Review

Extraction of lithium from primary and secondary sources by pre-treatment, leaching and separation: A comprehensive review

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Abstract

In this comprehensive review resources of lithium and status of different processes/technologies in vogue or being developed for extraction of lithium and associated metals from both primary and secondary resources are summarized. Lithium extraction from primary resources such as ores/minerals (spodumene, petalite and lepidolite) by acid, alkaline and chlorination processes and from brines by adsorption, precipitation and ion exchange processes, is critically examined. Problems associated with the exploitation of other resources such as bitterns and seawater are highlighted. As regards the secondary resources, the industrial processes followed and the newer developments aiming at the recovery of lithium from lithium ion batteries (LIBs) are described in detail. In particular pre-treatment of the spent LIBs, leaching of metals from the cathode material in different acids and separation of lithium and other metals from the leach liquors, are discussed. Although spent LIBs are currently processed to recover cobalt and other base metals but not lithium, there is a good prospect for the recovery of lithium in the coming years. Varying compositions of batteries for different applications require development of a suitable recycling process to recover metals from all types of LIBs.

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http://dx.doi.org/10.1016/j.hydromet.2014.10.012
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1. Introduction

Lithium is the 25th most abundant element (at 20 mg/kg) in the earth's crust. Lithium finds an application in rechargeable lithium ion batteries (LIBs) because of its very high energy density by weight and high electrochemical potential (3.045 V). With a present consumption level of ~22% of the total lithium produced in LIBs, it is expected to reach to ~40% by 2020 (Wang et al., 2012). Besides batteries, at present it has major applications in glass and ceramics (30%), greases (11%), metallurgical (4%) industries and also in chemicals/ pharmaceuticals, rubbers etc. (Garrett, 2004; Holdren, 1971). As per the Madrid Report of July 2010, lithium falls in the border-line of low-to-medium in supply and demand, primarily due to scanty resources (Tedjar, 2013). It is also understood that the demand for lithium is increasing further due to its application in nuclear and strategic areas. As per recent estimates of lithium reserves, out of 103 deposits with more than 1,000,000 t of lithium, each deposit has a different mineralogical composition and therefore, requires the appropriate technology to process (Gruber et al., 2011). In view of this, lithium is usually extracted from its mineral that is found in igneous rocks (chiefly spodumene) and from lithium chloride salts found in brine pools, while ignoring other resources including the low-grade ores.

The rising demand for lithium for various applications thus calls for prospecting and processing all viable resources. Lithium extraction from ores/minerals utilizes roasting followed by leaching, while its extraction from brines includes evaporation, precipitation, adsorption and ion exchange (Garrett, 2004). Lithium can be extracted from LIBs by leaching followed by precipitation, ion exchange or solvent extraction and electrolysis (Shuva and Kurny, 2013). It is estimated that 250 t of ore (spodumene) or 750 t of brine or 25 t of lithium ion batteries of mobile phones and laptops or 256 batteries of electric vehicles (EVs) are required to produce 1 t of lithium (Tedjar, 2013). Lithium concentrate obtained mainly by the flotation of pegmatites (ore), is pulverized and leached in hot acid, and lithium is precipitated as lithium carbonate (Tahil, 2010). The processing of pegmatites is expensive as compared to that of the brines due to the heating and dissolution steps involved, but the higher metal concentration in pegmatites partly compensates for the cost. Because of the cost factor in the lithium extraction from brine compared to the ores, many deposits of spodumene are not currently being mined/processed. Lithium is also present in seawater, but the concentration is too low to be economical. As regards lithium metal, it can be produced by both carbothermic reduction and metallothermic reduction of oxide (at times hydroxide) and also by electrolysis of LiCl (Kipouros and Sadoway, 1998). In view of the scattered literature on the extraction of lithium from primary resources viz., ores, minerals and the brines, it is considered worthwhile to review the details and discuss critically the merits and demerits of various processes in vogue or being developed.

With the increasing use of LIBs in mobile phones, laptops, camcorders, tracking systems, military and medical devices and in large energy storage systems including that of transportation applications (>one million EVs expected by 2015), there will be a significant pressure on lithium resources and its supplies (Kuo, 2011). The disposal of spent batteries may involve landfilling, stabilization, incineration or recycling. In landfills, heavy metals have the potential to leach slowly into the soil, groundwater or surface water.

The methods for recycling spent LIBs are based mainly on pyro-/hydro-metallurgical processes (Li et al., 2009a). The disadvantage of all pyro-recycling processes is that lithium is not recovered. The traditional pyrometallurgical processes can burn off all the organic electrolyte and binder, and facilitate the leaching of valuable metals. In the hydrometallurgical processes, the dismantled electrodes are dissolved in concentrated acid and the metal rich leach solutions are treated to recover the individual metal by the different methods mentioned above. These processes may produce wastewater containing fluoride which is difficult to treat, and can pollute the environment due to the incomplete recycling of the organic binder and electrolyte. There is an inconsistent policy about the fate of discarded lithium ion batteries in e-waste that is distributed internationally. Lithium batteries also contain potentially toxic materials including metals, such as copper, nickel and lead, and organic chemicals, such as toxic and flammable electrolytes containing LiClO4, LiBF4, and LiPF6. Defunct Li-ion batteries are classified as hazardous due to their lead (Pb) (6.29 mg/kg), cobalt (163.544 mg/kg), copper (98.694 mg/kg) and nickel (9525 mg/kg) contents with exceeded limits of chromium, lead, arsenic and thallium (Bernardes et al., 2004; Kang et al., 2013). Human and environmental exposures to these chemicals are typically regulated during the manufacture of lithium batteries through occupational health and safety laws, and potential fire hazards associated with their transportation. These findings support the need for stronger government policies at the local, national, and international levels to encourage recovery, recycling, and reuse of lithium battery materials. In view of the above, efforts must be made to develop an environmentally benign and economically viable technology for recycling spent LIBs.

This review focuses on the primary and secondary resources of lithium available for exploitation and provides comprehensive details on the conventional/currently practiced lithium extraction methods vis-a-vis the resource type. The resources that are covered include ores/minerals/clays and brines/seawater and bittens, and lithium ion batteries for the hydrometallurgical recovery of lithium.

2. Resources of lithium

2.1. Primary resources — minerals/clays and brines

Lithium is produced from a variety of natural sources, e.g., minerals such as spodumene, clays such as hectorite, salt lakes, 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 lithium with higher content of FeO (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. Table 1 lists the principal commercial lithium minerals found in pegmatites along with their composition. 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.

Among the clay minerals, hectorite, a type of smectite is rich in lithium and magnesium, and generally contains 0.3 to 0.6% Li. The best

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Li content (wt%)</th>
<th>Theoretical Li content</th>
<th>Range in commercial minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spodumene</td>
<td>LiAlSiO3 or Li2O·Al2O3·4SiO2</td>
<td>3.73</td>
<td>1.9–3.3</td>
<td></td>
</tr>
<tr>
<td>Lepidolite</td>
<td>LiAlF6·2Li2O or LiF·KF·FeO·Al2O3·3SiO2</td>
<td>3.56</td>
<td>1.4–1.9</td>
<td></td>
</tr>
<tr>
<td>Amblygonite</td>
<td>LiAIF6PO4 or 2LiF·Al2O3·P2O5</td>
<td>4.74</td>
<td>3.5–4.2</td>
<td></td>
</tr>
<tr>
<td>Triphyllite</td>
<td>LiFePO4 or Li2O·2FeO·P2O3</td>
<td>4.40</td>
<td>2.5–3.8</td>
<td></td>
</tr>
<tr>
<td>Petalite</td>
<td>LiAlSiO3 or Li2O·Al2O3·8SiO2</td>
<td>2.27</td>
<td>1.6–2.21</td>
<td></td>
</tr>
<tr>
<td>Biktite</td>
<td>LiAlSiO·H2O</td>
<td>3.28</td>
<td>1.35–1.7</td>
<td></td>
</tr>
<tr>
<td>Eucryptite</td>
<td>LiAlSiO4</td>
<td>5.53</td>
<td>2.34–3.3</td>
<td></td>
</tr>
<tr>
<td>Montebrasite</td>
<td>Li2O·Al2O3·2SiO2</td>
<td>3.93</td>
<td>0.9–1.8</td>
<td></td>
</tr>
<tr>
<td>Jadarite</td>
<td>LiNaSiB2O7·(OH)</td>
<td>3.39</td>
<td>0.096–0.11</td>
<td></td>
</tr>
<tr>
<td>Zinnwaldite</td>
<td>LiFeAl2Si2O6·2H2O</td>
<td>1.7</td>
<td>1.21–1.3</td>
<td></td>
</tr>
<tr>
<td>Hectorite</td>
<td>Na3Co3(MgLi)·2SiO3(OH)</td>
<td>0.56</td>
<td>0.36</td>
<td></td>
</tr>
<tr>
<td>Zabulonite</td>
<td>Li2CO3</td>
<td>18.75</td>
<td>–</td>
<td></td>
</tr>
</tbody>
</table>

known hectorite deposit with 0.7% Li is in Hector, California. Flint clays and other high-alumina clays contain <0.01 to 0.5% Li. Jadarite is a newly discovered lithium-boron containing mineral found in Serbia (Mohr et al., 2012). These minerals are often concentrated to around 2%–4% Li for use in the ceramics and glass industry (Garrett, 2004).

Seawater contains about 0.1–0.2 mg/L Li (Bach and Wasson, 1981). Total amount of metallic lithium in seawater (globally) is estimated to be ~230 Gt. 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. Geothermal brines are underground brines naturally heated, e.g., in the Salton Sea California. 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). Almost 70% of the global lithium deposits are concentrated in South America’s ABC (Argentina, Bolivia and Chile) region. Table 2 details the geographical availability of various resources of lithium vis-a-vis lithium content and their locations. The lithium concentrations in the salars of Chile, Argentina, and Bolivia are in the range 0.04–0.16%. According to Yalkis and Tilton (2009) the resource of lithium is estimated to be 64 Mt. Chile has the world’s largest resource of brine (7.5 Mt, 1500–2700 mg/L Li) containing lithium, followed by Bolivia (resource: 9.0 Mt with 532 mg/L Li) and Argentina (resource: 2.6 Mt, 400–700 mg/L Li) and these three countries account for almost 80% of the world’s brine reserves (Mohr et al., 2012). Estimates of lithium resources are published extensively (Clarke and Harben, 2008; Kesler et al., 2011; Ono, 2009; Evans, 2010a, 2010b; USGS, 1980, 1986, 2005, 2009, 2010, 2011, 2012, 2013).

Lithium rock production began with lithium minerals (1899) in the USA (Garrett, 2004). Since the first lithium production from brines at Searles Lake, USA in 1936, brines are exploited largely in South America and China. The largest producer of lithium in the world is Chile where lithium is extracted from saline brine at the Atacama Salt Flat. Lithium production from brines is also at salt lakes in Tibet and Qinghai in China, besides at Nevada in the United States. Several newer installations (by 2013) are on various stages of exploration/operation for brine source which are: one more in China, six in Argentina, three in Chile and one in Bolivia (Clarke, 2013). Currently 8% of lithium is obtained from salt lake brines and sea by sedimentation. Significant quantities of lithium compounds and ore concentrates are also produced in Australia, Canada, Portugal, Russia and Zimbabwe. Currently, Australia produces lithium concentrate from spodumene at the mines in Mt Catlin, Western Australia. The 160,000 t/annum concentrate produced in Western Australia is processed to 16,000 t/annum lithium carbonate in its Chinese plant. Lithium carbonate is mostly produced from both ores and brines and the production figures are often expressed as lithium carbonate equivalent (LCE). Other chemicals such as lithium chloride and hydroxide are also produced in varying amounts.

In India small pocket deposits mostly comprising of lepidolite in pegmatites of mica fields are located. The maximum lithium content (lepidolite with 2–6% Li2O) is found in Jharkhand followed by that of Chhattisgarh (2.56% Li2O) and Rajasthan (2.25% Li2O as pegmatites in Udaipur, Bhilwara, Jadhpur 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 the Salal area, Jammu (Brown and Dey, 1955; Krishnaswamy, 1979; Roonwal et al., 2005).

### 2.2. Secondary resources — lithium ion batteries

Out of the various secondary resources, spent LIBs are the most prominent secondary source of lithium and other metals. To recycle these materials, it is desired to understand the construction/composition of the cells in brief and how they transform during their use.

Lithium ion battery is a term generally used for a battery which has lithium metal, lithium alloy or material absorbing lithium ions for its negative active material. LIB uses carbon as an anode and lithium ions exist in the carbon material; there is no metallic lithium at any state of charge during normal usage. Depending on their technical construction and properties batteries are categorized as either primary or secondary. From the legislative view point batteries are also categorized as portable (household) and vehicle or industrial batteries. Primary cells are constructed with metallic lithium. The metallic lithium in a non-rechargeable primary lithium battery is a combustible alkali metal that self-ignites at 178 °C, and when exposed to water/seawater reacts exothermically and releases 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 a chemistry that allows reversing the discharge reaction and are rechargeable. LIBs are of the rechargeable secondary type. The functional parts of LIBs are the cathode, anode, electrolyte and separator, which are housed in a protective metal casing.

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

$$\text{LiCoO}_2 + 6\text{C} \rightarrow \text{Li}_6\text{C}_6 + \text{Li}_{1-x}\text{Co}_x\text{O}_2.$$ (1)
The active mass (cathode, anode and electrolyte) of LIBs comprises of almost 40% of the weight whereas ~30% (wt) of these components are carbon (anode). A number of chemical species in the cathode material within the lithium-ion family have been reported including the type, structure of the materials used and their electrochemical properties which are listed in Table 3. Generally LIBs have a short life of 2–3 years whether they are used or not. The spent batteries are a good source of metals like Li, Co, Ni, etc. It is of interest to know whether they are used or not. The spent batteries are a good source of metals like Li, Co, Ni, Mn etc. and Olson (1978) have reviewed methods and techniques for the extraction of lithium from ores, brines and clays. Processes followed for the extraction of lithium from different resources have also been compiled in detail by Garrett (2004).

In order to process ores/concentrates, acid digestion with H2SO4 may be followed for decomposition of the silicate structure at 250–400 °C which is suitable for the processing of lepidolite, ambygolinite and zinnwaldite (Kondás and Jandová, 2006). In the sulfate process lithium minerals such as lepidolite are decomposed at high temperature in the presence of potassium and/or sodium sulfate. Alkali digestion is suitable for the decomposition of spodumene and lepidolite largely by the treatment of potassium carbonate to produce lithium hydroxide. In the alkaline/gypsum process the mineral is reacted with limestone or a mixture of calcium sulfate with calcium oxide and/or hydroxide by heating to convert silicate to soluble lithium aluminate from which LiOH or Li2CO3 can be obtained.

### Table 3

<table>
<thead>
<tr>
<th>Component</th>
<th>WL% of the total weight of the battery</th>
<th>Material</th>
<th>Structure</th>
<th>Properties/Merits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>39.1 ± 1.1</td>
<td>LiCoO2</td>
<td>Layered</td>
<td>High structural stability and can be cycled for &gt;500 times with 80–90% capacity</td>
</tr>
<tr>
<td>Anode</td>
<td>3.9 ± 0.1</td>
<td>Carbon</td>
<td>Hard carbon</td>
<td>Suitable for biomedical applications because of higher safety levels and lower</td>
</tr>
<tr>
<td>Electrolyte</td>
<td></td>
<td>Lithium salt like LiPF6, Li[PF3(C2F5)3]</td>
<td></td>
<td>cost</td>
</tr>
<tr>
<td>Plastic case</td>
<td>22.9 ± 0.7</td>
<td>Polyethylene terephthalate layers, a polymer layer and a polypropylene layer, layers of carbonized plastic</td>
<td></td>
<td>possesses high capacity with structural and thermal stability, and safe to use</td>
</tr>
<tr>
<td>Outer casing</td>
<td>10.5 ± 1.1</td>
<td>Stainless steel, aluminium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper foil</td>
<td>8.9 ± 0.3</td>
<td>Copper</td>
<td>~14 μm thick</td>
<td></td>
</tr>
<tr>
<td>Aluminium foil</td>
<td>6.1 ± 0.6</td>
<td>Aluminium</td>
<td>~20 μm thick</td>
<td></td>
</tr>
<tr>
<td>Polymer foil &amp;</td>
<td>5.2 ± 0.4</td>
<td>Polyethylene, polypropylene or composite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvent</td>
<td>4.7 ± 0.2</td>
<td>Ethylene carbonate, dimethyl carbonate &amp; diethyl carbonate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrical contact</td>
<td>2.0 ± 0.5</td>
<td>Aluminium and copper</td>
<td>Conductive</td>
<td></td>
</tr>
</tbody>
</table>

### Table 4

<table>
<thead>
<tr>
<th>Component</th>
<th>WL% of the total weight of the battery</th>
<th>Material</th>
<th>Structure</th>
<th>Properties/Merits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lepidolite conc.</td>
<td>2.0</td>
<td>Sulfation roasting</td>
<td>850</td>
<td>Room temp. (RT)</td>
</tr>
<tr>
<td>Lepidolite conc.</td>
<td>2.0</td>
<td>Sulfation roasting</td>
<td>850</td>
<td>Room temp. (RT)</td>
</tr>
<tr>
<td>Lepidolite conc.</td>
<td>2.55</td>
<td>Sulfation roasting</td>
<td>1000</td>
<td>Room temp. (RT)</td>
</tr>
<tr>
<td>Lepidolite conc.</td>
<td>1.79</td>
<td>Roasting with iron sulfate</td>
<td>850</td>
<td>Room temp. (RT)</td>
</tr>
<tr>
<td>Zinnwaldite conc.</td>
<td>0.96</td>
<td>Roasting with sodium sulfate</td>
<td>850</td>
<td>Room temp. (RT)</td>
</tr>
<tr>
<td>Petalite/Lepidolite</td>
<td>1.9</td>
<td>Calcination</td>
<td>1100</td>
<td>Room temp. (RT)</td>
</tr>
<tr>
<td>Spodumene</td>
<td>4.21</td>
<td>Calcination</td>
<td>1100</td>
<td>Room temp. (RT)</td>
</tr>
<tr>
<td>Spodumene</td>
<td>2.81</td>
<td>Roasting &amp; H2SO4 leaching</td>
<td>1050–1090</td>
<td>Room temp. (RT)</td>
</tr>
<tr>
<td>Montmorillonite clay</td>
<td>1.2% Li2O</td>
<td>Without roasting</td>
<td>–</td>
<td>Room temp. (RT)</td>
</tr>
</tbody>
</table>

### References

is obtained. Thus most of the alkaline processes involve either the heating of lithium minerals with alkali salts or in more advanced hydrothermal processes by decomposition in solutions containing Na2CO3, NaOH, Na2SO4 and/or other alkali salts at elevated temperature and pressure. Ion-exchange processes are applied for the processing of the leach liquors obtained from spodumene, petalite and partly from zinnwaldite. Tables 4–6 summarize recent work on lithium extraction from its minerals and clays by using different approaches.

3.1.1. Sulfation process

Sulfation roasting of lepidolite followed by water leaching was recently reported by Yan et al. (2012a). The lithium extraction efficiency of 91.6% could be achieved at a mass ratio of lepidolite/Na2SO4/K2SO4/CaO of 1:0.5:0.1:0.1 and roasting at 850 °C (Table 4). Roasting at 880 °C with a mass ratio of lepidolite/Na2SO4/CaCl2 of 1:0.5:0.3 resulted in improved recovery (~95% Li) of lithium (Yan et al., 2012a). The lithium extraction efficiency of 91.6% could be achieved at a mass ratio of lepidolite/Na2SO4/CaCl2 of 1:0.5:0.3 and roasting at 850 °C with a mass ratio of lepidolite/Na2SO4/CaCl2 of 1:0.5:0.3 resulted in improved recovery (~95% Li) of lithium (Yan et al., 2012a). The lithium extraction efficiency of 91.6% could be achieved at a mass ratio of lepidolite/Na2SO4/CaCl2 of 1:0.5:0.3 and roasting at 850 °C with a mass ratio of lepidolite/Na2SO4/CaCl2 of 1:0.5:0.3 resulted in improved recovery (~95% Li) of lithium (Yan et al., 2012a).

\[ \text{Li}_2CO_3 \rightarrow \text{Li}_2O + \text{CO}_2 \]

Lithium carbonate can be recovered by the addition of sodium carbonate to the solution after pH adjustment, purification and evaporation (Reaction 3).

\[ \text{Li}_2SO_4 + \text{Na}_2CO_3 \rightarrow \text{Li}_2CO_3 + \text{Na}_2SO_4 \]

The world’s first continuous plant to convert spodumene concentrate to lithium carbonate by calcination, roasting of calcine with H2SO4 and water leaching, was commissioned in 2012 by Galaxy Resources in China (Clarke, 2013). One of the drawbacks of the sulfuric acid method to treat lepidolite, petalite and zinnwaldite is the requirement of a high concentration of acid and complex purification processes, whereas spodumene needs to be converted to the more leachable β-phase at higher temperature.

### Table 5

Lithium extraction from its minerals/clays by alkali process.

<table>
<thead>
<tr>
<th>Raw material</th>
<th>% Li</th>
<th>Pre-treatment</th>
<th>Experimental conditions</th>
<th>% Li extraction</th>
<th>Li2CO3 purity (%)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lepidolite concentrate</td>
<td>1.4</td>
<td>Defluorination</td>
<td>Roasting temp. (°C), time (h)</td>
<td>860, 0.5 h</td>
<td>1</td>
<td>150</td>
</tr>
<tr>
<td>Zinnwaldite concentrate</td>
<td>1.4</td>
<td>Gypsum roast</td>
<td>950, 1 h</td>
<td>0.167</td>
<td>90</td>
<td>10:1</td>
</tr>
<tr>
<td>Zinnwaldite concentrate (tailing sample)</td>
<td>0.19</td>
<td>Gypsum roast</td>
<td>975</td>
<td>1</td>
<td>90</td>
<td>5:1</td>
</tr>
<tr>
<td>Zinnwaldite concentrate</td>
<td>1.21</td>
<td>Roasting with gypsum &amp; Ca(OH)2</td>
<td>825, 1 h</td>
<td>1</td>
<td>90-95</td>
<td>5:1</td>
</tr>
<tr>
<td>Zinnwaldite concentrate</td>
<td>1.29</td>
<td>Roasting with CaCO3</td>
<td>825</td>
<td>4</td>
<td>95</td>
<td>10:1</td>
</tr>
<tr>
<td>Montmorillonite clay–hectorite</td>
<td>0.3–0.6</td>
<td>Roasting with CaCO3, CaCO3–CaSO4</td>
<td>750</td>
<td>–</td>
<td>RT</td>
<td>–</td>
</tr>
</tbody>
</table>

### Table 6

Lithium extraction from its minerals/clays by chlorination process.

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Experimental conditions</th>
<th>% Li extraction</th>
<th>Product</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lepidolite</td>
<td>Roasting temp. (°C), time (h)</td>
<td>935</td>
<td>13</td>
<td>80</td>
</tr>
<tr>
<td>Spodumene (3.58% Li)</td>
<td>1000</td>
<td>4</td>
<td>10:1</td>
<td>80</td>
</tr>
<tr>
<td>Lepidolite concentrate (2.0% Li)</td>
<td>880</td>
<td>0.5</td>
<td>2.5:1</td>
<td>60</td>
</tr>
<tr>
<td>Spodumene (7.2% Li2O)</td>
<td>1100</td>
<td>2.5</td>
<td>–</td>
<td>~10</td>
</tr>
<tr>
<td>Lepidolite ore (3.70% Li2O)</td>
<td>With CaCO3 + CaCl2, 950</td>
<td>5</td>
<td>10:1</td>
<td>90</td>
</tr>
</tbody>
</table>
3.1.2. Alkaline process

In the alkaline process (Table 5), spodumene or lepidolite ore concentrates are ground and calcined with limestone at 825–1050 °C. The resulting calcine is crushed, milled and treated with water to yield lithium hydroxide which can be converted to chloride by reaction with hydrochloric acid. The recovery in this method is approximately 85–90% (Averill and Olson, 1978). The reaction during calcination of spodumene with limestone can be represented as:

\[
\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 (s) + \text{CaCO}_3 \rightarrow \text{Li}_2\text{O}_2 \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 (s) + \text{CO}_2 (g).
\] (4)

Lepidolite was pre-roasted at 860 °C under water steam atmosphere for defluorination followed by pressure leaching of the defluorinated mass in a lime–milk autoclave at 150 °C. In this process 98.9% lithium was extracted (Yan et al., 2012). During the roasting with steam formation of phases such as lithium aluminium silicate (beta-eucryptite) and leucite (KAlSiO₄) was noticed (Karsstetter, 1971) as per reaction (5)

\[
2\text{LiF} \cdot \text{K}_2\text{O} \cdot 3\text{SiO}_2 + 4\text{H}_2\text{O} \rightarrow 2\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{KAlSiO}_4 + 4\text{H}_2 + 2\text{F}_2.
\] (5)

Extraction of lithium from a zinnwaldite containing waste was investigated by Jandová et al. (2009). The concentrate (1.40% Li) obtained from dry magnetic separation of the waste (0.21% Li) was treated by the gypsum roasting method (with CaSO₄ and Ca(OH)₂). About 96% Li was leached out from the sinter made at 950 °C. Earlier the concentrate prepared from this waste by gravity and dry magnetic separation, was roasted by the gypsum roasting method at 975 °C and water leached to recover ~93% Li (Kondás and Jandová, 2006). In another study Jandová et al. (2010) reported that the roasting of the above concentrate with CaCO₃ and Na₂O gives a high purity of separated leach liquor by either converting the alkaline liquor to the carbonated solution by CO₂ bubbling or by solvent extraction with LIX54 and TOPO as an extractant followed by stripping with diluted H₂SO₄. The first method provided a higher yield. Siame and Pascoe (2011) obtained recovery of ~84% Li from the roasted zinnwaldite concentrate at 1050 °C with limestone, gypsum and sodium sulfate. A similar process was reported by Vu et al. (2013) from zinnwaldite by sintering with CaCO₃ powder at 825 °C, followed by water leaching and precipitation.

Crocker and Lien (1987) reported the recovery of ~85% Li by roasting montmorillonite type clays (0.3–0.6% Li) with KCl–CaCO₃ or CaCO₃–CaSiO₃ followed by water leaching. Lithium silicate in the clay was converted to Li₂SO₄ by roasting a pelletized mixture of clay, limestone and gypsum at 900 °C in a direct gas-fired rotary roaster (Lien, 1985). Formation of lithium sulfate may be represented by reactions (6) and (7)

\[
\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{SiO}_2 \rightarrow \text{CaSiO}_3 + \text{SO}_2 + \frac{1}{2} \text{O}_2.
\] (6)

\[
\text{Li}_2\text{Si}_2\text{O}_5 + \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{Li}_2\text{SO}_4 + 2\text{SiO}_2.
\] (7)

The initial product obtained from the alkaline process is lithium hydroxide which can be converted to carbonate or chloride salt.

3.1.3. Chlorination process

A less common method is the chlorination process in which the ore is roasted in the temperature range 880–1100 °C in the presence of chlorine gas or HCl depending upon the type of mineral treated (Table 6). For instance chlorination of lepidolite with HCl can be achieved at lower temperature (935 °C) while giving a high yield (~99%) of lithium during leaching as compared to the roasting of spodumene (Löf and Lewis, 1942). Lithium in spodumene can be converted to LiCl almost quantitatively at higher temperature (1100 °C) in 2.5 h with Cl₂ gas (Barbosa et al., 2014); the recovery is found to be quite low (58%) at the lower temperature (1000 °C) (Peterson and Gloss, 1959). In the chlorination process, when the ore is sintered with NH₄Cl and CaCl₂ in a furnace at 750 °C, ~98% of the lithium contained in spodumene is converted to its chloride which can be water leached (Zelikman et al., 1996). Vyas et al. (1975) reported a similar process using CaCO₃ and CaCl₂ to roast Indian lepidolite at 950 °C by which 80% Li was recovered as LiCl. The chlorination process with calcium chloride and/or sodium chloride with lepidolite (M = Li, K, Rb, Cs) may be represented as:

\[
2\text{NaCl} + 6\text{SiO}_2 + \text{M2O} + \text{Al}_2\text{O}_3 \rightarrow 2\text{NaAlSi}_3\text{O}_8 + 2\text{MCl}.
\] (8)

\[
\text{CaCl}_2 + 2\text{SiO}_2 + \text{M}_2\text{O} \rightarrow \text{CasIO}_3 + 2\text{MCl}.
\] (9)

\[
\text{CaCl}_2 + 2\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{M}_2\text{O} \rightarrow \text{CaAlSi}_2\text{O}_6 + 2\text{MCl}.
\] (10)

Chlorination roasting with a mixture of CaCl₂ and NaCl gives a better lithium extraction yield because of its lower melting point than either of the agents, which increases the fluidity of chloride melt. This allows diffusion of the chlorinating agent to the surface of the lepidolite facilitating the lithium extraction selectively and yielding a pure product. Crocker and Lien (1987) also reported a process for selective chlorination of hectorite (0.3–0.65% Li) in clays with limestone at 750 °C using 20 wt.% HCl.

3.1.4. Other processes

Chlorination roasting of ores requires corrosion-resistant equipment. To overcome this drawback the autoclave method is used. Chen et al. (2011b) reported a process to treat β-spodumene obtained in the calcination of α-spodumene, by sodium carbonate solution in an autoclave at a liquid/solid ratio of 4 and Na/Li of 1.25 at 225 °C. During pressure leaching lithium carbonate and analcime slurry are formed according to reaction (11).

\[
\beta - \text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 + \text{Na}_2\text{CO}_3 + \text{nH}_2\text{O} \rightarrow \text{Li}_2\text{CO}_3 + \text{Na}_2\text{SiO}_3 \cdot \text{nH}_2\text{O}.
\] (11)

The slurry was leached in carbon dioxide to form lithium bicarbonate which on heating produced lithium carbonate of 99.6% purity as per reactions (12) and (13).

\[
\text{Li}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow 2\text{LiHCO}_3.
\] (12)

\[
2\text{LiHCO}_3 \rightarrow \text{Li}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}.
\] (13)

Medina and El-Naggar (1984) developed an alternate method of chlorination to treat spodumene with a recovery of ~87% Li by roasting at 1150 °C with a mixture of 8:1 (wt.) tachyhydrite:spodumene followed by water leaching. Because the production of lithium carbonate from spodumene is energy intensive and expensive, lithium carbonate is mostly produced from the brines.

3.2. Lithium extraction from brines/sea water/bitterns

In order to meet the growing demand of lithium, brines and bitterns have received increasing attention. Tables 7 and 8 elaborate the summary of work carried out recently for the extraction of lithium from sea water/brines/bitterns. Production process for brine-water lithium costs 30% to 50% less than that of the mined ores (Abe, 2010). As mentioned earlier, lithium carbonate is produced from brines by an evaporative concentration and refining method. Firstly, brine is concentrated by solar evaporation over a year in a pond to crystallize sodium, potassium and magnesium chlorides. During the refining process calcium carbonate is roasted and then added to the solution of LiCl for the removal of...
Various types of adsorbents have been used for selective lithium recovery from seawater and brines. In the adsorption method certain inorganic-ion-exchangers such as the spinel-type manganese oxide (H$_{1.6}$Mn$_{1.6}$O$_4$) prepared from the precursor, Li$_3$Mn$_{2}$O$_4$ by hydrothermal and reflux methods, showed the maximum uptake of 40 mg Li/g of adsorbent from the seawater, the highest among the inorganic adsorbents (Chitrakar et al., 2003). The very fine size (nano-size range) of the synthesized manganese oxide was found to be responsible for its high adsorption capacity towards lithium as compared to other adsorbents. Adsorption of lithium from seawater by a spinel type Li$_3$Mn$_2$O$_4$ produced low purity (~33%) Li$^+$ ions contaminated with Na$^+$ (Yoshizuka et al., 2006). Chung et al. (2004, 2008) synthesized nano-manganese oxide (Li$_{1.33}$Mn$_{1.67}$O$_4$) through a gel process. The ion sieve-type adsorbent containing magnesium after acid treatment was medium (pH of seawater being ~8) for Li$^+$ in the presence of alkali and alkaline earth ions. For instance Kitajou et al. (2003) reported the separation of Li$^+$ from a large amount of Na$^+$ by the spinel-type Li$_3$Mn$_2$O$_4$ whereby Li$^+$ was concentrated 400 times leaving most Na$^+$ in the seawater. Extraction/separation of lithium from brines and such resources is summarized in Table 7.

The basic approaches for the separation of mineral products (K, Mg, Na, Ca, Li) from the seawater comprises of flotation (using anionic collectors), sorption, ion exchange, solvent extraction etc. as described by Koyanaka and Yasuda (1977). The existing evaporation process for lithium recovery from brine lakes is time consuming and suffers from low recovery efficiency. Besides, tremendous burden is posed on the environment due to waste generation and substantial water consumption.

### Table 7

<table>
<thead>
<tr>
<th>Source/Raw Material</th>
<th>Adsorbent used</th>
<th>Conditions</th>
<th>Adsorption/Remarks</th>
<th>Product</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seawater (Li 0.15 mg/L)</td>
<td>H$<em>{1.6}$Mn$</em>{1.6}$O$_4$</td>
<td>Adsorbent: 200 mg, sea water: 50 L, 30 °C, 15 days</td>
<td>Max. uptake: 40 mg Li/g adsorbent</td>
<td>LiCl</td>
<td>Chitrakar et al. (2001)</td>
</tr>
<tr>
<td>Seawater (Li 0.15 mg/L)</td>
<td>Nap-MnO$_2$</td>
<td>Recovery—264 g LiCl in 791 g dried precipitated salt (816 m$^3$ seawater)</td>
<td>Adsorption: 88% Li by adsorbent I and 89% Li by adsorbent II. Equil. solubility: 30.3 mg/g (I) and 33.1 mg/g (II).</td>
<td>LiCl</td>
<td>Yoshizuka et al. (2002)</td>
</tr>
<tr>
<td>Artificial seawater (Li 0.02 mg/L)</td>
<td>Ion-sieve type Mn-oxide spinels: H$<em>3$Mg$</em>{0.5}$Mn$<em>{1.5}$O$<em>4$ (I), HZn$</em>{0.5}$Mn$</em>{1.5}$O$_4$ (II)</td>
<td>Adsorption at 0.4 M HCl, 5 days</td>
<td>Equil. solubility: 30.3 mg/g (I) and 33.1 mg/g (II).</td>
<td>LiCl</td>
<td>Chung et al. (2004)</td>
</tr>
<tr>
<td>Seawater (1 mmol/L Li)</td>
<td>H$_2$MnO$_4$</td>
<td>60 °C, 24 h</td>
<td>Loading capacity: 1.53 mmol/g sorbent</td>
<td>Li salt</td>
<td>Wajima et al. (2012)</td>
</tr>
<tr>
<td>Brine (Salars de Uyuni, Bolivia)</td>
<td>Li$<em>4$Mg$</em>{0.5}$Mn$_{1.5}$O$_4$</td>
<td>24 h, pH 6.5</td>
<td>Adsorption capacity: 23–25 mg/g adsorbent</td>
<td>Li$_2$CO$_3$</td>
<td>Chitrakar et al. (2013)</td>
</tr>
<tr>
<td>Seawater (Li 0.125 mg/L)</td>
<td>Surface deposition on corrosion product of Al</td>
<td>30 °C, 10 days</td>
<td>34% Li</td>
<td>–</td>
<td>Takeuchi (1980)</td>
</tr>
<tr>
<td>Salt lake bitterns</td>
<td>Hydrated alumina: LiOH = 2 M ratio</td>
<td>pH 5.8</td>
<td>Adsorption: 0.6–0.9 mg/g sorbent</td>
<td>–</td>
<td>Dong et al. (2007)</td>
</tr>
<tr>
<td>Egyptian bitterns (19.5, 55, 8.8 mg/L)</td>
<td>Al(OH)$_3$</td>
<td>30 °C, pH 9</td>
<td>Adsorption capacity: 123 mg/g adsorbent</td>
<td>LiAlO$_2$</td>
<td>Hawash et al. (2010)</td>
</tr>
<tr>
<td>Brine (Salar de Hombre Muerto, Argentina)</td>
<td>Hydrated alumina</td>
<td>LiCl solution—1% Li (20 times conc.) by solar evaporation.</td>
<td>Adsorbed Li eluted by acid and precipitated by sodium carbonate</td>
<td>Li$_2$CO$_3$</td>
<td>Clarke (2013)</td>
</tr>
</tbody>
</table>

### Table 8

<table>
<thead>
<tr>
<th>Source/Raw material</th>
<th>Process</th>
<th>Conditions</th>
<th>Recovery (%)/Remarks</th>
<th>Product (% purity)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic solution, Geothermal water (Li = 10 mg/L)</td>
<td>Precipitation</td>
<td>pH 12.5 for [Al]: 50–1000 mg/L</td>
<td>70% Li</td>
<td>–</td>
<td>Yoshinaga et al. (1986)</td>
</tr>
<tr>
<td>Synthetic solution (2.5 M LiCl, 0.3 M CaCl$_2$ and 0.15 M MgCl$_2$)</td>
<td>Precipitation followed by IX using Poly BDI® (94% Li$^+$, Lewatit® (TP 207), Dowex®(Y92))</td>
<td>Precipitation with 1.8 M Na$_2$CO$_3$ at 80 °C, 50°C, 30 min</td>
<td>Good usable volume cap. of resin TP207: 564 g/L; 56% yield</td>
<td>Li$_2$CO$_3$ (99.9)</td>
<td>Bukowsky et al. (1991)</td>
</tr>
<tr>
<td>Seawater (0.12–0.16 mg/L Li)</td>
<td>Integrated ion-exchange method</td>
<td>pH 12.8</td>
<td>Li salt solution</td>
<td>–</td>
<td>Nishihama et al. (2011), Onishi et al. (2010)</td>
</tr>
<tr>
<td>Seawater (0.18–0.20 mg/L Li)</td>
<td>Two stage precipitation</td>
<td>1st stage pH: 11.5–12.5; 2nd stage: Na$_2$CO$_3$ at 100 °C</td>
<td>Recovery of pure lithium carbonate</td>
<td>Li$_2$CO$_3$ (99.4)</td>
<td>Uem and Hirato (2012)</td>
</tr>
<tr>
<td>Uyuni Salar brine, Bolivia, 15–18 g/L Mg, 0.7–0.9 g/L Li</td>
<td>Two stage precipitation with lime &amp; Na-oxalate</td>
<td>1st stage pH: 11.3, 2nd stage: sodium oxalate, 80–90 °C</td>
<td>Precipitation as Li$_2$CO$_3$</td>
<td>Li$_2$CO$_3$ (99.55)</td>
<td>An et al. (2012), Tran et al. (2013)</td>
</tr>
<tr>
<td>Brine from Salar de Hombre Muerto, Argentina (high Mg/Li ratio)</td>
<td>Precipitation (2.5 g/L LiCl from solar pond) with lime and Na$_2$SO$_4$</td>
<td>Separation of Mg as hydroxide and Ca as sulfate</td>
<td>Precipitation as Li$_2$CO$_3$</td>
<td>Li$_2$CO$_3$ (99.55)</td>
<td>An et al. (2012), Tran et al. (2013)</td>
</tr>
<tr>
<td></td>
<td>Electrochemical</td>
<td>LiCl salt feed for Li extr. in a chemical plant</td>
<td>LiCl</td>
<td>–</td>
<td>Zhao et al. (2013)</td>
</tr>
</tbody>
</table>
then generated which selectively adsorbed lithium (~30.3 mg/g adsorbent) from seawater. When a polymeric membrane reservoir containing an inorganic ion-exchange adsorbent inside it with zinc was used, lithium recovery from seawater was very effective and kinetically favored with adsorption of 33.1 mg Li/g sorbent (Chung et al., 2008). This adsorbent had excellent lithium adsorption of 89% of 400 mg Li in a day only; the desorption efficiency being 92.88% by dipping in 4 L of 0.5 M HCl solution in a day. By using Mg-doped manganese oxide, Chitrakar et al. (2013) also observed very fast adsorption equilibrium (within 24 h) for effective recovery of lithium from solar brine (Table 7).

Recently Wajima et al. (2012) prepared HMn2O4 by elution of spinel-type lithium di-manganese-tetra-oxide (LiMn2O4) and examined the kinetics of lithium adsorption. The intermediate, LiMn2O4, was also synthesized from LiOH·H2O and Mn3O4 by acid treatment. Lithium ions were eluted using 0.2 M HNO3 in 80% methanol solution containing 15–18 g/L Mg and 0.7–0.9 g/L Li saturated with sodium, chloride and sulfate. In a 2-stage precipitation process, magnesium and sulfate were removed as Mg(OH)2 and gypsum (CaSO4⋅2H2O) at pH 11.3 by lime in the first stage. Residual magnesium after lime precipitation and almost all soluble calcium were then removed by the addition of sodium oxalate. In the second stage 99.6% lithium carbonate was precipitated at 80–90 °C using sodium carbonate. Residual Li+ from the solution was quantitatively extracted in the presence of other alkali metals by a mixture of commercial β-diketones (LIX-51) and TBP (Miyai et al., 1988). A 2-stage lime precipitation process to treat seawater was reported by Um and Hirato (2012) to separate lithium from magnesium and sodium, whereas Clarke (2013) mentioned the use of precipitation method to remove the two metals (magnesium and calcium) from the solar brine of Argentina to produce LiCl which was further processed to recover lithium.

3.2.2. Precipitation process

Some of the precipitation and other processes used for lithium recovery from seawaters/brines are summarized in Table 8. Among various co-precipitating agents used, aluminium salts show the best performance for lithium recovery from geothermal water. The appropriate pH for lithium recovery is 10–13 and use of NaAlO2 seems better than AlCl3. With a high purity NaAlO2 solution as co-precipitating agent, about 98–99% Li recovery was achieved at pH 11.5 from Ca- and SiO2-free geothermal water (Yoshinaga et al., 1986).

Despite being the richest lithium resource (10.2 Mt) Uyuni salar brine containing a high magnesium concentration (Mg/Li mass ratio ~21.2:1) causes difficulties in lithium production. The high magnesium content represents a significant metal value which should be recovered with lithium. Consequently, calcium and magnesium had to be removed from the brine by using oxalic acid before the production of lithium. The Mg-oxalate produced was suitable for use as a precursor for the production of MgO by roasting (Tran et al., 2013). An et al. (2012) developed a hydrometallurgical process to recover lithium from Uyuni salar brine containing 15–18 g/L Mg and 0.7–0.9 g/L Li saturated with sodium, chloride and sulfate. In a 2-stage precipitation process, magnesium and sulfate were removed as Mg(OH)2 and gypsum (CaSO4⋅2H2O) at pH 11.3 by lime in the first stage. Residual magnesium after lime precipitation and almost all soluble calcium were then removed by the addition of sodium oxalate. In the second stage 99.6% lithium carbonate was precipitated at 80–90 °C using sodium carbonate. Residual Li+ from the solution was quantitatively extracted in the presence of other alkali metals by a mixture of commercial β-diketones (LIX-51) and TBP (Miyai et al., 1988). A 2-stage lime precipitation process to treat seawater was reported by Um and Hirato (2012) to separate lithium from calcium and magnesium, whereas Clarke (2013) mentioned the use of precipitation method to remove the two metals (magnesium and calcium) from the solar brine of Argentina to produce LiCl which was further processed to recover lithium.

3.2.3. Ion exchange/Solvent extraction process

For high magnesium and calcium containing brines or brines solvent extraction or ion exchange can be used. After selective stripping/elution lithium can be precipitated out. A combined process consisting of solar evaporation and ion exchange for the extraction of lithium was proposed by Steinberg and Dang (1975, 1976). The Dowex resin was used for selective extraction of its H+ with the cations present in sea water in the order: K+, Na+, Li+ and Mg2+. Lithium ions were eluted using 0.2–0.5 M HCl and eluted LiCl was transferred into an electrolyser to produce lithium. Strelow et al. (1974) separated lithium from sodium, beryllium and many other elements by eluting lithium with 1 M HNO3 in 80% methanol from a column of AG50W-XS, a sulfonated polystyrene cation-exchange resin. Samples were loaded onto a column 20 cm3 AG50W-XS (200–400 mesh) resin column and then eluted with a mixed acid–methanol solution (1 M HNO3 and 80% methanol) which ensured an extremely good separation of lithium from sodium in a single column pass.

Earlier studies showed that organic ion-exchange resins exhibited low selectivity for lithium ions (Abe and Hayashi, 1984; Alberti and Massucci, 1970; Ho et al., 1978). However, Bukowsky et al. (1991) demonstrated that precipitation followed by ion exchange can be effectively used for separation and recovery of lithium from a synthetic solution of calcium and magnesium chlorides. Recently Nishihama et al. (2011) applied SK110 resin (sulfonated type) from a concentrated solution to remove divalent metal ions (Mg2+, Ca2+, Sr2+ and Mn2+) due to their higher sorption capacity compared to that of mono-valent ions. The separation of Li+ from the resultant solution with Na+ and K+ was achieved in a packed column of impregnated resin containing...
1-phenyl-1,3-tetradecanone (C₁₅H₂₉DK)/tri-n-octylphophine oxide (TOPO). Li₂CO₃ was precipitated from the concentrated Li⁺ solution by a (NH₄)₂CO₃ solution with an overall yield of 56% and a purity of >99.9%. Earlier this group reported selective adsorption of Li⁺ in aqueous chloride media using a novel synergistic solvent impregnated resin (SIR) containing both 1-phenyl-1,3-tetradecanone (C₁₅H₂₉DK) and TOPO (Onishi et al., 2010). About 94% Li⁺ was adsorbed by SIR containing 0.66 mmol/g of each extractant at pH 12. Almost 96.9% Li⁺ was eluted with a 1.0 mol/L HCl solution with 99.8% purity at a bed volume (BV) of 2.7.

Nelli and Arthur (1970) patented a selective liquid extraction process for lithium from batters of high magnesium content. In the presence of strong chloride and HCl, lithium was converted into stable lithium tetra chloroferrate (Cl₄FeLi₂), which can be extracted by a number of solvents. About 90% Li was extracted with a mixture of 20% TBP and 80% diisobutyl ketone in 7 counter current stages. Any co-extracted magnesium was recycled back to the initial extraction step by washing with water in 4 stages. Finally lithium tetra chloroferrate was stripped in 5 counter current stages. The strip water with ~2 M NaCl was contacted with a mixture of solvent (20% D2EHPA and 30% TBP in benzene) in 6 stages to remove FeCl₃. The raffinate in this step is the product containing ~0.36% Li, 200 mg/L Mg and 20 mg/L Fe. The second solvent is then recycled back to the initial extraction step by washing with water in 6 stages.

Separation of lithium and magnesium is difficult because they exhibit many chemical similarities. However, by utilizing the high charge density of Mg²⁺ which is twice that of Li⁺ with almost the same ionic radius and many chemical similarities, Zhao et al. (2013) reported a separation method using LiFePO₄/FePO₄ as electrodes (Table 8). Lithium exhibits its easy hydrated properties, Zn₂⁺ is stripped of its FeCl₃ with about 0.3 parts of water in 6 stages. The aqueous solution is then treated with Na₂CO₃ to obtain Li₂CO₃. Plastics and paper can then be separated from the rest of the materials (Cu, steel and plastics) can then be separated from the rest of the materials (Cu, steel and plastics). The large pieces are mechanically treated while the battery is submerged in a process solution of lithium brine, after which ferrous and nonferrous metals are recovered. Li-ion fluff (mixture of steel and plastics) can then be separated from the rest of the materials (Cu–Co and slurry). Copper is extracted in the next step and lithium carbonate. Besides organics, H₂ formed by reaction with lime, burns off at the surface of the process bath. Sludge from LIBs is sent to recover cobalt. The large pieces are mechanically treated while the batteries are submerged in a process solution of lithium brine, after which ferrous and nonferrous metals are recovered. Li-ion fluff (mixture of steel and plastics) can then be separated from the rest of the materials (Cu–Co and slurry). Copper is extracted in the next step and lithium brine is treated with Na₂CO₃ to obtain Li₂CO₃. Plastics and paper floating at the top are recovered for disposal or recycling. The filtered carbon

3.3. Extraction of lithium from secondary resources — lithium ion batteries

Secondary resources like spent batteries have lithium compounds coupled with valuable metals such as cobalt, nickel, manganese etc. which can be economically viable to recycle, whereas low value elements such as iron and phosphorus will be a greater challenge to create a profitable recycling program. 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; 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 the other component being the lithium hydroxide. Sony uses incineration which is followed by hydrometallurgical techniques. The industrial processes in vogue developed for recycling LIBs are described in brief.

3.3.1. Major industrial processes

3.3.1.1. AEA technology. A patented process developed in the UK aims at the recovery of all battery materials (Lain, 2002). The casing of the battery is first removed in N₂ and cells are cut mechanically to remove other components wound into a spiral. The anode, cathode and separators are shredded (~1 cm² size) to leach the electrolyte and the solvent in acetonitrile at 50 °C. The electrolyte and the solvent are recovered by evaporation of the leach liquor and acetonitrile is recycled back. The binder-PVDF is dissolved in NMP (N-methyl-2-pyrrolidone) and filtered to separate it from electrode material (Al, Cu, steel and plastics). The NMP is evaporated from the filtrate and recycled back. Residue is back-washed and the suspended particulate (LiCoO₂ and carbon) is electrolysed with LiOH as electrolyte. LiCoO₂ is reduced adjacent to the cathode to form COO while increasing the concentration of LiOH (Fig. 2) which is recovered by decantation. The reaction can be represented as:

\[ e^- + H_2O + LiCo(III)O_2 \rightarrow Co(II)O + Li^+ + 2OH^- \]  

3.3.1.2. Toxco process (Canada). A variety of batteries is processed in cryogenic conditions (in liquid nitrogen) to reduce the reactivity and mechanical and hydrometallurgical approaches are utilized to recover metal values (McLaughlin and Adams, 1998). The process flow-diagram is shown in Fig. 3. Large batteries are sheared into three pieces in a caustic bath, which neutralizes any acidic components and dissolves the lithium salts. The salts precipitated and dewatered in filter press, are used to produce lithium carbonate. Besides organics, H₂ formed by reaction with lithium, burns off at the surface of the process bath. Sludge from LIBs is sent to recover cobalt. The large pieces are mechanically treated while the batteries are submerged in a process solution of lithium brine, after which ferrous and nonferrous metals are recovered. Li-ion fluff (mixture of steel and plastics) can then be separated from the rest of the materials (Cu–Co and slurry). Copper is extracted in the next step and lithium brine is treated with Na₂CO₃ to obtain Li₂CO₃. Plastics and paper floating at the top are recovered for disposal or recycling. The filtered carbon
cake from the sludge is un-economical to reuse or even to burn off. Cobalt in the spent LIBs presents higher economic worth.

3.3.1.3. Accurec GmbH (Germany) process. The process involves mechanical treatment to separate the electrode material which is treated by pyro-metallurgy to recover the Co–Mn alloy and lithium chloride (Sojka, 1998). Electronics and plastic casings are removed followed by vacuum thermal treatment and pyrolysis to take care of the electrolyte and solvent including conductive salts (Fig. 4). The batteries are then crushed and by employing sieving, magnetic as well as air separator, aluminium, copper and steel are removed. The remaining electrode material is agglomerated with the addition of a binder and pressed to briquettes, which are smelted (reduction) in a furnace to obtain two fractions, the metallic Co–Mn alloy and lithium containing slag. By acid leaching of the slag lithium can be extracted as lithium chloride/carbonate.

3.3.1.4. Sony/Sumitomo (Japan) process. In this process untreated LIBs are calcined at 1000 °C by which the cells open and inflammable components such as the plastic casing and organic solvent burn off. The residue consisting of metallic and metal pieces of iron, copper and aluminium can be magnetically separated. The remaining fraction is mainly carbon powder and active cathode material (LiCoO₂ and/or LiCoO₂Ni₁−ₓO₂). The powder is treated at the Sumitomo plant by hydrometallurgical methods to recover cobalt; lithium is not targeted. Cobalt oxide of high quality is recovered to use directly in the fabrication of new LIBs and the metallic scraps such as copper and stainless steel can be used as the by-products. Large batteries can also be handled but needs to be punctured prior to introduction to the furnace (Gaines and Cuenca, 2000; Lupi et al., 2005).

3.3.1.5. Recupyl process (France). This is also called as the Valibat process for recycling LIBs. Mechanical preparation of the spent batteries is performed under an inert atmosphere to reduce the reactivity of lithium. Plastics, steel and copper are then separated by physical treatment. The fine powder obtained by screening is suspended in stirred water for subsequent leaching and hydrolysis step. Filtering the hydrolyzed solution produces an alkaline solution of lithium salt and a suspension of

Fig. 3. Tosco’s hydrometallurgical recycling process for LIBs.

Fig. 4. Flow-sheet of Accurec recycling process.

Fig. 5. Recupyl process for LIBs recycling.
metal oxides and carbon. Lithium is precipitated as Li₂CO₃ using the CO₂ obtained from the mechanical treatment. The suspension of metal oxides is dissolved in H₂SO₄. Copper is cemented out by the steel shots (Tedjar and Foudraz, 2007). The purified solution is oxidized by NaClO to precipitate cobalt(III) hydroxide (Fig. 5) and cobalt is separated by electrolysis. The remaining lithium in the solution is precipitated with CO₂ gas.

3.3.1.6. Batrec Industrie AG process (Switzerland). The company Batrec mainly runs a mechanical processing plant for LIBs. In this process batteries are crushed in CO₂ gas atmosphere and the released lithium is neutralized. With the completion of the neutralization step, the protective environment is released and subsequently treated in a gas scrubber to reduce the emission during the process. Scrap material is leached and washed in acidified aqueous liquid and leach liquor is further processed for the recovery of different chemical substances. Metal containing a solid fraction can be separated from liquid and treated to remove impurities. The flowsheet of the process is presented in Fig. 6.

### Table 9

<table>
<thead>
<tr>
<th>Material</th>
<th>Leaching conditions</th>
<th>Extraction/Separation—parameters</th>
<th>Highlights (with merits/demerits)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cylindrical-shaped LIBs</td>
<td>4 M H₂O, 80 °C, 1 h</td>
<td>SX with 0.29 M D2EHPA and 0.90 M PC-88A</td>
<td>SX: &gt;99.9 Co and 12.6% Li with 0.9 M PC-88A. High selectivity with PC 88A. Co(OH)₂ separated easily. Ni₃CoₓMₓ, a precursor to cathode material</td>
<td>Zhang et al. (1998)</td>
</tr>
<tr>
<td>Spent LIBs</td>
<td>4 M H₂O, 80 °C, 1 h</td>
<td>SX with 0.29 M D2EHPA and 0.90 M PC-88A</td>
<td>SX: &gt;99.9 Co and 12.6% Li with 0.9 M PC-88A. High selectivity with PC 88A. Co(OH)₂ separated easily. Ni₃CoₓMₓ, a precursor to cathode material</td>
<td>Contestabile et al. (2001)</td>
</tr>
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<td>LIBs</td>
<td>4 M H₂O, 80 °C, 1 h</td>
<td>SX with 0.29 M D2EHPA and 0.90 M PC-88A</td>
<td>SX: &gt;99.9 Co and 12.6% Li with 0.9 M PC-88A. High selectivity with PC 88A. Co(OH)₂ separated easily. Ni₃CoₓMₓ, a precursor to cathode material</td>
<td>Contestabile et al. (2001)</td>
</tr>
<tr>
<td>LIBs</td>
<td>3 M H₂O, 80 °C, 1 h</td>
<td>SX with 0.29 M D2EHPA and 0.90 M PC-88A</td>
<td>SX: &gt;99.9 Co and 12.6% Li with 0.9 M PC-88A. High selectivity with PC 88A. Co(OH)₂ separated easily. Ni₃CoₓMₓ, a precursor to cathode material</td>
<td>Contestabile et al. (2001)</td>
</tr>
<tr>
<td>Ash from LIBs</td>
<td>4 M H₂O, 90 °C, 18 h</td>
<td>SX with 0.29 M D2EHPA and 0.90 M PC-88A</td>
<td>SX: &gt;99.9 Co and 12.6% Li with 0.9 M PC-88A. High selectivity with PC 88A. Co(OH)₂ separated easily. Ni₃CoₓMₓ, a precursor to cathode material</td>
<td>Contestabile et al. (2001)</td>
</tr>
</tbody>
</table>

3.3.2. Recent development in recycling of lithium ion batteries

Spent LIBs containing lithium and other metals are mostly treated by the hydrometallurgical process which is used at times in combination with pyrometallurgical treatment. This may have integrated pre-treatment steps like pyrolysis or mechanical processing, i.e. crushing and material separation. In order to investigate the extraction of cobalt, nickel, manganese etc. from LIBs by such processes thermodynamic aspects particularly the stability regions of different phases in aqueous solution under redox conditions may be examined. For this standard Eh–pH diagrams of Li–H₂O, Co–H₂O, Mn–H₂O and Ni–H₂O systems can be referred from literature (Pourbaix, 1966; Schweitzer and Pasterfield, 2010).

Leaching of LIBs are carried out with different acids like HCl (Contestabile et al., 2001; Zhang et al., 1998), H₂SO₄ (Aktas et al., 2006; Dorella and Mansur, 2007; Kang et al., 2010a,b; Nan et al., 2005; Shin et al., 2005; Swain et al., 2007), HNO₃ (Lee and Rhee, 2002, 2003), and a few organic acids like DL-malic acid (Li et al., 2010a), citric acid (Li et al., 2010b) etc. The binder (PVDF) which links the cathode material, LiCoO₂ with aluminium foils does not dissolve easily in the organic reagents such as fatty hydrocarbon or alcohol at room temperature making the leaching reactions more difficult to proceed. The important developments in the recycling of the spent lithium ion batteries are presented in Table 9.
While H2O2 facilitated the dissolution of Co(II) which was reduced (2001; Joulié et al., 2014; Shuva and Kurny, 2013; Zhang et al, 1998). In the presence of a reducing agent such as hydrogen peroxide material of spent LIBs was achieved with a 4 M solution of HCl. Most processes reported, optimum extraction of metals from the cathode, metal leaching was possible even in 3 M HCl (Contestabile et al., 2006).

### 3.3.2.1. Extraction and recovery of metals from spent LIBs in other organic/inorganic acid systems.

### Table 10

<table>
<thead>
<tr>
<th>Material</th>
<th>Leaching conditions</th>
<th>Extraction/Separation parameters</th>
<th>Highlights (with merits/demerits)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIBs waste</td>
<td>2 M acid + 15 vol% H2O2</td>
<td>75 °C, 167 h, 50 g/L</td>
<td>–</td>
<td>Leaching (%): 95 Co and 100 Li. Harmful gas—SOx, generated.</td>
</tr>
<tr>
<td>Square-shaped LIBs</td>
<td>3 M acid</td>
<td>70 °C, 4 h, 200 g/L</td>
<td>Precipitation &amp; SX using Acorga M5640 and Cyanex 272</td>
<td>Precipitation: 90% Co; SX: ~57% Cu by Acorga M5640, 97% Co by Cyanex 272</td>
</tr>
<tr>
<td>LIBs</td>
<td>6% acid + 1% H2O2</td>
<td>65 °C, 33.3 g/L</td>
<td>Precipitation with NH3, at pH 5. Co/Li separation by diluted (0.72 M) Cyanex 272</td>
<td>Leaching (%): ~55 Al, 80 Co and 95 Li; Extraction (%): ~85 Co by Cyanex 272</td>
</tr>
<tr>
<td>LIB wastes</td>
<td>2 M acid + 5% H2O2</td>
<td>75 °C, 100 g/L</td>
<td>SX by 0.5 M Cyanex 272, pH 5.35 and O/A = 1 in 1-stage</td>
<td>Leaching (%): 93 Co and 94 Li; CoSO4 solution: 99.99% pure.</td>
</tr>
<tr>
<td>Spent LIBs</td>
<td>4 M acid + H2O2</td>
<td>80 °C, 4</td>
<td>Precipitation using ethanol, ethanol/solution = 3:1; 15 min, room temperature</td>
<td>Co recovery: 92% as CoO4 and 85% as Co(OH)2 by adding Li(OH)2 at pH 10. Separation factor (Co/Li): 497 at pH 5</td>
</tr>
<tr>
<td>Synthetic solution</td>
<td>10 mol/L Co(II) and 20 mol/L Li2SO4</td>
<td>–</td>
<td>SX by Cyanex 272 and DP-8R</td>
<td></td>
</tr>
<tr>
<td>Spent LIBs</td>
<td>2 M acid + 6% H2O2</td>
<td>60 °C, 100 g/L</td>
<td>Precipitation at pH 6.5 for Cu, Fe and Al by 50% saponified 0.4 M Cyanex 272, pH 6, O/A = 2</td>
<td>Leaching (%): ~99 Co, SX: 99.9% Co in 2 stages. Separation factor 750 (Co/Li) and Co/Ni at pH 6.</td>
</tr>
<tr>
<td>Spent LIBs</td>
<td>1 M acid + 30% H2O2</td>
<td>80 °C, 714 g/L</td>
<td>Precipitation by 1 M citric acid, 2 h, 65 °C; calcined at 450 °C, 4 h</td>
<td>Max. Co leaching (%): 88.3, Crystalline LiCoO2 synthesized</td>
</tr>
<tr>
<td>Spent LIBs</td>
<td>4 M acid + 10% H2O2</td>
<td>85 °C, 100 g/L</td>
<td>SX by 25% P507</td>
<td>SX: 98% Co and removal of 97% Ni and Li.</td>
</tr>
<tr>
<td>Spent LIBs</td>
<td>3 M + 0.25 M Na2S2O3</td>
<td>90 °C, 67 g/L</td>
<td>–</td>
<td>&gt;99% leaching</td>
</tr>
</tbody>
</table>

on the leaching and separation of metals from the leach solutions are summarized in Tables 9–11.

#### 3.3.2.1. 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 with a 4 M solution of HCl (Table 8). In the presence of a reducing agent such as hydrogen peroxide, metal leaching was possible even in 3 M HCl (Contestabile et al., 2001; Joulié et al., 2014; Shuva and Kurny, 2013; Zhang et al, 1998). While H2O2 facilitated the dissolution of Co(II) which was reduced from Co(III), the dissolution of lithium was also promoted because of the presence of the two metals in the same oxide. The separation and recovery of metals from the leach liquors, was carried out either by solvent extraction involving PC-88A, Cyanex 272 etc. to produce the pure metal salts or the metals that were selectively precipitated as Co(OH)2 and Li2CO3 from the leach solutions. Thus, Zhang et al. (1998) 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. Out of sulfurous acid, hydroxyl amine hydrochloride and hydrochloric acid, HCl was found to be the most suitable lixiviant for economic reasons. The leaching efficiency of ~99% of Co and Li in a 4 M HCl solution was achieved. The complete extraction of cobalt from the leach liquor by 0.90 M PC-88A in 1 stage at pH 6.7 and O/A of 0.85:1, scrubbing of lithium by 30 g/L Co at O/A 10:1 and

### Table 11

<table>
<thead>
<tr>
<th>Material</th>
<th>Leaching reagent</th>
<th>Leaching conditions</th>
<th>Highlights (with merits/demerits)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIBs</td>
<td>1 M HNO3 + 1.7 vol% H2O2</td>
<td>1 °C, 75 °C, 20 g/L</td>
<td>Leaching (%): 95 Co and Li. Harmful gas—NOx generated.</td>
<td>Lee and Rhee (2002, 2003)</td>
</tr>
<tr>
<td>LIBs</td>
<td>1 M HNO3 + 1.0 vol% H2O2</td>
<td>1 °C, 80 °C, 20 g/L</td>
<td>Leaching (%): 90 Co and 100 Li. Harmful gas—NOx generated.</td>
<td>Li et al. (2011)</td>
</tr>
<tr>
<td>Spent LIBs</td>
<td>1.5 M oxalic acid + 2% H2O2</td>
<td>0.67 °C, 90 °C, 20 g/L</td>
<td>Leaching (%): 90 Co and 100 Li. Acid can be recycled and reused.</td>
<td>Li et al. (2010a)</td>
</tr>
<tr>
<td>Spent LIBs</td>
<td>1.25 M citric + 1% H2O2</td>
<td>0.25 °C, 90 °C, 20 g/L</td>
<td>Leaching (%): ~90 Co and 100 Li. Simple and environmental friendly process.</td>
<td>Li et al. (2010b)</td>
</tr>
<tr>
<td>Cylindrical spent LIBs of mobile phone</td>
<td>1.25 mol/L ascorbic acid</td>
<td>0.33 °C, 70 °C, 25 g/L</td>
<td>Leaching (%): 94.8 Co and 98.5 Li. Reducibility of ascorbic acid displaced H2O2.</td>
<td>Li et al. (2012)</td>
</tr>
</tbody>
</table>
stripping of cobalt from the loaded organic with 2 M H2SO4 at O/A 5:1, produced high purity cobalt sulfate. About 80% lithium was recovered as Li2CO3 by precipitation with saturated soda solution at 100 °C. The leaching reaction of the waste LiCoO2 with HCl solution can be represented as:

\[ 4\text{LiCoO}_2(s) + 12\text{HCl}(aq) \rightarrow 4\text{LiCl}(aq) + 4\text{CoCl}_2(aq) + 6\text{H}_2\text{O}(l) + \text{O}_2(g) \]  

A laboratory scale process involving leaching of LiCoO2 in HCl and precipitation of cobalt hydroxide was developed by Contestabile et al. (2001). The active material of spent LIBs was dissolved in N-methylpyrrolidone at 100 °C to separate aluminum and copper foil. From the leach liquor, carbon powder was removed by filtration and Co(OH)2 was precipitated out from the solution at pH 6–8. In another study over 95% dissociation of Ni, Co and Mn was reported when the battery material of 120 μm size was leached at a higher acid concentration (6 M HCl) and lower temperature (60 °C) in the presence of H2O2 (Li et al., 2009b). Cobalt from the solution was cemented out by iron powder and iron was removed as goethite. Finally chlorides of Ni, Mn and Co were added in the purified solution to prepare the precursor of the cathode material (Ni2Co2Mn2) directly through co-precipitation with ammonium bicarbonate. The leaching of metals from the cathode material in 4 M HCl at 80 °C with a metal recovery of 99% was also reported by Wang et al. (2009). Manganese in the leach liquor was precipitated at a molar ratio of Mn2+ to KMnO4 2 for pH 2 followed by selective precipitation of nickel with dimethylglyoxime (DMG) at pH 9. Cobalt was recovered as hydroxide at pH 11 and Li2CO3 was then precipitated; purity of the metals being 96.97% Li, 98.23% Mn, 96.94% Co and 97.43% Ni. A recent study by Shuva and Kurny (2013) demonstrated the reductive dissolution of cathode powder in 3 M HCl in the presence of 3.5% H2O2. Over 95% cobalt was precipitated as hydroxide at pH 11–12, leaving lithium (93%) in the leach solution.

Processing of battery ash obtained from the pyrolysis of spent LIBs by HCl leaching was also attempted. Lin et al. (2003) patented a pyrometallurgical process of waste LIBs combined with hydrometallurgical processing. The ash with metal and metal oxides was dissolved in 3–6 M HCl containing NaCl. Copper and cobalt were separated out using membrane electrolysis. Then Fe(OH)3 and Al(OH)3 were recovered at pH 5–7 followed by the precipitation of lithium carbonate. Recently Joullé et al. (2014) reported the high leaching efficiency (~100%) of Li, Ni, Co and Al from the Li–Ni–Co–Al oxide ash of spent LIBs by 4 M HCl at 90 °C with chloride ions promoting the dissolution. Co(II) in the leach liquor was oxidized to Co(III) with NaClO and recovered as Co2O3·3H2O by selective precipitation at pH 3 (Eqs. (16) and (17)). Nickel hydroxide was then precipitated at pH 11.

\[ 2\text{Co}^{2+} + \text{ClO}^- + 2\text{H}_2\text{O} \leftrightarrow 2\text{Co}^{3+} + \text{Cl}^- + 3\text{H}_2\text{O} \]  

\[ 2\text{Co}^{3+} + 6\text{OH}^- \rightarrow \text{Co}_2\text{O}_3\cdot3\text{H}_2\text{O} \]  

3.3.2.2. Metal extraction/recovery from sulfuric acid leach liquors. In most leaching processes with sulfuric acid, hydrogen peroxide was used as a reductant (Castillo et al., 2002; Dorella and Mansur, 2007; Jha et al., 2013a,b; Kang et al., 2010a, 2010b; Shin et al., 2005). In some cases alkali leaching followed by acid leaching was considered to remove aluminium. Metals from the leach solutions were separated and recovered by solvent extraction using PC-88A/P507, Cyanex 272 and Acogra M5640 and precipitation processes very similar to that of the HCl system. The fine sized electrodes were initially contacted with N-methyl pyrrolidone (NMP) to dissolve the binder and separate active material (LiCoO2) from Al and Cu foils (Castillo et al., 2002). The LiCoO2 powder was leached in 4 M H2SO4 at 80 °C to dissolve Co and Li, and Co(OH)2 was recovered from the leachate by the addition of sodium hydroxide.

Shin et al. (2005) reported almost quantitative leaching of cobalt and lithium with 2 M H2SO4 in the presence of a high amount of H2O2 (15 vol%) at 75 °C and 50 g/L pulp density (Table 10). Reductive leaching of the mechanically treated LIBs in 6% v/v H2SO4 and 1% H2O2 solution resulted in a relatively lower recovery of metals (~55% Al, 80% Co and 95% Li) (Dorella and Mansur, 2007). Kang et al. (2010a, 2010b) also reported the reductive leaching of LIBs with H2SO4. The reactions of LiCoO2 with H2SO4 and in the presence of H2O2 are shown below:

\[ 4\text{LiCoO}_2(s) + 6\text{H}_2\text{SO}_4(aq) \rightarrow 4\text{CoSO}_4(aq) + 2\text{Li}_2\text{SO}_4(aq) + 6\text{H}_2\text{O}(l) + \text{O}_2(g) \]  

\[ 2\text{LiCoO}_2(s) + 3\text{H}_2\text{SO}_4(aq) + \text{H}_2\text{O}_2(aq) \rightarrow 4\text{CoSO}_4(aq) + \text{Li}_2\text{SO}_4(aq) + 4\text{H}_2\text{O}(l) + \text{O}_2(g) \]  

The leaching efficiency of cobalt depends on the reductant concentration. Among other reducing agents, Na2SO3 helped in the leaching of >99% of the metals (Co and Li) in 2 M sulfuric acid at 90 °C in 3 h (Wang et al., 2012).

Safe dismantling procedures of spent lithium ion batteries have often been described in the literature (Nan et al., 2005; Tanii et al., 2003). Zhu et al. (2011) applied a mechanical separation process to recover copper from these batteries. The anodes from the batteries were separated by mechanical treatment, pulverization and sieving. Almost 92% of copper in anode particles was recovered by a gas-fluidized bed separator.

In the alkali–acid leaching process, the cathode was first treated with 10% (w/w) NaOH at 30 °C to dissolve Al, followed by reductive leaching of ~97% Co and 100% Li with H2SO4 and H2O2 (Ferreira et al., 2009; Nan et al., 2005). Acogra M5640 and Cyanex 272 were used to selectively extract and recover 98% Cu and 97% Co, respectively from the solutions. About 90% Co was recovered as oxalate with <0.5% impurities. LiCoO2 positive electrode material with a good electrochemical performance was synthesized by using the recovered compounds.

From the sulfate leach liquor of spent LIBs, 96% copper was recovered as CuSO4·3H2O with ethanol at a volume ratio of 3:1. Cobalt was recovered in two steps. During the first step, 92% of the cobalt was recovered as Co2O3 by the use of ethanol at a volume ratio of 3:1. The remaining Co in the second step was recovered as Co(OH)3 by the addition of Li(OH)2 at pH 10 (Aktas et al., 2006). Lithium, which remained in the solution, was then recovered to the extent of 90% as Li2SO4 by the addition of ethanol (3:1 volume ratio). Aluminium was recovered as Al(OH)3 with 99% recovery efficiency. It was shown that metals could be precipitated/separately by the ethanol/sulfate precipitation technique depending on their concentrations present in the solution.

The waste cathodic active material generated during the manufacturing of LIBs was also leached in H2SO4 in the presence of H2O2 (Swain et al., 2007). During the separation of Co/Li in a 2-step SX process with 1.5 M Cyanex 272 at O/A 1.6, about 85% Co was recovered. The remaining cobalt was extracted in 0.5 M Cyanex 272 at O/A 1 and pH 5.35. The purity of cobalt sulfate in solution was found to be 99.99%. Earlier, Swain et al. (2006) reported the highest separation factor (Co/Li) of 62 during extraction with saponified Cyanex 272 from a synthetic solution at pH 6.9.

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):

\[ \text{M}_2\text{aq}^2+ + \text{A}_{org}^- + 2(\text{HA})_{org}^- \rightarrow 2\text{M}_{2}^-\text{A}_{org} + \text{H}_3\text{O}^+ \]  

Cobalt is extracted as [CoA2−3HA]org with 65% Na-Cyanex 272. Cobalt can be completely stripped from the loaded organic with 0.01 M H2SO4 to produce cobalt sulfate of ~99% purity.

By acid leaching of waste cathodic material and SX with Cyanex 272, Swain et al. (2008) produced a pure cobalt sulfate solution (99.99%). In another study quantitative separation of Co(II)/Li 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). Very recently, leaching of lithium and cobalt from cathodic material of waste mobile phone batteries in sulfuric acid in the presence of H₂O₂ and separation of metals by Cyanex 272 were reported (Jha et al., 2013a, 2013b). Chen et al. (2011a) recovered cobalt oxalate from the spent LIBs by using an alkali–acid leach process. After roasting the spent LIBs at 700–800 °C to burn off carbon and the binder, and leaching with NaOH to remove Al, and leaching with H₂SO₄ in the presence of 10 (v/v)% H₂O₂ could recover 95% Co and 96% Li. Iron removal (99.99%) as jarosite solution with saponite was also reported by Suzuki et al. (2012). About 95% Co(II) was extracted selectively from the purified solution with saponified 25 wt.% FSO₇(2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) at pH 3.5 and stripped with 9 MH₂SO₄. Cobalt oxalate was produced from the strip liquor with a purity of 99.9%. Co₃O₄·2H₂O and Li₂CO₃ were also produced by a combination of acid leaching, SX and precipitation from spent mobile phone batteries (Jian et al., 2012). From the leach solution of the used batteries, Co(OH)₂ was precipitated and was converted to Co₃O₄ by heating (Yamaji et al., 2011). A sp e r r e a c t i o n (23) and (24). Lithium was recovered as carbonate (47% Co) is obtained by precipitation, whereas without solvent extraction the product containing 36–37% (w/w) Co is obtained. Lithium is recovered by crystallization (yield 80%) with 98% purity. The process with solvent extraction shows economical outputs (gross margin and payback time) than the one without solvent extraction.

**Copper precipitation (>)98.5% with NaOH was followed by solvent extraction to recover Co(II) while removing 97% Ni and Li (Zhu et al., 2012). About 95% Co(II) was extracted selectively from the purified solution with saponified 25 wt.% FSO₇(2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) at pH 3.5 and stripped with 9 MH₂SO₄. Cobalt oxalate was produced from the strip liquor with a purity of 99.9%. Co₃O₄·2H₂O and Li₂CO₃ were also produced by a combination of acid leaching, SX and precipitation from spent mobile phone batteries (Jian et al., 2012). From the leach solution of the used batteries, Co(OH)₂ was precipitated and was converted to Co₃O₄ by heating (Yamaji et al., 2011) as per reactions (23) and (24). Lithium was recovered as carbonate by adsorption with 2% MnO₂ (11.7 mg Li/g).

\[
\ce{CoSO_4 + 2NaOH -> Co(OH)_2 + Na_2SO_4} \tag{23}
\]

\[
\ce{3Co(OH)_2 + 1/2 O_2 -> Co_3O_4 + 3H_2O} \tag{24}
\]

The advantage of vacuum pyrolysis to prevent the escape of toxic gases and lower the decomposition temperature of organics while protecting oxidation of metals in LIBs, was applied by Sun and Qiu (2011). The cathode material was treated in a vacuum furnace at 600 °C for 30 min with the residual gas pressure of 1.0 kPa. Over 99% Co and Li were recovered from peeled Co–Li oxide by leaching with 2 M H₂SO₄ at 80 °C. Paulino et al. (2008) examined two approaches for recycling spent Li/MnO₂ and LIBs. In the first process ~90% Li was recovered by precipitation at 500 °C followed by leaching with H₂SO₄ and H₂O₂ at 90–100 °C, and solvent extraction. The second process involved fusion with KHSO₄ at 500 °C and water leaching with H₂O₂ at 90 °C. Cobalt and manganese were precipitated at pH ~9 followed by precipitation of LiF by KF solution.

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 powder is leached in H₂SO₄ in the presence of 50% excess of a reducing agent, glucose — a waste product of the food factory. Iron, aluminium and copper are partially precipitated as hydroxides at pH 5.0. Using solvent extraction high purity cobalt carbonate (47% Co) is obtained by precipitation, whereas without solvent extraction the product containing 36–37% (w/w) Co is obtained. Lithium is recovered by crystallization (yield 80%) with 98% purity. The process with solvent extraction shows economical outputs (gross margin and payback time) than the one without solvent extraction.

**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 was also utilized to treat the leach solutions of spent LIBs (Pranolo et al., 2010). In the first stage Fe(III), Al(III) and Cu(II) were extracted using Ionquest 801 and Acorga M5640, and the raffinate containing cobalt, nickel and lithium was treated with 15% (v/v) Cyanex 272 to separate out Al, Co and Li in the raffinate. Aluminium is then selectively extracted by PC-88A in the pH range 2.5–3.0. Cobalt(II) and lithium(I) are separated by PC-88A/TOA rather than Acorga M5640 due to its higher stripping efficiency (>98%), although Acorga M5640 provides higher cobalt selectivity.

3.3.2.3. 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 LiCoO₂ as a cathode active material (Lee and Rhee, 2002, 2003). Reductive leaching in 1 M HNO₃ with 1.7 vol.% H₂O₂ at 75 °C extracted ~95% Li and 95% Co (Table 11). The molar ratio of lithium to cobalt in the leach liquor was adjusted to 1.1 by adding a fresh LiNO₃ solution. Then, 1 M citric acid solution was added to prepare a gelatinous precursor. LiCoO₂ was obtained with the gel precursor calcined in a crucible at 450 °C for 4 h.

![Fig. 7](image-url) Fig. 7. SX separation of Al, Cu and Li from sulfate media (Suzuki et al., 2012).
Recycling of Li-ion and polymer batteries while producing LiCoO$_2$, as a cathode material was investigated by Lupi and Pasquali (2003). The process consists of cathodic paste leaching, Co–Ni separation by SX and recovery of Ni by electrowinning. The separation of Ni/Co was performed by solvent extraction using saponified 0.5 M Cyanex 272. Nickel was electrowon at a current density of 250 A/m$^2$, 50 °C and pH 3–3.2 with an electrolyte of 50 g/L Ni and 20 g/L H$_2$BO$_3$. Elaborating further, Lupi et al. (2005) reported the current efficiency and energy consumption of 87% and 2.96 kWh/kg for nickel under the above conditions as compared to the figures of 96% and 2.8 kWh/kg, respectively for cobalt at the same current density and temperature, but at pH 4–4.2 from a solution containing manganese and (NH$_4$)$_2$SO$_4$.

3.3.2.4. Metal extraction using organic acids/reagents. For the sustainable management of the secondary resource such as LIBs, organic acids such as mL-malic acid, citric acid etc. which have mild acidity, are suggested for the leaching of metals (Table 11). Li et al. (2010a) reported that mL-malic acid can dissolve lithium and cobalt of LIBs fairly rapidly under aerobic and anaerobic conditions as compared to the mineral acids like HCl, HNO$_3$ and H$_2$SO$_4$ and the waste solutions can be treated easily. Almost 100% Li and >90% Co were leached out with 1.5 M mL-malic acid and 2.0% H$_2$O$_2$ at 90 °C in 40 min. Leaching of lithium and cobalt in citric acid was also reported after separating the anode and cathode material by the treatment of NMP (Li et al., 2010b). Nearly 100% Li and >90% Co were extracted in 1.25 M citric acid and 1.0% H$_2$O$_2$ at 90 °C.

Recently ultrasonic assisted leaching of cobalt and lithium from spent LIBs in the presence of ascorbic acid was investigated (Li et al., 2012). Leaching efficiencies of as high as 94.8% for Co and 98.5% for Li were achieved with 1.25 M ascorbic acid solution at 70 °C (Table 11). Sun and Qiu (2012) used oxalic acid as both leachant and precipitant to separate and recover cobalt and lithium from the spent LIBs. Cathode material consisting of LiCoO$_2$ and CoO from the dismantled batteries, was peeled off from the aluminium foils after vacuum pyrolysis at 600 °C. Leaching was performed using 1 M oxalate at 80 °C with the reaction efficiency of >98% of LiCoO$_2$ while separating cobalt and lithium. The reaction with oxalate for leaching and precipitation proceeds as:

\[ 3\text{H}_2\text{C}_2\text{O}_4 + \text{LiCoO}_2(\text{s}) \rightarrow \text{LiHC}_2\text{O}_4 + \text{Co(HC}_2\text{O}_4)_2 + 2\text{H}_2\text{O} + 2\text{CO}_2(\text{g}) \]  

(26)

\[ 4\text{H}_2\text{C}_2\text{O}_4 + 2\text{LiCoO}_2(\text{s}) \rightarrow \text{LiC}_2\text{O}_4 + 2\text{CoC}_2\text{O}_4(\text{s}) + 4\text{H}_2\text{O} + 2\text{CO}_2(\text{g}) \]  

(27)

During the oxalate leaching Co$^{3+}$ was reduced to Co$^{2+}$ which was dissolved and precipitated as cobalt(II) oxalate (Sun and Qiu, 2012). The reduction of Co$^{3+}$ to Co$^{2+}$ is also believed to proceed by the reaction of CO$_2$ radicals generated from oxalic acid (Hoffman and Simic, 1973). The electrochemical performance of nano-Co$_3$O$_4$ anode material prepared from the spent LIBs was evaluated by Hu et al. (2013). From the leach liquor obtained from the alkali and acid process, Al(OH)$_3$, MnOOH, Cu(OH)$_2$ and Ni(OH)$_2$ were removed at a pH > 5 which was followed by the precipitation of CoC$_2$O$_4$ at pH 2 by adding a saturated solution of (NH$_4$)$_2$C$_2$O$_4$. The product CoC$_2$O$_4$ was used to synthesize nano-Co$_3$O$_4$ by the sol–gel method.

The roasting of batteries under reduced pressure at 650 °C was reported by Kondas et al. (2006), which was followed by the leaching of Li$_2$CO$_3$ at ambient temperature and crystallization of pure Li$_2$CO$_3$. A process for the recycling and synthesis of LiCoO$_2$ from the incisors bound of Li-ion batteries was developed by Liu et al. (2006). Firstly, LiCoO$_2$ was separated from aluminium foil with dimethyl acetamide (DMAC). Polyvinylidene fluoride and carbon powders in the active material were then eliminated by roasting at 450 °C for 2 h and 600 °C for 5 h, respectively. Finally LiCoO$_2$ was obtained by adding a certain amount of Li$_2$CO$_3$ in the recycled LiCoO$_2$ and calcining it at 850 °C for 12 h.

4. Conclusions

Lithium is one of the rare metals with a variety of applications and demand for lithium is expected to increase with the ever increasing use of electronic and electronic devices/hybrid electric vehicles. A few established technologies are in vogue to produce lithium in the desired form from its primary resources like its minerals and brine, whereas limited exploitation of lithium resources from seawater and bitterns calls for their intensified tapping. Extraction of lithium from its minerals and clays is fraught with high mining costs and involves high energy, while extraction from brine and bitterns/seawater needs a long time for evaporation. Hence these processes need to be adequately modified to yield efficiency and better economic returns.

Extraction processes from secondary resources like batteries depend on the chemistry of the battery material. Most processes involve dismantling of LIBs, separation of cathode and anode materials, leaching of valuable metals like Co, Li, Ni, Mn etc. from the cathode material in different mineral acids, and separation and recovery of metals from the solutions by solvent extraction/Ix/preparation. At present no lithium extraction is industrially practiced from LIBs. Therefore, a sufficient scope exists not only to reduce the process steps followed currently but also to improve the efficiency of metal extraction and separation, including lithium recovery. Points that may be considered include process intensification to save energy and improve the kinetics of leaching, while addressing the problem of selectivity and examining the use of unexplored/synergistic solvents with an ultra high metal loading capacity to cut down the process steps. There is a need to develop appropriate technology which can address the limitation of current processes for extraction of all valuable metals from its primary as well as secondary resources.

Acknowledgements

The authors are thankful to the Director, CSIR-National Metallurgical Laboratory (NML), Jamshedpur, India for giving permission to publish the paper.

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