A Review on the Separation of Lithium Ion from Leach Liquors of Primary and Secondary Resources by Solvent Extraction with Commercial Extractants

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Abstract: The growing demand for lithium necessitates the development of an efficient process to recover it from three kinds of solutions, namely brines as well as acid and alkaline leach liquors of primary and secondary resources. Therefore, the separation of lithium(I) from these solutions by solvent extraction was reviewed in this paper. Lithium ions in brines are concentrated by removing other metal salts by crystallization with solar evaporation. In the case of ores and secondary resources, roasting followed by acid/alkaline leaching is generally employed to dissolve the lithium. Since the compositions of brines, alkaline and acid solutions are different, different commercial extractants are employed to separate and recover lithium. The selective extraction of Li(I) over other metals from brines or alkaline solutions is accomplished using acidic extractants, their mixture with neutral extractants, and neutral extractants mixed with chelating extractants in the presence of ferric chloride ($FeCl_3$). Among these systems, tri-n-butyl phosphate (TBP)- methyl isobutyl ketone (MIBK)-$FeCl_3$ and tri-n-octyl phosphine oxide (TOPO)- benzoyltrifluoroacetone (HBTA) are considered to be promising for the selective extraction and recovery of Li(I) from brines and alkaline solutions. By contrast, in the acid leaching solutions of secondary resources, divalent and trivalent metal cations are selectively extracted by acidic extractants, leaving Li(I) in the raffinate. Therefore, bis-2,4,4-trimethyl pentyl phosphinic acid (Cyanex 272) and its mixtures are suggested for the extraction of metal ions other than Li(I).

Keywords: lithium resources; lithium; solvent extraction; commercial extractants; separation

1. Introduction

1.1. Applications and Resources

Lithium is an indispensable element in the manufacture of the electrode materials for batteries. It is also widely used in the fields of ceramic glass, enamels, adhesive, lubricant greases, metal alloys, air-conditioning and dyeing [1]. Therefore, the demand for lithium metal and its compounds has significantly increased. Albema [2] reported that lithium consumption reached 150,000 t in 2012 and is expected to increase by 50% by 2020. The increase in the demand of lithium and its compounds is related to their applications to nuclear energy and lithium-ion batteries [3]. The global market of lithium products for tradition and energy usage is shown in Table 1. Lithium-ion batteries represent about 37% of the rechargeable battery world market [1].

Lithium is found in several primary resources such as different ores, clays, brines and seawater [4]. A distribution of lithium among these resources shows that continental brines are the biggest resources (59%) of lithium, followed by pegmatite and spodumene (25%), hectorite (7%) and geothermal brines,

oilfield brines and jaderite (3%) [4]. Liu et al. [5] reported that brines are rich in lithium and account for over 80% of lithium reserves in the world. There are about 20 minerals containing lithium but only four minerals, namely lepidolite ($KLi_{1.5}Al_{1.5}[Si_3O_{10}][F,OH]_2$), spodumene ($LiO_2 \cdot Al_2O_3 \cdot 4SiO_2$), petalite ($LiO_2 \cdot Al_2O_3 \cdot 8SiO_2$) and amblygonite ($LiAl[PO_4][OH,F]$), occur in sufficient quantities for commercial interest as well as industrial importance [4,6]. The geological features of pegmatite, brine and other types of lithium deposits and their potential for large scale and long-term production were reviewed by Kesler et al. [7]. The authors reported that total amount of lithium in these deposits is enough to meet the estimated lithium demand for the next century. The increase in demand for lithium-ion batteries results in a massive amount of scrap during the manufacture of lithium-ion batteries [8]. Therefore, the recycling of the scrap and spent lithium-ion batteries is important to recover lithium and other valuable metals [9]. In particular, spent lithium-ion batteries contain 2–7 wt % lithium and other valuable metals [10].

Table 1. Applications in traditional uses and energy of lithium and lithium compounds [2].

	Applications	Market Size	Lithium and Lithium Compounds
Traditional uses	Glass/ceramics	46 kt	• Spodumene • Li_2CO_3
	Greases/lubricants	18 kt	• LiOH
	Chemical synthesis	11 kt	• Li organometallics fed by Li metal LiCl
Energy	Portable electronics and other handheld devices	48 kt	• BG Li_2CO_3 • BG LiOH • BG Li metal • BG electrolyte salts • BG LiCl • BG alloys • BG specialty compounds
	Plug-in hybrid and hybrid electric vehicles		
	Battery electric vehicles (BEVs)		
	Grid and other power storage applications		

Total Global Lithium Carbonate Equivalent (LCE) Market: 160 kt (2014); kt: kiloton; BG: battery grade.

1.2. Lithium Recovery

Lithium demand is predominantly driven by the expansion of the battery industry. Therefore, the recovery of lithium from primary and secondary resources has attracted much attention to either meet lithium requirements or minimize waste disposal problems [4]. Pyrometallurgy and hydrometallurgy processes are commonly employed in the recovery of lithium from primary and secondary resources [4,11,12]. Although pyrometallurgical processes are techno-economically feasible, they require intensive investment and cause environment pollution [4]. Hydrometallurgical processes including acid/alkaline leaching followed by solvent extraction, ion exchange, and precipitation are considered to be promising methods, for the recovery of lithium in a pure lithium carbonate (Li_2CO_3) and lithium hydroxide (LiOH) form due to technological advantages such as smaller scale, minimal energy investment, minimal toxic gas emission and waste management efficiency [1]. In leaching solutions, Li(I) exists as a cationic species with other metal ions such as Na(I), K(I), Ca(II), Mg(II), etc. These metals have nearly identical ionic radii and thus the separation of Li(I) from the leaching solutions becomes more difficult [13–15]. For the purpose of the separation and recovery of lithium from solutions in the presence of impurities, solvent extraction, ion exchange, and precipitation have been widely employed [16–21]. In the precipitation method, impurities such as Mg(II), Ca(II) and Ni(II) should be removed before the production of lithium [16]. Precipitation has several drawbacks, such as the lower purity of the products due to the co-precipitation of other metals and slow kinetics. Ion exchange offers high separation efficiency of Li(I) from brines but the application of this method is limited in the large scale owing to the low loading capacity of resins [17,18]. Considering the high separation and recovery efficiency, low cost and easy operation, solvent extraction is commonly regarded as a favorable method to recover Li(I) from lithium resources [19–21]. Some commercial

extractants have been employed for the recovery of Li(I) from the leaching solutions of primary and secondary resources [19–21]. Crown ethers and their derivatives employ ether oxygens as donor atoms ("hard base"), which coordinate well with alkali metal cations ("hard acids") on the basis of the hard-soft acid-base (HSAB) principle [1]. Although the highly selective extraction efficiency of lithium can be obtained from the solution containing K(I), Na(I), Rb(I) and Cs(I) using crown ethers, the application of these extractants is limited due to their high cost [1]. Therefore, finding commercial extractants with a low cost and high extraction efficiency is needed for the recovery of Li(I) from lithium resources. Some review papers have been published on the recovery of lithium from primary and secondary resources by hydrometallurgy and pyrometallurgy. However, little data has been reported in these review papers on the solvent extraction of Li(I) with promising extractants [4,12]. Swain [1] reviewed the separation and purification of lithium from brines and alkaline solutions by solvent extraction and supported liquid membrane, while physical and chemical processes for the recycling of spent lithium-ion batteries were summarized by Ordonez et al. [11]. Generally, the comparison of the extraction performance of commercial extractants for the separation of lithium from different leach liquors of primary and secondary resources is scarce in the reported literature. For this purpose, the present work reviewed the separation of lithium from leach liquors of primary and secondary resources by solvent extraction with commercial extractants and their mixtures.

2. Pretreatment and Leaching of Primary and Secondary Resources

In brines, the weight percentages of Li(I) are generally 0.01–0.2 wt %, while large amounts of chloride salts of sodium, potassium, calcium, and magnesium are also present [16]. Therefore, in recovery of lithium from brines, a process of solar evaporation is widely employed to remove Na(I), K(I), Ca(II) and Mg(II) through the evaporation and crystallization of these salts [16,22]. The salts of Na(I), K(I), Ca(II) and Mg(II) are crystallized in the sun while lithium remains in the solution. After liquid-solid separation between crystallized salts and the aqueous solution containing lithium, this process is repeated several times to remove water and salts until the concentration of lithium in the solution reaches a required concentration [16,19,22]. Then the concentrated brines are fed into further purification steps such as solvent extraction, ion exchange, and precipitation to produce pure lithium products [6].

Alkaline and sulfuric acid processes are widely used in the recovery of lithium from ores and clays [6,23–30]. In alkaline processes, the roasting of the ores such as lepidolite, zinnwaldite, spodumene, and montmorillonite with $Na_2SO_4/CaSO_4/CaCO_3/(CaSO_4 + Ca(OH)_2)$ at 850–1100 °C followed by water leaching is commonly employed to recover lithium [23–26,29,30]. Most of Li(I) was leached by this method and pure lithium carbonate products were obtained by evaporation and precipitation with sodium carbonate [23–26,29,30]. Several researchers suggested a possible process to recover lithium from petalite concentrate as a solution of lithium sulfate by following three main steps: (i) calcination; (ii) the roasting of the calcines with sulfuric acid; and (iii) water leaching [6,27,28]. The solutions of lithium sulfate were subsequently converted to lithium carbonate as a final lithium product by the addition of sodium carbonate to the solutions after pH adjustment, purification and evaporation [12]. However, disadvantages of sulfuric acid processes are the requirement of a strong acid concentration and complicated purification processes. The recovery efficiency of Li(I) from ores and clays by calcination and roasting followed by water leaching is summarized in Table 2.

Spent lithium-ion batteries are made up of valuable metals (Co(II), Ni(II) and Li(I)), organic chemical products and plastics. Thus, preliminary mechanical separation processes and thermal treatments are carried out to treat the outer cases and shells and to concentrate the metallic fraction before applying hydrometallurgical processes (acid/alkaline leaching, solvent extraction, precipitation and electrochemical processes) [11]. Lithium cobalt oxide ($LiCoO_2$) is commonly used as an active cathode material, which is very difficult to dissolve by common leaching reagents. Various inorganic acids (HCl, HNO_3 and H_2SO_4) and organic acids (citric acid, oxalic acid, ascorbic acid and 2-hydroxybutanedioic acid (DL-malic acid) have been employed to dissolve the active cathode

materials [11]. In order to enhance the leaching efficiency of metals in spent lithium-ion batteries and to reduce acid consumption, the addition of reducing agents such as H_2O_2 and $NaHSO_3$ is required in leaching processes [31–36]. Among the inorganic acids, HCl leaching offers a higher leaching efficiency of Co(II), Li(I) and Ni(II) than that of H_2SO_4 and HNO_3 systems [33]. Organic acids are found to be more effective in dissolving Li(I) and Co(II) from the spent lithium-ion batteries and to release lower emissions of toxic gases than inorganic acids. However, the main disadvantage of organic acids is their high cost [34]. A summary of the operational conditions for the leaching of Li(I), Co(II) and other metals from spent lithium-ion batteries using inorganic and organic acids is shown in Table 3.

Table 2. Summary of the pretreatment and leaching of ores and clays by alkaline processes.

Ores/Clays	Pretreatment and Leaching Condition		Li Leaching, %	Ref.
	Calcination and Roasting	Water Leaching		
Petalite	Calcination: 1050–1100 °C Roasting: 93% H_2SO_4; 250 °C; 1 h	-	85	[6]
	Calcination: 1100 °C; 2 h Roasting: H_2SO_4; 300 °C; 1 h	S/L = 1/7.5; 320 rpm; 1 h; 50 °C	97	[27]
Spodumene	Calcination: 1050–1090 °C, 0.5 h Roasting: H_2SO_4	S/L = 4; 225 °C; 1 h	96	[28]
Zinnwaldite	Roasting: $CaSO_4$ + $Ca(OH)_2$; 950 °C; 1 h	S/L:1/10; 10 min; 90 °C	96	[23]
	Roasting: $CaCO_3$; 825 °C; 1 h	S/L: 1/5; 1 h; 90–95 °C	85	[29]
	Roasting: $CaSO_4$ + $Ca(OH)_2$; 975 °C	S/L:1/5; 1 h; 90 °C	93	[24]
	Roasting: $CaCO_3$; 825 °C; 1 h	S/L: 1/10, 400 rpm; 4 h, 95 °C	84	[30]
Clay	Roasting: $CaSO_4$; 1050 °C, 1 h Roasting: Na_2SO_4; 850 °C, 1 h	S/L: 1/10; 10 min; 85 °C	8497	[25]
Lepidolite	Roasting: Na_2SO_4 + K_2SO_4 + CaO; 850 °C, 0.5 h	S/L: 1/2.5; 0.5 h; room temperature	92	[26]

* S/L: solid-liquid ratio.

Table 3. Summary of operational conditions for Li(I), Co(II) and other metals leaching from spent lithium-ion batteries using inorganic and organic acids.

Type of Acid	Leaching Condition	Leaching Efficiency, %		Ref.
		Li(I)	Others	
Inorganic acids	Ultrasonic power: 90 W 2M HCl/H_2SO_4; S/L: 1/40; 5 h; 60 °C	97 (H_2SO_4) 98 (HCl)	Co: 48 (H_2SO_4) Co: 76 (HCl)	[34]
	2M $HCl/H_2SO_4/HNO_3$; S/L:5%w/v; 18h; 25 °C	80 (HCl) <80 (H_2SO_4) >80 (HNO_3)	Co, Ni, Al: >60 (HCl) Co, Ni, Al: ≤40 (H_2SO_4) Co, Ni, Al: ≤40 (HNO_3)	[33]
	4M HCl; S/L: 1/50; 1 h; 80 °C	>99%	Co, Mn, Ni: >99	[37]
	3M HCl + 3.5%v/v H_2O_2; S/L: 1/20; 1 h; 80 °C	89%	Co: 89%	[38]
	1M H_2SO_4 + 30%v/v H_2O_2; S/L: 1/1.4; 2 h; 80 °C	-	Co: 88	[39]
	2M H_2SO_4 + 6%v/v H_2O_2; S/L:1:10; 1 h; 60 °C; 300 rpm	-	Co: >99%	[40]
	2M H_2SO_4 + 5%v/v H_2O_2; S/L: 1/10; 0.5 h; 75 °C	94	Co: 93	[8]
	6%v/v H_2SO_4 + 5%v/v H_2O_2; S/L: 3/10; 1 h; 65 °C	95	Co: 80 Al: 55	[41]
	2M H_2SO_4 + 15%v/v H_2O_2; S/L: 1:20; 10 min; 75 °C; 300 rpm 4M H_2SO_4 + 10%v/v H_2O_2; S/L: 1/10; 2 h; 85 °C	100 96	Co: 95 Co: 95	[42] [31]
	2M H_2SO_4 + 4%v/v H_2O_2; S/L: 1:10; 2 h; 70 °C	99	Co: 100 Ni: 99 Mn: 98	[36]
	1M H_2SO_4 + 0.0075M NaHSO3; S/L: 1/50; 4 h; 95 °C	97	Co: 92 Ni:96 Mn:88	[35]
	1M HNO_3 + 1.7%v/v H_2O_2; S/L: 1:50; 1 h; 75 °C	95	Co: 95	[43]

Table 3. *Cont.*

Type of Acid	Leaching Condition	Leaching Efficiency, %		Ref.
		Li(I)	Others	
Organic acids	2M citric acid + 1.25%v/v H$_2$O$_2$ S/L: 3/100; 2 h; 60 °C	92	Co: 81	[32]
	Ultrasonic power: 90 W 2M citric acid + 0.55M H$_2$O$_2$; S/L: 1/40; 5 h; 60 °C	98	Co: 96	[34]
	1.25M citric acid + 1%v/v H$_2$O$_2$; S/L: 1/40; 0.5 h; 90 °C; 300 rpm	100	Co: >90	[44]
	1.25M ascorbic acid; S/L: 1/40; 20 min; 70 °C	99	Co: 95	[45]
	1.5M DL-malic acid+ 2%v/v H$_2$O$_2$; S/L: 1/40; 40 min; 90 °C	100	Co: 90	[46]
	1M oxalic acid; S/L: 1/66.7; 2.5 h; 95 °C; 400 rpm	98	Co: 97	[47]

3. Separation of Li(I) from Leach Liquors of Primary and Secondary Resources by Solvent Extraction

3.1. Selective Extraction of Li(I) from Brines/Alkaline Solutions

Lithium exists in leach liquors as a cationic species, Li$^+$, which is difficult to selectively extract due to its strong tendency to be hydrated [20]. Various acidic and neutral commercial extractants (see Table A1) have been used to extract Li(I) from brines, sea waters and alkaline solutions. The extraction and separation of Li(I) from brines and alkaline solutions by commercial extractants are summarized in Table 4. Hano et al. [21] reported the extraction of Li(I) from geothermal water containing Na(I), K(I), Mg(II) and Ca(II) using single D2EHPA (di-(2-ethylhexyl)phosphoric acid) and MEHPA (mono-2-ethylhexyl-phosphonic acid). The highly selective extraction of Li(I) over Na(I) and K(I) was obtained, while Mg(II) and Ca(II) were well extracted by these extractants compared to Li(I), Na(I) and K(I). The authors also found that the addition of TBP to D2EHPA/MEHPA led to the selective extraction of Li(I) from the geothermal water. Although commercial acidic extractants offer a high separation factor between lithium and other monovalent metal cations from brines and seawaters, the application of these extractants is limited due to their low extraction efficiency [21].

Table 4. Summary of the extraction and separation of Li(I) from brines and alkaline solutions by commercial extractants.

Extractants	Condition	Remarks	Ref.
HBTA-TOPO	Li(I): 0.14 g/L pH = 11.2	97% of Li(I) was extracted with form complexes of Li.2BTA.TOPO; scrubbing with 0.5M HCl; stripping of Li(I) with 2.5M HCl; regeneration of the organic phase was achieved by washing with NaOH	[48]
Thenoyltrifluoracetone (TTA)-TOPO in kerosene	Li(I): 1 mg/L pH = 10.6	Mg^{2+} had a strong effect on Li(I) extraction; 70% Li(I) was extracted from Mg(II)-free aqueous solution	[48]
TTA-1, 10-phenanthroline (Phen) in chlorobenzene	Li(I): 0.01–0.1 mol/L pH = 6.5–11.6	Li(I) was extracted in the wide phen concentration while the extraction of K(I) and Na(I) was only possible in a high phen concentration	[49]
TTA-TOPO in m-xylene/MIBK/n-henxane/ benzene/chloroform	Li(I): 5.8.10^{-4}M NH$_4$Cl: 0.1M, pH = 9	Extraction efficiency of Li(I) followed the sequence: m-xylene > benzene > MIBK > n-hexane > chlorofrom; extracted sepecies were Li.TTA.2TOPO	[50]
β-carbonyl amide (NB2EHOTA)-TBP-FeCl$_3$	HCl: 0.05M; Li(I): 2 g/L Fe(III)/Li(I):1.3 MgCl$_2$: 4.8M	Separation factor of Li(I)/Mg(II) was higher than 450; extracted sepecies were (LiFeCl$_4$.2TBP.NB2EHOTA).4TBP.NB2EHOTA	[51]
Dioctyl phthalate (DOP)/ acetyl tributyl citrate(ATBC)/ tri-n-butyl citrate(TBC)-TBP-FeCl$_3$	HCl: 0.05 Li(I): 1.86 g/L Fe(III)/Li(I):1.3 MgCl$_2$: 4.8	Li(I) extraction efficiency was in the order of DOP > ATBC > TBP;after three stages, 99.5% Li was extracted with extracted species of LiFeCl$_4$.2TBP.0.1DOP; separation factors of Li(I)/Mg(II), Li(I)/Na(I) and Li(I)/K(I) were 31,458, 1259 and 16,508, respectively	[15]

Table 4. *Cont.*

Extractants	Condition	Remarks	Ref.
TBP/MIBK-FeCl$_3$-keosene	LiCl: 0.025–0.05 mol/L MgCl$_2$: 3.5–4 mol/L FeCl$_3$: 0.025–0.09 mol/L	Extracted species were LiFeCl$_4$.TBP and LiFeCl$_4$.2MIBK	[52]
TBP -FeCl$_3$-keosene	Li(I): 0.2 mol/L Fe(III)/Li(I): 1.0–1.9 MgCl$_2$/CaCl$_2$/NH$_4$Cl	Fe(III) extraction was a precondition of Li(I) extraction; the extraction efficiency of Li(I) followed the sequence: MgCl$_2$ > CaCl$_2$ > NH$_4$Cl; MgCl$_2$ at Fe(III)/Li(I) = 1.9 was the optimum condition for Li(I) extraction	[3]
TBP-MIBK-FeCl$_3$	Li(I): 0.05 mol/L Mg(II): 4.74 mol/L SO$_4{}^{2-}$: 0.12 mol/L Cl–9.43 mol/L	98% Li(I) was extracted at a high Mg(II)/Li(I) molar ratio; Mg(II) scrubbing with LiCl/NaCl; Li(I) stripping with HCl/NaCl; regeneration of the organic phase was obtained by washing with NaOH/NaCl	[53]
α-acetyl-m-dodecylacetophenone (LIX 54) - a mixture of four trialkylphosphine oxides (Cyanex 923)	pH = 11 Li(I): 1 g/L Na(I): 20–80 g/L	High separation of Li(I) at a high Na(I) concentration (SF = 110–1500); 95% of Li(I) was extracted after three stages; extracted species was LiR Cyanex 923	[54]

Several authors have reported the extraction of Li(I) using a mixture of chelating and neutral extractants such as TBP and TOPO in kerosene [29,54,55]. Neither Li(I) nor Na(I) was extracted by LIX 54, TOPO and Cynanex 923, while some mixed systems consisting of LIX 54 and neutral extractants (TOPO and Cyanex 923) showed synergism for the selective extraction of Li(I) from Na(I) and K(I) in sulfate or chloride solutions [29,54,55]. The extraction efficiency of Li(I) by the mixture of LIX 54 and Cyanex 923 was higher than that by the mixture of LIX 54 and TOPO because the solubility of Cyanex 923 was higher in organic diluents than that of TOPO. In the extraction with the mixture of LIX54 and Cyanex 923, LIX 54 played the role of extractant and Cyanex 923 acted as a synergist. The extracted species of Li(I) by the mixture of LIX 54 and Cyanex 923 were found to be LiR(Cynanex 923), where R denotes the deprotonated LIX54. HCl solutions with moderate acidity can strip Li(I) from the loaded organic mixtures. The recovered LiCl in the HCl stripping processes is one of the products for the market and an intermediate for the production of either lithium hydroxide or carbonate [54].

The extraction efficiency of Li(I) from brines/alkaline solutions was enhanced by the employment of neutral extractants such as TBP and MIBK dissolved in kerosene in the presence of ferric chloride (FeCl$_3$) [3,52,56,57]. In these extraction processes, FeCl$_3$ plays the role as a co-extracting agent, which leads to a great increase in the extraction of lithium [49]. The stepwise extraction reactions can be represented by Equations (1) and (2) [3,52,56,57]. In concentrated chloride solutions, ferric chloride exists as FeCl$_4{}^-$, which is extracted by neutral extractants to form extracted species (HFeCl$_4$nL) through an ion association mechanism (see Equation (1)). Then ion exchange reaction occurs between the hydrogen in HFeCl$_4$ nL and the Li(I) in the aqueous phase, as represented by Equation (2). Zhou et al. [52] reported that the extraction capacity of TBP for Li(I) is much higher than that of MIBK. The difference between the extraction of Li(I) by TBP and that by MIBK might be related to the interaction performance between FeCl$_4{}^-$ and an effective functional group P = O in TBP or C = O in MIBK [52].

$$FeCl_{4(aq)}{}^- + H_{(aq)}{}^+ + nL_{(org)} = HFeCl_4\ nL_{(org)} \tag{1}$$

$$Li_{(aq)}{}^+ + HFeCl_4\ nL_{(org)} = LiFeCl_4\ nL_{(org)} + H_{(aq)}{}^+ \tag{2}$$

where L denotes the neutral extractants (TBP/MIBK) and the subscripts (aq) and (org) denote the aqueous and organic phases, respectively.

Equation (1) indicates that the formation of FeCl$_4{}^-$ is a prerequisite for the extraction of Li(I) to occur; thus a certain concentration of chloride ions is required for FeCl$_4{}^-$ to form. As chloride ion sources, MgCl$_2$, CaCl$_2$ and NH$_4$Cl were tested for the extraction of Li(I) by TBP [3]. The extraction efficiency of Li(I) was in the order of MgCl$_2$ > CaCl$_2$ > NH$_4$Cl due to the competitive effect of Mg^{2+}, Ca^{2+}, and NH$_4{}^+$ with Li$^+$ and the salting out effect of the three salts [3]. In fact, when salting out agents (MgCl$_2$, CaCl$_2$ and NH$_4$Cl) are added to the solution, some of water molecules are attracted by the

salt ions, resulting in a decrease in the amount of free water molecules. The increase in the fraction of hydrogen ions accelerates the extractability of iron (see Equation (1)) and thus the extraction efficiency of Li(I) is improved with $MgCl_2$, $CaCl_2$ and NH_4Cl added as chloride sources (see Equation (2)). Zhou et al. [3] reported that $MgCl_2$ has a stronger salting-out effect than $CaCl_2$ and NH_4Cl, so $MgCl_2$ is suggested as a promising chloride resource for the extraction of lithium by $TBP/kerosene/FeCl_3$. The main disadvantage of using the $TBP-FeCl_3$ system in kerosene as a diluent is a significant loss of the extractant to the aqueous phase during extraction at high TBP concentrations [15]. Moreover, the formation of a third phase occurs at low TBP concentrations due to the low solubility of the extracted species in an inert diluent, such as kerosene [3]. It has been demonstrated that 2-octanol, a polar diluent, has strong intermolecular forces with the extracted complexes, while MIBK has low density and viscosity. Thus, MIBK and 2-octanol were used in $TBP-FeCl_3$ systems as diluents to prevent the formation of the third phase [22,56]. According to the obtained results from the reported literature, the extraction efficiency of Li(I) was in the order of $TBP-FeCl_3$-MIBK > $TBP-FeCl_3$-kerosene > $TBP-FeCl_3$-2-octanol [22,56]. This means that the use of MIBK as a diluent in the $TBP/FeCl_3$ system not only prevents the formation of a third phase but also enhances the extraction efficiency of Li(I) from chloride solutions by synergistic extraction with TBP and MIBK [22].

In the extraction process of Li(I) from salts containing high Mg(II)/Li(I) ratios, the co-extraction of Mg(II) by TBP necessitates the employment of a scrubbing step to remove Mg(II) from the loaded organic phase [22]. The stripping process of $TBP-FeCl_3$-MIBK consists of three steps: (i) the scrubbing of Mg(II) from the loaded organic phase using LiCl + NaCl solution; (ii) the stripping of Li(I) using HCl + NaCl solution; and (iii) the regeneration of the organic phase using NaOH + NaCl [22]. Ji et al. [15,51] developed synergistic extraction systems to enhance the extraction efficiency of Li(I) from saturated $MgCl_2$ solutions using TBP-dioctyl phthalate/β-carbonyl amide-$FeCl_3$. The advantages of dioctyl phthalate/β-carbonyl amide in $TBP-FeCl_3$ systems are good stability, low to negligible solubility and low corrosiveness towards instruments. Dioctyl phthalate reacts with $LiFeCl_4$, thus reducing the polarity of Li(I) complex and increasing the solubility of these molecules [15]. An almost complete extraction of Li(I) was obtained without phase separation problems by controlling the concentration of TBP and dioctyl phthalate in the mixture of TBP-dioctyl phthalate-$FeCl_3$ [51]. In these extraction processes, the saturated concentration of $MgCl_2$ in the aqueous phase is required to form $FeCl_4^-$ [51]. However, the aqueous phase with saturated $MgCl_2$ would be viscous, which could lead to a kinetic problem in mixer-settler operations.

TTA forms ion-pairs with TOPO to offer a synergistic effect for the extraction of Li(I) from seawater in the absence of Mg(II), which reacts with TTA to form magnesium chelate that is insoluble in solvent [58]. However, the extraction and separation efficiency of Li(I) by TTA-TBP/TOPO is still low because of the high co-extraction of other metals like Na(I), K(I) and Ca(II). Strong selectivity for Li(I) over Na(I) and K(I) was obtained by employing TTA in the presence of phen [49]. The extracted species of Li(I) can be represented as Li(TTA)(phen), and the separation factor between Li(I) and Na(I) by TTA-phen systems was much higher than that by TTA-TOPO systems [49]. Although the employment of the TTA-phen system resulted in the selective extraction of Li(I) from the aqueous solutions containing Na(I) and K(I), the application of this system is limited due to the high toxicity, high price, high water solubility, and poor solubility in conventional diluents [1]. Zhang et al. [48] reported an innovative application of synergistic extraction system HBTA and TOPO to extract Li(I) from alkaline brine. Most of Li(I) was extracted over Na(I) by this system without the formation of a third phase or emulsification. The extraction reactions of Li(I) by HBTA-TOPO can be represented by Equations (3)–(5). With high capacity and stability, a simple extraction process, and good regeneration efficiency, HBTA-TOPO is recognized as a promising system for Li(I) extraction from alkaline brine [48]. A process for the recovery of Li(I) as LiCl from alkaline brine with HBTA-TOPO is represented in Figure 1.

$$HBTA_{(org)} + OH_{(aq)}^- = BTA_{(org)}^- + H_2O_{(aq)} \tag{3}$$

$$BTA_{(org)}^- + Na_{(aq)}^+ + mTOPO_{(org)} = NaBTA \cdot mTOPO_{(org)} \tag{4}$$

$$\text{NaBTA mTOPO}_{(org)} + \text{Li}_{(aq)}^+ = \text{LiBTA TOPO}_{(org)} + (m-1)\text{TOPO}_{(org)} \tag{5}$$
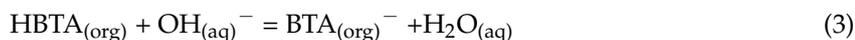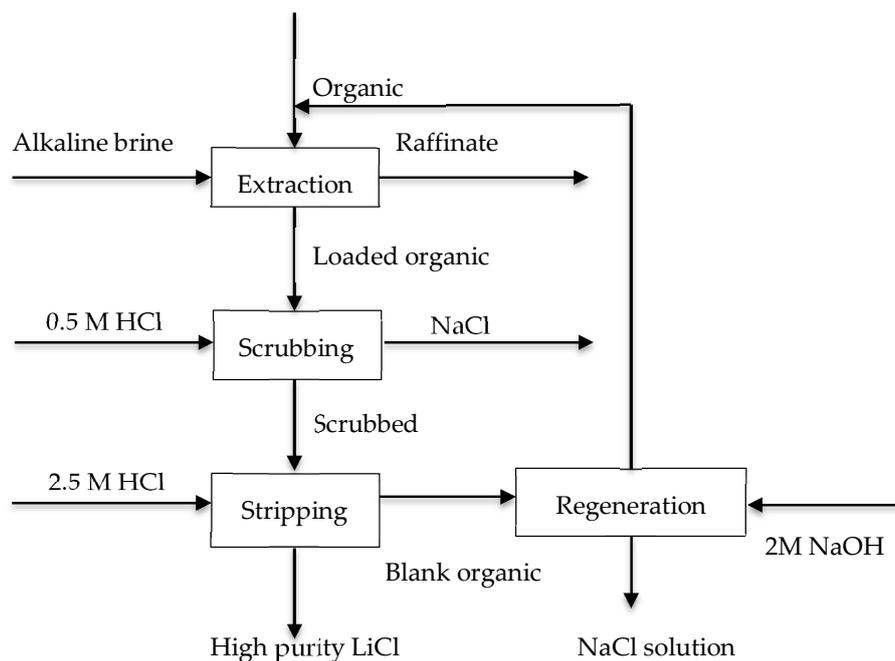
Figure 1. Flow-sheet of lithium extraction from alkaline brine with the HBTA-TOPO-kerosene system [48].

3.2. Selective Extraction and Recovery of Li(I) from Leach Liquors of Secondary Resources

The leach liquors of spent lithium-ion batteries contain large amounts of Co(II), Li(I) and small amounts of Ni(II), Cu(II), Al(III) and Fe(III) as cationic metal ions, which can be extracted by commercial acidic extractants (see Table A1). Swain [1] reported that divalent/trivalent metal cations have stronger affinities for acidic extractants than lithium ions; thus, it is difficult to selectively extract Li(I) over the divalent/trivalent metals by acidic extractants. Various kinds of single acidic extractants and their mixtures have been used to separate and recover Co(II) and Li(I) from leach liquors of spent lithium-ion batteries [8–10,59–64]. Zhang et al. [65] used D2EHPA and PC88A (2-ethylhexyl 2-ethylhexyphosphonic acid) in kerosene to separate Co(II) and Li(I) from HCl leaching solutions. PC88A was found to be more effective in selectively extracting Co(II) over Li(I) than D2EHPA in terms of lower co-extraction efficiency of Li(I), but low phase disengagement occurred at high PC88A concentrations [65]. Other researchers found that Cyanex 272 can selectively extract Co(II) over Li(I) from either acidic or alkaline solutions [8,59–61]. Although the extraction efficiency of Co(II) was enhanced with Cyanex 272 concentration, the increase in the viscosity of the organic phase caused some problems in phase disengagement [8]. Moreover, high co-extraction of Li(I) at high Cyanex 272 concentrations led to great difficulty in the scrubbing process. Since the increase in the viscosity ultimately decreased the rate of mass transfer, the Cyanex 272 extraction system should be operated at the maximum loading capacity to avoid phase disengagement problems [62,63]. On the other hand, the saponification of Cyanex 272 was found to be helpful in maintaining the extraction rate [62]. Most of Co(II) was selectively extracted over Li(I) and Ni(II) from reductive leaching solutions (H_2SO_4 + H_2O_2) of spent lithium-ion batteries using saponified Cyanex 272 without phase disengagement problems [40]. Nayl et al. [10] reported that Cyanex 272 existed as a dimer, while its saponified form existed as a monomer. Therefore, the saponification reaction of Cyanex 272 and the extraction reactions between monovalent/divalent metal ions and saponified Cyanex 272 can be represented as follows:

$$\text{Na}^+_{(aq)} + \frac{1}{2}(\text{HA})_{2(org)} = \text{NaA}_{(org)} + \text{H}^+_{(aq)} \tag{6}$$

$$M^{2+}_{(aq)} + A^-_{(org)} + 2(HA)_{2(org)} = (MA_2\,3HA)_{(org)} + H^+_{(aq)} \tag{7}$$

$$M^+_{(aq)} + A^-_{(org)} + 2(HA)_{2(org)}) = (MA\,2HA)_{(org)} \tag{8}$$
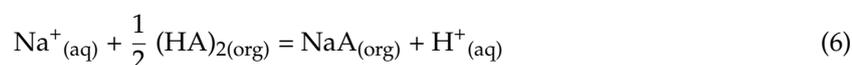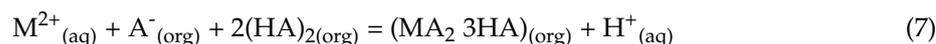
Generally, the recovery of pure Li(I) and Co(II) from leach liquors containing impurities such as Al(II), Fe(III), Cu(II), Ni(II) and Mn(II) consists of the following steps: (i) the elimination of some impurities such as Fe(III), Cu(II) and Al(III) by solvent extraction or precipitation; (ii) the selective extraction of Mn(II) and Co(II) by solvent extraction; (iii) the separation of Ni(II) by ion exchange; and (iv) the precipitation of Li(I) from the raffinate as lithium carbonate [9,10,64,66]. A conceptual process flowsheet for the recovery of Li(I) and other metals from leach solutions of spent lithium-ion batteries is presented in Figure 2. The mixture of 5-nonylsalicylaldoxime (Acorga M5640) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (Ionquest 801) has a synergistic effect of selectively extracting Cu(II), Al(III) and Fe(III), leaving Co(II), Ni(II) and Li(I) in the raffinate. After extracting Al(III), Cu(II) and Fe(III), the selective extraction of Co(II) over Ni(II) and Li(I) was obtained by employing Cyanex 272/Na-Cyanex 272. A small amount of the co-extracted Li(I) (<20%) into the organic phase was scrubbed using Na_2CO_3 solution and then the complete stripping of Co(II) was achieved using acidic solutions. Finally, an ion-exchange resin such as Dowex M4195 was employed to load Ni(II), leaving Li(I) in the effluent [66]. Zhao et al. [63] reported that the mixture of Cyanex 272 and PCC8A has synergistic effect on the selective extraction of Co(II) and Mn(II) over Li(I) from simulated sulfuric acid. The addition of EDTA (ethylenediaminetetraacetic acid) to the mixtures of Cyanex 272 and PC88A suppressed the extraction efficiency of Co(II), while the extractability of Mn(II) was slightly increased. Therefore, the mixture of Cyanex 272-PC88A-EDTA was considered to be a promising system for the separation of Co(II) and Mn(II) in terms of extraction efficiency and stripping properties [63]. A process for the recovery of Li(I), Co(II) and Mn(II) from spent lithium-ion batteries is shown in Figure 3. According to this process, Li(I) can be recovered as a precipitate of Li_2CO_3 by adding sodium carbonate after the separation of all of the metals from the leach liquors.
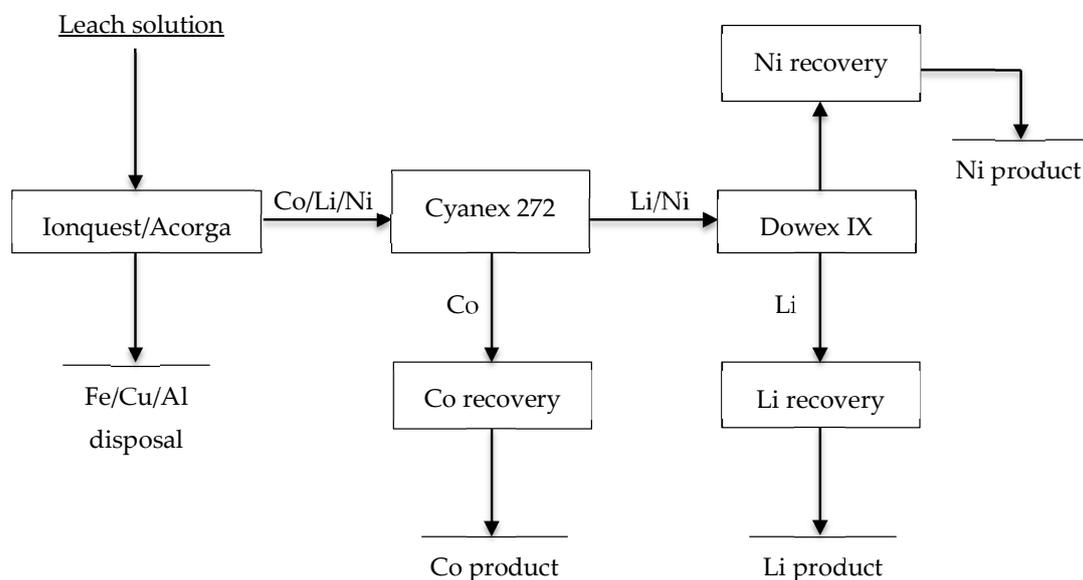

Figure 2. A conceptual process flow-sheet for the recovery of Co(II), Ni(II) and Li(I) from spent battery leach solutions [66].
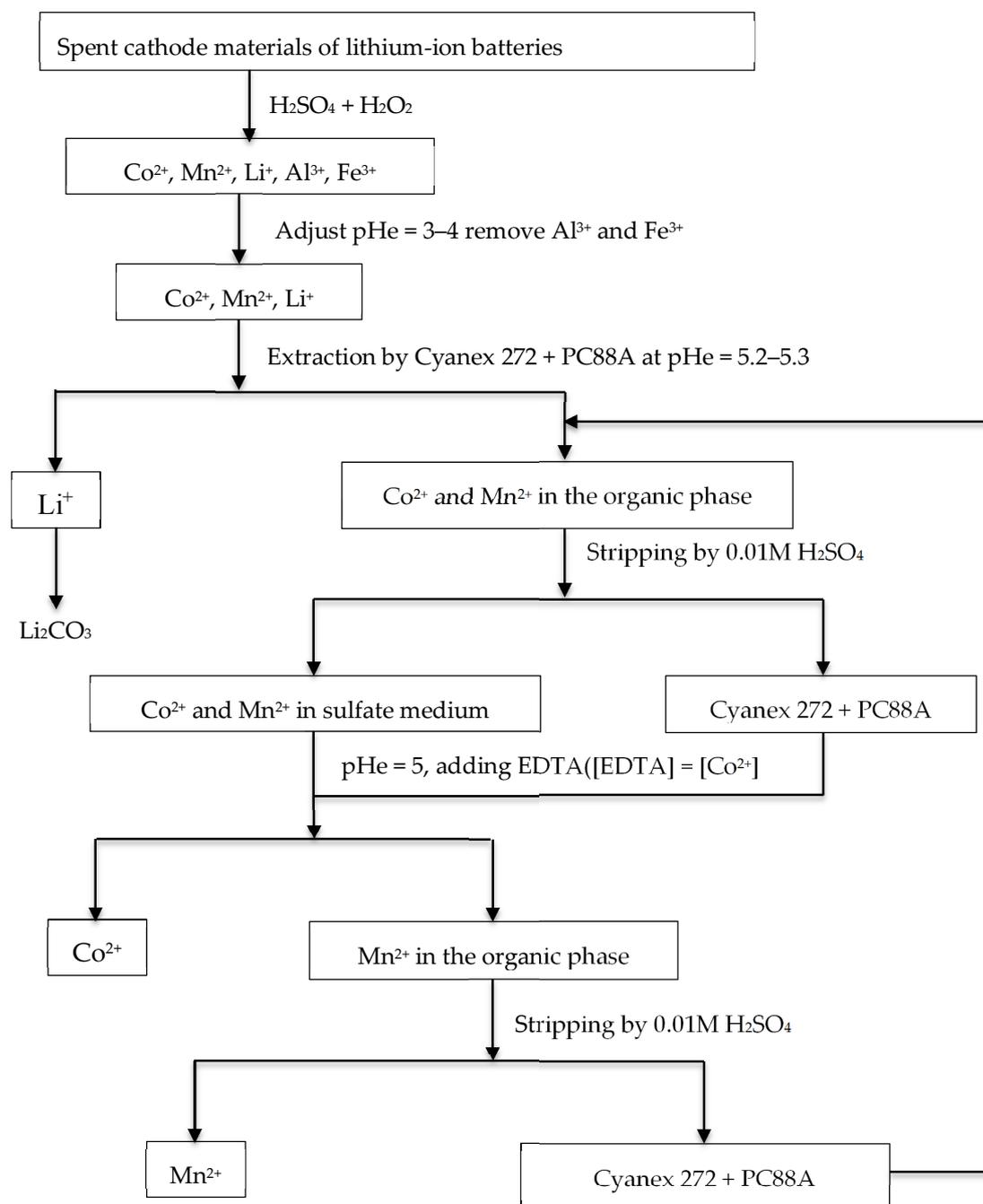
Figure 3. Flow-sheet for the separation of Co^{2+}, Mn^{2+} and Li^+ from each other in order to recycle the spent cathode materials of lithium-ion batteries (LIBs)[63].

4. Conclusions

This paper presents a review of the separation of lithium from leach liquors of primary and secondary resources by solvent extraction with commercial extractants and their mixtures. Solar evaporation is employed to concentrate lithium ions in brines by removing the salts of Na(I), Ca(II), Mg(II) and K(I), while acid and alkaline leaching processes are employed to dissolve lithium and other metals from primary and secondary resources. Several commercial extractants are then employed to separate lithium ions from the leach liquors of primary and secondary resources. Li(I) was selectively extracted over monovalent metal cations from brines or alkaline solutions by single acidic extractants and the mixture of acidic and neutral extractants. However, the extraction efficiency of lithium by

these extractants was low. The mixture of neutral extractants, TBP/TOPO, and chelating extractants in the presence of $FeCl_3$ had a synergistic effect on the extraction and separation efficiency of Li(I) from chloride solutions containing Na(I), Ca(II), K(I) and Mg(II). The small amount of co-extracted divalent metal cations in the TBP/TOPO system was scrubbed and then LiCl was obtained by the stripping process. In the acidic leaching solutions of secondary resources, divalent/trivalent metal cations are selectively extracted over Li(I) by single acidic extractants, which renders the recovery process of Li(I) complicated. Therefore, these divalent/trivalent metal cations should be separated before Li(I) purification. Among the acidic extractants and their mixtures, the Cyanex 272 system showed a high extraction performance for these divalent and trivalent metals cations. From the raffinate, Li(I) can be recovered as Li_2CO_3 by adding sodium carbonate.

Appendix A

Table A1. Structure of commercial extractants used for the extraction and recovery of lithium in the reported literature.

Extractants	Structure of the Compound
D2EHPA Di-2-ethylhexyl phosphoric acid	
PC88A 2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester	
MEHPA Mono-2-ethylhexyl phosphoric acid	
Cyanex 272 Bis-2,4,4-trimethyl pentyl phosphinic acid	
LIX 54 ∝-acetyl-m-dodecylacetophenone	
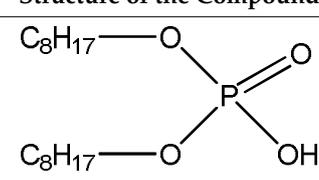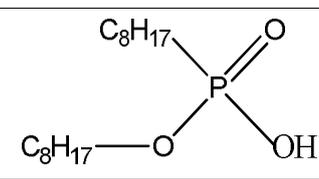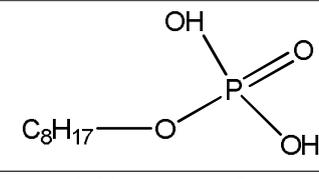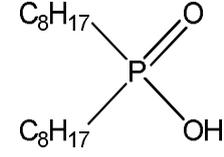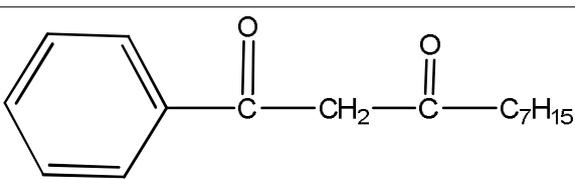
Table A1. *Cont.*

Extractants	Structure of the Compound
MIBK Methyl isobutyl ketone	(structure)
TBP Tri-n-butyl phosphate	(structure)
TOPO Tri-n-octyl phosphine oxide	(structure)
Cyanex 923 Mixture of main trialkyl phosphine oxides	$R'R_2P{=}O$ (31%) $R_2'RP{=}O$ (42%) $R_3'P{=}O$ (14%) $R_3P{=}O$ (8%) $R,R' = [CH_3(CH_2)_7]-normal\ octyl$
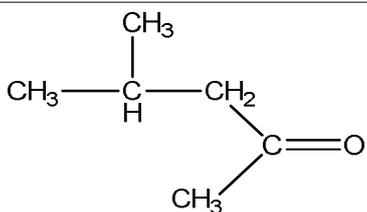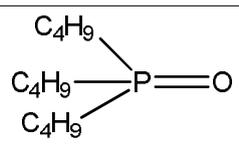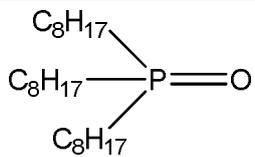
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