al., 1986
		<i>Hydro-Desulfurization</i>	--	--	5.26-11.6	--	--	--	Pradhan et al., 2013
	<b>Tailing</b>	<i>Cu-based (g/t)</i>	--	15.41	8.81	590.8	163.2	16.10	Chen et al., 2014a
		<i>Zn-based</i>	--	0.05-2	--	--	0.1-8	--	Evdokimov and Evdokimov, 2014
		<i>Mn-tailings</i>	--	--	--	2-10	--	--	Souza et al., 2016
	<b>Others</b>	<i>Granulated Slag</i>	--	5-6	0.5-1.0	--	--	--	Agrawal et al., 2004
		<i>Ash</i>	--	--	--	--	60-85	--	Jha et al., 2001
		<i>EAF Dust</i>	--	--	--	2-5	17-22	--	Caravaca et al., 1994
		<i>Reverts</i>	--	0.05-1.4	0.1-11	--	--	--	Jones, 2013
		<i>Anode Slime</i>	--	0.13	0.06-23	--	--	--	Agrawal et al., 2004
		<i>Jarosite residue</i>	--	--	--	--	3-5	--	
		<i>Dross</i>	<i>Zn Dross</i>	--	--	--	--	9.3-9	--
<i>Al Dross</i>	--		--	--	0.3	0.5	--		



## HYDROMETALLURGICAL PROCESSING OF SPENT BATTERIES FOR THE RECOVERY OF METALLIC VALUES

<b>Effluents</b>	<i>Bleed Stream</i>	<i>Cu/Ni based (g/L)</i>	--	--	9.5	--	--	--	Agrawal et al. 2008
	<i>Pickle Liquor</i>	<i>SS Plant (g/L)</i>	--	--	3-6	--	--	--	Gálvez et al., 2006
		<i>Galvanizing plant (g/L)</i>	--	--	--	--	100-120	--	Sinha et al., 2014
		<i>Brass Plant (g/L)</i>	--	--	0.01	--	25	--	Sinha et al., 2012
	<i>Electroplating</i>	<i>Ni Based(g/L)</i>	--	--	1-5	--	--	--	Tanaka et al., 2008
		<i>Zn Based(ppm)</i>	--	--	--	--	520	--	Jha et al 2005
	<i>Mine Effluents</i>	<i>ETP</i>	--	--	0.95	--	--	--	Valiente et al., 1991
		<i>Zn mines(ppm)</i>	--	--	--	90	1800	--	

**Table 1.4:** Material compositions of some battery types by weight (%) (UNEP, 2013)

<b>Materials</b>	<b>Primary Batteries</b>		<b>Secondary Batteries</b>					<b>Li-ion</b>	<b>Li-Polymer</b>
	<b>Zn-Alkaline</b>	<b>Ni-Cd</b>	<b>NiMH batteries</b>						
			<i>Button</i>	<i>Cylindrical</i>	<i>Prismatic</i>	<i>HEV</i>			
<i>Fe</i>	5-30	40-45	31-47	22-25	6-9	36	24.5	1	
<i>Ni</i>	--	18-22	29-39	36-42	38-40	23		2	
<i>Zn</i>	15-30	--	--	--	--	--	--	--	
<i>Mn</i>	10-25	--	--	--	--	--	--	--	
<i>Cd</i>	--	16-18	--	--	--	--	--	--	
<i>Co</i>			2-3	3-4	2-3	4	27.5 (LiCoO <sub>2</sub> )	35 (LiCoO <sub>2</sub> )	
<i>Li</i>	--	--	--	--	--	--			
<i>RE</i>			6-8	8-10	7-8	7		16	
<i>Cu</i>	--	--	--	--	--	--	14.5	15	
<i>Al</i>	--	--	--	--	--	--		--	
<i>K</i>			1-2	1-2	3-4	--	--	--	
<i>Trace metals</i>	--	--	--	--	--	2	--	15	
<i>Graphite/carbon</i>	--	--	2-3	<1	<1		16	---	
<i>Plastics/Polymer</i>	--	--	1-2	3-4	16-19	18	14	3	
<i>H<sub>2</sub>O</i>	--	--	8-10	15-17	16-18	--	--	--	

### 1.3.1. Lithium Ion Batteries and Recovery of Metals

The spent LIBs are the most prominent secondary source of lithium and other metals. Prior to recycling, it is desired to understand the construction/ composition of the cells in brief and how they transform during the use.

Lithium ion battery is a term used for the battery which has lithium metal, lithium alloy or material adsorbing lithium ions for the negative active material. LIBs use carbon as anode and lithium ions exist in the carbon material; there is no metallic lithium at any state of charge during normal usage. Depending on the technical construction and properties batteries are categorized as either primary or secondary. From the legislative view point batteries are also categorized as portable (household), vehicle or industrial batteries. Primary cells are constructed with metallic lithium. These are non-rechargeable and combustible because alkali metal self-ignites at 178 °C, and react exothermically with water releasing hydrogen. Primary batteries are single-use as irreversible discharge reactions occur in the cells and after use they are disposed off. Secondary battery cells have chemistry that allows reversing the discharge reaction and are rechargeable, like the LIBs. The functional part of LIBs is: cathode, anode, electrolyte and separator which are housed in a protective metal casing.

Cathode is aluminium plate coated with the cathode material, like lithium metal oxide. The typical composition of LIBs is provided in Table 1.5. The most common cathode material is  $\text{LiCoO}_2$ , but  $\text{LiNiO}_2$  and  $\text{LiMn}_2\text{O}_4$  are also used. While the anode is a copper plate coated with graphite, polyvinylidene fluoride (PVDF) binds the electrode coating to the plate. As regards recycling, the mechanical sorting by size is generally used for LIBs. Shredding or sorting has widely been used to increase the surface area, liberate the components / materials, achieve material segregation, and improve the efficiency of subsequent processes. The pre-treatment steps proposed include cutting battery cases etc. (Contestabile et al., 2001; Li et al., 2010b; Chen et al., 2011) and the cryogenic treatment to prevent explosion. Under water explosion to dismantle spent LIBs was also applied (Yamaji et al., 2011). Nan et al. (2005) described the use of a custom dismantling machine to separate the outer steel cans from the contained materials, while Li et al. (2014) used ultrasonic machine to

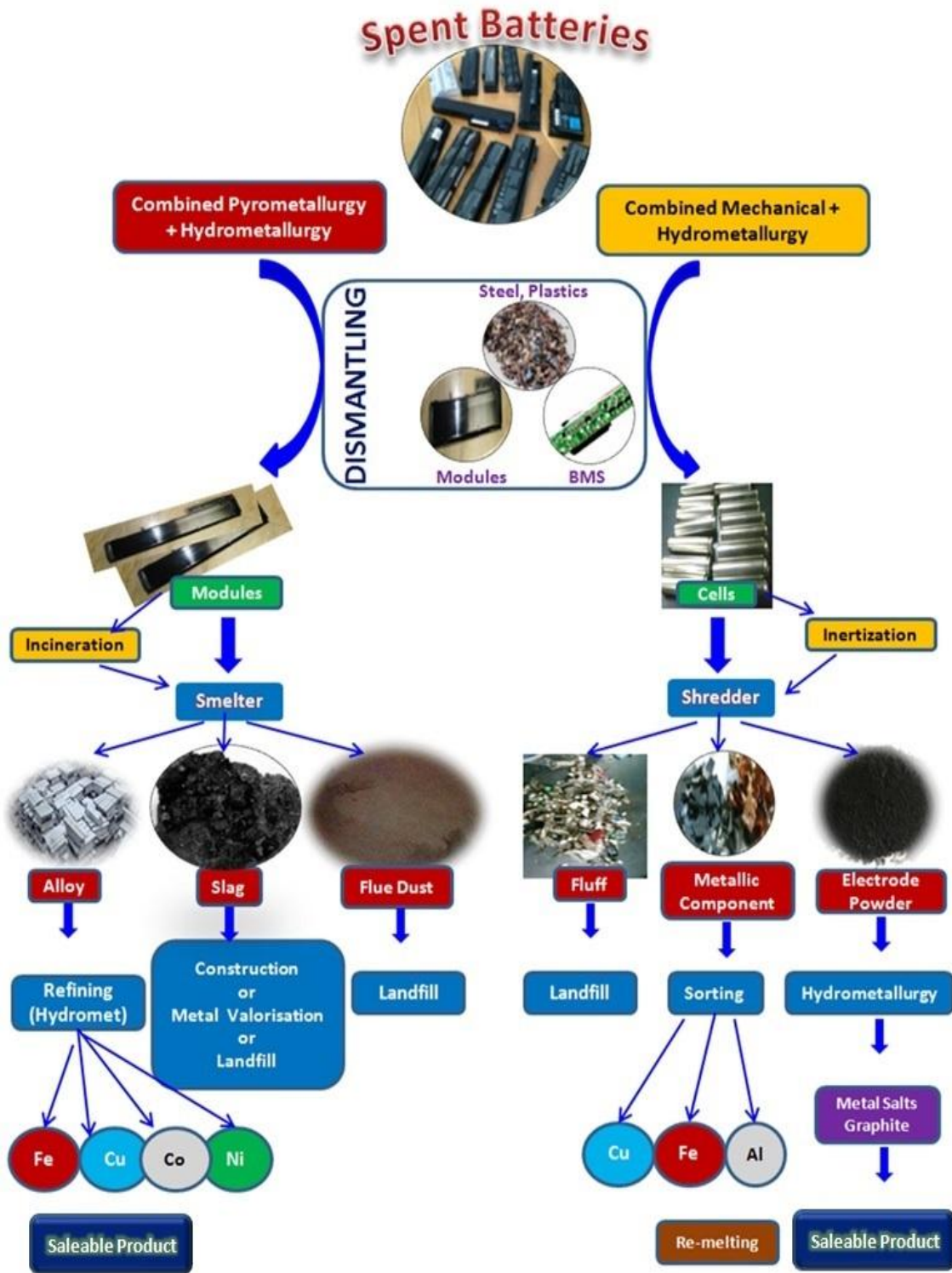


Fig. 1.1: A schematic of proposed processing route for battery waste

separate cathode materials from the Al-foils and separate carbon power from the Cu-foils. A series of two stage thermal treatments, shredding, screening, and acid leaching process was applied by Lee and Rhee (2003).

The chemical reaction in the cell expressed below shows the forms in which lithium and cobalt can be present in the spent LIBs.



The active mass (cathode, anode and electrolyte) of LIBs comprises of almost 40% of the weight whereas ~ 30% (wt) of these components is carbon (anode). Generally LIBs have short life of 2-3 yrs whether they are used or not. It is claimed (Georgi-Maschler et al., 2012) that more than a third of the production cost for LIBs arises from the cost of materials. The valuable metals contained in LIBs include lithium, iron, aluminium, cobalt, nickel and copper. The recovery of cobalt, nickel and copper may affect the economic value of any battery recycling process, which needs to be confirmed with a detailed cost analysis of the selected options.

**Table 1.5:** Composition of spent LIBs after dismantling (Ekberg and Petranikova, 2015)

Component	Element (% wt)	Composition (Mass%)
<i>Cathode</i>	Li	3.14-6.54
	Co	43.3-54
	C	--
	Al	10.2-11.1
	Ni	0.8-1.14
	Mn	0.97
	Cu	0.7
<i>Anode</i>	C	--
	Li	0.5-0.8
	Co	0.05-0.32
	Cu	40.7-52.64
	Al	0.05-2

LIBs contain toxic and flammable components as well as valuable metals (Li, Ni, Cu and Co). Recovery of metals from the used LIBs seems attractive instead of disposal in landfills. Rising demand of lithium and other metals for various applications thus calls for prospecting and processing all viable resources. Lithium can be extracted from spent LIBs by leaching followed by precipitation, ion exchange or solvent extraction and electrolysis (Shuva and Kurny, 2013). It is estimated that 250 t of spodumene or 750 t of brine or 28 t of LIBs of mobile phones and laptops or 256 electric vehicle (EVs) batteries are required to produce 1 ton of lithium (Tedjar, 2013).

World over several companies viz., Toxco, OnTo, Sony, ACCUREC, etc. are currently performing and improving battery recycling processes. Though Toxco and Sony were the first to recycle LIBs which they still continue, several others also started processing such materials recently (Espinosa et al., 2004 a, b; Gaines and Cuenca, 2000; Li et al., 2009a). The Toxco process is designed for all types of lithium containing wastes. The main product is targeted as appropriate (cobalt / other base metals) and other component being the lithium hydroxide. Sony uses incineration which is followed by the hydrometallurgical techniques. The industrial processes in vogue /developed for recycling LIBs are briefly described in Table 1.6.

**1.3.1.1. Recent development in recycling of lithium ion batteries:** Spent LIBs are mostly treated by the hydrometallurgical process and at times in combination with pyrometallurgy. This has integrated pre-treatment steps like pyrolysis or mechanical processing, i.e. crushing and material separation. The thermodynamic aspects particularly the stability regions of different phases in aqueous solutions need to precede the process of metal extraction. For this standard Eh-pH diagrams of Li-H<sub>2</sub>O, Co-H<sub>2</sub>O, Mn-H<sub>2</sub>O and Ni-H<sub>2</sub>O systems can either be referred from literature or reconstructed (Pourbaix, 1966; Schweitzer and Pesterfield, 2010).

The LIBs can be leached in different acids, like HCl (Zhang et al., 1998a; Contestabile et al., 2001), H<sub>2</sub>SO<sub>4</sub> (Shin et al., 2005; Nan et al., 2005; Dorella and Mansur, 2007; Swain et al., 2007; Aktas et al., 2006; Kang et al., 2010 a, b), HNO<sub>3</sub>

(Lee and Rhee, 2002; 2003), and a few organic acids like DL-malic acid (Li et al., 2010 a), citric acid (Li et al., 2010b; Chen and Zhou, 2014), etc. The binder (PVDF) which links the cathode material,  $\text{LiCoO}_2$  with aluminium foils does not dissolve easily in the common organic reagents making the leaching more difficult. Details on leaching and recovery of metals from spent LIBs are summarized in Tables 1.7-1.9.

*Metal extraction /recovery from hydrochloric acid leach liquors:* In most processes reported, optimum extraction of metals from the cathode material of spent LIBs was achieved in 4 M HCl (Table 1.7). In the presence of a reducing agent such as hydrogen peroxide, metal leaching was possible even in 3 M HCl (Zhang et al., 1998a; Contestabile et al., 2001; Shuva and Kurny, 2013; Joulié et al., 2014). While  $\text{H}_2\text{O}_2$  facilitates the dissolution of Co(II) which is reduced from Co(III), the dissolution of lithium is also promoted. The separation and recovery of metals from the leach liquors were carried out by SX involving PC-88A, Cyanex 272, etc. to produce pure metal salts or  $\text{Co(OH)}_2$  and  $\text{LiCO}_3$ . Thus, Zhang et al. (1998a) used the steps such as leaching of cathode materials of spent LIBs in HCl, separation of Co/Li by solvent extraction (PC-88A) and recovery of cobalt as sulfate and lithium as carbonate. The leaching efficiency of > 99% of Co and Li in 4 M HCl was achieved while producing high purity  $\text{CoSO}_4$  by SX process. About 80% Li was precipitated as  $\text{Li}_2\text{CO}_3$  with saturated soda solution at 100 °C. The leaching reaction of the waste  $\text{LiCoO}_2$  with HCl solution can be represented as:



The leaching of  $\text{LiCoO}_2$  in HCl and precipitation of cobalt hydroxide, were reported by Contestabile et al. (2001). The active material of spent LIBs was dissolved in N-methylpyrrolidone at 100 °C to separate aluminium and copper foils. From the leach liquor, carbon powder was removed and  $\text{Co(OH)}_2$  was precipitated at pH 6-8. Leaching with 6 M HCl and 60 °C in the presence of  $\text{H}_2\text{O}_2$  dissolved over 95% Ni, Co and Mn (Li et al., 2009b). By adding chlorides of Ni, Mn and Co in the leach solution, cathode precursor ( $\text{Ni}_x\text{Co}_y\text{Mn}_z$ ) was co-precipitated. The reductive HCl

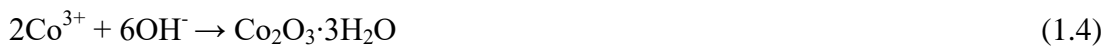
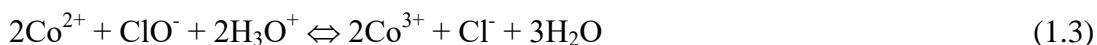
**Table 1.6:** Major industrial process for recycling of the lithium ion batteries (UNEP, 2013; Saloojee and Lloyd, 2015).

<b>Technology</b>	<b>Pre-treatment</b>	<b>Dismantling</b>	<b>Extraction Process</b>	<b>Recovered product</b>
<i>AEA Technology Inc., UK</i>	Dismantling in N <sub>2</sub> atmosphere, followed by mechanical separation	Aceto-nitrile to dissolve electrolyte & solvent NMP is used to dissolve binder	Electrolysis (evaporation/recycle of solvents)	-CoO -LiOH
<i>Accurec Recycling, Germany</i>	Mechanical pre-treatment	Vacuum thermal treatment & pyrolysis; followed by sieving & magnetic separation	Reduction smelting of electrode briquettes	Co-Mn alloy Li rich slag
			Acid leaching of slag	LiCl/Li <sub>2</sub> CO <sub>3</sub>
<i>Umicore, Belgium/Sweden</i>	-	Smelting	Sulfuric acid leaching of molten metal	-NiSO <sub>4</sub> - CoCl <sub>2</sub>
<i>Batrec Industrie AG Process, Switzerland</i>	Crushed in CO <sub>2</sub> atmosphere	Neutralization of gases by air and collection	Acidified leaching followed by SX	Metal salts
<i>Sumitomo Electric SONY, Japan</i>	Calcination at 1000°C	Magnetic separation of metallic/non-metallic fractions	Acid leaching	CoO
<i>Recupyl, France</i>	Mechanical treatment in inert gas atmosphere	Physical treatment to separate steel, Cu, plastic & fines	Leaching of fines at pH>12 followed by H <sub>2</sub> SO <sub>4</sub> leaching, precipitation of Li using CO <sub>2</sub>	-Li <sub>2</sub> CO <sub>3</sub> -Li <sub>3</sub> PO <sub>4</sub> -Co(OH) <sub>3</sub>
<i>Retriev, Canada (Formerly TOXCO)</i>	Milling and Tabling (removes steel)	Mixing/Holding	Precipitation of enriched brine by Soda	-Li <sub>2</sub> CO <sub>3</sub> -Cu-Co product

leaching of metals from the cathode material and their recovery, were also reported elsewhere (Wang et al., 2009; Shuva and Kurny, 2013).

Processing of battery ash obtained from the pyrolysis of spent LIBs by HCl leaching was patented by Lin et al. (2003). The membrane electrolysis could separate Cu and Co from the solution of ash (metal and oxides) leached in HCl containing NaCl.

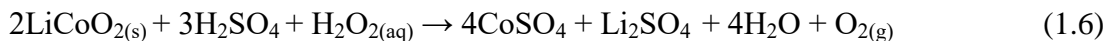
Recently Joulié et al. (2014) reported the high leaching efficiency (~100%) of Li, Ni, Co and Al from the oxide ash in 4 M HCl with chloride ions. Cobalt was oxidized to Co(III) with NaClO and recovered as  $\text{Co}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  by selective precipitation at pH 3 (Eq. 1.3,1.4) followed by precipitation of nickel hydroxide at pH 11 .



Compared to the most studies reported on metal extraction from the cathodic material, Guo et al. (2016) recently reported the leaching of 99.4% Li from anodic material in 3 M HCl.

*Metal extraction /recovery from sulfuric acid leach liquors:* Leaching in sulfuric acid uses mostly hydrogen peroxide as a reductant (Castillo et al., 2002; Shin et al., 2005; Dorella and Mansur, 2007; Kang et al. 2010a; Jha et al., 2013a, b). In some cases alkali leaching followed by acid leaching was considered to remove aluminium. Metals from the leach solutions were separated by using PC-88A/P507, Cyanex 272 and Acorga M5640 very similar to that of the HCl system (Table 1.8). The binder of the electrode material was dissolved in N-methyl pyrrolidone (NMP), and the active material ( $\text{LiCoO}_2$ ) was leached in 4 M  $\text{H}_2\text{SO}_4$  (Castillo et al., 2002). Reductive leaching of cobalt and lithium in varying concentrations of  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  was also reported (Shin et al., 2005; Kang et al., 2010a). Relatively lower recovery of metals (80% Co and 95% Li) by leaching the mechanically treated LIBs in 6 (v)%  $\text{H}_2\text{SO}_4$  with low amount of  $\text{H}_2\text{O}_2$  was observed (Dorella and Mansur, 2007). The reactions of  $\text{LiCoO}_2$  with  $\text{H}_2\text{SO}_4$  and in the presence of  $\text{H}_2\text{O}_2$  are shown below:





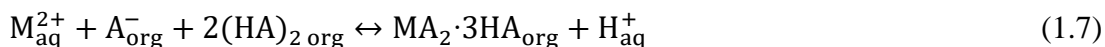
The leaching efficiency of cobalt depends on the reductant concentration. With the reducing agent,  $\text{Na}_2\text{S}_2\text{O}_3$  leaching was >99% (Co and Li) in 2 M  $\text{H}_2\text{SO}_4$  at 90 °C (Wang et al., 2012).

Safe dismantling procedures of spent lithium ion batteries have often been described (Tanii et al., 2003; Nan et al., 2005). Zhu et al. (2011) applied mechanical separation (gas fluidized bed) to recover ~92% of copper in anode particles.

In the alkali–acid process, the cathode was first treated with 10% (w/w) NaOH to dissolve Al, followed by reductive leaching with  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  (~97% Co and 100% Li) (Nan et al., 2005; Ferreira et al., 2009). Acorga M5640 and Cyanex 272 were used to selectively extract and recover 98% Cu and 97% Co, respectively.  $\text{LiCoO}_2$  was synthesized from the recovered Co and Li with a good electrochemical performance.

Using the ethanol /sulfate precipitation method depending on their concentrations, 96% Cu was reclaimed as  $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$  at ethanol: sulfate volume ratio of 3:1. Cobalt was recovered in two steps; 92% as  $\text{CoSO}_4$  at a ratio of 3:1 (step-I) and rest in step-II as  $\text{Co}(\text{OH})_2$  by adding  $\text{Li}(\text{OH})_2$  at pH 10 (Aktas et al., 2006). About 90% Li and 99% Al were also recovered as  $\text{Li}_2\text{SO}_4$  and  $\text{Al}(\text{OH})_3$ , respectively.

The waste cathodic active material generated during the manufacturing of LIBs was also leached in  $\text{H}_2\text{SO}_4$  in the presence of  $\text{H}_2\text{O}_2$  (Swain et al., 2006; 2007). Separation of Co/Li with high efficiency was achieved using a saponified Cyanex 272 in a 2-step SX process. The mechanism by which a metal ion is extracted from an aqueous solution using a partially saponified cation exchange extractant is as follows (Ritcey and Ashbrook, 1984):



Cobalt is extracted as  $[\text{CoA}_2 \cdot 3\text{HA}]_{\text{org}}$  with 65% Na-Cyanex 272. Cobalt can be completely stripped from the loaded organic with 0.01 M  $\text{H}_2\text{SO}_4$  to produce cobalt sulfate of >99% purity.

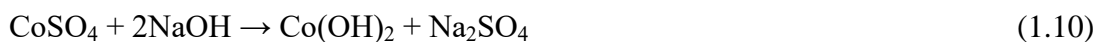
By acid leaching of waste cathodic material and SX with Cyanex 272, Swain et al. (2008) produced pure cobalt sulfate solution (99.99%). Co(II)/Li separation was reported using the supported liquid membrane (SLM) with a mixed extractant containing Cyanex 272 and DP-8R as the mobile carrier (Swain et al., 2010). Reductive sulfuric acid leaching of metals from waste mobile phone batteries and separation of Co/Li by Cyanex 272, were also reported (Jha et al., 2013a, b). Chen et al. (2011) recovered cobalt oxalate by the alkali–acid leach process after roasting spent LIBs at 700–800 °C to burn off carbon and binder. After dissolving Al in NaOH leaching, ~95% Co and 96% Li could be reclaimed in acid leaching from which ~99.99% iron was removed as jarosite with a loss of <1% Co in the pH range 3-3.5. The precipitation reaction is shown below:



Complete removal of manganese with ammonium persulfate at pH 4 and 70 °C is as follows:



Copper precipitation (>98.5%) with NaOH was followed by SX to remove 97% Ni and Li with the saponified 25wt. % P507 (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester), and recover 99.9% pure Co(II) oxalate (Zhu et al., 2012).  $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Li}_2\text{CO}_3$  were also produced by a combination of acid leaching, SX and precipitation from spent mobile phone batteries (Jian et al., 2012).  $\text{Co}(\text{OH})_2$  was precipitated from the leach liquor and was converted to  $\text{Co}_3\text{O}_4$  (Yamaji et al., 2011) as per reactions (1.10-1.11). Lithium was recovered as carbonate by adsorption with 2%  $\text{MnO}_2$  (11.7 mg Li/g).



Advantage of vacuum pyrolysis (at ~600 °C) preventing both the escape of toxic gases and oxidization of metals while lowering the decomposition temperature of organics, was applied by Sun and Qiu (2011). Over 99% Co and Li were recovered from peeled Co-Li oxide by leaching with 2 M  $\text{H}_2\text{SO}_4$ . Paulino et al. (2008) examined

two approaches, i) calcination of spent batteries at 500 °C followed by reductive leaching at 90-100 °C, and solvent extraction, and ii) fusion with  $\text{KHSO}_4$  at 500 °C and water leaching with  $\text{H}_2\text{O}_2$  at 90 °C. Cobalt and manganese were precipitated at  $\text{pH} > 9$  followed by precipitation of  $\text{LiF}$  by  $\text{KF}$ .

Extraction of Co and Li from a material of a large scale mechanical pre-treatment and recycling plant in Northern Italy is described by Granata et al. (2012). The leaching in  $\text{H}_2\text{SO}_4$  with 50% excess of a reductant, glucose—a waste product of food factory, was followed by partial precipitation of Fe, Al and Cu (hydroxides) at  $\text{pH} 5.0$ , and cobalt recovery by SX and precipitation (as carbonate, 47% Co). Lithium salt was crystallized (yield 80%) with 98% purity. Suzuki et al. (2012) developed a process in which Acorga M5640 extracted Cu, Al extracted by PC-88A, and Co/Li was separated by PC-88A/TOA with higher stripping efficiency (>98%).

Synergistic extraction and separation of Co(II) and Mn(II) with Li(I) from simulated sulfuric acid leaches of waste cathodic materials using a mixture of Cyanex 272 and PC-88A in n-heptane have been investigated by Zhao et al. (2011). A mixed extractant system (Ionquest 801, Acorga M5640, Cyanex 272) and an ion exchange resin (Dowex M4195) were utilized to treat the leach solutions of spent LIBs (Pranolo et al., 2010). Apart from extracting the valuable metals from spent LIBs,  $\text{LiCoO}_2$  was also synthesized (Li and Zeng, 2011). The solvent N-methyl-2-pyrrolidone (NMP) was used to dissolve the PVDF agglomerate from Co-Li membrane to separate aluminium foils. About 88% Co was recovered during the leaching with sulfuric acid at 80 °C. Then, 1 M citric acid solution was added at 65 °C to prepare a gelatinous precursor from which  $\text{LiCoO}_2$  was obtained by calcination at 450 °C.

*Metal extraction /recovery from nitric acid leach liquors:* Mechanical, thermal, hydrometallurgical and sol–gel steps were applied to recover Co/Li from spent LIBs and synthesize  $\text{LiCoO}_2$  as cathode active material (Lee and Rhee, 2002, 2003). The reductive leaching ( $1\text{M HNO}_3 + 1.7 \text{ vol.}\% \text{ H}_2\text{O}_2$ ) at 75 °C extracted ~ 95% Li and 95% Co (Table 1.8). By adjusting the Li /Co molar ratio in the leach liquor at 1.1 with a  $\text{LiNO}_3$  solution and then adding 1 M citric acid, the obtained gelatinous precursor was calcined at 950 °C to produce crystalline  $\text{LiCoO}_2$ . Recovery of ~100% Co and Li from the spent batteries in nitric acid and  $\text{H}_2\text{O}_2$  was achieved at 80 °C by Li et al.

(2011). Pollution due to harmful NO<sub>x</sub> gases is a major problem in this system. The dissolution of LiCoO<sub>2</sub> in nitric acid is found to be controlled by surface chemical reaction kinetics with apparent activation energy of 52.32 and 47.72 kJ /mol for Co and Li, respectively (Lee and Rhee, 2003). The leaching reaction with HNO<sub>3</sub> can be represented as:



Recycling of Li-ion and polymer batteries while producing LiCo<sub>x</sub>Ni<sub>(1-x)</sub>O<sub>2</sub> as a cathode material was also investigated by Lupi and Pasquali (2003). The process consists of cathodic paste leaching, Co-Ni separation by SX and Ni recovery by electrowinning. Ni and Co were separated by using saponified Cyanex 272. Ni was electrowon at a current density of 250 A/m<sup>2</sup>, 50 °C and pH 3-3.2 with current efficiency and energy consumption of 87% and 2.96 kWh/kg as against the figures of 96% and 2.8 kWh/kg, respectively for cobalt at pH 4-4.2 from a solution containing manganese and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (Lupi et al., 2005).

*Metal extraction using organic acids/reagents:* For the sustainable management of the secondary resource such as LIBs, organic acids such as DL-malic acid, citric acid etc. which have mild acidity are suggested (Table 1.9). Li et al. (2010a) reported rapid dissolution of lithium and cobalt from LIBs in DL-malic acid under aerobic and anaerobic conditions. Almost 100% Li and >90% Co were leached out with 1.5 M malic acid and 2.0% H<sub>2</sub>O<sub>2</sub> at 90 °C: the leaching efficiency in citric acid being similar after separating the anode and cathode material by treatment with NMP (Li et al., 2010b).

The ultrasonic assisted leaching of metals in the presence of ascorbic acid was investigated (Li et al., 2012); the leaching efficiencies being 94.8% for Co and 98.5% for Li with 1.25 M ascorbic acid at 70 °C (Table 1.9). Sun and Qiu (2012) used oxalic acid as both leachant and precipitant to separate and recover cobalt and lithium. The cathode material (LiCoO<sub>2</sub> and CoO) from the dismantled batteries after vacuum pyrolysis at 600 °C, was leached in 1 M oxalate at 80 °C. The reaction efficiency was

>98% of LiCoO<sub>2</sub> while separating Co and Li. The reaction with oxalate for leaching and precipitation proceeds as:



During the oxalate leaching Co<sup>3+</sup> is reduced to Co<sup>2+</sup> which is dissolved and precipitated as cobalt(II)-oxalate. The reduction of Co<sup>3+</sup> to Co<sup>2+</sup> is also believed to proceed by the reaction of CO<sub>2</sub> radicals generated from oxalic acid (Hoffman and Simic, 1973).

The ultrasonic-assisted recovery of metals from the cathode active materials of spent LIBs in different acids was studied (Li et al., 2014). Out of the acids, H<sub>2</sub>SO<sub>4</sub>, HCl and citric acid, the leaching with 0.5 M citric acid with 0.55 M H<sub>2</sub>O<sub>2</sub> was found (using 90 W ultrasonic power) to be more efficient than the other two acids. The high leaching efficiency is ascribed to the unique cavitation action of the ultrasonic waves and ultrasonic-assisted leaching with the citric acid.

The electrochemical performance of nano-Co<sub>3</sub>O<sub>4</sub> anode material prepared from the spent LIBs by sol-gel method was evaluated by Hu et al. (2013). The product CoC<sub>2</sub>O<sub>4</sub> obtained from the alkali-acid leaching and precipitation by (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, was used to synthesize nano-Co<sub>3</sub>O<sub>4</sub>. Roasting of batteries under reduced pressure at 650 / 450 °C followed by leaching in organic acids and synthesis of Li<sub>2</sub>CO<sub>3</sub>, were reported (Kondás et al., 2006; Liu et al., 2006).

Use of a mixed acids, citric / tartaric (chelating agent) and ascorbic acid (reducing agent) was also examined to process the batteries (Nayaka et al., 2016 a, b). The leaching efficiency of Li and Co was >95%. Co was separated from the leach solution as Co-oxalate and Li as LiF. Recent study on the leaching of metals from treated cathode active material from the commercial LIB pack of HEVs may be mentioned (Ku et al., 2016). Ammonium sulfite as a reductant enhanced the leaching kinetics of Ni and Co. Co and Cu can be preferentially dissolved in a mixture of 1M NH<sub>3</sub>, 0.5 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub> and 1 M (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> at 80 °C leaving Mn and Al.

### 1.3.2. Nickel Metal hydride (NiMH) batteries

Nickel metal hydride (NiMH) batteries were developed in 1989 and commercialized primarily in Japan in 1990 to replace NiCd systems. They have high electrochemical capacity, as well as safety and good environmental compatibility. In addition, NiMH batteries are found to be efficient in a wide range of temperatures ( $-20$  to  $60$  °C), and possess long lives (500–1000 cycles) and low self-discharge rates. The positive electrode is a porous nickel coated with nickel oxy-hydroxide whilst the anode is made of a hydrogen storage alloy based on mischmetal (mainly Ce, La, Pr, and Nd) on a metal-mesh substrate. An inert insulating layer made of polypropylene or polyamide separates the two electrodes and KOH is used as electrolyte. Their working is based on the anodic and cathodic reactions (Eqn.1.15, 1.16):



Thus during the discharge, active material at the cathode, NiOOH gets reduced to Ni(OH)<sub>2</sub> and hydrides of La-Ni alloy (an AB<sub>5</sub>-type alloy) at anode are oxidized to its un-hydride alloy. The standard potential for the reaction at the anode is +0.490 V and that at the cathode is -0.828 V. Thus, the cell voltage works out to be 1.318 V and the nominal voltage is 1.2 V.

The alloy of LaNi<sub>5</sub> family has a typical composition, MmNi<sub>3.6</sub>Co<sub>0.7</sub>Mn<sub>0.4</sub>Al<sub>0.3</sub> (Mm stands for mischmetal, a mixture of REs, La, Ce, Nd and Pr with similar chemical properties). This type of electrochemical system is not too harmful to the environment as against Ni-Cd and Pb-acid batteries, in spite of high metal contents as they comprise of a complex polymetallic deposit (Lupi and Pilone, 2002; Muller and Friedrich, 2006). The electrodes of NiMH batteries constitute several metals of economic values.

It is estimated that nickel bearing scrap totaling 4.4-4.6 million tons per year is collected and recycled. These scraps may contain almost 350,000 t of nickel (or one-

**Table 1.7:** Extraction and recovery of metals from spent LIBs in hydrochloric acid system

Material	Leaching Conditions				Extraction / separation-parameters	Highlights (with merits/demerits)	References
	Acid concentration (M)	Temp. (°C)	Time (h)	Pulp density (g/L)			
Cylindrical-shaped LIBs	4	80	1	100	SX with 0.29 M D2EHPA and 0.90 M PC-88A	SX: > 99.9 Co and 12.6% Li with 0.9 M PC-88A, Higher selectivity with PC 88A.	Zhang et al., 1998a
Spent LIBs	4	80	1	100	Precipitation: pH 6-8 with 4 M NaOH, Synthesis of precursor material by co-precipitation.	Co(OH) <sub>2</sub> separated easily. Ni <sub>x</sub> Co <sub>y</sub> Mn <sub>z</sub> a precursor to cathode material	Contestabile et al., 2001
LIBs	4	80	1	20	Precipitation: pH 2 with KMnO <sub>4</sub> for Mn(II),. pH 9 for Co by DMG and Li <sub>2</sub> CO <sub>3</sub>	Purity (%): 96.9 Li, 98.23 Mn, 96.94 Co and 97.43 Ni	Wang et al., 2009
Spent battery material	6 + 3% H <sub>2</sub> O <sub>2</sub>	60	2	120	Precipitation: <i>Cu removal</i> : 30 °C, Iron powder (Femol/Cumol=1.5), 30 min <i>Fe removal</i> : pH 4, 90 °C, 6 h <i>Ni, Co, Mn</i> by (NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	Recovery (%):~ 95%Ni, Co and Mn Precipitation: 99% Cu, Fe Ni <sub>x</sub> Co <sub>y</sub> Mn <sub>z</sub> a precursor to cathode material	Li et al., 2009a
LIBs	3 M acid + 3.5% H <sub>2</sub> O <sub>2</sub>	80	1	50	Precipitation : pH 11-12 with NaOH for Co; Na <sub>2</sub> CO <sub>3</sub> at 100 °C for Li	Recovery (%): 95 Co and 93 Li in precipitate	Shuva and Kurny, 2013
Ash from LIBs	4	90	18	50	Precipitation by NaClO at pH 3 and base addition at pH 11	Recovery (%): 100 Co and 99.99 Ni. HCl gives higher leaching efficiency.	Joulié et al., 2014
Spent LIBs of mobile	3+ 0.3 M H <sub>2</sub> O <sub>2</sub>	80	1.5	20	--	Recovery:99.4% Li	Guo et al., 2016

**Table 1.8:** Extraction and recovery of metals from spent LIBs in sulfuric acid system

Material	Leaching Conditions				Extraction / separation-parameters	Highlights (with merits/demerits)	References
	Acid concentration	Temp. (°C)	Time (h)	Pulp density(g/L)			
LIBs waste	2 M acid + 15 vol.% H <sub>2</sub> O <sub>2</sub>	75	0.167	50	-	Leaching (%): 95 Co and 100 Li. Harmful gas- SO <sub>x</sub> generated.	Shin et al., 2005
Square-shaped LIBs	3 M acid	70	4	200	Precipitation & SX using Acorga M5640 and Cyanex 272	Precipitation: 90% Co SX: ~97% Cu by Acorga M5640, 97% Co by Cyanex 272	Nan et al., 2005
LIBs	6 % acid + 1% H <sub>2</sub> O <sub>2</sub>	65		33.3	Precipitation with NH <sub>3</sub> at pH 5. Co/Li separation by diluted (0.72 M) Cyanex 272	Leaching (%): ~ 55 Al, 80 Co and 95 Li. Extraction (%):~85 Co by Cyanex 272.	Dorella and Manusr, 2007
LIB wastes	2 M acid + 5% H <sub>2</sub> O <sub>2</sub>	75	0.5	100	SX by 0.5 M Cyanex 272, pH 5.35 and O/A = 1 in 1-stage	Leaching (%): 93 Co and 94 Li. CoSO <sub>4</sub> solution: 99.99% pure.	Swain et al., 2007
Spent LIBs	4 M acid + H <sub>2</sub> O <sub>2</sub>	80	4		Precipitation using ethanol, ethanol/solution = 3:1; 15 min, room temperature	Co recovery: 92% as CoSO <sub>4</sub> and 8% Co as Co(OH) <sub>2</sub> by adding Li(OH) <sub>2</sub> at pH 10.	Aktas et al., 2006
Synthetic solution (10 mol/L Co(II) and 20 mol/L Li <sub>2</sub> SO <sub>4</sub> )	-	-	-	-	SX by Cyanex 272 and DP-8R	Separation factor (Co/Li): 497 at pH 5	Swain et al., 2010
Spent LIBs	2 M acid + 6% H <sub>2</sub> O <sub>2</sub>	60	1	100	Precipitation at pH 6.5 for Cu, Fe and Al SX by 50% saponified 0.4 M Cyanex 272, pH 6, O/A = 2	Leaching (%): >99 Co, SX: 99.9% Co in 2 stages; Separation factor 750 (Co/Li) and Co/Ni at pH 6.	Kang et al., 2010a
Spent LIBs	1 M acid + 30% H <sub>2</sub> O <sub>2</sub>	80	2	714	Precipitation by 1M citric acid, 2 h, 65 °C; calcined at 450 °C, 4 h	Max. Co leaching (%): 88.3; Crystalline LiCoO <sub>2</sub> synthesised	Li and Zeng, 2011
Spent LIBs	4 M acid + 10% H <sub>2</sub> O <sub>2</sub>	85	2	100	SX by 25% P507 Precipitation by ammonium oxalate, pH 1.5	SX: 98% Co and removal of 97% Ni and Li.	Chen et al., 2011
Spent LIBs	3 M + 0.25 M Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	90	3	67	-	> 99% leaching	Wang et al., 2012



**Table 1.9:** Extraction and recovery of metals from spent LIBs in other organic/inorganic acid systems

Material	Leaching reagent	Leaching Conditions			Highlights (with merits/demerits)	References
		Time (h)	Temp. (°C)	Pulp density (g/L)		
LIBs	1 M HNO <sub>3</sub> +1.7 vol.% H <sub>2</sub> O <sub>2</sub>	1	75	20	Leaching (%): 95 Co and Li. Harmful gas-NO <sub>x</sub> generated.	Lee and Rhee, 2002; 2003
LIBs	1 M HNO <sub>3</sub> +1.0 vol.% H <sub>2</sub> O <sub>2</sub>	1	80	20	Leaching (%): 100 Co and Li. Harmful gas-NO <sub>x</sub> generated.	Li et al., 2011
Spent LIBs	1.5 M DL-Malic acid + 2% H <sub>2</sub> O <sub>2</sub>	0.67	90	20	Leaching (%): 90 Co and 100 Li. Acid can be recycled and reused.	Li et al., 2010a
Spent LIBs	1.25 M citric acid + 1% H <sub>2</sub> O <sub>2</sub>	0.25	90	20	Leaching (%): >90 Co and 100 Li. Simple and environmental friendly process.	Li et al., 2010b
Cylindrical spent LIBs of mobile phone	1.25 mol/L ascorbic acid	0.33	70	25	Leaching (%): 94.8 Co and 98.5 Li. Reducibility of ascorbic acid displaced H <sub>2</sub> O <sub>2</sub> .	Li et al., 2012
Spent LIBs	0.4 M tartaric acid and 0.02M ascorbic acid	5	80	2	Leaching: >95%Li, Co Precipitation:Co-oxalate	Nayaka et al., 2016b
Spent LIBs	0.5 M citric acid with 0.55 M H <sub>2</sub> O <sub>2</sub> + 90 W ultrasonic power	5	60	25	Leaching: >96% Co and ~ 100% Li	Li et al., 2014

quarter of the total demand) annually which is mainly used by the stainless steel industry (Naik, 2008). The nickel scrap processing industry consists of four or five major players operating internationally to ensure collection of such scraps from every corner of the globe. Moreover, batteries contain a variety of materials that can be reused as a secondary raw material. Though standard methods are used for recycling of traditional batteries, but for some like newer nickel-hydride and lithium systems, recycling methods are still in the early stages. With huge opportunity for development, it follows that collecting and recycling of the batteries will be important.

Approximately 7% of a typical NiMH battery is made up of REs. This equates to around 1 g of REs per AAA battery, 60 g for a household power tool and 2 kg for a HEV battery (Tunsu and Retegan, 2016). The fact that in a HEV battery the REs are present mainly at one of the electrodes (anode), is a definite advantage for their recovery. Separation of the anodic material from the cathodic material allows easier separation of REs, lower chemical consumption and higher product purity. The metals present in various types of NiMH batteries are given in Table 1.10.

Unlike the pyrometallurgical processes in which the loss of REMs in the slag phase is an issue, the hydrometallurgy provides complete recovery of metals at high purity, low-energy requirements and minimal air emissions besides, showing flexibility and selectivity. In order to get homogeneous raw material some pre-treatment/ mechanical separation is often used.

**Table 1.10:** Composition of various types of Ni-MH batteries (Heegn et al., 2003)

Batteries	Battery type	Elemental composition (wt.%)											
		REs					Base Metals						
		La	Ce	Nd	Pr	Y	Ni	Fe	Co	Al	K	Mn	C
Portable NiMH batteries	Button Cells	6-8					29-39	31-47	2-3	--	1-2	--	2-3
	Prismatic cells	8-10					36-42	22-25	3-4	--	1-2	--	<1
	Cylindrical cells	7-8					38-40	6-9	2-3	--	3-4	--	<1
HEV NiMH batteries	Cathode	--	--	--	--	0.9	64.7	--	5.7	0.1	0.2	0.2	--
	Anode	20.2	7.4	2.4	1	0.7	52.3	0.1	3.6	1.5	0.4	5.6	--

**1.3.2.1. Pre-treatment/Dismantling/ mechanical separation:** The pre-treatment consists of manual dismantling or mechanical processing including grinding, classification and separation using difference in density, weight, size, magnetic properties, etc. (Ferreira et al., 2009; Huang et al., 2011; Al-Thyabat et al., 2013). This improves the recovery efficiency of target metals. The electrodes are separated manually or using some physical /mechanical treatment. Mechanical treatment is efficient and flexible with high throughput, but consumes considerable amount of energy (Huang et al., 2011; Al-Thyabat et al., 2013). Bertuol et al. (2006) used the magnetic separation to recycle spent NiMH batteries.

Tanabe et al. (2016) recovered valuable materials from spent NiMH batteries using spouted bed elutriation, an alternative initially tried for spent LIBs (Bertuol et al., 2015). The elutriation can be realized based on the difference in particle size and/or density. While using spouted bed elutriation Bertuol et al. (2015) processed spent LIBs, Tanabe et al. (2016) could separate different materials (polymer, metals and powder - the active materials of anode and cathode) present in the spent NiMH batteries using grinding, sieving and spouted bed elutriation. Having estimated the quantity of each component by manual dismantling, mechanical processing was used to yield three different fractions: 24.2% of metals, 28.2% of polymers and 42% of powder (positive and negative electrodes) - out of which ~37 wt.% is composed of Ni-based alloy. The best results on laboratory scale (86% metal yield, 5.6% process loss), was obtained by hammer milling, magnetic separation, knife milling, magnetic separation and size separation.

An effective physical separation process is necessary prior to chemical processing of metals. Hence crushing at low temperature and magnetic separation were applied for bookshelf-type Ni-MH batteries; the optimum treatment flow with 3-stage magnetic separation to recover anodic, cathodic, iron and plastic components was demonstrated (Tsunekawa et al., 2007). Earlier mineral processing techniques involving hammer and knife milling, magnetic and size separation were applied to recover Ni-based alloys from such batteries (Tenorio and Espinosa, 2002).

**1.3.2.2. Recent development in recycling of nickel metal hydride batteries:** In order to recycle spent Ni-MH batteries from the point of view of resource recovery, especially the base and rare earth metals, the hydrometallurgical processes were worked out on different scales; the details are described here in brief.

*Metal extraction /recovery from HCl leach liquors:* Table 1.11 highlights the processes developed to extract metals from NiMH batteries in HCl. Out of the mineral acids used to leach valuable metals from the spent NiMH batteries, best results were obtained with 4 M HCl (Lyman and Palmer, 1993; 1995). The REMs could be recovered from the resulting chloride solution, whereas, Co and Ni were recovered as oxalate.

Leaching of spent batteries with HCl and separation of REs by D2EHPA, and electrochemical recovery of a Ni-Co alloy (Tzanetakis and Scott, 2004a;b) or separation by Cyanex 923 to reclaim the rare earths (Larsson et al., 2012, 2013), were reported. Use of an ionic liquid (IL), tricaprylmethyl ammonium chloride (Aliquat 336, [A336][Cl]) was reported by Larsson and Binnemans (2014) to extract Co, Mn, Fe and Zn from the HCl leachate of electrode materials in step-I, followed by using its nitrate analogue, [A336][NO<sub>3</sub>] to extract the REs from the concentrated chloride solution in step-II. Larsson and Binnemans (2015) further used the tricaprylmethyl ammonium nitrate with/ without a neutral extractant, Cyanex 923 to recover REMs which form the extractable nitrate complexes directly from the aqueous phase.

Using 12 M HCl, Fernandes et al. (2013) extracted Ni, Co and lanthanides from the spent Ni-MH batteries followed by SX and precipitation of lanthanides as oxalates. The leaching characteristics of constituent metals in the electrodes were applied to treat the batteries of HEVs; recovered base metals and yttrium, the only RE from the cathodic material (Larsson et al., 2013).

*Metal extraction /recovery from sulfuric acid leach liquors:* Table 1.12 highlights the attempts made for the extraction of metals from the spent NiMH batteries in sulfuric acid.

Rodrigues and Mansur (2010) utilized a two-stage leaching process both with 8% v/v sulfuric acid and without any addition of  $H_2O_2$  at 30 °C. The leach-I yield was 80-85% for Ni and 95-100% for Co, and leach-II recovered ~87% REs and ~100% Ni; REs were precipitated with NaOH. Dissolved La and Ce from industrial scale grinding of batteries (<500 mm) in two sequential leaching steps, were also selectively precipitated at pH <2 yielding La-Ce-sulfates with 99% recovery.

The leaching of the mixed materials of positive and negative electrodes with 3 M  $H_2SO_4$  at 95 °C was reported (Li et al., 2009). The low solubility of  $RESO_4$  at high temperature separated REs (~94.8%) from the base metals. Fe, Zn and Mn (and remaining 5.2% REs) were then separated from Ni and Co by SX with 20% P204. REs were recovered as  $RECl_3$  from the alkali treated filter cake, and spherical  $Ni(OH)_2$  was synthesized from the Co/Ni solutions obtained from SX with Cyanex 272; recovery efficiency of metals exceeded 98%.

Spent NiMH batteries were characterized and recovery of metal was studied through mechanical processing and magnetic separation. By this process nickel alloys could be efficiently recovered (Bertuol et al., 2006). The leaching of NiMH accumulators with 2 M  $H_2SO_4$  at 90 °C and selective precipitation of metals from the solution, were investigated by Bertuol et al. (2009). Precipitation being an easier and economical process option than solvent extraction was exemplified with the high recovery of REs as double sulfate salt (~98%) in the pH range 0.8-1.2. The second precipitation at pH 7 removed ~ 100 % Fe and >70% Zn along with co-precipitation of ~10 % Ni and ~9 % Co. Pure solutions of Ni and Co separated by SX could be electrowon to produce the metal cathodes (Ni and Co).

Zhang et al. (1998b, 1999) proposed a conceptual hydrometallurgical flowsheet for the separation and recovery of metals such as Ni, Co and rare earths from the spent batteries. The electrode material was dissolved in 2 M  $H_2SO_4$  at 95 °C with a leach efficiency of 97% Ni, 100% Co and 96% REs, followed by solvent extraction (SX) with 25% D2EHPA and 20% Cyanex 272, and precipitation with oxalic acid. Innocenzi and Vegliò (2012a) reported a two-step leaching process for complete extraction of La and Ce with 1-2 M  $H_2SO_4$  in 1-3 h at 25-80 °C, followed by

precipitation with NaOH. Acid leaching using 2 M H<sub>2</sub>SO<sub>4</sub> was performed by Pietrelli et al. (2002) to dissolve the Ni-MH electrode material at 20 °C. Thereafter REs were precipitated at pH <1.5 by alkali addition showing ~80% recovery.

The above reports stress on the leaching of primarily the base metals present in the spent Ni-MH batteries by H<sub>2</sub>SO<sub>4</sub> or HCl while recording the dissolution of REMs together as one entity. Particularly the information on the kinetics and mechanism of leaching of all the metals and detailed characterization studies is very scanty. The approach of reporting leaching kinetics of all the constituent REMs as one entity and considering the universal model (chemical reaction controlled) (Yang et al., 2014), seems to be a complete approximation. The chemical reaction of each rare earth and base metal in any acid would vary depending on the size (for light and heavy REs), the type of phases, and their association with each other. Apart from optimizing the process parameters, investigating the kinetics and mechanism of leaching base metals present in the spent LIBs as well as in spent NiMH batteries, and also that of REs in NiMH batteries in an acid, is clearly an area worth pursuing and has been considered in the present thesis.

#### **1.4. Kinetics of leaching:**

To find out the nature of interaction between the particles of battery material and the lixiviant, an attempt may be made to fit the kinetic data obtained from the leaching experiments at different temperatures in the shrinking core models. Data on the extraction of different metals can be tested using the shrinking core models based on the chemical, diffusion and mixed control (Levenspiel, 1972).

The shrinking core model considers that the rate controlling step for metal dissolution process is either the surface chemical reaction, or diffusion through the solution boundary or through the ash or a solid product layer. For the substrate particles of spherical geometry and the process controlled by surface chemical reaction, the integrated equation of the model can be expressed as (Levenspiel, 1972):

$$1-(1-x)^{1/3} = k_c.t \quad (1.17)$$

When the process is controlled by diffusion through the ash layer or the product layer, the integrated equation of the shrinking core model can be given as:

$$1-(2/3)x-(1-x)^{2/3} = k_d \cdot t \quad (1.18)$$

where  $x$  is the fraction reacted,  $k_c$  and  $k_d$  are the rate constants, and  $t$  is reaction time. According to Eq. (1.17) and Eq. (1.18), when the process is chemically controlled, the plot of  $1-(1-x)^{1/3}$  versus  $t$  is a straight line with a slope  $k_c$ . Similarly, for the process controlled by diffusion through a solid ash / product layer, the plot of  $1-(2/3)x-(1-x)^{2/3}$  vs.  $t$  is also a straight line with a slope  $k_d$ .

The mixed control model may also proceed in a diffusion controlled process and takes the form:

$$1-(2/3)x-(1-x)^{2/3} + m \{1-(1-x)^{1/3}\} = k_d \cdot t \quad (1.19)$$

where  $k_d$  is the specific rate constant and  $m$  is a constant.

Kinetic data can also be analyzed by using empirical model of the leaching that may proceed by the surface diffusion of lixiviant on the substrate particles, and governed by the logarithmic rate law (Levenspiel, 1972; Kim et al., 2011) as:

$$(-\ln(1-x))^2 = k_l \cdot t \quad (1.20)$$

where  $k_l$  is the specific rate constant for the model. The relation between the specific rate constant determined from Eq. (1.17, 1.18, 1.19 and 1.20) and the temperature can be expressed by the Arrhenius equation (1.21) from which the activation energy can be estimated.

$$k = A e^{-E_a / RT} \quad (1.21)$$

where  $k$  is the reaction rate constant,  $A$  the frequency factor,  $E_a$  the apparent activation energy and  $R$  ( $8.3145 \text{ JK}^{-1}\text{mol}^{-1}$ ) is the gas constant.

**Table 1.11:** Extraction and recovery of metals from spent NiMH batteries in HCl system

Material	Leaching Parameters				Extraction/separation method	Highlights	References
	Conc. (M)	t (min)	T (°C)	PD			
Spent NiMH batteries	20%	100	50-70	10	Precipitation using oxalic acid at pH 0.4-0.6 followed by calcination at 810 °C	Leaching (%): 95.2 REs ; Ppt: 99% pure RE-oxides	Yang et al., 2014
Spent batteries	6	120	60	12.5	Leaching studies	Leaching: 97% Ni, 95% Co, 96% Mn	Li et al., 2009c
Cylindrical AA NiMH batteries	4	180	95	Not given	SX with 25% D2EHPA at pH=2.5	Leaching (%): 98 Ni, 100 Co & 99 REs; SX: 100% REs; Electrolytic Co	Tzanetakis and Scott, 2004a
					Electrochemical deposition at low current densities		Tzanetakis and Scott, 2004b
Spent NiMH	3	180	95	S/L=1/9	2-stage SX: 25% D2EHPA, O/A 3:1, pH 2; REs precipitation with ammonia: pH 2-3.	Leaching (%): 96 Ni, >99 REs, 100 Co	Zhang et al., 1998b
Spent cell phone batteries	12	100	40	150 g/L	SX: pure TBP for Fe(III) & Zn, 10% Alamine 336 for Co, 20% PC 88A for REs; REs oxalates: pH 0.5.	Leaching(%): ~100 all, SX & ppt: >99.9% REs	Fernandes et al., 2013
AB2 type NiMH batteries	4	360	75		--	Leaching (%): 76.5 Ni, 88.4 Co, 53.8 Fe	Lyman and Palmer, 1993



**Table 1.12:** Extraction and recovery of metals from spent NiMH batteries in sulfuric acid system

Material	Leaching Parameters				Extraction/separation method	Highlights	References
	Conc. (M)	t (h)	T (°C)	PD			
Black mass of spent batteries	Stage I:2 Stage II:1	3 1	80 25	15 15	Precipitation: pH 1.6	Leaching (%): 100 Mn, Co & Zn; 99 Ni & REs	Innocenzi and Vegliò, 2012
Spent NiMH batteries	3 + 3% wt. H <sub>2</sub> O <sub>2</sub>	5	70	-		Leaching (%):80-85 Ni & 95-100 Co	Aly et al., 2012
NiMH spent batteries	Stage I:2 Stage II:1	3 1	80 25	15 15	2-stage SX: 20% DEHPA	Leaching: SX: 99% Ni & Zn; 98% Mn	Innocenzi and Vegliò, 2012b
NiMH batteries (50% cylindrical and 50% prismatic batteries)	Stage I:8% Stage II:8%	1 1	30 30	10 10	Precipitation with NaOH & SX (0.5 M D2EHPA / 0.6 M Cyanex 272)	Stage I: 80-85% Ni, 95-100% Co Stage II: 87% REs, 100% Ni	Rodrigues and Mansur, 2010
Cylinder shaped Ni-MH batteries	3	4	95	L/S=7.5/1	SX: 20% P204, 20% Cyanex 272 for Co/Ni separation	Leaching: < 90% Ni, Co, Fe, Mn, Zn; 5% REs	Li et al., 2009d
Cylindrical NiMH accumulators	2	4	90	S/L=1/20	Precipitation with NaOH: pH 0.8-1.2 followed by pH 7	Leaching (%): 82.6 Ni, 92.3 Co, 95.7 Zn, 53.3 Fe, 91 Mn, 83.3 Ce, 84 La, 86.4 Pr; Precipitation: 98% REs (pH<1.2) 100 Fe, 70 Zn( pH 7)	Bertuol et al., 2009
Cylinder shaped Ni-MH batteries	1 + 0.6% H <sub>2</sub> O <sub>2</sub>	2d	RT	S/L=1/20	SX (5-stage): 10% N1923 + 4% isooctanol; Oxalate ppt: 70 °C & pH 1.5	SX: 99.98% REs	Yun et al., 2015
Spent NiMH batteries	2	2	20	10	Precipitation using NaOH at pH <1.5	Leaching (%), Anode: 76.6 Ni, 97.6 Co, 1.0 Fe, 99.7 Mn, 92.5 La, 93 Ce, 91.8 Pr, 95.6 Nd Cathode:100 Ni, Co, Mn & Zn, 15 Fe; Precipitation: 80% REs as double sulfate salts	Pietrelli et al., 2002

Table 1.12 Contd.

HEV batteries	pH=1	--	30	--	--	Leaching (%): 73 Ni, 100 others	Larsson et al., 2013
Spent NiMH batteries	1	4	RT	S/L=1/20	Precipitation with NaOH up to pH = 1.2, followed by SX using D2EHPA	Leaching (%): 91.5 Ni, 92.6 Co & >97.5 REs; SX (%): 99 REs, 99.9 Fe, ~99 Zn & >60 Mn.	Dvořák and Vu, 2015
Electrode materials of prismatic cells of NiMH spent batteries	2	2	80	S/L=1/10	Precipitation with NaOH at pH<1.5	Leaching (%) :88.3 Ni, 98.8 Co & Mn, 100 Zn, 92.5 La, 93 Ce, 91.8 Pr, 95.6 Nd; 88% REs ppt	Pietrelli et al., 2002
Cylindrical and prismatic cells of NiMH (AB5 and AB2) and NiCd spent batteries.	2	1.15	20	S/L=1/10		Leaching (%): 84.5 Ni, 93.6 Mn, 92.6 Co, 82 REs	Pietrelli et al., 2005
Spent NiMH batteries	3 N +8% H <sub>2</sub> O <sub>2</sub>	3	90	S/L=1/1.5	Precipitation: Ni with diacetyl dioxime, NH <sub>3</sub> or caustic soda.	Leaching (%): 99.9 Ni, 99.4 Co	Rabah et al., 2008
Anode scraps of hydrogen-nickel battery	3	4	95	100 g/L	SX : 20% PC-88A	Leaching: <95% SX: 98.9 REs, 98.4 Ni, 98.5 Co	Wu et al., 2010
Spent NiMH batteries	2	2	25	S/L=1/10	Adsorption using MgFe-LDH-A, adsorbent wt/10 mL=0.1 g, 2h, 25 °C	Leaching (%):85 Ni, 98 Co and 95 REs (after II stage) Adsorption: 98% La and Nd	Gasser and Aly, 2013
Spent NiMH batteries	1 + 0.6% H <sub>2</sub> O <sub>2</sub>	48	RT	L/S=20/1	SX (5 stage): 10% N1923, A/O 1.5, pH 1.5; RE- oxalates : 70 °C & pH 1.5.	SX: 99.98% REs PPT: 99.77% pure RE-oxalates	Yun et al., 2015

### **1.5. Objectives and scope of the work:**

The objective of the work presented in the thesis is to investigate the dissolution of valuable metals from the secondary resources such as spent rechargeable batteries and to understand the governing mechanism. For this, two types of spent batteries namely, lithium ion batteries (LIBs) and nickel metal hydride batteries (NiMH) have been chosen to dissolve the constituent metals. Apart from this, use of a process intensification step has also been explored to study the possibility of selective leaching of some of the metals present in the electrode materials. Literature study reveals the prospects of utilizing such spent batteries as an important secondary resource because of the merits of high metal content encouraging 'resource recovery' and environmental friendliness entailing 'waste minimization'. The research reported in the thesis covers the following aspects:

1. Characterization of spent battery materials (LIBs and NiMH) with respect to the chemical composition, phase identification /association and structural /morphological observations.
2. Optimization of parameters for acid leaching of the cathode active material of spent LIBs to extract base metals such as Li, Ni, Co, Mn and Fe in absence and presence of reducing agents; also a comparison of the role and efficiency of the reducing agents.
3. Separation of the extracted metals from the leach liquors by suitable routes.
4. Optimization of parameters for acid leaching of the electrode material of spent NiMH batteries to extract base metals viz., Ni, Co, Mn, Fe, Zn and rare earth metals (La, Ce, Pr, Nd, Sm), followed by separation of extracted metals.
5. Process intensification (by acid baking-leaching) for selective extraction of the constituent metals from the cathode active material of spent LIBs.
6. Process intensification (through acid baking-leaching) for selective extraction of the constituent metals from the electrode material of spent NiMH batteries.
7. Correlation of leaching kinetics and mechanism by suitable models and process characterization using physico-chemical techniques.

At the end, a conclusion of the thesis is given. The thesis also summarizes the scope for future work in this area in brief.