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Review

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

Pratima Meshram [a,b], B.D. Pandey [a,*], T.R. Mankhand [b]

[a] CSIR—National Metallurgical Laboratory, Jamshedpur 831 007, India
[b] Dept. of Metallurgical Engineering, IIT, BHU, Varanasi 221 005, India

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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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* Corresponding author.
E-mail address: bd_pandey@yahoo.co.uk (B.D. Pandey).

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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 1,00,000 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 28 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 $LiClO_4$, $LiBF_4$, and $LiPF_6$. 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 bitterns, and lithium ion batteries for the hydrometallurgical recovery of lithium.

Table 1
Principal commercial lithium minerals with composition[a].

Mineral	Formula	% Lithium content	
		Theoretical	Range in commercial minerals
Spodumene	$LiAlSi_2O_6$ or $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$	3.73	1.9–3.3
Lepidolite	$LiKAl_2F_2Si_3O_9$ or $LiF \cdot KF \cdot Al_2O_3 \cdot 3SiO_2$	3.56	1.4–1.9
Amblygonite	$LiAlFPO_4$ or $2LiF \cdot Al_2O_3 \cdot P_2O_5$	4.74	3.5–4.2
Triphylite	$LiFePO_4$ or $Li_2O \cdot 2FeO \cdot P_2O_5$	4.40	2.5–3.8
Petalite	$LiAlSi_4O_{10}$ or $Li_2O \cdot Al_2O_3 \cdot 8SiO_2$	2.27	1.6–2.21
Bikitaite	$LiAlSi_2O_6 \cdot H_2O$	3.28	1.35–1.7
Eucryptite	$LiAlSiO_4$	5.53	2.34–3.3
Montebrasite	$Li_2O \cdot Al_2O_3 \cdot 2SiO_2$	3.93	0.9–1.8
Jadarite	$LiNaSiB_3O_7(OH)$	3.39	0.096–0.1
Zinnwaldite	$LiKFeAl_2F_2Si_3O_{10}$ or $LiF \cdot KF \cdot FeO \cdot Al_2O_3 \cdot 3SiO_2$	1.7	1.21–1.3
Hectorite	$Na_{0.3}(Mg,Li)_3Si_4O_{10}(F,OH)_2$	0.56	0.36
Zabuyelite	Li_2CO_3	18.75	–

[a] Industrial Minerals and Rocks (2006), Norton and Schlegel (1955), Schaller (1937), and Siame and Pascoe (2011).

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 lepidolite 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