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Review

Technology for the Recovery of Lithium from Geothermal Brines [†]

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Abstract: Lithium is the principal component of high-energy-density batteries and is a critical material necessary for the economy and security of the United States. Brines from geothermal power production have been identified as a potential domestic source of lithium; however, lithium-rich geothermal brines are characterized by complex chemistry, high salinity, and high temperatures, which pose unique challenges for economic lithium extraction. The purpose of this paper is to examine and analyze direct lithium extraction technology in the context of developing sustainable lithium production from geothermal brines. In this paper, we are focused on the challenges of applying direct lithium extraction technology to geothermal brines; however, applications to other brines (such as coproduced brines from oil wells) are considered. The most technologically advanced approach for direct lithium extraction from geothermal brines is adsorption of lithium using inorganic sorbents. Other separation processes include extraction using solvents, sorption on organic resin and polymer materials, chemical precipitation, and membrane-dependent processes. The Salton Sea geothermal field in California has been identified as the most significant lithium brine resource in the US and past and present efforts to extract lithium and other minerals from Salton Sea brines were evaluated. Extraction of lithium with inorganic molecular sieve ion-exchange sorbents appears to offer the most immediate pathway for the development of economic lithium extraction and recovery from Salton Sea brines. Other promising technologies are still in early development, but may one day offer a second generation of methods for direct, selective lithium extraction. Initial studies have demonstrated that lithium extraction and recovery from geothermal brines are technically feasible, but challenges still remain in developing an economically and environmentally sustainable process at scale.

Keywords: lithium; geothermal brines; critical materials; extraction technologies

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1. Introduction

Lithium is a light and reactive metal that is the principal component in one of the most promising forms of high-energy-density batteries [1–3]. Current technology for all-electric vehicles is based on lithium-ion batteries and electric vehicles are expected to gain an ever-increasing share of the car market, so lithium demand and production are expected to grow proportionately with vehicle demand [1,2]. In addition to use for electric vehicle batteries, lithium batteries are slated for used in grid-scale storage for intermittent renewable energy generation such as wind and solar [4]. Lithium is also a critical component for ceramics, glass, metallurgy, air treatment products, pharmaceuticals, and polymers [4]. Lithium is used to make alloys with other metals including lead, copper, silver, magnesium, silicon, and aluminum. The alloys most commonly used in aerospace applications are lithium–aluminum alloys containing 1–3 weight % of lithium. Lithium–aluminum alloys are reported to generate weight savings of 5%, increased stiffness up to 7%, and increased strength of up to 30% relative to non-lithium-containing aluminum alloys [5]. Due to this variety of uses, lithium is on the list of critical materials necessary for the economy and security of the United States and was the focus of recent executive orders relating to critical minerals and relevant supply chains [6–8].

Lithium has a low density of 0.53 g/cm^3, an ionic charge of +1, and an ionic radius of 0.79 angstrom (Å). For comparison, sodium has an ionic charge of +1 but a larger ionic radius of 0.99 Å, and magnesium has an ionic charge of +2 and a smaller ionic radius of 0.72 Å [9]. Lithium is a lithophilic element (i.e., an element that forms silicates or oxides and is associated with the Earth's crust) that concentrates in hydrothermal fluids and therefore can be found concentrated in areas subject to volcanic influences (Figure 1) [9]. In solution, lithium occurs as soluble, positively charged lithium ions (Li^+).

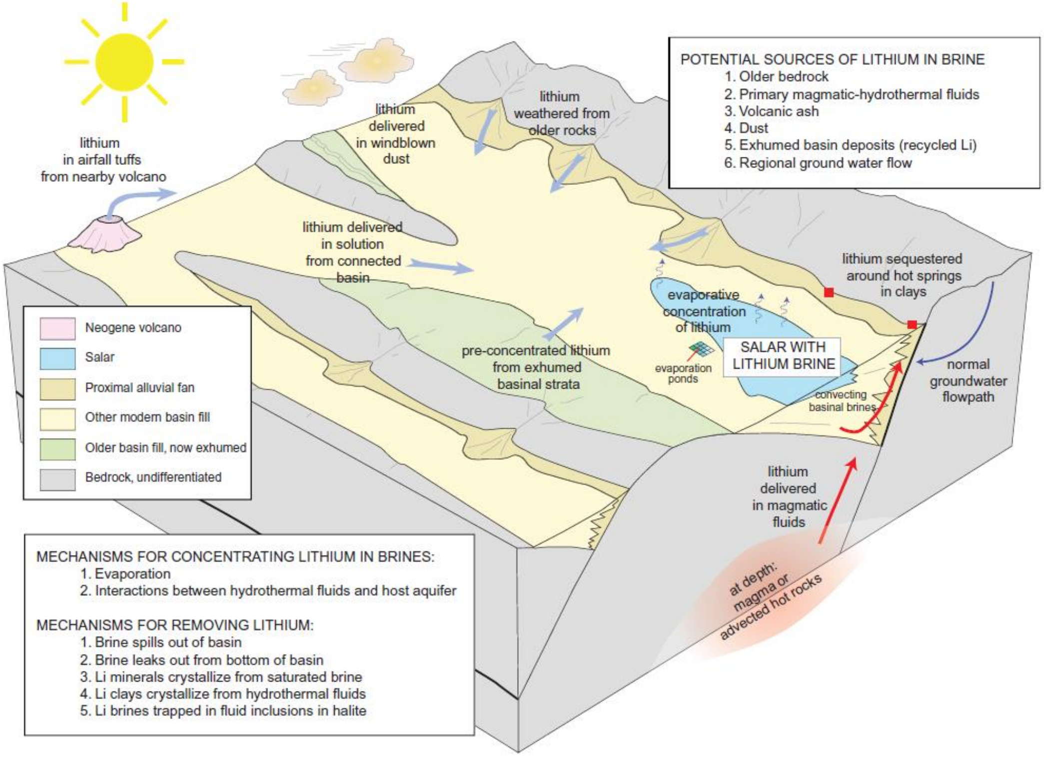


Figure 1. Summary diagram of the geological, geochemical and hydrological features of lithium brine [9]. Lithium can be found concentrated in areas subject to volcanic influences. Reproduced with permission of the Society of Economic Geologists, Inc. Munk et al. (2016) Chapter 14: Lithium brines: A global perspective, Reviews in Economic Geology, v. 18, 339–365.

1.1. Lithium Resources

Lithium is found in three main types of deposits: saline subsurface waters (continental brines), hydrothermally altered clays (sedimentary deposits), and pegmatites (crystalline hard rock). Lithium-bearing minerals are mainly phosphates and complex aluminosilicates [10]. Commercially important lithium-bearing minerals include spodumene, lepidolite, petalite, and amblygonite [10,11]. World lithium reserves are estimated to be 21 million metric tons of lithium and the world lithium resource base is estimated to be 86 million metric tons of lithium [12]. The US lithium resource base is estimated at 7.9 million metric tons of lithium, which includes lithium in continental brines (including geothermal brines), sedimentary deposits, and pegmatites [12]. New resource estimates for Thacker Pass (potentially 22.4 million metric tons) suggest that lithium resources in the US may be higher than current USGS estimates [13].

The primary commercial sources of lithium are hard rock deposits in Australia and China, and brine deposits in Argentina, Chile, and China [12,14]. These countries account for the majority of lithium production worldwide [14]. Brine deposits account for between 50 and 75 percent of the world's lithium production (Figures 2 and 3) [4,9,10,15,16]. Major brine deposits occur in the US (Figure 4 and Table 1), but commercial production of brine lithium occurs predominantly in South America [2,9–11,15,17].

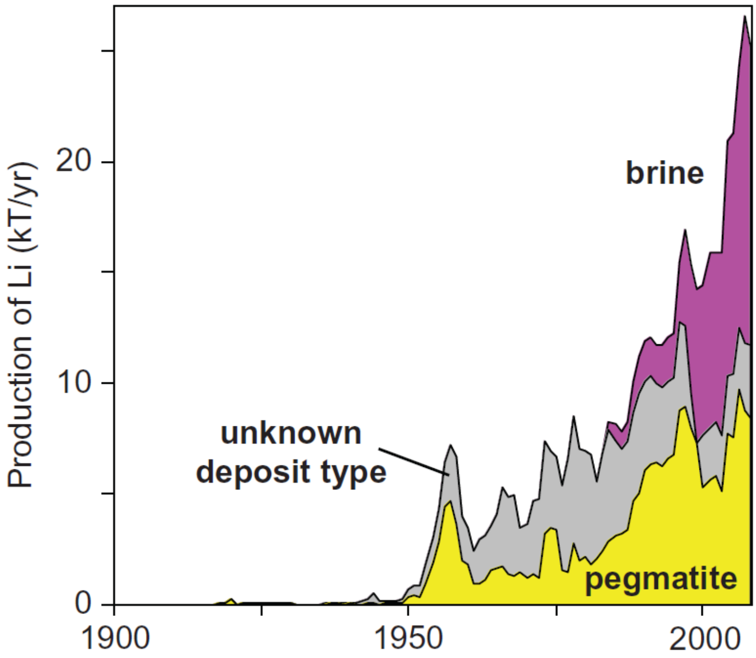
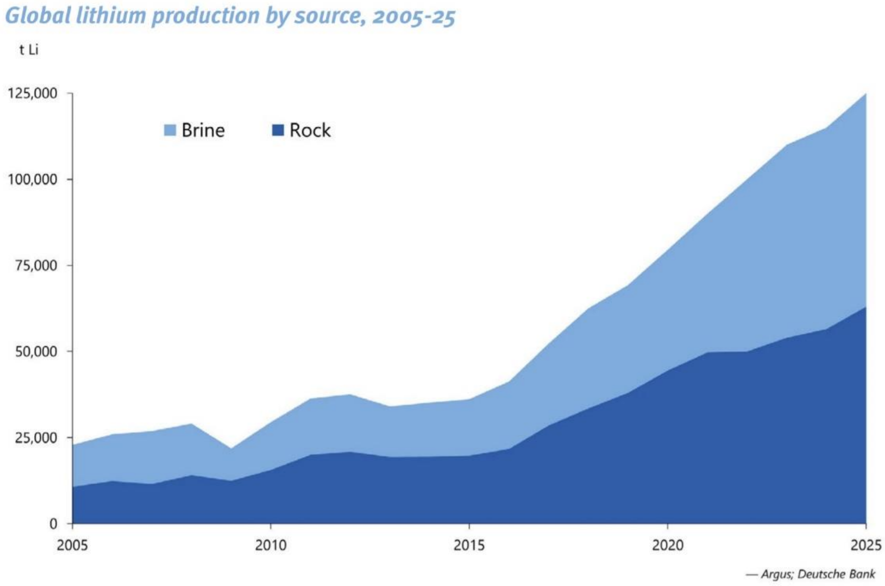


Figure 2. Lithium production since 1900 [9]. Lithium is found in three main deposit types: pegmatites, continental brines, and hydrothermally altered clays. Lithium mining increased exponentially starting in the 1950s due to its use as a component in modern materials, including in metal alloys, specialty glass, and ceramics. Reproduced with permission of the Society of Economic Geologists, Inc. Munk et al. (2016) Chapter 14: Lithium brines: A global perspective, Reviews in Economic Geology, v. 18, 339–365.


Global lithium production by source, 2005-25

— Argus; Deutsche Bank

Figure 3. Distribution of worldwide Li production from brine and hard rock sources [16]. Brines are expected to become an increasingly important source of lithium. Reproduced with permission from Argus Media Ltd.

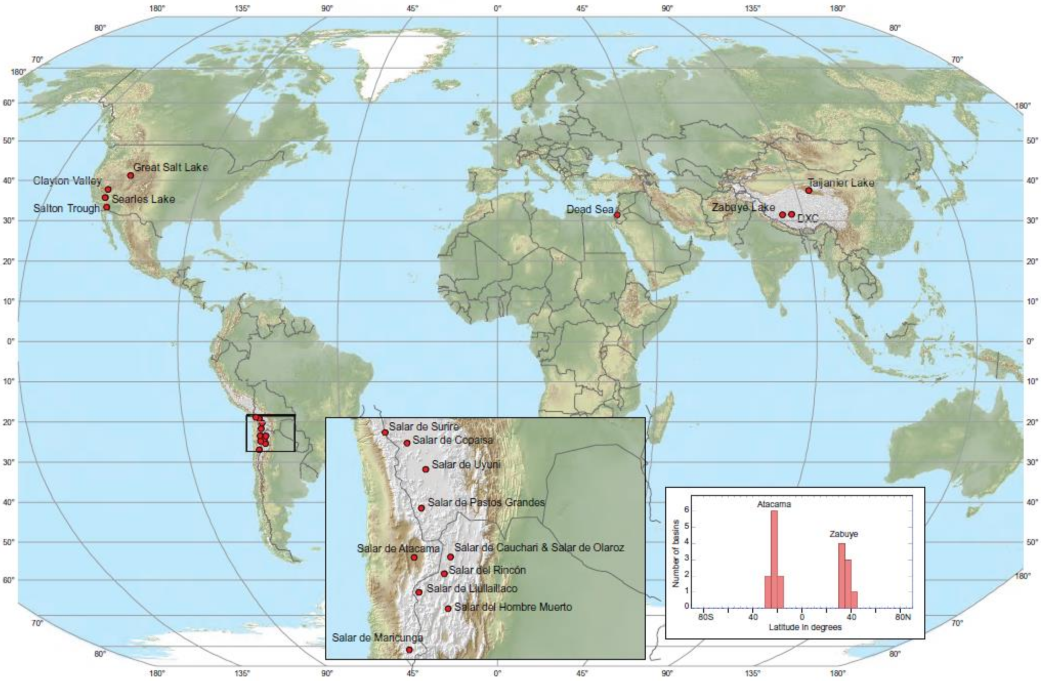


Figure 4. World map of lithium brine deposits [9]. Currently, lithium is produced from brines mostly in South America and Asia. Reproduced with permission of the Society of Economic Geologists, Inc. Munk et al. (2016) Chapter 14: Lithium brines: A global perspective, Reviews in Economic Geology, v. 18, 339–365.

Table 1. Lithium and magnesium concentrations in prominent salar and salt lake brines [17]. Separation of lithium and magnesium are important for recovery of battery-grade lithium. Table reproduced from [17]; some calculated ratios have been corrected.

Deposit Name	**Country**	**Li^+ (wt.%)**	**Mg^{2+} (wt.%)**	**Mg^{2+}/Li^+ Ratio**
Salar de Atacama	Chile	0.157	0.965	6.15
Maricunga	Chile	0.092	0.74	8.04
Uyuni	Bolivia	0.0321	0.65	20.2
Cauchari	Argentina	0.062	0.18	2.90
Olaroz	Argentina	0.09	0.18	2.00
Hombre Muerto	Argentina	0.062	0.089	1.44
Rincon	Argentina	0.034	0.04	1.18
Silver Peak	USA	0.03	0.04	1.33
Great Salt Lake	USA	0.006	0.8	133
Bonneville	USA	0.0057	0.4	70.2
Salton Sea	USA	0.022	0.028	1.27
Searles Lake	USA	0.0083	0.034	4.10
Smackover	USA	0.038	0.75	19.7
Clayton Valley	USA	0.0163	0.019	1.17
East Taijinar	China	0.085	2.99	35.2
West Taijinar	China	0.021	1.28	64
Yiliping	China	0.022	2.0	91
Zabuye	China	0.97	0.001	0.001
Da Qaidam	China	0.02	1.3	65
Dead Sea	Israel	0.002	3.4	1700
Fox Greek	Canada	0.01	0.1	10
Sua Pan	India	0.002	-	-
Chott Djerid	Tunisia	0.00024	0.0143	59.6

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In 2019 and 2020, world production of lithium was approximately 86,000 and 82,000 metric tons, which was approximately 10% less than in 2018, demonstrating that year-to-year production can fluctuate significantly, even as demand increases steadily [12,14]. The only current lithium production in the United States is reported to be from a brine operation in Nevada [14]. The Silver Peak, NV, lithium brine operation produced approximately 2200 metric tons of lithium carbonate equivalent (LCE) in 2020, representing approximately 410 metric tons of lithium or approximately 20% of annual domestic consumption [12,14,18]. Lithium carbonate is a key ingredient in many lithium batteries that is traded in markets, so LCE is a common unit of measure for lithium production, especially in industry and economic analysis.

1.2. Lithium Demand Is Expected to Grow

Between 1975 and 2005, world lithium production increased by approximately 5-fold [4]. Average lithium demand rose by 6% annually between 2000 and 2008, driven by needs in both the battery and aluminum applications [2]. The increased demand for lithium is driven by two types of battery uses: (1) the rapidly growing production of electric vehicles—many countries will require a switch to an all-electric vehicle fleet within the next 10–20 years, and (2) the increased demand for battery energy storage to offset the intermittent nature of important renewable energy sources, such as solar and wind [19,20]. A 2020 World Bank study (Figure 5) predicted that increased demand will result in an increase in lithium production from 447 thousand tons LCE in 2018 to over 2 million tons LCE in 2050, representing an increase of 488% [20]. One key uncertainty is how new innovations in battery technology will affect the demand for lithium, particularly the impact on lithium demand beyond 2030 [20].

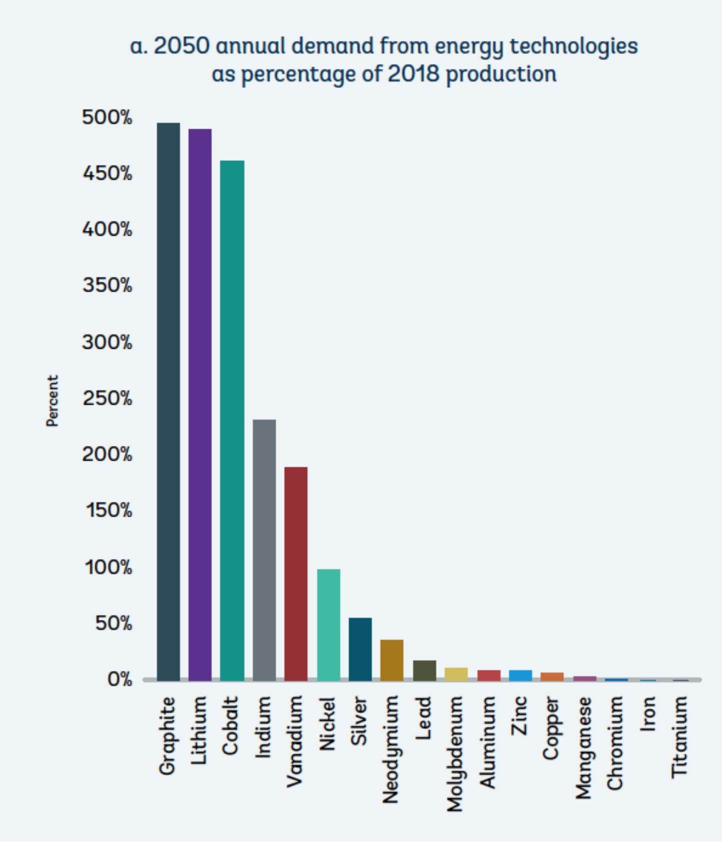

Figure 5. Predicted increase in worldwide demand for lithium and other battery materials due to growth of the EV and battery storage markets [20]. It is estimated that lithium demand in 2050 will be over 2 million tons LCE [20]. Creative Commons Attribution (CC BY 3.0 IGO).

Lithium markets can be volatile, as overproduction can lead to drops in the price of lithium [21]. A recent study by Cochilco (the state mining agency in Chile) predicts that the growing EV market will drive up the global demand of lithium by a factor of 5 over the next ten years, from a current production level of 317 thousand tons lithium carbonate equivalent (LCE) to 1790 thousand tons LCE in 2030 [16]. The increased demand for EV batteries is indicated by Tesla's announcement to build a 30 GWh lithium battery "gigafactory" in Texas (in partnership with Northvolt), and the new partnership between Daimler and the Chinese battery company Farasis Energy [16]. It is anticipated that there will be significant growth in US lithium production as part of this market shift.

There is strong interest in developing domestic lithium production in the United States, which is the location of significant lithium deposits and high electrical vehicle demand [3,4,9,19]. In the future, it is expected that lithium production will develop globally in response to regional lithium demand for vehicle batteries and other uses (Figure 6) [2,22].

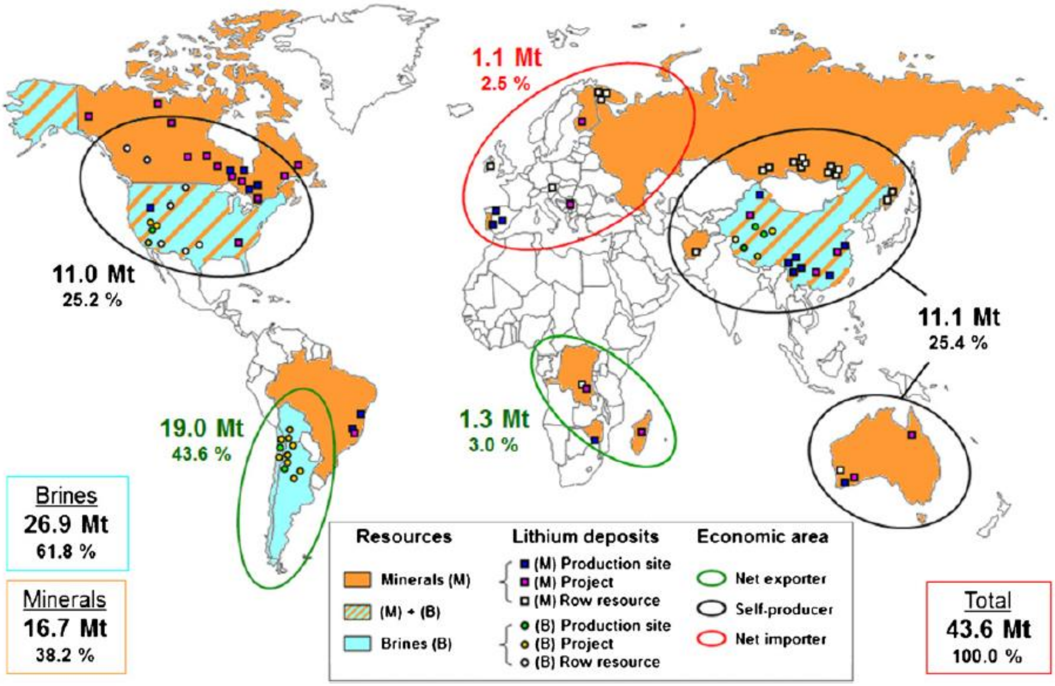

Figure 6. Projected lithium resources by source type (brine vs. hard rock) [2]. It is expected that lithium production will develop globally in response to lithium demand [2,22]. Reprinted from Renewable and Sustainable Energy Reviews, v. 16(3), Grosjean et al., Assessment of world lithium resources and consequences of their geographic distribution on the expected development of the electric vehicle industry, 1735–1744., Copyright 2012, with permission from Elsevier.

1.3. Potential for Geothermal Brine to Supply Demand

Geothermal fluids are recognized as potentially important brine sources for lithium [23–25]. As part of the US Department of Energy GeoVision study, geochemistry data were compiled from a number of published and unpublished sources, including the US Geological Survey, representing samples from over 2000 geothermal wells and hot springs [23,24,26]. Of these samples, approximately 1200 had reported lithium concentrations and the distribution of lithium concentrations from this study is depicted in Figure 7. The majority of these samples (>900) had lithium concentrations less than 1 ppm, and only 35 samples have lithium concentrations greater than 20 ppm [23,24]. All of the geothermal brine samples with lithium concentrations above 20 ppm were from the Salton Sea KGRA in the Imperial Valley of California [23,24]. Using data from previous studies, we estimate average concentrations of lithium in Salton Sea post-flash geothermal brines to be approximately 200 mg/L (Table 2).

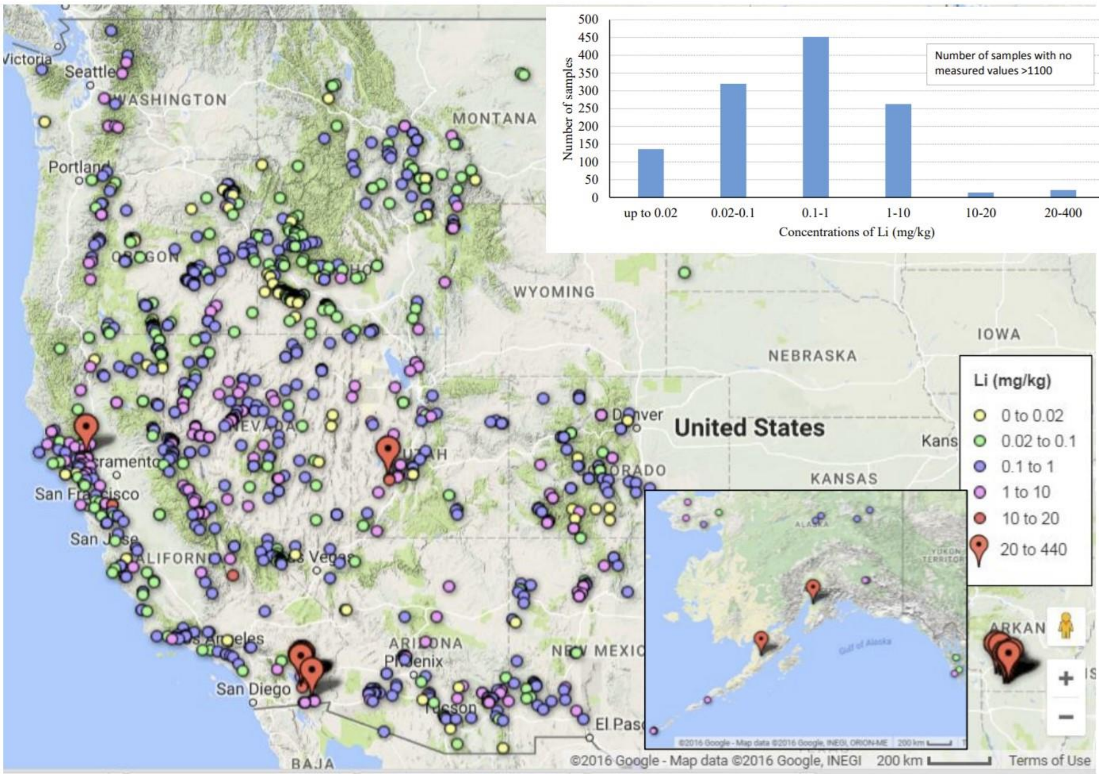

Figure 7. Distribution of geothermal brine samples with measured Li concentrations [23,24]. Geothermal brines are expected to be a significant source of domestic lithium production in the future.

Table 2. Salton Sea geothermal brine chemical composition. Average calculated values reported in the literature representing post-flash geothermal brines [27–35].

Element or Analyte	Mean (mg/L)	SD	%RSD	N
Cl	142,015	18,853	13	13
Na	49,249	5578	11	13
Ca	25,684	3050	12	13
K	14,467	3370	23	13
Fe	1347	653	48	13
Mn	1201	393	33	13
Zn	463	169	36	12
Sr	434	67	15	12
B	298	69	23	11
Ba	205	57	28	11
Li	202	39	20	13
Rb	110	52	47	4
Mg	109	192	176	13
Br	91	28.0	31	9
Pb	84	19	23	12
Cs	20	2.9	15	4
I	17	3.6	21	3
F	15	0.6	4	3
As	9.0	3.6	40	3
Cu	4.1	2.3	57	10
Al	2.4	1.2	51	5
Cd	1.9	0.5	27	7
Ag	1.6	0.7	43	3
SiO_2	342	133	39	7
NH_4	311	111	36	8
SO_4	58.6	37.3	64	9
TDS	24,300	2800	12	13

SD: Standard deviation; %RSD: percent relative standard deviation; N: number of measurements included in calculation.

The potential production of lithium from a number of geothermal fields in the US was estimated using the range of lithium concentrations in produced brines and the annual brine production from operating wells (Table 3) [24]. Neupane and Wendt [24] assumed that the fields would operate 90% of the time and that lithium recovery from the brine would be 80%. The fields are grouped in Table 3 by geologic setting and the fields in the non-volcanic portion of the Great Basin generally have low lithium contents (typically less than 3 ppm), those on the margins of the Great Basin that are associated with Quaternary volcanism generally have slightly higher concentrations, while those in the Imperial Valley generally have the highest values, with some values exceeding 100 ppm. Of the fields studied, only three geothermal fields (Roosevelt, East Mesa, and Salton Sea) were shown to have brine concentrations greater than 10 ppm and that the Salton Sea geothermal field, with its hypersaline brines, was the only field with reported lithium contents greater than 100 ppm [24]. Neupane and Wendt concluded that the Salton Sea field represents by far the largest potential lithium geothermal brine resource in the US, with annual potential production levels of 6 to 32 thousand tons lithium per year (equivalent to 34 to 168 thousand tons LCE) at existing brine flow rates [24]. Toba et al. [36] used dynamic economic modeling and estimated that geothermal lithium production could reach approximately 70,000 metric tons LCE by 2030.

Table 3. Lithium concentrations and potential lithium (as Li) production from selected operating geothermal fields in the US (adapted from Neupane and Wendt [23,24]).

Geothermal Field	Brine Li Concentration (ppm)	Brine Production (mt/d)	Annual Potential Li Production (mt) *
Volcanic margins of the Great Basin			
Casa Diablo	0.3–4	65,660	5–69
Roosevelt	16–27	24,490	100–170
Steamboat	6.4–10	20,830	35–55 †
Non-volcanic Great Basin			
Beowawe	2.1–2.6	22,960	13–16
Bradys	0.19–3.3	43,190	2–37
Desert Peak 1 and 2	1.4–5.6	11,090	4–16
Dixie Valley	0.38–2.65	52,610	5–37
Neal	0.3	51,060	4
Raft River	1.2–3	34,400	11–27
San Emidio	2.2–2.5	23,130	13–15
Soda Lake	0.05–1.7	23,150	0.3–10
Stillwater	1.5–2.1	28,030	11–15
Tuscarora	0.6–0.7	31,300	5–6
Wabuska	0.26–0.53	14,150	1–2
Imperial Valley			
East Mesa	0.8–40	190,640	41–2000
Heber	2.8–6.6	133,760	98–230
Salton Sea	90–440	273,130	6460–31,580

* Assume 80% recovery efficiency and 90% operation time. Values are in metric tons of Li/year. † Note that reported production of Li for Steamboat by Neupane and Wendt [23,24] is off by a factor of 10.

1.4. Resource Estimates for the Salton Sea Geothermal Field

Lithium resource production estimates for the Salton Sea KGRA are based on extraction of lithium from brines assuming either current geothermal energy capacity or future total geothermal energy potential. The current installed capacity of the Salton Sea geothermal field is just under 400 MWe and consists of the combined 350 MWe capacity of 10 power plants operated by CalEnergy and the 49 MWe John Featherstone plant operated by EnergySource. The proven and predicted sizes of the Salton Sea geothermal reservoir are quite a bit larger. Kaspereit et al. [37] suggest that the proven resource is 990 MWe, with a total resource of 2250 MWe potentially developable, and with an additional 700 MWe that could be accessible as the Salton Sea continues to recede.

Recent academic studies estimated the potential production rate for lithium from the Salton Sea geothermal field to be thousands of metric tons of lithium per year based on the currently installed geothermal power capacity (Table 3) [23,24]. CalEnergy estimates a potential annual lithium production of 90 thousand tons LCE from their existing 350 MWe field and estimates that an additional 700 MWe of geothermal power could be developed that could produce an additional 210 thousand tons of LCE per year [38]. EnergySource has plans for a lithium extraction facility at their John Featherstone plant with the objective of eventually producing up to 16 thousand tons of LCE per year [39,40]. EnergySource estimated that a total of approximately 100 thousand tons of LCE could be produced annually from the Salton Sea region [39].

Resource estimates for the Salton Sea KGRA have also been calculated based on brine concentrations and the estimated reservoir volume. McKibben et al. [41] estimate that the proven lithium reserves from the Salton Sea geothermal field are on the order of 2 million metric tons of lithium (or over 10 million metric tons of LCE). This would be comparable with other world-class lithium deposits (Table 4) [12,14,42].

Table 4. World-class lithium deposits for pegmatites, continental brines, tuffs, jadarite, and lithium clays [42].

Deposit	Type	Location	Main Owner	Li (Kt)	Grade (wt.% Li)	Resource/ Reserve
Greenbushes	Pegmatite	Greenbushes (Australia)	Tianqi Lithium	943	1.091	R
Wodgina	Pegmatite	Pilbara (Australia)	Mineral Resources	826	0.543	R
Earl Grey	Pegmatite	Goldfields (Australia)	Kidman Resources and SQM	658	0.697	R
Pilgangoora	Pegmatite	Pilbara (Australia)	Pilbara Minerals	628	0.580	R
Grota do Cirilo	Pegmatite	Mina Gerais (Brazil)	Sigma Lithium	293	0.641	r (M + I)
Whabouchi	Pegmatite	Quebec (Canada)	Nemaska Lithium	220	0.604	R
Arcadia	Pegmatite	Harare (Zimbabwe)	Prospect Resources	164	0.608	R
Tanco	Pegmatite	Manitoba (Canada)	Sinonime Rare Metals	110	1.180	R
Atacama	Brine	Atacama (Chile)	SQM; Albemarle	6300	0.184	R
Uyuni	Brine	Ororu and Potosí (Bolivia)	COMIBOL	3600	0.045	R
Zhabuye	Brine	Tibet (China)	Tibet Shigatse and Tianqi	1500	0.100	R
Centenario	Brine	Salta (Argentina)	Eramet	921	0.045	r (M + I)
Hombre Muerto	Brine	Catamarca (Argentina)	Livent	835	0.071	R
Olaroz/Cauchari	Brine	Jujuy (Argentina)	Orocobre	345	0.053	R
Cauchari	Brine	Jujuy (Argentina)	Lithium Americas and Exar	282	0.069	R
Maricunga	Brine	Atacama (Chile)	Minera Salar Blanco	269	0.117	R
3Q	Brine	Catamarca (Argentina)	Neo Lithium	243	0.079	R
Rincon	Brine	Salta (Argentina)	Argosy Minerals	203	0.032	R
Clayton Valley	Brine	Nevada (USA)	Pure Energy Minerals	41	0.012	R
Sonora	Li-Clay	Sonora (Mexico)	Bacanora and Ganfeng	845	0.229	R
Thacker Pass	Li-Clay	Nevada (USA)	Lithium Americas	582	0.236	R
Rhyolite Ridge	Li-Clay	Nevada (USA)	Ioneer Resources	209	0.170	r (M+I)
Falchani	Li-Tuff	Puno (Peru)	Plateau Energy Metals	146	0.296	r (I)
Jadar	Jadarite	Jadar (Serbia)	Rio Tinto	435	0.836	r (I)

R = reserve; r = resource, M = measured; I = indicated. Reproduced with permission of the Mineralogical Society of America. Bowell et al. (2020) Classification and characteristics of natural lithium resources. Elements, 16(4), 259–264.

1.5. Resource Estimates for Other US Geothermal Fields

Several studies have shown that the potential for lithium production from other geothermal fields in the US is much lower than the Salton Sea KGRA [23–26,43]. Brines from the Roosevelt field in Utah and East Mesa in California have significant lithium concentrations; however, the potential production from these fields is estimated to be an order of magnitude lower than the Salton Sea KGRA (Table 3) [23,24,26]. The Brawley geothermal field in California has deep hypersaline brines that may contain elevated lithium concentrations [44], but currently the Brawley geothermal field is tapping shallower, lower temperature, and lower salinity fluids.

One study measured geothermal brine lithium concentrations and estimated the total resource potential from producing geothermal fields in Nevada and Utah [25,43]. The Roosevelt geothermal field in Utah was found to have significant lithium concentrations (20–30 mg/kg), but the other geothermal fields included in that study had less than 0.5 mg/kg lithium [25,43]. Lithium resources in geothermal fields were estimated by multiplying the average concentrations of lithium in produced fluids by the areal extent of production wells and assuming a reservoir thickness of 1 km, and a porosity of 15% [43]. Using this method, the Roosevelt field was calculated to have a lithium inventory of 7 thousand tons (37 kilotons lithium carbonate equivalent) [43]. Note that this estimate assumes that all lithium contained within the reservoir could be produced and extracted.

1.6. Lithium in Geothermal Brines Outside of the US

The abundance and resource potential of lithium in geothermal brines is also under investigation in other regions of the world (e.g., [45]). Millot et al. [46] conducted an extensive review of the lithium concentrations of brines associated with geothermal systems throughout Europe. They identified six systems with lithium concentrations greater than 90 ppm (Figure 8). Lithium demand is expected to be high in Europe, especially in the face of EU greenhouse gas emission targets, and several projects are underway to characterize and develop geothermal lithium sources in Europe, especially in France and Germany [45,47–50]. Resource assessments of lithium in geothermal brines and studies of direct lithium extraction technologies are also ongoing in Japan and New Zealand [51–54].

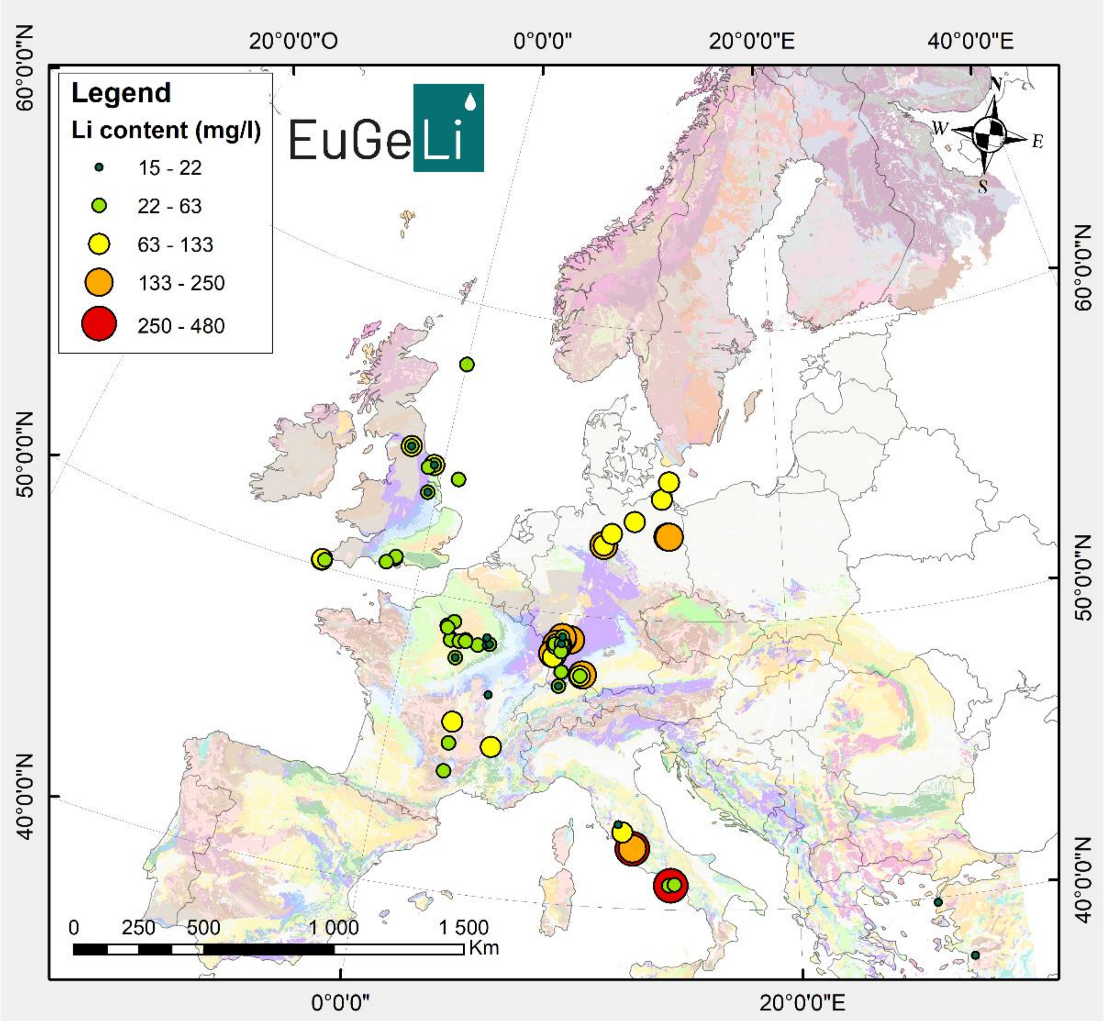

Figure 8. Distribution and abundance of Li in geothermal brines in Europe [46,48]. Significant geothermal lithium resources have been identified in Europe. Reproduced with the permission of the authors.

1.7. Current Practices for Lithium Extraction from Brine: Evaporative Concentration

Under current practices, lithium chloride (LiCl) and lithium carbonate (Li_2CO_3) are produced from brines by evaporative concentration followed by further refining [4,5,55,56]. Lithium hydroxide ($LiOH{\cdot}H_2O$) is typically produced from refined lithium carbonate. Lithium-containing brine deposits occur as groundwater under ancient endorheic lake beds (salt-pans or salt-flats or salars) and are commonly referred to as "salar brines" [4,9]. Wells are drilled to access the underground brine deposits and the salar brine is then pumped to the surface and distributed to evaporation ponds. The brine remains in the evaporation pond for a period of months or years until most of the liquid water content has been removed through solar evaporation [4,57]. Salar brines typically contain high concentrations of magnesium, potassium, and sodium as well as many other elements, including boron, in addition to lithium [4,57]. Brine operations usually consist of a series of large, hydraulicly connected evaporation ponds where lithium brines are concentrated. Potassium and other metals and salts are precipitated and extracted from earlier ponds in the series and evaporation continues in later ponds until an optimal target lithium concentration is reached [55,57–59]. Extracted metals and salts that are not economically valuable are disposed of as tailings or may be stored for later processing [58]. Main by-products are potash for the fertilizer industry and bischofite (mineral hydrous magnesium chloride), which is used for road paving [5,57]. Reverse osmosis (RO) can be used to concentrate the lithium brine as a supplement or alternative to the evaporation process [57]. During the evaporation process, the lithium concentration is increased from approximately 2000 mg/L to up to 6% in the final brine [5].

The brine is concentrated by solar evaporation to crystallize sodium, potassium and magnesium chlorides, leaving a concentrated solution of lithium chloride [56]. This lithium chloride solution is further refined at associated facilities to remove both bulk and trace impurities [5,9,57]. Conversion of lithium chloride to lithium carbonate or lithium hydroxide occurs at associated facilities or may involve the sale of partially refined products to lithium markets [16,18,59]. Refining of the lithium chloride solution includes chemical addition to promote the precipitation of magnesium hydroxide ($Mg(OH)_2$), which is then removed by filtration (e.g., [56]). Other processes may be applied to remove boron or other impurities, depending on the purity required for the chloride or carbonate product (e.g., [57,60,61]). A generalized flowsheet of lithium carbonate production from a concentrated salar brine is shown in Figure 9 [56]. Other versions of this process include variations such as using solar evaporation to concentrate the brine to approximately 3% lithium chloride, then treating it with lime and calcium chloride to convert impurities such as boron, magnesium and sulfate to a calcium borate hydrate, magnesium hydroxide and calcium sulfate dihydrate [52]. Production of lithium carbonate using salt ponds is estimated to cost 30% to 50% less than lithium obtained from hard rock mines [56,62].

1.8. Future Practices: Direct Extraction of Lithium from Brines

Although the use of open ponds for evaporation and concentration of lithium brines is nominally inexpensive, the evaporation process is time consuming, land intensive and wasteful of water [21]. The development of new brine resources from undeveloped lithium brine deposits is likely to meet significant environmental and social barriers to implementation, particularly in the US, and evaporation ponds are not considered environmentally sustainable [19]. Furthermore, geothermal energy production requires that lithium be recovered from brines without significant losses of water, since water is a valuable resource that must be reinjected to maintain energy production at geothermal facilities, and reinjection also provides a safe means of disposing of the other produced brine constituents back into the reservoir.

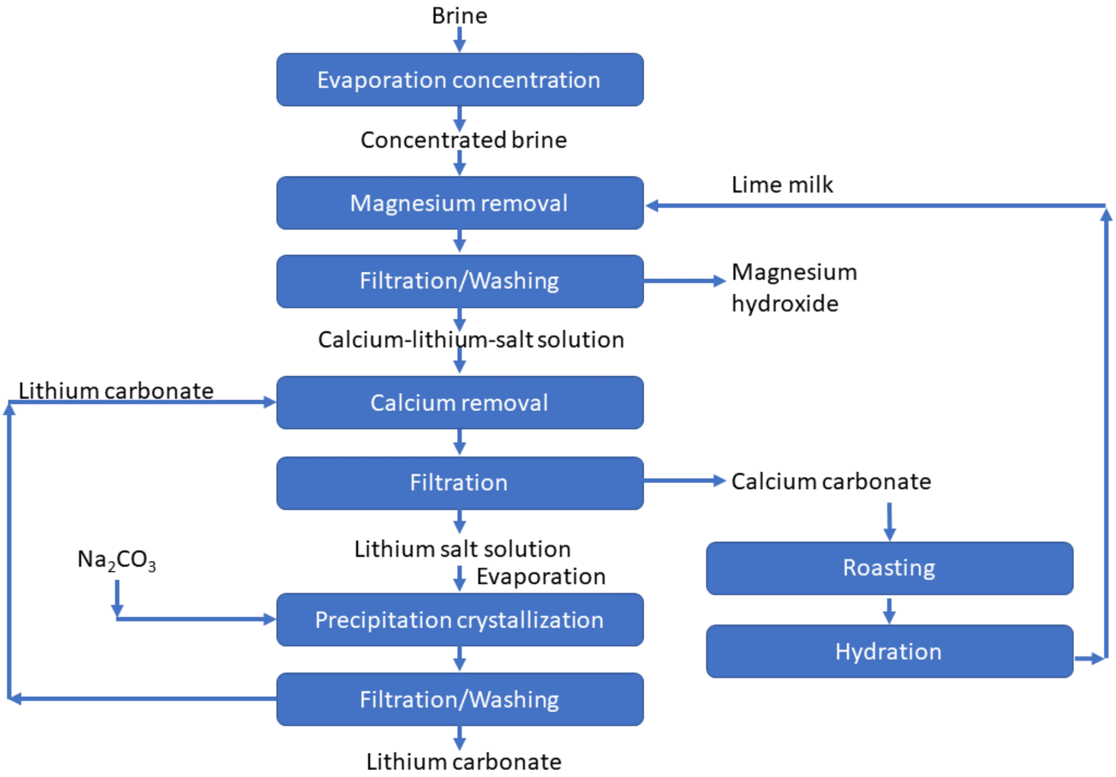

Figure 9. Flow-chart for lithium extraction as lithium carbonate from salar brine, adopted from [56]. Reprinted (modified) from Hydrometallurgy, v. 150, Meshram et al., Extraction of lithium from primary and secondary sources by pre-treatment, leaching and separation: A comprehensive review, 192–208, Copyright 2014, with permission from Elsevier.

For both geothermal and conventional lithium resources, there is interest in developing technology and processes for the “direct extraction” of lithium from brines. In direct extraction, lithium is concentrated from solution by a technological means, as opposed to evaporative concentration (e.g., [63,64]). The ideal direct lithium extraction technology would be one that can specifically pluck lithium ions out of complex geochemical soup, while leaving all other salts and metals in solution. However, as discussed below, selective extraction of lithium from brine is challenging. It is recognized that direct lithium extraction will have higher upfront capital costs than evaporation ponds [21]. Direct lithium extraction has been employed profitably to produce lithium chloride from brines in Argentina and China and it is estimated that approximately 12% of the world’s lithium supply in 2019 was produced using direct lithium extraction technology [64]. Direct extraction processes will require careful attention to competitive operating costs at scale, but it is believed that geothermal lithium production, using direct lithium extraction and recovery, will be competitive within the current global commodity supply curves, especially if other commodities (e.g., metals) can be harvested along with lithium [21].

1.9. Objective of This Paper

The objective of this paper is to examine and analyze direct lithium extraction technology in the context of developing sustainable lithium production from geothermal brines. In this review, we focus on the application of the technology to geothermal brines; however, applications to other brines (such as coproduced brines from oil wells) are considered.

The approach taken was to review the fundamentals of lithium recovery technology and examine applied processes envisioned or utilized for extracting lithium from brines. We interpret the results of fundamental and applied studies in the context of geothermal lithium production, with a focus on the Salton Sea KGRA. The focus of this paper is on industrial or commercial processes and associated technologies, rather than on basic research. The information examined includes patents, patent applications, industrial reports, and scientific literature. This examination shows that there is a vibrant nascent industry growing around direct extraction of lithium from brines and that application of direct lithium extraction to geothermal brines has unique challenges.

2. Technology for the Direct Extraction of Lithium from Brine

Techniques and technologies applied for the direct extraction of lithium from brines include precipitation, well-established sorption technologies such as ion-exchange resins, emerging novel sorbents, such as metal oxides, solvent separation using solvents commonly used for metal extraction, and novel solvents specific to lithium, such as crown ethers. Direct lithium extraction methods may use membranes and electrochemical processes to enhance lithium extraction. In this section we discuss the variety of technologies and techniques that have been used or are under development for extraction of lithium from brine. Other studies have examined technologies and techniques for lithium recovery from hard rock and clay resources [10,11].

2.1. Concentration and Precipitation

It is possible to use simple and well-understood chemical precipitation reactions to recover lithium from brine. Some of the precipitation and other processes used for lithium recovery from seawater and brines are summarized in Table 5 [56]. Lithium can be recovered by lime precipitation; however, for a variety of precipitation methods that have been tested, aluminum salts are reported to show the best performance for lithium recovery from geothermal water [56,65]. Using a Salton Sea geothermal brine, Schultze and Bauer [65] precipitated over 99% of the lithium in by adding a solution of $AlCl_3$ and increasing the pH to 7.5 with lime slurry (see Section 3, below). Meshram et al. [56] reported that the appropriate pH for lithium recovery is 10–13 and the use of $NaAlO_2$ produced better recoveries than $AlCl_3$. With a high-purity $NaAlO_2$ solution as a precipitating agent, approximately 98–99% lithium recovery was achieved at pH 11.5 from a silica (SiO_2) and calcium-free geothermal water [56].

Table 5. Precipitation methods for extraction of lithium [56].

Source/Raw Material	Process	Conditions	Recovery (%)/Remarks	Product (% Purity)	References
Synthetic solution, geothermal water (Li = 10 mg/L)	Precipitation	pH 12.5 for {Al}: 50–100 mg/L	70% Li		[66]
Synthetic solution (2.5 M LiCl, 0.3 M $CaCl_2$ and 0.15 M $MgCl_2$)	Precipitation followed by IX using Poly BN® R45HTLO (MC50), Lewatit® (TP 207), Dowex® (Y80)	Precipitation with 1.8 M $NaCO_3$ at 80 °C IX-50 °C, 30 min	Good usable volume cap. of resin TP207: 56.4 g/L	Li salt solution	[67]
Seawater (0.12–0.16 mg/L Li)	Integrated ion-exchange method	1st stage: sorption on λ-MnO_2, 150 days (264 g LiCl in 816 m^3 seawater): 2nd stage: Sep. of Mg(II), Ca(II), Sr(II) and Mn(II) with SK110 resin (pH 9)	56% yield	Li_2CO_3 (>99.9)	[68,69]
Seawater (0.18–0120 mg/L Li)	Two-stage precipitation	1st-stage pH: 11.5–12.5 2nd stage: Na_2CO_3 at 100 °C	Recovery of pure lithium carbonate	Li_2CO_3 (99.4)	[70]
Uyuni Salar brine, Boliva, 15–18 g/L Mg, 0.7–0.9 g/L Li	Two-stage precipitation from lime and Na-oxalate	1st-stage pH: 11.3 2nd stage: sodium oxalate, 80–90 °C	Precipitation as Li_2CO_3	Li_2CO_3 (99.55)	[71,72]
Brine from Salar de Hombre Muerto, Argentina	Precipitation (2.5 g/L LiCl from solar pond) with lime and Na_2SO_4	Separation of Mg as hydroxide and Ca as sulfate	LiCl salt feed for Li extr. in a chemical plant	LiCl	[73]
Brine (high Mg/Li ratio)	Electrochemical	Electrolyte: 0.5 M NaCl, 10 h	~94% Li; Li sorption: 28.65 mg/g $LiFePO_4$		[74]

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Precipitation reactions are routinely used in geothermal power production, especially for the control of silica [75–78], but precipitation reactions may not be practical for direct extraction of lithium from geothermal brines. The non-selective nature of these types of reactions and the numerous competitive co-precipitates (such as calcium carbonates and iron hydroxides) will influence chemical reagent costs and may cause waste disposal problems. In addition, lithium extracted by precipitation will require extensive post-extraction purification and processing to meet standards for lithium battery production or other uses.

2.2. Organic Sorbents

2.2.1. Organic Ion-Exchange Resins

Using strong acid cation-exchange resins to selectively collect and recover lithium from seawater and other lithium-containing solutions has been investigated since at least the 1970s [56,79–83]. However, early studies showed that organic ion-exchange resins exhibited low selectivity for lithium ions [56,83]. A strong acid cation exchanger such as AmberSep™ G26 H Resin can be used to strip lithium from water; however, because lithium has a very low affinity for ion-exchange resins compared to most other cations, typical ion-exchange resins are not practical for use in lithium extraction and recovery [82,83]. Ion-exchange resins only become effective for selective lithium extraction when impregnated with inorganic, lithium-selective sorbents [6,84–87].

2.2.2. Ion-Imprinted Polymers and Other Organic Sorbents

Several investigators have investigated the synthesis and application of organic polymers that selectively extract lithium in preference to other metal ions. Metal selectivity may be imparted by including reactive or chelation sites in steric structures specifically sized, using an ion-imprinting process, to allow entry of lithium and not competing ions. For example, Ventura and others created a nanocomposite sorbent comprised of molecular sieve nanoparticles and lithium-imprinted polymeric resins for the selective recovery of lithium from geothermal brines [88,89]. They created beads of lithium- and manganese-imprinted polymers by crosslinking and polymerization of a metal chelate, where the metal acts as a template. To extract lithium and manganese from brines, lithium- and manganese-imprinted polymer beads were used as selective solid sorbents. Ion-imprinted polymers have selectivity toward the target metal ion due to the memory effect imparted by how they are manufactured. Metal ion selectivity is imparted by: (1) the affinity of the ligand for the imprinted metal ion, and (2) the size and shape of the generated cavities [88,89].

Variants of lithium-imprinted polymers are being developed by the company Materials Research LLC [90,91]. They have an active program for critical materials extraction and recovery, including processes for extracting lithium from geothermal brines, but they have not yet developed commercial products [90–92]. One project includes scaling-up the manufacturing process for the sorbent and conducting a pilot study that includes the design and testing of a transportable, skid-based pilot system for the production of lithium carbonate from geothermal brine. The project will be conducted with synthetic brine, but may include testing against actual geothermal brines [90]. The goals of this project are to gain experience in a large-scale facility operation using these novel sorbents, adapt the process based on lessons learned, update the energy and material balance for the process, and to refine process economics [90].

Lu et al. [93] developed lithium-imprinted polymers that contained crown ether structures (Figure 10). These polymers were used as membranes for the selective separation of lithium from sodium and potassium, where the lithium was adsorbed to crown ether sites on the membrane while the other ions were not retained [93]. Crown ether moieties are also used in other ion-imprinted polymers designed for lithium adsorption [94].

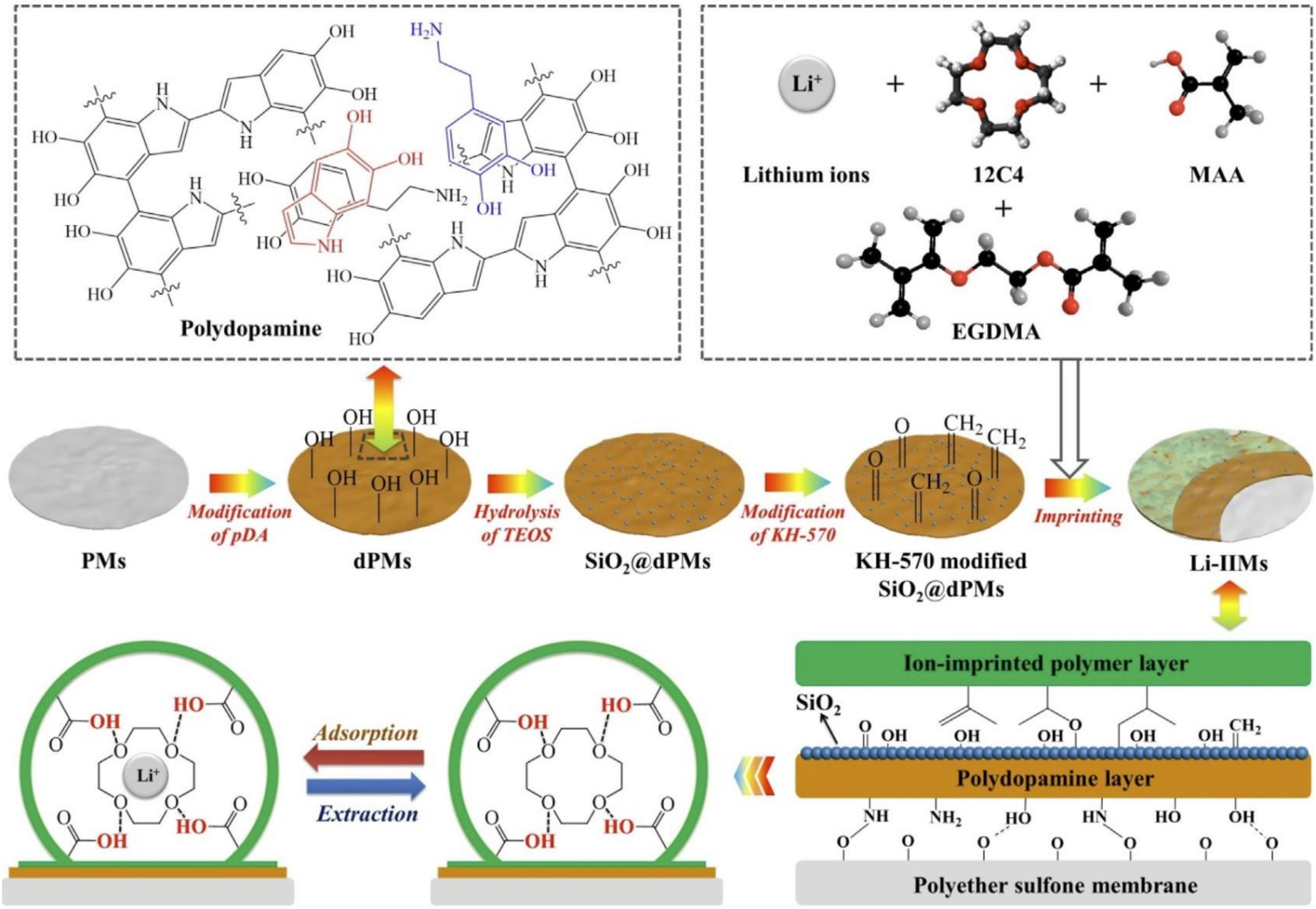

Figure 10. Schematic diagram for the preparation of an ion-imprinted polymer membrane [93]. Reprinted from Applied Surface Science, v. 427, Lu et al., Multilayered ion-imprinted membranes with high selectivity towards Li+ based on the synergistic effect of 12-crown-4 and polyether sulfone, 931–941, Copyright 2018, with permission from Elsevier.

Karp [95] investigated the chromatographic separation of lithium from brine with an organic sorbent as the stationary phase. The process involves the use of a Zwitterionic stationary phase and brine and freshwater as mobile phases. Lithium and other dissolved salts intercalate with the Zwitterionic group on the stationary phase and are retained on in relation to the bulk mobile phase. The rate at which a salt moves down the column depends on their Van der Waals radius, charge, and solubility [95]. Lithium was separated from other ions based on their differing affinities for the Zwitterion stationary phase [95].

2.3. Inorganic Molecular Sieve Ion-Exchange Adsorbents

Inorganic crystalline solids, including various aluminum hydroxides (AlOH), aluminum oxides (AlOx), manganese oxides (MnOx), and titanium oxides (TiOx), have been shown to be selective lithium sorbents [80]. Many of the lithium sorbents under investigation for use in direct lithium extraction from brines are used as cathode materials in lithium-ion batteries (Table 6) [56]. Dow Chemical Company first proposed using microcrystalline AlOH embedded in anion-exchange resins for the selective removal of lithium from brines [79]. Ooi, Miyai and co-workers first proposed the use of manganese oxides (MnOx) as sorbents for the recovery of lithium from seawater [96,97]. TiOx materials are used in lithium-ion batteries and their application to the recovery of lithium from brines has been proposed more recently [80,98–101]. The properties of inorganic crystalline sorbents have been scientifically investigated and efforts are underway to apply these solid sorbents in engineered systems to the selective recovery of lithium from natural and industrial fluids, including geothermal brines [102].

Table 6. Materials used for lithium-ion batteries are also used as adsorbents [56].

Component	Wt.% of the Total Weight of the Battery	Material	Structure	Properties/Merits
Cathode	39.1 ± 1.1	$LiCoO_2$	Layered	High structural stability and can be cycled >500 times with 80–90% capacity retention
		$LiMn_2O_4$	Spinel	Attractive for ecological and economic reasons; discharges ~3 V
		$LiNiO_2$	Layered	Cheaper and possesses higher energy density (15% higher by volume, 20% higher by weight), but less stable and less ordered as compared to $LiCoO_2$
		$LiFePO_4$	Olivine	Suitable for biomedical applications because of higher safety levels and lower cost
		Li_2FePO_4F	Olivine	
		$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O$	Layered/spinel	Possesses high capacity with structural and thermal stability, and safe to use
		$Li(Li_aNi_xMn_yCo_z)O_2$	Layered/spinel	
Anode		Carbon	Graphite	Low cost and availability. It has the ability to reversibly absorb and release large quantity of Li (Li:C) = 1:6
		Hard carbon	Microspheres	

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Crystalline metal structures are selective for the sorption of lithium because they have numerous cation-exchange sites that are protected inside a crystal matrix that serves as a molecular sieve. The molecular sieve selectively allows small lithium ions to access internal ion-exchange sites, whereas larger cations are excluded from internal sites. Feng and coworkers showed that the predominant reaction for the sorption of lithium by MnOx was via ion exchange, rather than oxidation-reduction (redox) reactions [103,104]. Investigations showed that the selective adsorption capacity of MnOx was due the crystalline structure acting as a molecular sieve that allowed lithium ions to enter into the crystalline lattice, but sterically hindered the entrance of other ions (e.g., [80,103–107]). A similar steric hindrance mechanism has been proposed for intercalation of lithium ions in TiOx and AlOH crystals as well (e.g., [80,99–101,108–114]).

2.3.1. Aluminum Hydroxides

Crystalline aluminum trihydroxides ($Al(OH)_3$), such as gibbsite, bayerite, and nordstrandite, can form layered intercalation matrices with lithium [108,109,115,116]. Amorphous $Al(OH)_3$ can be reacted with lithium chloride at elevated temperature to form crystalline $LiCl{\cdot}2Al(OH)_3$, which can adsorb lithium ion from lithium-containing brines [86,87]. Burba [87] showed that, under an appropriate range of initial concentrations and temperatures, crystalline hydrous aluminum oxides (AlOx) can be reacted directly with lithium salts to form crystalline lithium salt aluminates. Cations (lithium, magnesium, and transition metals) lie in the octahedral voids of the AlOH layers (Figure 11) [108,109,116]. As discussed in other sections, AlOH can be added to zeolite, resins, and other materials to make lithium sorbents [6,84–87,117–119].

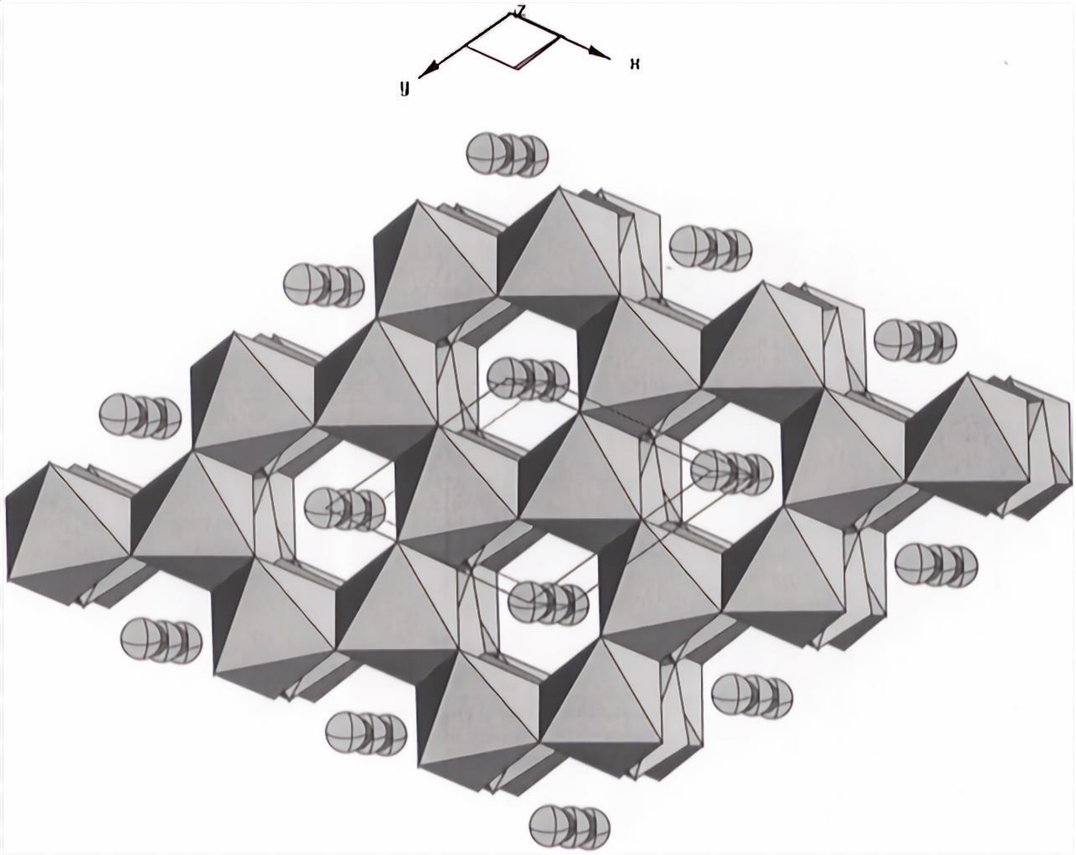


Figure 11. Schematic of an Al(OH)$_3$ layer, showing octahedral holes that allow lithium to enter [108]. Reprinted with permission from Besserguenev, A.; Fogg, A.; Francis, R.; Price, S.; O'hare, D.; Isupov, V.; Tolochko, B. Synthesis and Structure of the Gibbsite Intercalation Compounds [LiAl$_2$ (OH)$_6$] X (X = Cl, Br, NO$_3$) and [LiAl$_2$ (OH)$_6$] Cl-H$_2$O Using Synchrotron X-ray and Neutron Powder Diffraction. Chem Mater 1997, 9, 241–247. Copyright 1997 American Chemical Society.

For example, Isupov [109] showed that when aqueous lithium salts interact with gibbsite, the lithium cations penetrate between the layers from the periphery to the center of the crystal along the direction parallel to the basal planes. In this case, the lithium cations are incorporated into the voids of the interlayer space because the crystalline structure forms interlayer voids that are comparable in size to the lithium cation and considerably smaller than water molecules or other common ions [109]. This molecular sieve effect explains the non-intercalation of other metal ions into gibbsite. In the case of other salts such as NaCl, KC1, and CaC1$_2$, the Na$^+$ (R = 0.97 A), Ca^{2+} (R = 0.99 A), and K$^+$ (R = 1.3 A) cations are larger than the octahedral voids and their inclusion in the lattice would require deformation of the aluminum hydroxide layer [109]. For MgCl$_2$, which has a radius smaller than lithium, the intercalation seems to be retarded due to a considerably higher solvation energy of the Mg^{2+} cation compared to that of lithium [109]. In a similar fashion, alkali and alkaline earth cations (Na$^+$, K$^+$, Ca^{2+}, etc.), which are large relative to the octahedral voids, are not intercalated into aluminum trihydroxides [108,109]. In the intercalation process, the cations, anions, and water molecules are first incorporated into the interlayer space of aluminum hydroxide, followed by subsequent transition of lithium into the voids of the layer [109].

AlOH has been proposed for use as a lithium sorbent by a number of researchers; however, sorption capacities for AlOH sorbents are reported to be less than 8 mg/g [110,117,118,120]. One effective variant of AlOH sorbents are layered lithium-aluminum double hydroxides (Figure 12), which have been demonstrated as effective for removal of lithium for complex solutions. However, the stability of the sorbent for repeated sorption-extraction cycles may impact the practical application of this sorbent [80,114,116,120–127]. Some fundamental information, including detailed sorption isotherms, has not yet been published for AlOH sorbents [80].

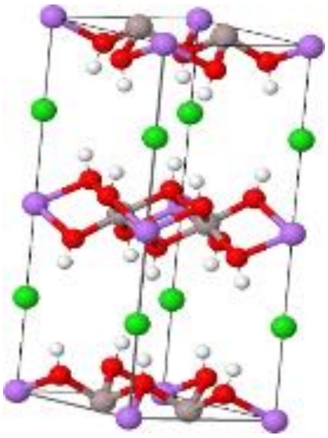


Figure 12. Crystal structure of lithium–aluminum double hydroxide (Li $Al_2(OH)_6$ Cl) [126]. Li, Al, Cl, O, and H represented as purple, gray, green, red, and white, respectively. Reproduced with permission from Wiley. Wu, L.L. et al. (2019) Lithium–aluminum-layered double hydroxide chlorides (LDH): Formation enthalpies and energetics for lithium-ion capture. J Am Ceram Soc 2019, 102, 2398–2404.

Paranthaman et al. [114] tested a layered AlOH for the treatment of geothermal brines in a bench-scale column. Brine was pumped through the column, where lithium was sorbed, and then the column was eluted in two steps, first a wash to remove ions other than lithium, then an acid treatment to recover the lithium chloride from the sorbent. The researchers reported a recovery efficiency of greater than 90%, a Li/Na selectivity ratio of ~50, and a Li/K selectivity ratio over 200 [114]. However, in some cases, aluminate-based adsorbents are reported to have lithium recoveries below 60% [128].

Simbol, Inc. developed processes and technology for the direct extraction of lithium from Salton Sea geothermal brines. The project included the development of improved aluminum-based sorbents for the extraction of lithium from geothermal brines [129,130]. The project involved developing methods for the manufacture of sorbents and their testing for sorption of lithium under a variety of conditions, mostly with synthetic geothermal brines [129,130]. Although the sorbents that were developed and tested were not described in the reports, it is likely that they are variations of AlOH sorbents, specifically a lithium aluminate intercalate [131,132]. Three variants of sorbents were discussed. Sorbent-P was a modification or improvement of a proprietary Simbol sorbent, probably a lithium aluminate intercalate [129–131]. Sorbent-S was Sorbent-P precipitated on an undefined inert substrate [129,130]. Sorbent-A was developed using a new method of synthesis and was considered a substantial advancement over prior materials, but the specific improved properties (i.e., loading capacity, physical robustness) that qualified it as improved were not reported [129,130]. Sorbent-A was manufactured in 50 kg batches (300 kg total) and used in pilot studies, discussed below [129,130]. Subsequent to this project, Simbol filed patents for a lithium aluminate intercalate stabilized in a polymer matrix [132], but it is not certain if that is the same sorbent that was used in pilot tests (discussed in applications section, below) [129,130].

AlOH sorbents have been tested for extraction of lithium from geothermal brines and are proposed for use as part of a direct lithium extraction process [133–135] (see Section 3, below). It is not certain that any company is actively marketing AlOH sorbents specifically for lithium extraction and recovery; however, DuPont advertises AmberLite™ IRN9687 Li/OH Ion-Exchange Resin for this purpose and presumably holds patents (from Dow) on resins that contain AlOH sorbent [79,82,83,85–87]. AlOH sorbents are being used for lithium extraction from salar brines in Argentina and are being tested against geothermal fluids in Europe [45,64,136]. There are numerous patents related to these sorbents (Tables 7 and 8) and AlOH products, including natural sorbents and precursor chemicals of AlOH sorbent manufacture, are available from chemical suppliers. Intellectual property developed by Simbol, Inc. and All American Lithium LLC (Table 7) are currently being marketed under the name of Terralithium, a partnership between All American Lithium and Oxy Low Carbon Ventures [137,138].

Table 7. Patents associated with Simbol Technology or S. Harrison.

Year	US Patent or Application	Inventor	Assignee	Title
2013	8,435,468	S. Harrison and R. Blanchet	Simbol, Inc.	Process for preparing highly pure lithium carbonate and other highly pure lithium-containing compounds
2013	8,574,519	S. Harrison and R. Blanchet	Simbol, Inc.	Processes for preparing highly pure lithium carbonate and other highly pure lithium-containing compounds
2013	8,454,816	S. Harrison and S. Mohanta	Simbol, Inc.	Selective recovery of manganese and zinc from geothermal brines
2013	8,518,232	S. Harrison, S. Mohanta, C. K. Sharma and E. Geler	Simbol, Inc.	Selective recovery of manganese, lead, and zinc
2013	8,597,521	S. Harrison	Simbol, Inc.	Selective removal of silica from silica containing brines
2014	2014/0239221	S. Harrison and J. Burba III	Simbol, Inc.	Treated geothermal brine compositions with reduced concentrations of silica, iron and lithium
2014	8,637,428	S. Harrison, C. K. Sharma, B. E. Viani and D. Peykova	Simbol, Inc.	Lithium extraction composition and method of preparation thereof
2014	8,741,256	S. Harrison	Simbol, Inc.	Preparation of lithium carbonate from lithium chloride containing brines
2014	2014/0239224	J. L. Burba, R. F. Stewart, B. E. Viani, S. Harrison, C. E. Vogdes and J. G. S. Lahlouh	Simbol, Inc.	Sorbent for lithium extraction
2014	8,753,594	J. L. Burba, R. F. Stewart, B. E. Viani, S. Harrison, C. E. Vogdes and J. G. S. Lahlouh	Simbol, Inc.	Sorbent for lithium extraction
2015	2015/0152309	S. Harrison and J. Burba	Simbol, Inc.	Treated geothermal brine compositions with reduced concentrations of silica, iron and lithium
2015	9,222,149	S. Harrison	Simbol, Inc.	Preparation of lithium carbonate from lithium chloride containing brines
2015	9,034,295	S. Harrison	Simbol, Inc.	Preparation of lithium carbonate from lithium chloride containing brines
2015	9,074,265	S. Harrison and R. Blanchet	Simbol, Inc.	Processes for preparing highly pure lithium carbonate and other highly pure lithium-containing compounds
2015	9,057,117	S. Harrison and S. Mohanta	Simbol, Inc.	Selective recovery of manganese and zinc from geothermal brines
2015	9,051,827	S. Harrison	Simbol, Inc.	Selective removal of silica from silica containing brines
2015	2015/171109	J. L. Burba, R. F. Stewart, B. E. Viani, S. Harrison, C. E. Vogdes and J. G. S. Lahlouh	Simbol, Inc.	Improved sorbent for lithium extraction
2016	9,238,851	S. Harrison, S. Mohanta, C. K. Sharma and E. Geler	Simbol, Inc.	Selective recovery of manganese, lead and zinc
2016	9,249,478	S. Harrison, C. K. Sharma and P.-Y. Lan	Simbol, Inc.	Selective recovery of manganese, lead and zinc

Table 7. *Cont.*

Year	US Patent or Application	Inventor	Assignee	Title
2017	9,764,318	S. Harrison, C. K. Sharma and M. S. Conley	Alger Alternative Energy, LLC	Porous activated alumina-based sorbent for lithium extraction
2017	9,644,866	S. Harrison and J. Burba	Simbol, Inc.	Treated brine compositions with reduced concentrations of potassium, rubidium, and cesium
2017	9,650,555	S. Harrison and J. Burba	Simbol, Inc.	Treated geothermal brine compositions with reduced concentrations of iron and silica
2017	9,644,126	S. Harrison and J. Burba	Simbol, Inc.	Treated geothermal brine compositions with reduced concentrations of silica, iron, and zinc
2019	10,266,915	M. P. Paranthaman, R. R. Bhave, B. A. Moyer and S. Harrison	UT-Battelle, LLC, Alger Alternative Energy, LLC	Composition for recovery of lithium from brines, and process of using said composition
2019	2019/0275473	R. R. Bhave, S. Harrison, B. A. Moyer and M. P. Paranthaman	UT-Battelle, LLC, All American Lithium LLC	Lithium extraction composite for recovery of lithium from brines, and process of using said composition
2019	10,190,030	S. Harrison and J. Burba	Alger Alternative Energy, LLC	Treated geothermal brine compositions with reduced concentrations of silica, iron and lithium
2019	10,328,424	S. Harrison, C. V. K. Sharma and M. S. Conley	All American Lithium LLC	Porous activated alumina-based sorbent for lithium extraction
2020	2020/0047124	R. R. Bhave, V. Deshmane, N. N. Linneen, S. Harrison, M. Paranthaman and B. A. Moyer	UT-Battelle, LLC, All American Lithium LLC	Forward osmosis composite membranes for concentration of lithium-containing solutions
2020	2020/0086271	S. Harrison, D. L. Howe and B. J. Dougherty	All American Lithium LLC	Processes for producing lithium compounds using forward osmosis

Table 8. Other patents or patent applications associated with the extraction of lithium from brines.

Year	US Patent or Application	Inventor	Assignee	Title
1978	4,116,858	J. M. Lee and W. C. Bauman	The Dow Chemical Company	Recovery of lithium from brines
1979	4,159,311	J. M. Lee and W. C. Bauman	The Dow Chemical Company	Recovery of lithium from brines
1980	4,221,767	J. M. Lee and W. C. Bauman	The Dow Chemical Company	Recovery of lithium from brines
1980	4,183,900	J. M. Lee and W. C. Bauman	The Dow Chemical Company	Recovery of Mg++ from brines
1981	4,271,131	P. M. Brown, S. R. Jacob and D. A. Boryta	Foote Mineral Company	Production of highly pure lithium chloride from impure brines
1981	4,261,960	D. A. Boryta	Foote Mineral Company	Removal of boron from lithium chloride brine
1982	4,347,327	J. M. Lee and W. C. Bauman	The Dow Chemical Company	Recovery of lithium from brines
1984	4,472,362	J. L. Burba	The Dow Chemical Company	Regeneration of crystalline lithium aluminates
1987	4,636,295	D. L. Ball and D. A. D. Boateng	Cominco Ltd.	Method for the recovery of lithium from solutions by electrodialysis
1987	4,684,404	G. I. Kalocsai	Kaljas Pty. Limited	Dissolution of noble metals
1989	4,879,042	D. N. Hanson and S. Lynn	Hanson and Lynn	Method of crystallizing salts from aqueous solutions
1990	4,891,130	F. Pitts	Engelhard Corporation	Process for removing metals from aluminosilicate materials

Table 8. *Cont.*

Year	US Patent or Application	Inventor	Assignee	Title
1993	5,229,003	W. P. C. Duyvesteyn	BHP Minerals International Inc., Sunnyvale, Calif.	Recovery of base materials from geothermal brines
1993	5,219,550	P. M. Brown and D. A. Boryta	Cyprus Foote Mineral Company	Production of low boron lithium carbonate from lithium-containing brine
1994	5,364,822	J. L. Carey	BP Chemicals Limited	Process for the recovery of group VIII noble metals
1995	5,389,349	W. C. Bauman and J. L. Burba	Bauman and Burba	Recovery of lithium values from brines
1997	5,599,516	W. C. Bauman and J. L. Burba	FMC Corporation	Recovery of lithium values from brines
1999	5,868,935	K. K. Sirkar, Z. Yang and A. K. Guha	New Jersey Institute of Technology	Method and apparatus for extraction and recovery of ions from solutions
1999	5,951,843	M. Itoh, Y. Inaguma and S. Iijima	NGK Spark Plug Co., Ltd.	Method and apparatus for extracting lithium by applying voltage across lithium-ion-conducting solid electrolyte
2001	6,280,693	W. C. Bauman and J. L. Burba	FMC Corporation	Composition for the recovery of lithium values from brine and process of making/using said composition
2003	2003/0231996	J.-Y. Shiu, J.-R. Lin, D.-C. Lee, Y.-M. Chen and C.-C. Liu	Industrial Technology Research Institute	Method for adsorbing lithium ions from a lithium-containing aqueous solution by a granular adsorbent
2004	2004/0074774	I.-L. Chang, Y.-L. Jiang, J.-Y. Shiu and J.-R. Lin	Industrial Technology Research Institute	Process for producing lithium concentrate from brine or seawater
2004	6,764,584	I.-L. Chang, Y.-L. Jiang, J.-Y. Shiu and J.-R. Lin	Industrial Technology Research Institute	Process for producing lithium concentrate from brine or seawater
2007	7,288,242	H. Tasaki and Y. Kajiya	Nikko Materials Co., Ltd.	Lithium-containing complex oxide and method of producing same
2007	7,217,406	K. Tsukuma and M. Kuniyoshi	Tosoh Corporation	Lithium–manganese composite oxide granular secondary particle, method for production thereof and use thereof
2010	7,713,662	M. Tabuchi, Y. Oka, T. Takeuchi and K. Tatsumi	National Institute of Advanced Industrial Science and Technology	Lithium–manganese-based composite oxide containing titanium and nickel
2010	2010/0147768	R. S. Addleman, J. T. Bays, T. G. Carter, S. A. Fontenot, G. E. Fryxell and D. W. Johnson	University of Oregon, Battelle Memorial Institute	Renewable sorbent material and method of use
2011	2011/0123427	D. A. Boryta, T. F. Kullberg and A. M. Thurston	Boryta, Kullberg and Thurston	Production of lithium compounds directly from lithium-containing brines
2012	2012/0288426	A. Rezkallah	Rezkallah	Method for separation of monovalent metals from multivalent metals
2013	8,444,744	M. Narisako, T. Yamaoka, D. Kobayashi and N. Higuchi	JX Nippon Mining and Metals Corporation	Method for separating and recovering nickel and lithium
2014	8,641,992	D. E. Galli, D. Humana, M. d. l. M. Otaiza, C. d. R. Cachagua and R. E. Santillan	ADY Resources Limited	Process for recovering lithium from a brine
2014	8,691,169	W. Perez, H. A. C. Barrientos, C. Suarez and M. Bravo	Minera Exar S.A.	Method for the production of battery-grade lithium carbonate from natural and industrial brines
2014	8,883,012	F. Boodoo, F. C. Sousa, J. A. Dale and C. M. Iesan	Purolite Corporation	Reduced fouling of reverse osmosis membranes
2014	8,795,614	U. Chon, G. C. Han, K. H. Kim, C. H. Song and K. Y. Kim	Research Institute of Industrial Science and Technology	Method for economical extraction of magnesium, boron and calcium from lithium-bearing solution
2015	9,062,385	Z. Zhongwei and L. Xuheng	Central South University	Method and device for extracting and enriching lithium

Table 8. *Cont.*

Year	US Patent or Application	Inventor	Assignee	Title
2015	9,147,918	M. Ueda	Empire Technology Development LLC	Effective recovery of lithium from lithium-ion battery waste
2015	8,945,275	C. H. Sonu, M. J. Lee, S. C. Ahan, B. K. Jeon and B. E. Kim	LS-Nikko Copper Inc.	Method for recovering valuable metals from lithium secondary battery wastes
2015	2015/0147248	H. Laitala, J. Karonen and L. Haavanlammi	Outotec (Finland) Oy	Process and equipment for producing pure lithium-containing solution (Application)
2015	9,187,804	H. Ishida and S. Asano	Sumitomo Metal Mining Co., LTD.	Lithium recovery method
2016	2016/0190573	Y.-K. Sun and S.-J. Youn	IUCF-HYU (Industry-University Cooperation Foundation Hanyang University)	Lithium composite oxide and manufacturing method therefor
2016	2016/0214869	K.-S. Chung, B.-G. Kim, T. Ryu, J. Ryu, I.-S. Park and H.-J. Hong	Korea Institute of Geoscience and Mineral Resource	Underwater holding-type lithium-recovering apparatus and method thererof
2016	9,255,011	M. Kawata, H. Tanaka, K. Mitsuhashi, R. Kawarabuki, Y. Yamamoto, K. Kamiyama, A. Moriya and N. Sakai	Nittetsu Mining co., ltd.,Toyo Engineering Corporation, Sumitomo Corporation	Method for producing lithium carbonate
2016	9,260,316	D. H. Kim, J.-Y. Kim, j. Seok, S.-M. Chung and J. H. Son	POSCO	Titanium dioxide nanoparticle, titanate, lithium titanate nanoparticle, and preparation methods thereof
2016	9,370,749	R. S. Addleman, W. Chouyyok, X. S. Li, A. D. Cinson and A. A. Gerasimenko	Battelle Memorial Institute (Richland, WA)	Porous multi-component material for the capture and separation of species of interest
2017	9,725,787	H. Laitala, J. Karonen and L. Haavanlammi	Outotec (Finland) Oy	Process and equipment for producing pure lithium-containing solution (Patent)
2017	2017/0327384	M. Privitera and C. Borgese	PreProcess, Inc.	Removal of impurities from brine
2017	9,695,060	C. Levy, S. Marlin and Y. Boussant-Roux	Saint Gobain Centre de Recherches D’Etudes Europeen	Method for the production of an LMO product
2017	9,677,152	S. Asano, H. Ishida and T. Nakai	Sumitomo Metal Mining Co., LTD.	Method for recovering lithium
2018	2018/0280831	K.-S. Chung, B.-G. Kim, T.-G. Ryu, I.-S. Park and H.-J. Hong	Korea Institute of Geoscience And Mineral Resources	Onshore lithium-recovering apparatus for lithium-ion adsorption and desorption process and lithium-recovering method using the same
2018	9,963,760	J. Hu, W. Zhang, W. Zheng, G. Chen, X. Shi, X. Yongchang, H. Lv and C. Yuan	Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences	Backflow cascade novel process for producing lithium-7 isotope
2018	10,106,437	M. T. Hernandez, M. Abu-Dalo, G. Khanna and A. Quick	Tusaar Inc.	Metal removal system
2019	2019/0314784	V. Lecocq, F. A. P. Burdet, Y. F. Oudart and G. P. A. Maillet	Eramet, IFP Energies Nouvelles	Method for producing an adsorbent material and method for extracting lithium from saline solutions using the material
2019	10,392,258	Y. J. Song	Kangwon National University University-Industry Cooperation Foundation	Method of producing high-purity lithium carbonate and barium sulfate from discarded lithium secondary batteries
2019	10,478,751	K.-S. Chung, B.-G. Kim, T.-G. Ryu, I.-S. Park and H. Hye-Jin	Korea Institute of Geoscience and Mineral Resources	Onshore lithium-recovering apparatus for lithium-ion adsorption and desorption process and lithium-recovering method using the same
2019	10,450,633	L. Lien	Lien, Larry	Recovery of lithium from an acid solution

Table 8. *Cont.*

Year	US Patent or Application	Inventor	Assignee	Title
2019	10,511,068	F. Metz	Rhodia Operations, Paris (FR)	Process for recovering an electrolyte salt
2019	10,246,341	L. Yang, F. Mi, Y. Wang, Q. Hongyu, Y. Xu, Y. Liu, G. Yalin and J. He	Xiangtan University	Method for producing lithium carbonate from low-lithium brine by separating magnesium and enriching lithium
2019	10,315,926	J. Nakano, A. Nakano and J. P. Bennett	US Department of Energy	Selective lithium recovery as lithium carbonate from natural brines
2020	2020/0299805	P. M. Mceachern, N. Wong and M. Andric	Purlucid Treatment Solutions (Canada) Inc.	Method and apparatus for the treatment of water with the recovery of metals
2020	2020/0010334	R. E. Pellenbarg and K. R. Cousins	Board of Trustees of the California State University	Octamethylcyclotetrasiloxane interacts with lithium ions
2020	2020/0306696	M. Wang, Y. Zhao, Y. Li, H. Wang and H. Yang	Qinghai Institute of Salt Lakes, Chinese Academy of Sciences	Method for separation and enrichment of lithium
2020	10,604,414 B2	J. L. Featherstone, P. J. Hanson, M. J., Garska, and C. R. Marston	EnergySource Minerals LLC	System and process for recovery of lithium from a geothermal brine
2020	2020/0189925 A1	J. L. Featherstone, P. J. Hanson, M. J., Garska, and C. R. Marston	EnergySource Minerals LLC	Process for recovery of lithium from a geothermal brine
2020	US 2020/0189924 A1	J. L. Featherstone, P. J. Hanson, M. J., Garska, and C. R. Marston	EnergySource Minerals LLC	System for recovery of lithium from a geothermal brine
2021	WO 2021/119208 A1	P.O. Saboe, R.L. Prestangen, E.M. Karp, B. Pivovar	Alliance for Sustainable Energy, LLC	Hybrid thermal–chromatographic system for simultaneous mineral purification and desalination of saline waters

2.3.2. Manganese Oxides

MnOx sorbents for lithium often consist of spinel structures consisting of cubic close-packed oxides with eight tetrahedral and four octahedral sites per formula unit [103,139]. The octahedral spaces are larger than tetrahedral spaces for these structures. MnOx porous crystals may contain MnO_6 octahedral units shared by corners or edges [128]. For the preparation of manganese oxide porous crystals, metal ions and organic ions can be used as templates to control their pore dimensions in various synthesis processes (Figure 13) [139]. Manganese oxides show ion-sieve properties and the spinel-type ion-sieves have effective pore radii of approximately 0.7 Å (Figure 14), which makes it selective for adsorption of lithium [139]. Materials that are commonly used as templates for MnOx designed for lithium adsorption include lithium and magnesium; however, other metals may be used [99,101,104,140,141].

Miyai et al. [97] investigated HMnO(Mg) for the sorption of lithium from seawater. They found that HMnO(Mg) was selective for lithium over both monovalent and divalent cations, with a selectivity sequence of $Mg < Ca < Sr < Ba < Na = K << Li$ at pH 8. The MnOx sorbents of composition HMnO(Ca), HMnO(Sr), and HMnO(Ba) had lower selectivity and capacity for lithium. The uptake of lithium was positively correlated with increasing solution pH and adsorption temperature, and reached a maximum amount of 8.5 mg/g of lithium sorbed from seawater (i.e., 8.5 mg lithium per gram HMnO(Mg)). The adsorbed lithium could easily be eluted with a dilute acid solution. The lithium adsorptive capacity gradually decreased through repeated adsorption/elution cycles so that after 4 cycles, the HMnO(Mg) showed a lithium absorptivity approximately 60% of the initial value [96,97].

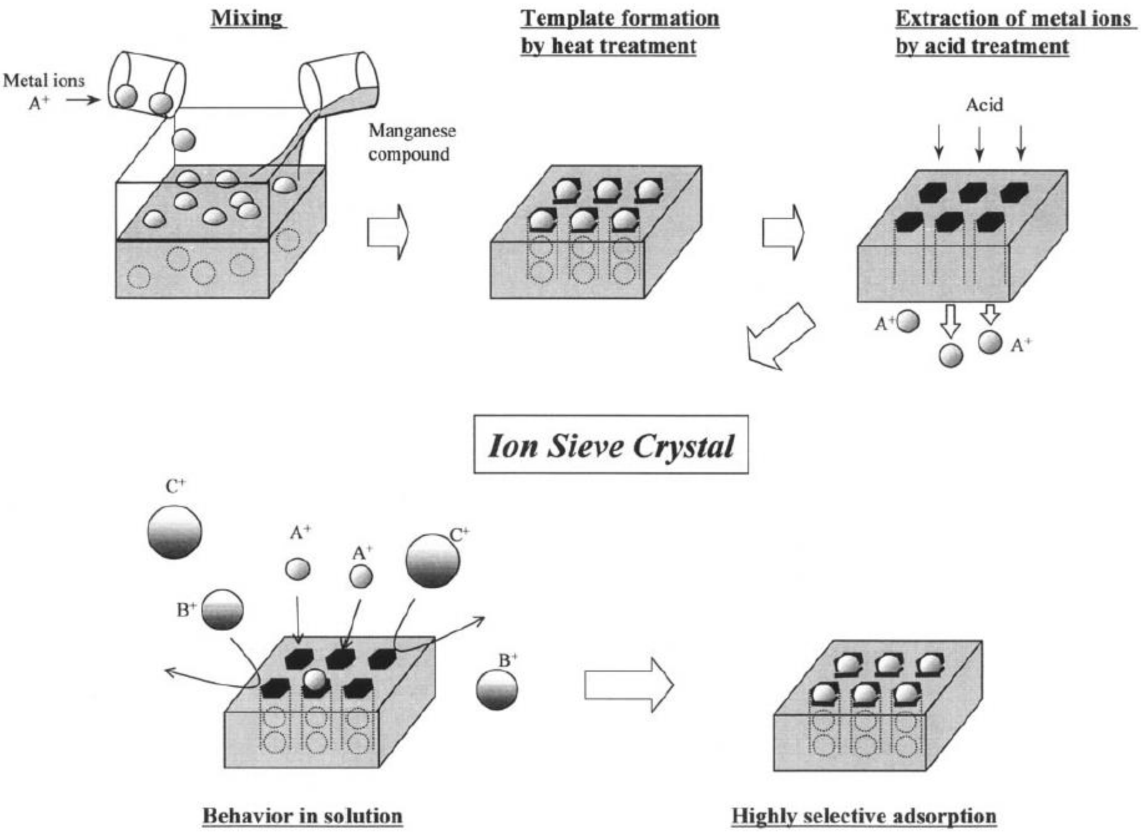


Figure 13. Schematic representation of synthesis of manganese oxide ion-sieve and ion-sieve behavior [139]. Republished with permission of the Royal Society of Chemistry, from Journal of Materials Chemistry, Manganese oxide porous crystals, Feng et al., v. 9(2), 319–333, 1999; permission conveyed through Copyright Clearance Center, Inc.

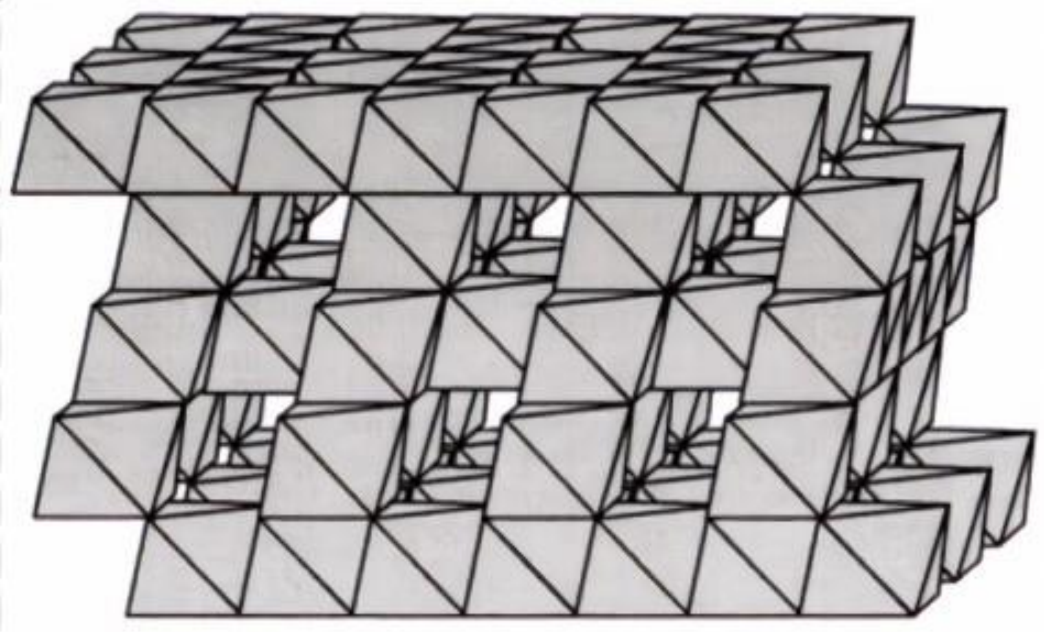


Figure 14. Structure of spinel-type manganese oxide, showing pores connecting 8a and 16c sites [139]. Republished with permission of the Royal Society of Chemistry, from Journal of Materials Chemistry, Manganese oxide porous crystals, Feng et al., v. 9(2), 319–333, 1999; permission conveyed through Copyright Clearance Center, Inc.

Recepoglu et al. [142] investigated the adsorption of lithium from geothermal water using both powdered and granulated forms of lambda-MnO_2 derived from spinel-type lithium manganese dioxide. The sorbents were tested using batch-equilibrium experiments, adsorption kinetics were measured, and intra-particle diffusion was found as the rate-controlling step [142]. Renew and Hansen [143] used a MnOx sorbent as part of a process train for the extraction of lithium from geothermal brines. Pretreatment for the removal of silica and divalent cations was considered critical to prevent coating of MnOx sorbent that would prevent lithium sorption [143].

Numerous investigations have concluded that MnOx crystals made with magnesium or lithium as the template metal (Figure 13) offer the best selectivity for lithium over monovalent and divalent cations [103,104,144–146]. Many variations of MnOx have been synthesized, characterized, and tested for lithium adsorption under a variety of conditions. Lithium sorption capacity has been improved by a number of modifications. For example, Liu et al. [107] synthesized $Li_{1.6}Mn_{1.6}O_4$, eluted Li^+ with acid, and made an ion-sieve $MnO_2 \cdot 0.5\ H_2O$ with an ion-exchange capacity of 10 mg/g at pH 10. Later formulations were made with additives and modifications that increased sorption capacity, such as spinel-type lithium antimony manganese oxides ($MnO_2 \cdot 0.10Sb_2O_5$ hydrates), formed by reacting an aqueous solution of manganese(II) and antimony(V) chlorides with lithium hydroxide, which has a reported exchange capacity of 38.9 mg/g for lithium [147]. Other variants include iron-doped MnOx with sorption capacities of 28 mg/g at pH 7.2 [148] and using tartaric acid to create spinel-structured nano-$Li_{1.33}Mn_{1.67}O_4$ with a 28.2 mg/g lithium uptake from artificial seawater that exhibits stability for at least five extraction cycles [149].

Li et al. [80] conducted a review of MnOx sorbents and identified maximum capacities of MnOx (as $Li_{1.33}Mn_{1.67}O_4$) as approximately 55 mg/g, but more typically in the range of 20 to 40 mg/g. Other studies found that raising pH to 10 increased sorption of lithium by a MnOx from approximately 6 mg to approximately 25 mg [150]. However, the actual performance of MnOx in complex solutions may be less than the experimental capacity observed in synthetic solutions. For example, Wang et al. [151] synthesized a variety of MnOx, including $LiMn_2O_4$, $Li_{1.66}Mn_{1.66}O_4$, and $Li_4Mn_5O_{12}$, and tested them for selective recovery of lithium from geothermal water. Wang et al. found that the powdery $Li_4Mn_5O_{12}$ worked best for low concentrations of lithium; however, this formulation had a maximum adsorption capacity of 8.98 mg/g when tested against actual geothermal brines [151].

Li et al. [80] concluded that MnOx ion-sieves exhibited a high ion-exchange capacity and high selectivity for lithium ions from various aqueous resources, but that the dissolution of the sorbent during the regeneration process with acid degrades the ion-exchange capacity and results in a poor cycling stability, which may limit MnOx potential for up-scaling. Stability of MnOx under acidic conditions is considered a limiting property for MnOx sorbents and alternative eluents that do not degrade the MnOx crystal structure are being investigated [152]. Industrial application of MnOx (and other inorganic sorbents) frequently focuses on improving the stability of the sorbents and using non-destructive regenerate solutions (see discussion of patents, below). At least one company (Lilac Solutions) is actively marketing MnOx sorbents and associated processes for lithium extraction from brines [153] and this product is being evaluated for application to geothermal brines [102].

2.3.3. Titanium Oxides

Crystal TiOx that have been used in batteries have also generated interest as molecular sieve/ion-exchange adsorbents for lithium [80,94,98]. TiOx spinel structures function in comparable ways to MnOx spinels, in that the pore radii of the crystal structure determine specificity and molecular sieving efficiency [101]. Shi et al. [111] demonstrated the synthesis of TiOx sorbents with a maximum capacity of 37 mg/g. Studies have demonstrated that TiOx were at least as effective as MnOx for the sorption of lithium ions from solution [80,94,99,100]. Spinel TiOx are more acid stable, potentially conferring robustness during cycling between sorption and stripping processes [80]. TiOx may have some advantages over MnOx, including being considered more environmentally friendly [80,101].

Chitrakar et al. [154] investigated the sorption of lithium ions from Salar de Uyuni (Bolivia) lake brine by layered H_2TiO_3, derived from Li_2TiO_3. They found H_2TiO_3 to have high lithium selectivity ($Li^+ \gg Na^+$, K^+, Mg^{2+}, Ca^{2+}) due to molecular sieving and an adsorptive capacity of 32.6 mg/g at pH 6.5. The sorption followed the Langmuir model, but the kinetics of sorption were slow, requiring a day to attain equilibrium at room temperature [100,154].

TiOx is still being investigated at a fundamental level in the laboratory [80,100,101] and few published studies have examined the efficacy of TiOx in complex brines [80,94]. However, processes using TiOx adsorbents for lithium extraction have been patented (Table 8), at least one company is marketing TiOx sorbents, and TiOx sorbents are being applied commercially for direct extraction of lithium from industrial brines [128,155–157]. For example, PurLucid is working in partnership with MGX Minerals and Eureka Resources to extract lithium from produced water from the Marcellus Shale in Pennsylvania and from produced waters from oil sands in Canada [157].

2.3.4. Other Metal Oxides

Activated alumina, an aluminum oxide (AlOx), has been proposed as a sorbent for lithium extraction from brines [131,132,158–164]. Harrison et al. [163] reacted porous activated alumina with lithium salts to form composite activated aluminum lithium intercalate sorbent materials. Ma et al. [165] proposed using high-alumina fly ash for lithium recovery from brines.

Snydacker et al. [166] applied high-throughput density functional theory (DFT) and specific ion interaction theory to predict a number of new lithium metal oxide compounds that seemed best suited for lithium extraction. They used the Open Quantum Materials Database and considered 77 candidate lithium metal oxide compounds that are stable or nearly stable in their lithiated states. Based on this approach, they identified compounds that thermodynamically release lithium while binding hydrogen in acid and that also release hydrogen while binding lithium in brine. They screened compounds to identify ones with selective binding of lithium relative to sodium in brine. As a result of this analysis, Snydaker et al. observed that most of these compounds either bind lithium in both acid and brine solutions or bind hydrogen in both acid and brine solutions [166]. The compounds that bind but do not release lithium are not suitable for lithium-ion exchange; however, nine compounds were identified as potential lithium extractants: $LiAlO_2$, $LiCuO_2$, Li_2MnO_3, $Li_4Mn_5O_{12}$, Li_2SnO_3, Li_4TiO_4, $Li_4Ti_5O_{12}$, $Li_7Ti_{11}O_{24}$, and Li_3VO_4. When the pH of the brine is adjusted to 10 to help drive hydrogen release, four additional compounds were found to be promising: Li_2TiO_3, $LiTiO_2$, Li_2FeO_3, and $Li_2Si_3O_7$. Four of the previously mentioned compounds were also identified as having potential for extracting lithium from seawater: Li_2MnO_3, $Li_4Mn_5O_{12}$, $Li_7Ti_{11}O_{24}$, and Li_3VO_4 [166].

2.3.5. Other Inorganic Sorbents

Other sorbents have also been proposed for lithium extraction from brines. Zeolite can be modified with AlOH and other chemicals to make lithium sorbates [117–119]. Belova [118] tested modified natural zeolites using aluminum hydroxide, hydrochloric hydroxylamine, or urotropin and found only AlOH-modified zeolite showed selectivity with regard to lithium ions. The zeolite modified with hydrochloric hydroxylamine or with urotropin was useful for sorption of boric acid from thermal brines [117,118]. Zeolites were found to be effective at removing potassium from geothermal brines; however, the zeolites had insufficient capacity and the form of potassium recovered was not valuable as fertilizer (potash), so the process was not considered economically viable [129,130].

Wisniewska et al. [119] investigated the possibility of extracting lithium from geothermal water using natural and synthetic zeolites. They found that lithium sorption was strongly pH dependent (increasing with pH). Treatment with polyacrylic acid (PAA) enhanced lithium sorption by the synthetic zeolite, but not the natural zeolite (clinoptilolite). The effect of PAA was attributed to dissociated carboxyl groups that then form polymer-metal complexes, increasing lithium-ion adsorption. However, treatment with PAA also increased sorption of sodium and divalent cations [119]. Wisniewska et al. demonstrated that the amount of adsorption on the surfaces of aluminosilicates depends on their structure (specific surface area size and porosity). The maximum recovery of lithium from geothermal water using zeolites (at pH 5.5) was approximately 50%, resulting in a sorption capacity of approximately 4.5 mg lithium per g clinoptilolite [119].

Titanium(IV) antimonate has been proposed as a cation-exchange sorbent for extracting lithium from seawater and hydrothermal brines [167,168]. Abe and coworkers [167,168] showed that the presence of ions such as potassium, calcium and magnesium interfered with the adsorption of lithium ions. However, they found that the presence of silica had no effect on the adsorption of lithium from hydrothermal water [168]. Spinel-type lithium antimony manganese oxide has also been shown to be an effective variant of MnOx for the sorption of lithium [144].

Thorium arsenate has been proposed as an adsorbent for lithium [169]. Alberti and Massucci [169] prepared crystalline $Th(HAsO_4)_2 \cdot H_2O$ by prolonged refluxing of a solution of thorium nitrate in arsenic acid. The hydrogen ion of this compound was reported to be completely exchanged by lithium ion but not by larger ions such as sodium or potassium, thus facilitating the separation of lithium from other alkali metal ions. Sorbed lithium was recovered using acid and the sorbent could be regenerated and used more than once [169].

Ho et al. [170] prepared and characterized an adsorbent based on filling the macropores of activated carbon with a tin oxide. Tin oxide, as well as hydrous tin oxide, had high selectivity for lithium and was used to separate lithium from the other alkali metals. They also tested a number of other hydrous oxides, including Al(III), Fe(III), Zr(IV), and Nb(V), but these metal oxides were not found to be effective for lithium adsorption [170].

In summary, investigations have been conducted using a wide variety of inorganic sorbents, including AlOH, MnOx, and TiOx sorbents, for direct extraction of lithium from solution [63,80,94]. Inorganic molecular sieve ion-exchange sorbents are considered promising for commercial application due to the perceived simplicity of the recovery of lithium from the sorbent and the potential of the sorbent to be reused over repeated cycles of lithium sorption and extraction [63,80,94]. MnOx and TiOx adsorbents are being actively commercialized and marketed for direct lithium extraction, but have not yet been proven for direct lithium extraction from geothermal brines [128,153,155–157]. AlOH sorbents have been tested for extraction of lithium from geothermal brines, and are being marketed for this purpose as part of a direct lithium extraction process (see Section 3, below).

2.4. Solvent Separations

Solvent extraction is a well-established technology for the separation of metals from aqueous solutions. Solvent extraction is economically used in the mining industry for the extraction and concentration of metals, particularly valuable or semi-valuable metals, such as copper and uranium [171–177]. Solvent extraction is economical for the extraction of metals from aqueous solutions due to the simplicity of the equipment and operation; however, chemical costs may be significant [172–175,177,178]. Typical hydrometallurgy processes employing solvent extraction include initial beneficiation (e.g., ammonia or acid leaching) followed by organic phase extraction [172,177,179]. It has been shown that solvent extraction techniques may be used to separate lithium quantitatively and selectively from aqueous solutions [17,53,63,180–183]. Solvent extraction techniques investigated for lithium extraction from brines fall broadly into three potentially overlapping categories: (1) crown ethers, (2) multicomponent systems consisting of an extractant, a synergistic co-extractant, and a diluent, and (3) ionic liquids [17,63,181]. Metals extracted into an organic, non-polar phase are typically recovered by use of an aqueous stripping agent, commonly an acidic solution, such as hydrochloric acid.

2.4.1. Crown Ether

Crown ethers and aza crown ethers have been shown to have selective reactivity with lithium [181]. Cation extraction by the polydentate structure of crown ether is governed by the structure (steric properties) of the ether and electrostatic interactions between cation and oxygens in the crown ether (Figure 15) [181]. Generally, cations are located in the center of crown ethers if there is a good match between ion radius and crown ether cavity size; however, a sandwich structure may be formed if the cation size is too large for the cavity size [63,181]. Crown ethers have oxygen atoms that act as a hard base and preferably binds to the lithium ion, which acts as a hard acid as per the Pearson acid–base concept [181].

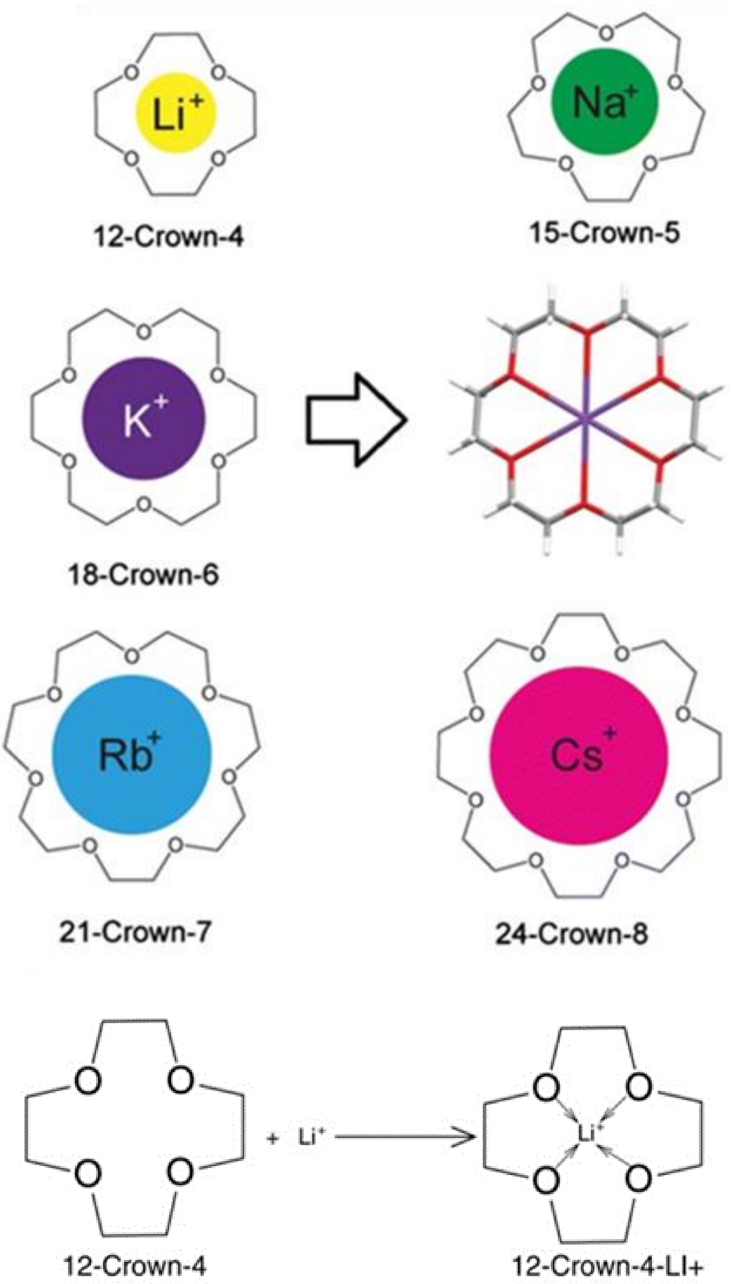
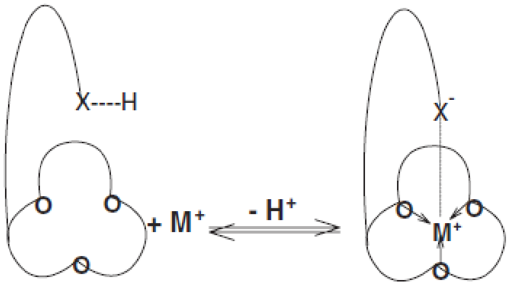


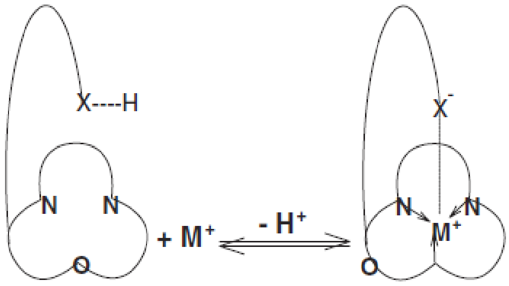
Figure 15. Structure of alkali cations with crown ether (top) and lithium complexation with crown ether (bottom) [181]. Reproduced with permission from Wiley. Swain, B. (2016), Separation and purification of lithium by solvent extraction and supported liquid membrane, analysis of their mechanism: a review. J. Chem. Technol. Biotechnol., 91: 2549–2562. https://doi.org/10.1002/jctb.4976, accessed on 1 September 2021.

Crown ethers with pendant side arms can form dynamic and three-dimensional complexes with extracted cations (Figure 16) [181]. Crown ethers with anionic ionizable pendant arms are known to form stronger complexes with cations than their neutral (but polar) counterparts [181]. Crown ethers with pendant arms form complexes with cations as shown generally in Figure 16 [181]. For both crown and aza crown ethers, there are three main groups of ionizable side arms: carboxylic acids, aromatic carboxylic acids, and phosphoric acids [181]. Neutral side arms include phenolic moieties, alcohols, and amines [17,63,181].

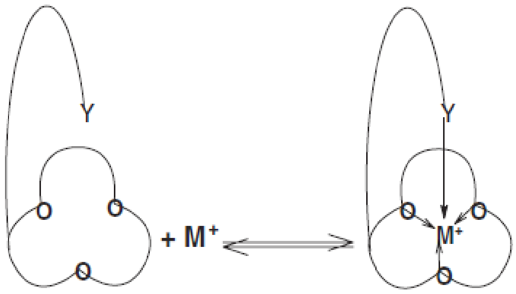
(a) Complexation of proton ionizable side chain crown ether with metal ions



(b) Complexation of proton ionizable side chain aza crown ether with metal ions



(c) Complexation of side chain crown ether with metal ions



(d) Complexation of side chain aza crown ether with metal ions

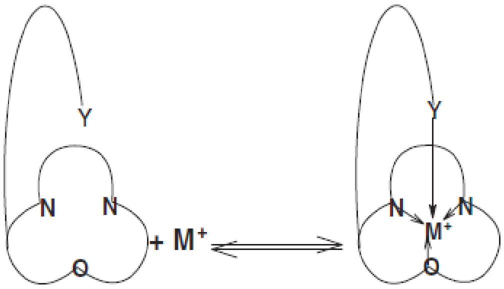


Figure 16. General mechanism of complexation of lithium by crown ether and aza crown ether with pendant side arms [181]. Reproduced with permission from Wiley. Swain, B. (2016), Separation and purification of lithium by solvent extraction and supported liquid membrane, analysis of their mechanism: a review. J. Chem. Technol. Biotechnol., 91: 2549–2562. https://doi.org/10.1002/jctb.4976, accessed on 1 September 2021.

The selectivity order for alkali metals by crown ether is dependent on the cavity size [181,184]. The bonding/extraction ability of crown ether toward lithium decreases as the crown ring size increases (Table 9 and Figure 15). Crown ethers and aza crown ethers of the structure 15-crown-5 or smaller have lithium selectivity, with 12-crown-4 and possibly 14-crown-4, with or without pendant arms, appearing to have the greatest selectivity toward lithium over competing alkali metals [17,63,181,184].

Table 9. Selectivity order of alkali metal cations with respect to various crown ethers [181,184].

Compound	Selectivity Order	Li^+/Na^+ Ratio
Benzo-12-crown-4	$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$	1.8
Benzo-14-crown-4	$Li^+ > Na^+ > K^+ > Rb^+$ (no Cs^+)	4.7
Dibenzo-14-crown-4	$Na^+ > Li^+ > K^+ > Rb^+ > Cs^+$	0.6
12-crown-4	$Li^+ > Na^+ > K^+ > Rb^+ \geq Cs^+$	1.7
13-crown-4	$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$	2.3
14-crown-4	$Li^+ >> Na^+$ (no K^+, Rb^+, Cs^+)	20
15-crown-4	$Li^+ > Na^+ > K^+ > Cs^+ > Rb^+$	3.5

Reproduced with permission from Wiley. Swain, B. (2016), Separation and purification of lithium by solvent extraction and supported liquid membrane, analysis of their mechanism: a review. J. Chem. Technol. Biotechnol., 91: 2549–2562. https://doi.org/10.1002/jctb.4976, accessed on 1 September 2021.

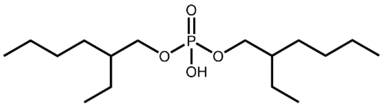
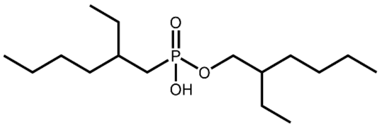
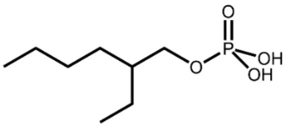
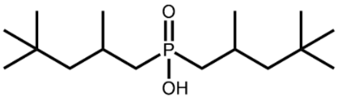
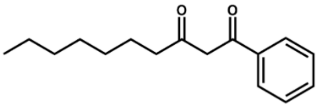
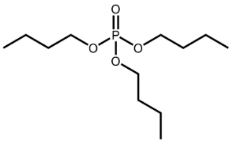
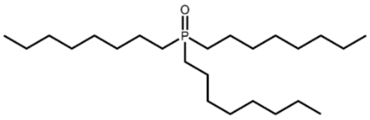
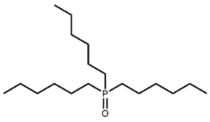
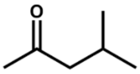
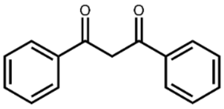
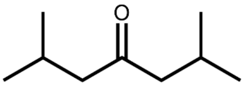
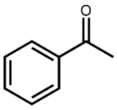
Modifications of crown ether extractions include attaching crown ethers to carbon nanotubes, and combining crown ethers with ionic liquid extraction or supercritical fluid extraction (see below) [17,63,181,185–190]. Several studies have investigated polymerized crown ethers for lithium extraction [191–196]. All of these approaches have shown some degree of success for selective extraction of lithium from simple solutions. Other ethers have also been shown to have selective chemistry with lithium [197,198].

Although crown ethers and aza crown ethers have had successful application in the laboratory, there are significant barriers to commercial application of crown ethers for extraction of lithium from geothermal brines. Crown ethers are expensive to manufacture and the selectivity of crown ethers for lithium in complex solutions has not been proven [17,63,181]. The level of pretreatment required (i.e., to remove base metals) before crown ether extraction of lithium is not known. There is a consensus that crown ethers are promising, but more research and the development of economical crown ethers for extraction of lithium are needed [17,63,181].

2.4.2. Multicomponent Solvent Systems

Organic solvent extractants applied by the mining and metallurgy industry typically contain multiple components, including an extractant (a metal chelating or binding reagent), a co-extractant (an adduct forming synergistic reagent), and a diluent (a bulk solvent). Example diluents are kerosene, xylene, and alkanes, such as dodecane [172,177,179,180,199]. Extractants include neutral species, such as ketones, beta-diketones, or ionizable species, such as organophosphates (Table 10). Extractants may have a variety of ionizable functional groups, including carboxylic acid, phosphoric acid, or amines [63,172,175,179]. A variety of organic and inorganic compounds, such tri-n-octyl phosphine oxide (TOPO) or ferric chloride, serve as synergistic adducts (see discussion below). In some cases, extractants, such as bis-2,4,4-trimethyl pentyl phosphinic acid (Cyanex 272), are used alone [177,179]. More frequently, synergistic mixtures, such as di-2-ethylhexylphosphoric acid (D2EHPA) and TOPO, are applied together to enhance selectivity or recovery efficiency [177].

Table 10. Solvents used for the extraction and recovery of lithium from brines and leachates, adapted from [63,179,200].

Extractants	CAS Number	Formula	Structural Formula
Di-(2-ethylhexyl)phosphoric acid (D2EHPA)	298-07-7	$C_{16}H_{35}O_4P$	
2-Ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A)	14802-03-0	$C_{16}H_{35}O_3P$	
Mono-2-ethylhexyl phosphoric acid (MEHPA)	1070-03-7	$C_8H_{19}O_4P$	
Bis-2,4,4-trimethyl pentyl phosphinic acid (Cyanex 272)	83411-71-6	$C_{16}H_{35}O_2P$	
1-Phenyldecane-1,3-dione (LIX 54)	68892-13-7	$C_{16}H_{22}O_2$	
Tri-n-butyl phosphate (TBP)	126-73-8	$C_{12}H_{27}O_4P$	
Tri-n-octyl phosphine oxide (TOPO)	78-50-2	$C_{24}H_{51}OP$	
Trialkyl phosphine oxides (mixture) (Cyanex 923)	100786-00-3	$C_{42}H_{90}O_2P_2$	
Methyl isobutyl ketone (MIBK)	108-10-1	$C_6H_{12}O$	
Dibenzoylmethane (DBM)	120-46-7	$C_{15}H_{12}O_2$	
2,6-Dimethyl-4-heptanone (DIBK)	108-83-8	$C_9H_{18}O$	
Acetophenone	98-86-2	C_8H_8O	

Adapted in part from Nguyen and Lee (2018) A Review on the Separation of Lithium Ion from Leach Liquors of Primary and Secondary Resources by Solvent Extraction with Commercial Extractants, Processes 6, 55; doi:10.3390/pr6050055, under Creative Commons Attribution 4.0 International Public License.

Solvent extraction was proposed for the extraction of lithium from aqueous solutions of alkali metal salts as early as 1954 [200]. Dibenzoylmethane (DBM) was identified as complexing with alkali metal ions to form chelate rings and it was shown that complex formation was more favorable for lithium (log K of ~6) than for sodium or potassium (log K $\leq$ 4) [200]. Lee et al. [180] extracted lithium from a solution of alkali metal salts using an adduct between DBM and TOPO. The resulting product had the form LiDBM·2TOPO or $Li_2(DBM)_2$·2HDBM·4TOPO, depending on the original solution composition. The chelated lithium was extracted with dodecane or p-xylene [180].

Hano et al. [53] investigated the solvent extraction of alkali and alkaline earth metals using the organophosphorus compounds D2EHPA and 2-ethylhexyl-phosphonic acid 2-ethylhexyl ester (PC88A) as extractants. Hano et al. [53] abbreviated 2-ethylhexyl-phosphonic acid 2-ethylhexyl ester as MEHPA, but this is more commonly an abbreviation for mono-2-ethylhexyl phosphoric acid (Table 10). Hano et al. [53] determined extraction equilibrium constants and composition of each metal complex in organic phase. The extractants were selective for lithium over other monovalent metal cations, but divalent metal cations had a stronger affinity than lithium. The addition of tri-n-butylphosphate (TBP) served to enhance solvent recovery of lithium. This effect was presumed to be due to the replacement of solvated extractant (D2EHPA or PC88A) by TBP. Changing the pH of the solution between 4 and 7 affected the extent of metal extraction, with a pH above 6 favoring lithium extraction. The organophosphorus solvents, with and without TBP, were used to extract lithium from geothermal waters from Japan. Lithium recovery was in the range of 50% for higher lithium waters; however, magnesium and calcium recoveries were almost 100% [53]. D2EHPA has been proposed for use in battery recycling to remove manganese, iron, aluminum, copper, and cobalt since D2EHPA is not selective for lithium in the presence of these other ions [201–204].

Other organophosphorus compounds have also been investigated for the direct extraction of lithium from solution. El-Eswed et al. [205] investigated the organophosphorus ligands phenylphosphonic, phenylphosphinic and bis(2-ethylhexyl) phosphoric acid and observed that by adding ammonia to the aqueous phase, lithium extraction increased as high as 90% with bis(2-ethylhexyl) phosphoric acid. Neutral extraction systems containing TBP, $FeCl_3$, and kerosene have been extensively investigated for lithium extraction [63,179,183,206,207]. In this solvent extraction approach, kerosene is the diluent, TBP serves as a neutral organophosphorus extractant, and $FeCl_3$ is the co-extraction reagent [63,179,183]. In the presence of excess chloride, TBP and $FeCl_3$ form $HFeCl_4$·2TBP, which will extract lithium via ion exchange to form $LiFeCl_4$·2TBP. In the extractant, lithium ion is coordinated to the oxygen atom of P=O in the TBP molecule [63]. The source of chloride influences lithium extraction, as it has been reported that $MgCl_2$ increases the recovery of lithium [63].

Organophosphorous compounds such Cyanex 272 and TBP have been tested for extraction of lithium from acid and alkaline leachate produced as part of lithium mining from ores and clays and battery recycling [179]. Several investigators reported successful extraction of lithium ion using a mixture of chelating and neutral extractants such as TBP and TOPO in kerosene [179]. However, extraction by TBP solvents does not appear to be selective.

The recovery of lithium from brines with high sodium concentrations has been studied for several extraction systems containing beta-diketone [63]. The synergism of these systems is based on the combination of beta-diketone as a chelate with a neutral solvation ligand. This process involves the displacement of protons by beta-diketone to form an ionized beta-diketone; then the ionized beta-diketone interacts with the lithium ion to form a chelating complex; finally, the complex forms an adduct with the neutral solvent [181]. Typically, the combination of beta-diketone and neutral ligand has an excellent performance for the lithium extraction and separation from alkali metal ions [63].

Pranolo et al. [208] demonstrated that commercially manufactured reagent mixtures (e.g., LIX 54) could also be used for separation of lithium from sodium in aqueous solution. They used LIX 54 and Cyanex 923 in ShellSol D70 diluent for lithium extraction with an efficiency of approximately 97% at pH 11 and a lithium to sodium separation factor of 1560 [208]. Lithium recovery was achieved with a 0.5 M HCl strip solution [208]. Other commercial extractants, such as D2EHPA, Cyanex 272, trioctylamine (TOA), diethylhexyl phosphoric acid (DEHPA) or 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A), are used in lithium-ion battery recycling for separating cobalt, copper, and lithium [17].

Solvent extraction has been extensively investigated for lithium-ion battery recycling. For example, Zhang et al. [209] used a beta-diketone extraction system composed of benzoyltrifluoroacetone (HBTA), TOPO and kerosene to recover lithium from spent lithium batteries. A three-stage countercurrent extraction process resulted in more than 90% of lithium being extracted by the organic phase. To remove non-target sodium, the lithium-loaded organic phase is eluted by dilute HCl solution, and then lithium is stripped by 6 M HCl to obtain a 4 M lithium solution [209]. Either lithium carbonate or lithium chloride can be prepared from the lithium-rich solution obtained from the process. The stripped organic phase was recycled and no "crud" or emulsification was observed during the process [209]. FT-IR spectroscopy was used to investigate the extraction mechanism of HBTA-TOPO. The thermodynamic study revealed lithium extraction is exothermic and that lower temperature favors lithium extraction [209].

Narisako et al. [210] proposed using alkyl phosphonate for solvent extraction of lithium for battery recycling. The method focused on co-extracting nickel and lithium using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester at a pH of 8.0 to 8.5 in a three-stage process where nickel and lithium are co-extracted into the organic phase. Other solvents that have been applied for the extraction of lithium include a variety of substituted nitrogen-heterocyclic analogues of phenanthrene (i.e., substituted benzo[h]quinolone) [211]. Additionally, isopropanol is used in the purification of precipitated lithium chloride [61].

2.4.3. Cyclic Siloxane

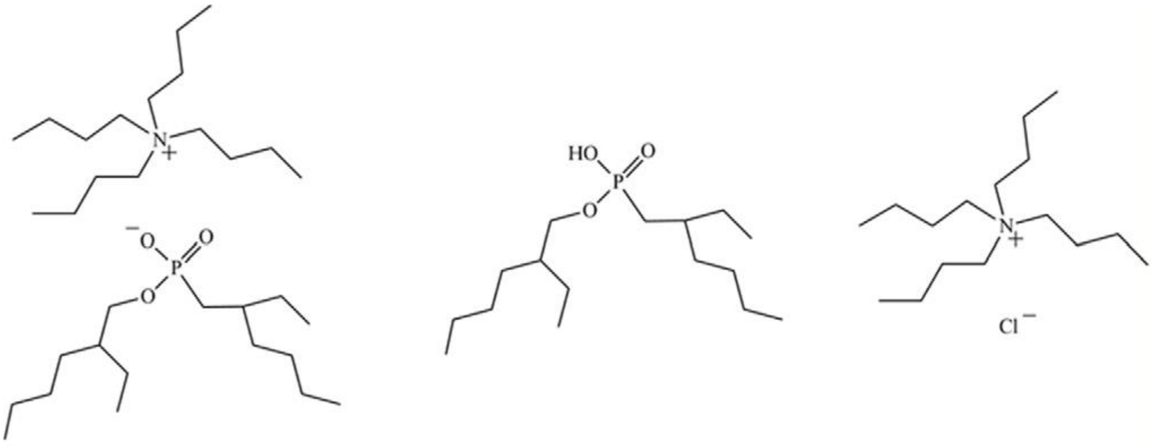
Ueda [212] used cyclic siloxane to remove and concentrate lithium ions as cyclic siloxane–lithium-ion complexes. The cyclic siloxane–lithium-ion complexes are extracted using liquid–liquid extraction and then recovered from the organic phase by filtering. Cyclic siloxanes are reported to form strong complexes with lithium ions with high selectivity. The cyclic siloxanes are selective for lithium ions, even though the equilibrium constant of the complex-forming reaction is moderate. Cyclic siloxanes are highly hydrophobic and can be effective in extracting lithium from water into organic solvents [212].

2.4.4. Ionic Liquids

Ionic liquids have been investigated for use in metal extraction from aqueous fluids, including extraction of lithium [17,63,181,185]. Ionic liquids have also been studied for the separation of lithium isotopes (^{6}Li/^{7}Li) [63,181,213]. Low-temperature or room-temperature ionic liquids, discussed here, are non-aqueous phase systems with anionic and cationic components that are liquid below 100 °C [185]. Ionic liquids can serve as the diluent, but may also have properties as an extractant or a co-extractant (Figures 17 and 18). Ionic liquids are of interest for metal extraction due to their unique physical properties and the possibility to choose numerous possible ligands as the anionic component [185]. Control of the speciation and thus chemical properties of the ionic liquid permits the attainment of extremely high activities of the ligands [185]. Room-temperature ionic liquids have attractive physical properties, including being non-volatile, non-combustible, of adjustable viscosity, and high thermal stability [63]. Ionic liquids have been investigated as replacements for traditional volatile organic solvents and as novel alternatives to more traditional extractants [63,185].

Shi and co-workers investigated imidazole ionic liquids as novel lithium extraction agents and as diluents in conjunction with reagents such as TBP [63,214–219]. They used the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate with TBP to extract lithium from salt lake brine [214]. This mechanism is a cation-exchange process resulting in the formation of $[Li\cdot 2TBP]^+$ in the ionic liquid system; however, the ionic liquid was not only the solvent, but also played the role of a synergistic reagent [63,214,215]. The extraction efficiency of lithium under optimal conditions was over 90% and lithium was effectively separated from magnesium [216,217]. These imidazole ionic liquids were also shown to have properties for the direct extraction of lithium ions, even in the absence of TBP [218,219]. Several ionic liquids have been investigated with varying results. For example, n-butyl pyridinium bis((trifluoromethyl)sulfonyl)imide was shown to have higher extraction efficiency for lithium, whereas tributylmethylammomium bis((trifluoromethyl)sulfonyl)imide had lower extraction efficiency, but superior properties for separating lithium from other cations [220].

Shi et al. [219] synthesized and tested tetrabutylammonium 2-ethylhexyl hydrogen-2-ethylhexylphosphonate for the extraction of lithium ion from aqueous solution (Figure 17) and found it effective for the separation of lithium from other alkali metals (Figure 19), but the ability of this ionic liquid to separate lithium from alkaline earth metals or other cations was not investigated [219]. The quantitative stripping of lithium ions from the loaded ionic liquid phase was carried out and the effect of hydrochloric acid concentration on stripping rate was investigated in detail [219].



$[N_{4444}][EHEHP]$ HEHEHP $[N_{4444}][Cl]$

Figure 17. Chemical structures of ionic liquids [219]. Reprinted from Journal of Molecular Liquids, v. 304, Shi et al., Solvent extraction of lithium from aqueous solution using an ammonium ionic liquid, 112756, Copyright 2020, with permission from Elsevier.

Zhou et al. [183] used the ionic liquid diethyl succinate to extract lithium from simulated salt lake brines with high Mg/Li ratios. In this study, diethyl succinate was used as a diluent, TBP acted as the extractant, and $FeCl_3$ was the co-extractant. The highest one-stage extraction efficiency of lithium was approximately 65%, with a maximum separation factor of 350. HCl + $MgCl_2$ and HCl + NaCl were used as washing and stripping agents, respectively. The effects of washing and stripping conditions on extraction and separation performance were also studied. $Mg(OH)_2$ and $MgCO_3$ were used as regeneration agents for the organic phase. The extraction efficiency of lithium ions remained at approximately 53% while reusing the organic phase ten times, demonstrating that the proposed extraction system could be recycled [183].

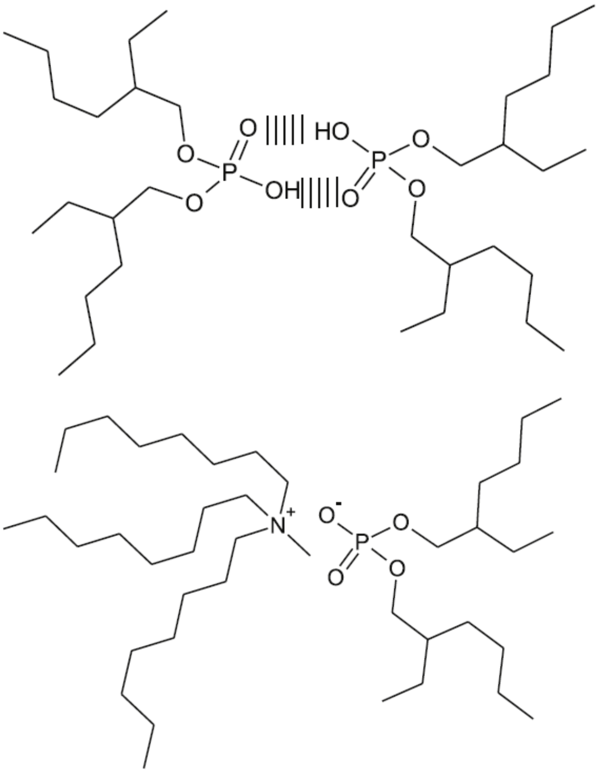


Figure 18. Ionic liquid extractant with co-extractant. Dimeric structure of DEHPA in solution (top) and mixture of DEHPA and Aliquat (bottom) [221]. Reprinted from Applied Geochemistry, v. 123, Zante et al., Solvent extraction of lithium from simulated shale gas produced water with a bifunctional ionic liquid, 104783, Copyright 2020, with permission from Elsevier.

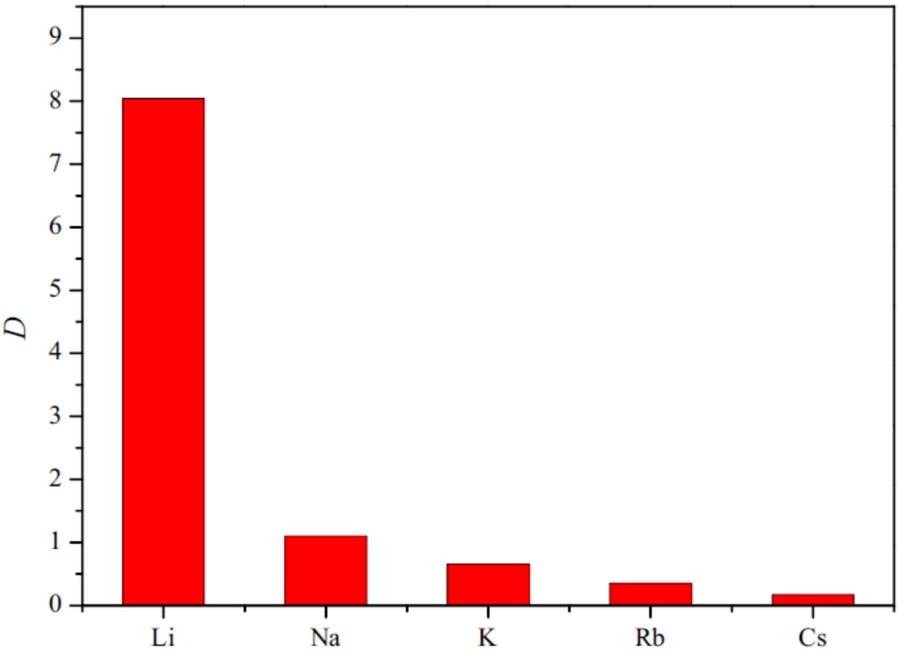


Figure 19. Selection of lithium over other alkali metal ions using an ionic liquid as the extractant and dichloromethane as the solvent [219]. The concentration factor “D” shows selectivity for lithium. Reprinted from Journal of Molecular Liquids, v. 304, Shi et al., Solvent extraction of lithium from aqueous solution using an ammonium ionic liquid, 112756, Copyright 2020, with permission from Elsevier.

Zante et al. [221] investigated the extraction of lithium from brines using the ionic liquid methyltrioctylammonium chloride (Aliquat-336) and the extractant DEHPA (Figure 18), dissolved in n-dodecane. These investigators targeted the extraction of lithium from produced waters from oil and gas wells and selected these reagents due to their commercial availability and relatively lower costs [221]. Lithium extraction was optimized by varying mixing time, aqueous phase acidity, ionic liquid concentration in the solvent phase, and aqueous lithium concentration. Stripping was accomplished with 0.5 molar HCl. A two-stage approach was developed to recover lithium from synthetic brine. In the first stage, divalent metals are removed using five successive cycles of extraction with 1 M DEHPA dissolved in n-dodecane. The second step employed a 1 M mixture of Aliquat-336 and DEHPA to remove 83% of the dissolved lithium in one cycle. This result was reported to be superior to other methods using other extractant combinations [221].

Although ionic liquids show promise for use in the selective extraction of lithium from geothermal brines, their application may be problematic. [185]. Loss of the ionic liquids into the extracted solution is a common problem [63]. When using ionic liquids as synergistic extraction agents, it was established that diluent losses were less with more hydrophobic ionic liquids, but that more hydrophobic liquids did not engage in the cation-exchange process as efficiently [63,209]. The extraction systems containing TBP as the extractant with imidazole ionic liquids as co-extractants and diluents appeared to suffer less dissolution loss than solutions without TBP [63,215,220]. Physical properties (such as viscosity) and solubilities with water will limit the choice of ionic liquids that can be used [185]. The high cost of these solvents also suggests that ionic liquids are better suited to small volume applications for extraction of high value metals [185]. However, the prospect of concentrating metals from large volumes of dilute aqueous solution into small volumes of ionic liquids is promising and interest in lithium extraction using these materials is an active area of research [63,183,185,222].

2.4.5. Modification of Solvent Extraction: Supported Liquid Membranes and Other Surfaces

Supported liquid membranes (SLM) are a variant of multicomponent solvent systems [223–225]. In SLM, a porous polymer support membrane holds a solution of the extractant mixture in its pores. SLM can be made with flat or hollow-fiber membranes. Modification of this idea include bulk liquid membranes, where a flat membrane separates a solvent phase from the aqueous phase, and emulsion liquid membranes, where surfactants are added to form emulsions that can be separated by a membrane [223]. Other modifications on solvent extraction include impregnation of resins or solid supports with extractants or extractant mixtures [68,202].

The SLM is formed by impregnating the pores of a thin, porous, polymeric membrane, such as those used in ultrafiltration, with an extractant in a diluent [223–225]. The stability of the liquid phase membrane is provided by capillary or surface forces between the support and the extractant mixture [223]. The impregnated membrane acts as a common interface between the feed and strip solutions, which are kept in compartments on the two sides of the membrane, thus aiding in selective transport of the diffusing species of interest through the membrane [223].

Ma and Chen [226] used the SLM technique to extract lithium from geothermal water. A mixture of extractants consisting of LIX 54 and TOPO were immobilized in a Celgard® 2500 membrane having 37–48% porosity. LIX 54, a mixture containing α-acetyl-m-dodecylacetophenone as a primary ingredient, is commonly used for extraction of copper from ammonia leaching solutions [226,227]. This SLM achieved 95% extraction of lithium in just 2 h; however, it exhibited stable performance for only up to 63 h before the flux dropped drastically [226]. The markedly decreased performance was attributed to the pressure difference over the membrane sheet, the solubility of the liquid membrane in the adjacent solutions, and emulsion of the liquid membrane into the aqueous solutions [80,226]. Using an SLM composed of LIX 54 and TOPO in kerosene, Bansal et al. [228] developed a mathematical transport model based on fundamental mass transfer and kinetics mechanisms that account for transport resistances for the extraction of lithium from dilute synthetic solution and geothermal water. The model is solved numerically and is used to investigate the effect of various extraction conditions and membrane support characteristics. Reasonable agreement is found between the experimental results reported in the literature and the model simulations [228].

Paredes and de San Miguel [229] proposed using a polymer inclusion membrane consisting of cellulose triacetate (CTA) treated with LIX-54-100 and Cyanex 923 to extract lithium from seawater. The membrane-mediated system is reported to selectively transport lithium against its concentration gradient due to a coupled hydrogen ion counter-transport reaction [229]. The membrane was reused up to 10 times before the separation efficiency dropped by 40% [229].

Stability of the liquid membrane is a common problem for SLM [181,199,230]. For example, Zante et al. [199] demonstrated the application of a SLM with high selectivity for separating lithium from sodium. Tests conducted using this synergistic extraction system, consisting of heptafluoro-dimethyloctanedione (HFDOD) and TOPO diluted in dodecane, indicated an extraction efficiency greater than 99% and a separation factor of over 400 for selectivity of lithium over sodium [199]. Experimental parameters that were studied included the initial lithium concentration, the Na/Li ratio, and the HFDOD to TOPO ratio in the SLM. Zante et al. found that high lithium permeation rates can be obtained even for low lithium concentrations and high sodium concentrations [199]. However, the membrane stability was found to be poor and there was significant loss of performances after just one cycle of use [199]. The organic phase leaked out of the SLM and the HFDOD to TOPO ratio was changed as the solvents dissolved into the aqueous phases [199]. Despite these drawbacks, the authors concluded that this SLM system showed promise for the extraction of lithium from solutions such as brines and seawater [199].

Sharma et al. [231] investigated the extraction of lithium from synthetically prepared seawater using D2EHPA and TBP as organic extractants in a hollow-fiber membrane. Synergistic effects were observed between D2EHPA and TBP. The equilibrium constant values for lithium, sodium and potassium ions were found to be 95.4×10^{-5} m^3/kmol, 4.6×10^{-5} m^3/kmol and 3.69×10^{-5} m^3/kmol, respectively. Hollow-fiber SLM experiments with low concentrations of lithium, sodium and potassium ions in the feed phase showed a higher flux for lithium ions than experiments conducted with higher concentrations of sodium and potassium [231]. Sharma et al. reported that model predictions were in good agreement with the experimental data [231].

Sirkar et al. [232] developed SLM using D2EHPA, anti-2-hydroxy-5-nonylacetophenone oxime (LIX 84), and TOA in a hollow-fiber configuration. Various combinations of these extractants in the SLM were effective for the extraction of copper, chromium, and zinc [232]. These and other results suggest that SLM or solvent systems made with extractants such as D2EHPA may also extract other metals as well as lithium, indicating post-extraction purification may be needed for geothermal lithium extracted using these reagents.

Song et al. [230] developed a lithium ion-selective membrane that was used with solvent extraction to concentrate lithium from a synthetic solution. They created a nanoporous ion-exchange membrane by blending polyether-sulfone (PES) with sulfonated poly-phenyl-ether ketone (SPPESK) that was utilized as the stabilizing barrier for SLM extraction. Song et al. [230] noted that the ratio between PES and SPPESK influenced membrane performance, and reported that at a PES/SPPESK ratio of 6/4 and a polymer concentration of 30% by weight, the membrane had a lithium-ion flux of 1.67×10^{-8} mol cm^{-2} s^{-1} at a lithium-ion feed concentration of 0.13 mol/L [230]. TBP in kerosene was used as the extractant and the membrane was noted for maintaining stability and function even after 50 days of solvent contact [230]. Based on these promising results, Song et al. predicted that the SPPESK/PES membrane for solvent extraction could be developed for lithium mining from brine and seawater in the near future [230].

2.4.6. Modification of Solvent Extraction: Supercritical Carbon Dioxide

Crown ethers have been used with supercritical carbon dioxide (CO_2) as a diluent [187,189,190]. Supercritical CO_2 is viewed as an attractive solvent because it allows extraction to be conducted at elevated temperature and pressure, thus reducing potential scaling problems that occur with geothermal brines [189,190]. The crown ethers methylene-14-crown-4 (M14C4) and fluorinated 14-crown-4 (F14C4) (Figure 20) were investigated extensivly for use with supercritical CO_2, with and without the synergistic extractant di(2-ethylhexyl) phosphoric acid (HDEHP) (Figure 20) [187,189,190]. In addition, Ruttinger et al. [187] experimented with tetraethylammonium perfluoro-1-octanesulfonate (TPFOS), based on its solubility in supercritical CO_2.

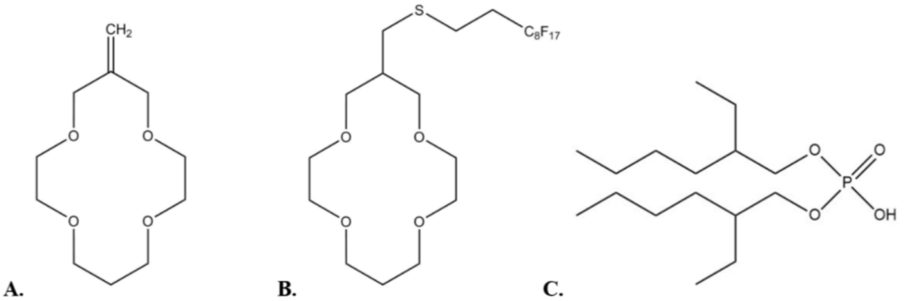


Figure 20. Crown ether and organophosphate extractants used with supercritical carbon dioxide as the solvent ((**A**). methylene-14-crown-4 (M14C4), (**B**). fluorinated 14-crown-4 (F14C4), (**C**). HDEHP [189,190]. Reprinted (adapted) with permission from Pálsdóttir, A. et al. Characterization of 14-Crown-4 Ethers for the Extraction of Lithium from Natural Brines: Synthesis, Solubility Measurements in Supercritical Carbon Dioxide, and Thermodynamic Modeling. Ind. Eng. Chem. Res. **2021**, 60, 7926–7934. Copyright 2021 American Chemical Society.

Pálsdóttir et al. [190] measured the solubility of crown ethers in supercritical CO_2 and found that M14C4 was more soluble than F14C4 at 60 °C and 205 bar, but that both crown ethers had order of magnitude higher solubilities than other crown ethers. These extractants were tested for lithium extraction from a synthetic geothermal brine with some success [189,190]. Ruttinger et al. [187] tested the extraction efficiency of supercritical carbon dioxide, cation exchangers, and 14-crown-4 ethers against a solution of 100 ppm lithium and 2300 ppm sodium, with a 50-fold excess of exchanger relative to the lithium concentration. For cation exchangers, they used both TPFOS and HDEHP. Molecular dynamics modeling was used to understand the mechanism of binding between lithium and combinations of 14-crown-4 ethers and cation exchangers [187]. Ruttinger et al. [187] reported good agreement between supercritical carbon dioxide extraction experiments conducted at 60 °C and 250 bar and corresponding computational predictions. Differences in the binding free energies of sodium and lithium to crown ethers determine the extraction selectivity and fluorine groups had a positive influence on optimizing extraction efficiency. $F_{14}C_4$ with TPFOS was determined to be a selective and efficient extraction system [187,189,190]. Chemical characteristics that were considered important for design of effective lithium extractants were (1) a fluorinated tail, (2) a sulfonic acid group, and (3) a proton as the cation that participates in the ion-exchange process [190]. The hypothesis that the addition of fluorinated groups to the crown ether or cation exchanger increases the binding free energy and, consequently, the extraction efficiency of the system was supported by results of the molecular dynamics modeling simulations and the experiments [187].

In summary, it can be concluded that ketone, beta-diketone and organophosphorus compounds have not been shown to be sufficiently selective for lithium to be practical for application to geothermal waters. However, these compounds are useful in pretreatment of lithium brines and leachates before lithium recovery, particularly for the removal of divalent cations and interfering or valuable metals. Solvent extraction steps are also likely to be important components of commercial geothermal lithium extraction processes. Other solvents, such as crown ethers and cyclic siloxanes, have been shown to have selective reactivity with lithium and appear promising in the laboratory, but are still in the early phases of development (i.e., are low TRL).

2.5. Membrane Separations Technology

Research on membrane separations in the context of direct lithium extraction include research on membranes that are specifically selective for allowing passage of lithium preferentially; less selective nanofiltration membranes that allow permeation of smaller monovalent ions, including lithium, but reject larger divalent ions; and membrane processes that remove water for concentration of all salts, including lithium [233–243]. Research on membranes that are designed to retain lithium by adsorption while allowing other ions to pass (e.g., [93]) is discussed in Section 2.3.

Principles governing the function and design of membranes that allow selective lithium permeation have recently been reviewed and described [233,235]. Major factors governing the selectivity of ion channels for lithium include the size of the nanochannel relative to the hydrated and bare lithium-ion radius, the surface charge of the channel, and the morphology of the channel [235]. Lithium-selective membranes are still under fundamental investigation and have not been proposed for use to extract lithium from geothermal brines.

Reverse osmosis (RO) and processes such as pervaporation can be used to concentrate lithium-containing brines [236,237]. RO serves the same function as evaporation or distillation in lithium processing (i.e., water removal), to concentrate brines before precipitation or other concentration steps. RO is not selective for lithium or any salt. In most cases, RO and other energy-intensive water removal processes are proposed as improvements over time-consuming evaporation in ponds [236,238]. It is not apparent that RO will ever be economical to apply directly to geothermal brines, due to the high concentrations and complexity of salts in these brines, but water concentration processes are likely be used in the subsequent purification of geothermally derived lithium chloride solutions (see Section 3, below).

As part of lithium recovery processes, membranes are often used or proposed for use to treat brines for the removal of divalent cations, metals, and other interfering substances before the process of concentrating, precipitating or otherwise extracting lithium [63,233,234]. Rejection of other ions (i.e., not allowing them to pass the membrane) occurs via size exclusion, membrane surface charge, or other chemical and physical properties [233]. Nanofiltration has been investigated extensively for the separation of lithium from magnesium and other interfering divalent cations [140,182,236,238–243]. For example, Wen et al. [239] used a spiral-wound Desal-5 DL 2540C membrane (GE Osmonics), which showed a 61–67% retention of the Mg^{2+}, while Li^{+} passed through the membrane, giving a Li^{+}/Mg^{2+} separation factor of 3.5. In similar studies, commercial membranes designed for desalination were tested against lithium brines [236,239,242]. For example, the Desal-DK membrane (GE Osmonics) showed a Li^{+}/ Mg^{2+} separation factor ranging between 2 and 3.2 depending upon the feed Li^{+} and Mg^{2+} concentrations and their ratio [236]. Other experiments include modification of membrane surfaces to change surface charge and other properties [182]. Variants on nanofiltration include hollow-fiber configurations [182,233]. Hollow-fiber filters have advantages over a flat-sheet configuration in that the hollow fibers have a high packing density, lower energy and maintenance costs, and are easier to fabricate [182]. The rejection order of this composite hollow-fiber membrane was magnesium chloride ($MgCl_2$) > magnesium sulfate ($MgSO_4$) > NaCl $\geq$ LiCl [182,233]. Because commercially available nanofiltration membranes have been used for the separation of divalent cations from lithium, it is likely that nanofiltration will be incorporated into some process for the commercial separation of lithium from geothermal brines [133–135,143,157,238,244].

Because geothermal brines are typically extracted at high temperatures, thermally robust membranes are required. Preliminary results reported by Li et al. [182] showed the potential of thermostable membranes to obtain a high lithium separation factor with nearly complete rejection of other monovalent and divalent cations in the brine solution.

In summary, while there are many published reports on membrane-based separation processes for lithium extraction, the technology is frequently being tested at the laboratory scale and is focused on pretreatment and the production of cleaner brines, rather than increasing the lithium concentration in the brine.

2.6. Electrochemical Separation

Electrodialysis is a membrane separation process that uses an electric field to aid the movement of ions across a semipermeable membrane. Electrodialysis is separate from the process of electrowinning, which is a metal extraction process that, to our knowledge, is not applied to lithium [34,173,245]. Electrodialysis for lithium extraction is dependent on the use of a lithium-selective membrane and has process components, such as anodes and cathodes, which are similar or analogous to technology in lithium-ion batteries [233,246,247]. Electrodialysis for lithium extraction can be used with SLM and potentially other modifications of solvent extraction technology [248,249]. Electrodialysis for lithium extraction can include the coating or construction of anodes or cathodes with metal oxides or other molecular sieve or lithium sorbent materials, which also has parallels with battery applications [243,250–254].

Ball and Boateng [246] used electrodialysis to separate lithium from multivalent cations, with a focus on magnesium. They treated brine containing a range of lithium concentrations (0.03 to 15 g/L) and ratios of magnesium to lithium as high as 60 to 1 using one or more electrodialysis cycles. In some cases, magnesium was also removed by lime precipitation. Membranes composed of styrene divinyl-benzene copolymer on a PVC base were functionalized with strong acidic groups such as sulphonic acid and trimethylamine derivatives. Electrodialysis is carried out at a pH below 7 with mixing. The number of electrodialysis steps needed for purification depends on the permeation selectivity of the membranes, the magnesium to lithium ratio in the feed, and the magnesium to lithium ratio in the concentrate [246].

Itoh et al. [255] proposed an electrodialysis method using a lithium-selective partition composed of TiOx crystals that would allow the selective passage of lithium. The system was composed of the TiOx partition, a perovskite-type lithium-ion-conducting solid electrolyte, a feed chamber for the lithium-containing brine, and a recovery chamber. A positive charge is applied to the feed side and a negative charge to the recovery side, which is filled with a simple salt or other conducting fluids [255].

Chang et al. [256] proposed combining adsorption and electrodialysis to enrich lithium ions in brine from a level of several ppm to approximately 1.5%. In an initial step, the brine is extracted with an adsorbent, so that the lithium content is increased to approximately 1200–1500 ppm. The lithium is recovered from the sorbent and purified by two stages of electrodialysis in series. Two stages of electrodialysis are required to reach concentrations of 1.5% [256].

Zhongwei and Xuheng [243] proposed using electrodialysis to separate lithium from manganese using an anion-exchange membrane and a cathode coated with an ion-sieve in the brine chamber. Ion-sieves were made of iron phosphate, manganese oxide, or various ratios of lithium, iron, manganese, and phosphate [243]. The electrolyte solutions were common salts. In one case, a composite membrane of MnO_2 was used as the ion-sieve cathode in a brine chamber containing lithium and manganese-rich salt lake brine and a graphite electrode was placed in the salt chamber as an anode. In this experiment, a voltage of 1.2 V was applied to the two electrodes at 5 °C for 12 h. The lithium-ion concentration in the brine chamber was reduced from 500 mg/L to 286 mg/L, the Mg^{2+} concentration was largely unchanged at approximately 1800 mg/L, and the MnO_2 ion-sieve had a lithium adsorption of 21.4 mg/g and a magnesium adsorption of only 1.8 mg/g [243]. In another case, a lithium iron phosphate ion-sieve was used as the anode in the salt chamber, and the iron phosphate ion-sieve was used as the cathode in the brine chamber. After electrodialysis, a lithium concentration of the brine chamber was reduced to 442.3 mg/L (from 500 mg/L), and the lithium concentration in the salt chamber was 57.8 mg/L [243].

Mroczek et al. [54] applied electrodialysis to geothermal brines from the Wairakei (NZ) geothermal power station (Figure 21). The geothermal fluid was first desilicated using electrocoagulation with aluminum electrodes and then lithium was extracted with electrodialysis. The influence of voltage, current, fluid temperature, and acidification on lithium extraction was measured in a laboratory electrodialysis unit [54]. Acid dosing was found to be essential to the electrodialysis process due to the alkalinity of the desilicated geothermal brine. The greatest extraction rates were obtained at a pH of approximately 2–4, and the highest extraction rate achieved was 0.28 mg/h·cm^2 using an active membrane with a three-membrane stack. Increased current increased the extraction rate, but had a negative effect on membrane lifetime [54].

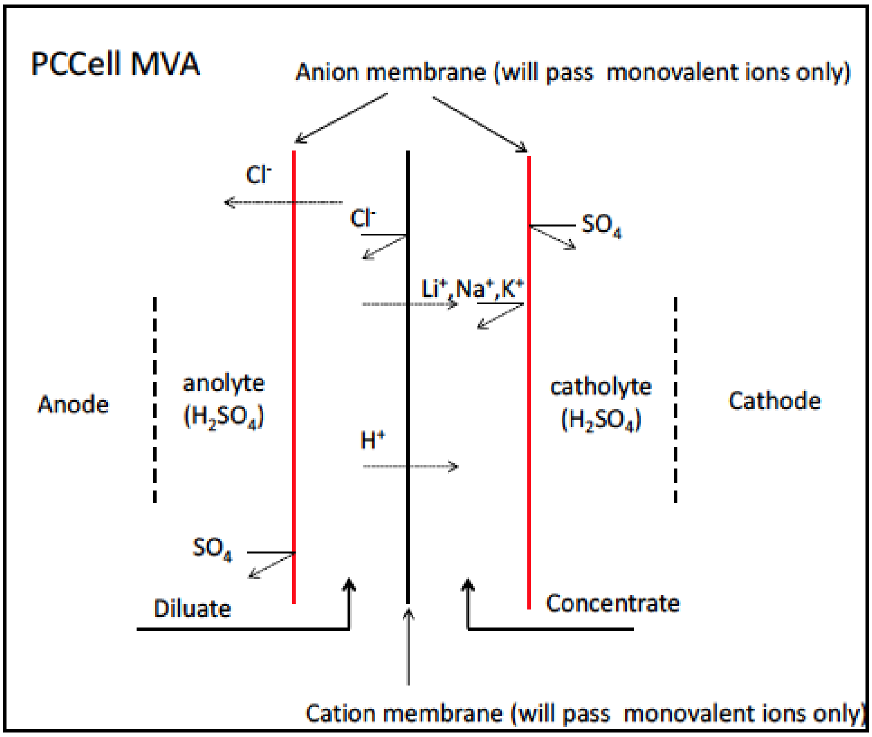


Figure 21. Schematic of an idealized electrodialysis (electrochemical) separation process [54].

Selective electrodialysis in the context of lithium extraction from water has been recently reviewed [234,257]. The extraction of lithium ion from salt lake brines can be achieved by electrodialysis using commercially available anion-exchange membranes (e.g., MA-7500 from Sybron and American Ionac) and lithium iron phosphate ($LiFePO_4$) and iron(III) phosphate ($FePO_4$) electrodes. Parameters such as pH and salt content influenced lithium extraction and lithium concentrations as high as 38.9 mg/g could be achieved [234,257]. The applied voltage, feed velocity, feed Li^+:Mg^{2+} ratio and pH all impacted the Li^+/Mg^{2+} separation factor [234,257]. In some cases, lithium recoveries over 95% were achieved and the Mg^{2+}/Li^+ mass ratio was decreased to 8 from 150 in the feed solution [234]. Li et al. concluded that selective electrodialysis was superior to nanofiltration for the fractionation of Mg^{2+}/Li^+ in solutions with a high initial mass ratio [234]. However, the poor durability of ionic membranes is a major issue preventing electrodialysis from becoming a widely applied technology for the recovery of lithium from brines [234,257].

3. Applications of Lithium Sorption Technology

As discussed above, there are a number of different approaches being investigated for the direct extraction of lithium from brines. The most advanced technologies are in the realm of solid adsorbents and most commercialized lithium recovery processes are based on using molecular sieve ion-exchange sorbents for the extraction of lithium.

3.1. Patented Lithium Adsorption Technology

There is a significant body of patented technology that is directed at developing or improving molecular sieve ion-exchange sorbents for the extraction of lithium from brine (Tables 7, 8 and 11). The earliest patents found date from the 1970s and describe AlOH-based sorbents [79,84,85]. These sorbents continue to be developed for commercial application (Table 7) (e.g., [131,132]). Molecular sieve ion exchange based on MnOx and other metal oxide sorbents are now patented and under development for application in geothermal systems (Tables 8 and 11) (e.g., [128,150,258]). To our knowledge, so far only aluminum-based sorbents have been applied at full or pilot scale for the extraction and recovery of lithium from geothermal brines [129,130,133–135], although both MnOx and TiOx adsorbents are being proposed for use in geothermal lithium demonstration projects. Aluminum-based adsorbents are reported to have recoveries below 60% for lithium in practice [128].

Table 11. Patents associated with Lilac Solutions or D. H. Snydacker.

Year	**US Patent or Application**	**Inventor**	**Assignee**	**Title**
2017	2017/0217796	D. H. Snydacker, V. I. Hegde, M. Aykol and C. M. Wolverton	Northwestern University	Compounds for lithium extraction via ion exchange
2017	2017/0229742	M. Aykol, S. Kim, S. Hao, Z. Lu, V. I. Hegde, D. H. Snydacker, S. J. Kirklin, D. Morgan and C. M. Wolverton	Northwestern University	Protective cathode coatings for lithium-ion batteries
2018	2018/0133619	D. H. Snydacker	Lilac Solutions, Inc.	Lithium extraction with coated ion-exchange particles
2018	10,150,056	D. H. Snydacker	Lilac Solutions, Inc.	Lithium extraction with coated ion-exchange particles
2019	2019/0256987	D. H. Snydacker, A. J. Grant and R. A. Zarkesh	Lilac Solutions, Inc.	Integrated system for lithium extraction and conversion
2019	2019/0044126	D. H. Snydacker, A. J. Grant and R. A. Zarkesh	Lilac Solutions, Inc.	Ion-exchange system for lithium extraction
2019	2019/0273245	D. H. Snydacker, A. J. Grant and R. A. Zarkesh	Lilac Solutions, Inc.	Ion-exchange system for lithium extraction
2019	10,505,178	D. H. Snydacker, A. J. Grant and R. A. Zarkesh	Lilac Solutions, Inc.	Ion-exchange system for lithium extraction
2019	2019/0046898	D. H. Snydacker	Lilac Solutions, Inc.	Lithium extraction with coated ion-exchange particles
2019	10,439,200	D. H. Snydacker, A. J. Grant and R. A. Zarkesh	Lilac Solutions, Inc.	Ion-exchange system for lithium extraction
2019	2019/0088991	V. I. Hegde, D. H. Snydacker and C. M. Wolverton	Northwestern University	Protective anode coatings for high energy batteries
2020	2020/0232105	D. H. Snydacker, A. J. Grant and R. A. Zarkesh	Lilac Solutions, Inc.	Integrated system for lithium extraction and conversion
2020	2020/0165699	D. H. Snydacker, A. J. Grant and R. A. Zarkesh	Lilac Solutions, Inc.	Ion-exchange system for lithium extraction
2020	2020/0289958	D. H. Snydacker	Lilac Solutions, Inc.	Lithium extraction with coated ion-exchange particles
2020	2020/0230591	D. H. Snydacker	Lilac Solutions, Inc.	Lithium extraction with porous ion-exchange beads

3.2. Modifications to Improve Sorbent Stability

There are a number of recognized barriers to the application of lithium sorption for the recovery of lithium from geothermal brines. One limitation is the physical durability and chemical stability of the sorbent [259]. In order to be usable in geothermal systems, sorbents need to be thermally stable, resistant to harsh chemical conditions, and must be able to be regenerated multiple times [151]. In most applications, the sorbent must have physical characteristics, such as particle size, wettability, and porosity, that allow application in an ion-exchange column or a counter current exchanger [260]. Regeneration typically involved the treatment of the lithium-impregnated sorbent with an acid solution to desorb lithium by displacing and extracting the sorbed lithium ions with hydrogen ions. In the case of inorganic ion-exchange materials, dissolution and degradation of materials during uptake in brines is also an issue [259]. The number of times the sorbent can be reused and regenerated and the stability of the sorbent under geothermal brine conditions, including high temperatures, will be a major driver for determining the economic sustainability of any adsorption-based process.

Several different approaches to stabilizing sorbents have been proposed. Snydacker [259] suggested coating MnOx sorbents to improve stability. Coating can be a variety of materials, such as phosphates, metal oxides, including titanium, nickel, and zirconium oxides, or carbon materials, including amorphous carbon [259]. Other suggested coatings include polymers, such as polystyrene and polydivinylbenzene, fluorides, fluoride polymers, and nitrides [259].

Ryu et al. [261] combined silica (SiO_2) with lithium MnOx ($Li_{1.33}Mn_{1.67}O_4$) by a high-energy milling technique and calcination in an effort to prevent manganese dissolution during acid regeneration. It was found that amorphous SiO_2 imparted stability to the spinel MnOx and reduced the level of Mn dissolution during the acid extraction of sorbed lithium [261]. The silica-MnOx composite was tested for recovery of Li^+ from lithium-spiked seawater and was found to have a sorption capacity of 43 mg/g [261], which is comparable to MnOx sorbents that are not in a matrix.

Resins and polymers have been proposed for use to make more robust and stable variants of metal oxide sorbents that can withstand repeated acid-extraction cycles [262–264]. Xiao et al. [264] made an ion-exchange bed sorbent synthesized from $Li_4Mn_5O_{12}$ ultrafine powder in a polyvinyl chloride binder using N-methyl-2-pyrrolidone as solvent. Polymer nanofibers composed of hydrophilic polyacrylonitrile or polysulfone-based units have been used to stabilize MnOx sorbent and found enhanced lithium sorption attributed to reduced interference for alkaline earth metals [265,266]. Other suggested stabilizing approaches include other polymers, such as polystyrene and polydivinylbenzene, fluoride polymers, and sulfonate polymers [259,267,268].

Chitosan has been suggested as a sorbent matrix for MnOx sorbents [269]. MnOx in a chitosan matrix was determined to have a maximum adsorption capacity of 55 mg/g, which is higher than that reported for MnOx sorbents in a silica matrix [151,261]. Ryu et al. [269] investigated a continuous flow column packed with an MnOx adsorbent in a chitosan matrix. They tested the recyclability of this system after extraction of lithium from the adsorbent using sulfuric acid and found that the sorption capacity decreased slightly after recycling the adsorbent three times [269].

Chung and co-workers proposed a number of ideas for using stabilized sorbent for the passive or active extraction of lithium from seawater [266,270]. In one case, a specifically designed solid holder for lithium sorbent was developed to be placed on the seafloor or towed behind boats to collect lithium from seawater [270]. In another case, fabricated electrospun composite nanofiber was employed as an adsorbent membrane filter as part of a continuous lithium extraction process from seawater [266]. This membrane filter was composed of a hydrophilic polyacrylonitrile matrix infused with the lithium sorbent $H_{1.6}Mn_{1.6}O_4$. This material was found to be mechanically suitable for use as a microfiltration membrane and effective at capturing lithium even at a high water flux [266]. The filter was tested in breakthrough experiments and was still separating lithium preferentially over Na^+, K^+, Mg^{2+} and Ca^{2+} after being cycled 10 times with stripping solution.

Similar approaches have been applied for sorbents other than MnOx. Ion-exchange resins can be used to stabilize AlOH sorbents [79,84–86,120]. Burba et al. [132] proposed mixing a lithium aluminate intercalate with up to 25% by weight of a polymer to form a stable matrix appropriate for use in ion-exchange columns. Wu et al. [126] included iron in formulation of layered aluminum double hydroxide chloride sorbents to improve sorbent stability [126]. Limjuco et al. [271] created a lithium adsorbent "foam" by incorporating TiOx in a polyvinyl alcohol matrix through a process of blending, lyophilization, and chemical cross-linking. This foam was used for the extraction of lithium from seawater and maintained its performance and mechanical integrity after several uses [271].

In summary, improving sorbent stability is an important and active area of research and innovation. Developing robust chemical and thermal stable variants of inorganic molecular sieve ion-exchange sorbents will be critical to the successful application of these materials to the extraction of lithium from geothermal brines.

3.3. Interfering Chemicals and Pretreatment Challenges

Geothermal fluids are complex solutions (Tables 2 and 12) [272]. Even the most selective molecular sieves adsorb undesirable minerals from lithium leachates or brines [17,120,128,273]. The initial brine composition determines the production process, which typically includes pretreatment steps (to prepare the brine for lithium extraction), the lithium extraction process (to concentrate the lithium), and post-treatment processing (to remove impurities from the recovered lithium) [9,273]. For geothermal brines, typical materials that must be removed or reduced in concentration before lithium extraction include silica, magnesium, calcium and other metals [128]. Major elements and compounds found in geothermal brines that can interfere with lithium extraction include other alkali metals (Na, K), alkaline earth metals (Mg, Ca, Sr, Ba), iron and base metals (Fe, Mn, Pb, Zn), and metalloids (B, Si, As) [168]. In Salton Sea brines, lithium is a minor element in a concentrated brine (Table 2), and the majority of the other more abundant elements may need to be removed or controlled before lithium can be adsorbed or otherwise extracted and recovered.

Typical applications of lithium sorbents for extraction of lithium from geothermal brine envision multiple steps, in addition to silica removal [76–78]. Figure 22 shows the complexity of the processes required to separate other minerals from lithium in treatment of geothermal brines [31,274,275]. Typical steps include removing alkaline earth metals from the brine; passing the treated brine through an ion-exchange column containing a molecular sieve lithium sorbent; eluting the lithium ions from the molecular sieve using a strong acid solution; and collecting the resulting lithium-rich eluate fluid from the ion-exchange reactor column [128].

Table 12. Chemical composition of geothermal brines [272]. Values are reported in mg/kg.

	Li	**Na**	**K**	**Rb**	**Cs**	**Mg**	**Ca**	**Sr**	**Ba**	**Fe**	**B**	**Al**	$\mathbf{SiO_2}$	$\mathbf{NH_3}$	**F**	**Cl**	**Br**	**I**	$\mathbf{CO_2}$	$\mathbf{H_2S}$	$\mathbf{SO_2}$
Salton Sea	194	53,000	16,700	170	20	33	27,400	411	203	1560	257	2	>461	333	15	151,000	99	20	1600	15	64
Brawley	219	47,000	12,600	67	19	114	21,500	1043	992	3733	221	0.5	>430	725	0.5	134,000	87	6	14,600	45	25
Imperial	327	65,500	12,450			400	23,700		2260	4160	282	4.2	>510			131,000					
Coso	45	2850	927			<0.35	75	2.8			119		>711	4	2	5730			7800	160	5
Dixie Valley	2	407	64			0.007	8	0.4		<0.01	9.9	1.5	>599	1.8	15.5	438	0.32		4300		196
Roosevelt	27	2190	400			0.3	10	1.4			27		>650		5	3650	2				69
Cerro Prieto	27	8300	2210	11	39	0.5	521	16	11	1.5	9.4	0.05	>864		2.4	16.03	17.7	0.6	44		2
Miravalles	6	2300	300	1	0.7	0.7	60				60		>600	1.7	1.6	3950					60
El Tatio	44	4800	800		17	0.7	250				206		>740		3	9000			5500		30
Hvergerdi	0.3	212	27	0.04	<0.02		1.5			0.1	0.6		>480	0.1	1.9	197	0.45		55	7.3	61
Broadlands	11.7	1050	210	2.2	1.7	0.1	2.2			<0.01	48		>805	2.1	7.3	1740	5.7	0.8	128	<1	8
Wairakei	13.2	1250	210	2.9	2.5	0.04	12			<0.01	29		>670	0.2	8.4	2210	5.5	0.3	17	1	28
Rotokawa	10.2	1525	176				50				102		>430	3.2	6.6	2675		0.2	55		120
Ohtake	4.7	1210	137			0.1	46			0.03		0.28	>460			1750					138
Salak	17	5000	990	5	4.5	0.1	320	4.5	0.3	<0.4	312	0.1	>510	4	0.9	9100			5000	1.5	7
Monte Amiata	21.9	1977	558	2.1	0.7	<0.5	128	2.4		1.6	7300	0.31	>700	439		4135	8.4	4.1			26
Milos	81	31,500	9500			4	4380	70	37	19	125		>950		4	65,400			280	2.4	20
Cheleken	215	76,140	409		14	54	19,710	400	235	2290	390			409		157,000	120		32		309

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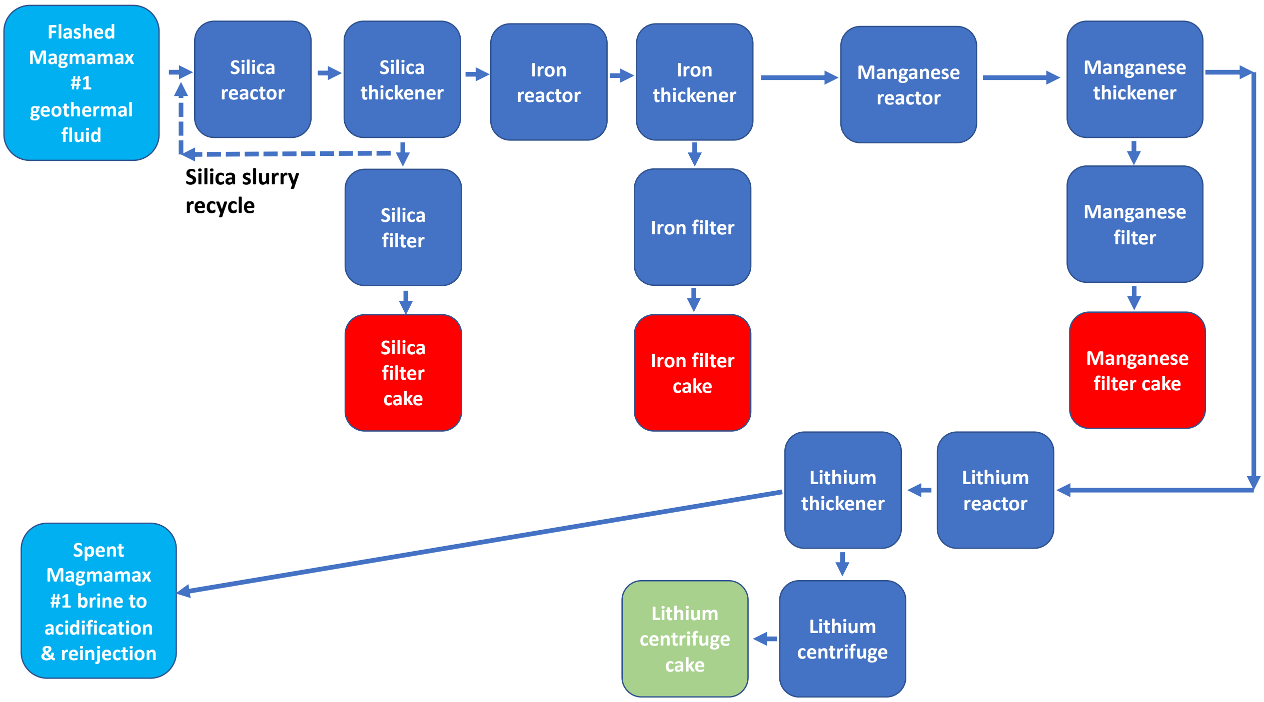

Figure 22. Process developed by Hazen International for the extraction of lithium from Salton Sea geothermal fluids, adopted from [31]. Reprinted (modified) from Geothermics, v. 11(4), Maimoni, Minerals recovery from Salton Sea geothermal brines: A literature review and proposed cementation process 239–258, Copyright 1982, with permission from Elsevier.

3.3.1. Alkali Metals

Alkali metals other than lithium often occur in brines at concentrations many times greater than lithium (Tables 2 and 12) [272]. In most cases, inorganic metal oxide sorbents (i.e., MnOx, TiOx) were found to be preferentially selective for lithium over sodium or potassium [154,264,276]. However, due to the much higher concentrations of sodium and potassium than lithium in typical brines, it is possible for these elements to reduce the efficiency of lithium sorption [166,276].

For maximum economic value, the final lithium product, such as lithium carbonate, lithium chloride, or lithium hydroxide, must be essentially free of sodium, potassium, and other impurities. For example, electrolyte-grade lithium chloride requires levels of sodium at or less than 0.006% [273]. The separation of lithium from sodium and potassium often occurs after other pretreatment steps. Strongly acidic cation-exchange resins (e.g., Dowex, AG50W-XS) have been used to separate sodium and potassium from lithium [56]. Lithium was separated from sodium in a single pass using AG50W-XS, a sulfonated polystyrene cation-exchange resin, which was regenerated with one molar HNO_3 in 80% methanol [56]. Some applications involve the removal of potassium as part of the pretreatment or preparation of the feed solution for the lithium extraction process [57,154,277]. Potassium is also removed and recovered as potentially valuable potash [57,129,130].

Laboratory studies were conducted to determine if potassium could be extracted from geothermal brines using ion exchange and recovered as sellable fertilizer (i.e., potash) [129,130]. Fourteen candidate cation-exchange materials were tested, including natural zeolite, modified natural zeolite, synthetic clinoptilolite, synthetic zeolite W, synthetic crystalline silicotitanate, niobium-substituted silicotitanate, and synthetic tin antimonates [130]. Uptake capacity, uptake selectivity, stripping efficiency, stripping selectivity and overall selectivity of the exchangers were measured. Bench column testing showed that zeolites could be used to selectively extract and recover potassium from geothermal brines at 95 °C. It was concluded that ion exchange could be used to recover potassium from geothermal brine; however, the overall process was not considered cost effective [129,130]. Potash recovery from geothermal brines was proposed for the Cerro Prieto geothermal field [278].

3.3.2. Alkaline Earth Metals

Commercial deployment of molecular sieve sorbents in mineral recovery has been hampered by the cost of conditioning feedstock (pretreatment) to remove alkaline earth metals, particularly calcium and magnesium [128]. Separation of lithium from magnesium is critical to achieving high recovery efficiency and purity of the final lithium product [17,120,128,262]. For example, the richest lithium resource in the world, the Uyuni salar brine, contains a high magnesium concentration (Table 1), which causes difficulties in lithium production [56]. Calcium and magnesium may be removed from brine by a variety of methods and magnesium has a significant resource value if it can be recovered as magnesium oxide as part of a lithium extraction and recovery process.

Removal of magnesium and calcium adds cost to lithium recovery [57,279]. Xu et al. [17] reviewed methods for separating magnesium and lithium in the context of recovering lithium from salt lake brines. Techniques for the separation of magnesium from lithium include precipitation, adsorption, solvent extraction, nanofiltration membrane, electrodialysis, and electrochemical methods [17]. Xu et al. [17] concluded that a combination of techniques would be needed in order to achieve the high separation selectivity, stability, low cost, and environmentally friendly characteristics needed for successful lithium extraction.

Ion-exchange resins may be applied for the separation of alkaline earth metals from alkali metals [59,280,281]. For example, Nishihama et al. [59] extracted lithium from seawater with a granulated-MnO_2 adsorbent, with a recovery efficiency of lithium of approximately 33% and then purified the eluent stream with a strongly acidic cation-exchange resin to remove divalent metal ions, then removed sodium and potassium with a diketone/TOPO impregnated resin, and lastly recovered lithium as precipitates of Li_2CO_3 using a $(NH_4)_2CO_3$ saturated solution. The yield of recovered Li_2CO_3 with their process was 56% with more than 99.9% purity [59].

Separation of lithium from divalent cations can also be achieved by precipitation. Bukowsky et al. [58] 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. Laitala et al. [282] proposed using precipitation and solvent extraction to prepare brines for lithium extraction. The process for producing a clean lithium solution involves first-stage magnesium and calcium removal by bulk precipitation of carbonates, sulfates or hydroxides with sodium carbonate or calcium hydroxide. This is followed by a second-stage polishing step of selective liquid–liquid extraction using a dialkyl phosphoric acid mixture (e.g., di-2-ethyl hexyl phosphoric acid) to remove residual calcium and magnesium from the lithium-containing solution. After the extraction step, magnesium and calcium concentrations in the aqueous phase are reported to be less than 0.01 g/1 [282]. Perez et al. [273] used two-stage precipitation of magnesium with calcium hydroxide to precipitate virtually all of the magnesium in the form of magnesium hydroxide, but also significant quantities of calcium in the form of gypsum ($CaSO_4{\cdot}2H_2O$) and boron in the form of calcium borate ($CaB_2O_4{\cdot}6H_2O$). Magnesium can be removed from lithium brines by using oxalic acid precipitation. The resulting Mg-oxalate that was removed from the brine was suitable for the production of magnesium oxide by roasting [56].

Li and Binnemans [283] tested neodecanoic acid and D2EHPA as co-extracts to remove magnesium from concentrated brines in the context of producing battery-grade Li_2CO_3 and found that this solvent mixture could remove over 85% of the magnesium, but also extracted up to 6% of the lithium. A mixture of the beta-diketone HPMBP and Cyanex 923 were more selective for magnesium extraction over lithium, yielding a separation factor of over 1000 [283]. Other beta-diketones (HTTA and HDBM) were not as effective.

When using a three-stage batch counter-current extraction process, Li and Ninnemans found that the HPMBP and Cyanex 923 mixture removed 100% magnesium with only 0.6% co-extraction of lithium [283].

Li et al. [182] used a composite nanofiltration (NF) membrane with a positively charged polyetherimide skin layer to separate magnesium ion from lithium in simulated brine. The NF membrane was treated with EDTA to modify the positively charged PA-B NF membrane in order to improve the permeation selectivity of lithium against magnesium. Renew and Hansen [143] used nanofiltration to separate divalent from monovalent cations, followed by membrane distillation to concentrate the lithium in the brine, and the Mn-oxide sorbent to recover the lithium from the brine.

3.3.3. Iron and Base Metals

Numerous transition and post-transition metals co-occur with lithium in geothermal brines (Tables 2 and 12). Of particular concern are iron and the so-called base metals, which may occur in high concentration, may form scales or precipitates (e.g., iron, manganese), and may be toxic (e.g., lead). Management of metals, especially as precipitate solids, can be expensive, especially if they contain toxic or regulated elements. Alternatively, recovery of valuable metals in a purity or composition that is saleable could potentially benefit the economics of lithium recovery [48,284].

Maimoni [31] reviewed prior investigations that examined lithium extraction from Salton Sea geothermal brines and proposed that recovery of valuable metals could be achieved with precipitation and cementation reactions. Christopher et al. [275] investigated the recovery of iron, manganese, zinc, and lead from Salton Sea geothermal brines. They recovered iron as a magnetic oxide product containing 68% Fe. Manganese, zinc, and lead were recovered as a mixed oxide product containing 47% Mn, 18% Zn, and 2.8% Pb [275]. Manganese and zinc have been identified as attractive targets for economic metals recovery [130,275,284–286].

Laboratory studies were also conducted to examine zinc and manganese extraction and recovery from both synthetic and Salton Sea geothermal brines [129,130]. Manganese and zinc were recovered by precipitation as hydroxides at pH 8 to 9 with a removal efficiency of approximately 95% [130]. Sulfuric acid was used to dissolve the precipitate solids to produce a manganese and zinc sulfate solution. Zinc was separated from the manganese by solvent extraction, but the solvent was not identified [129,130]. The resulting zinc sulfate was purified by cementation with zinc dust and converted to zinc metal by electrowinning [129,130]. The manganese sulfate from geothermal brines was not purified further, but it was shown with synthetic solutions that manganese oxide (MnO_2) could also be produced by electrowinning [129,130]. The process was considered economical and was apparently incorporated into pilot testing [129,130,270].

MidAmerican Energy Holding Co. [287] conducted laboratory-scale studies to determine the best technique for removal of the manganese from the spent brine produced from energy and mineral extraction plants they operated in the Salton Sea KGRA. They determined that solvent extraction was the best approach for manganese removal. They used an aliphatic-hydrocarbon solvent trade named Orfom SX-11 in mixture with di-(2-ethy\hexyl) phosphoric acid and Aliquat-336. Prior to use, the organic phase was equilibrated with aqueous NaOH so that the extractant solution contained the ion-pair, QL, where Q is the quaternary amine and L is the organic phosphate [287]. When this solvent was mixed with the aqueous brine, the ligand (L) complexed manganese and transferred it to the organic phase [287]. The metal was stripped from the organic phase with aqueous HCl. The final product, manganese dioxide, was produced by electrolytic oxidation [287]. This solvent process separates manganese from all of the significant constituents of the brine except iron and calcium. These metals in high concentrations interfere in the electrolytic production of manganese oxide, so additional studies were conducted on their removal [287].

Metals recovery is a key part of lithium battery recycling operations and there may be applications for technology and processes developed for lithium battery recycling in geothermal lithium applications. For example, Sonu et al. [288] used solvent extraction to recover valuable metals such as cobalt, nickel, manganese, and lithium from acid leachate of secondary battery-related wastes. Powdered battery waste was leached using sulfuric or hydrochloric acid, with or without hydrogen peroxide to produce a solution containing lithium, manganese, cobalt, and nickel. Manganese was recovered using D2EHPA as an extracting agent, cobalt was recovered after manganese by extraction with Cyanex 272, and nickel was then recovered using neodecanoic acid [288]. A solution containing only lithium was obtained after the nickel extraction step and it was proposed that lithium would be recovered in a form of Li_2CO_3 by addition of sodium carbonate [288]. Solvent extraction to separate metals from lithium brines is a common approach in battery recycling [201,209,210,212,288–291].

3.3.4. Metalloids and Other Elements

Silica

High concentrations of silica occur in hot geothermal brines (Tables 2 and 12) and geothermal power plants have silica control processes as part of their normal operations [76,77,287]. Typical approaches to silica control include precipitation of silica as crystalline or amorphous silica at the head of the power plant or acidification to keep the silica in solution [77,287]. It is recognized that silica is a major scale-forming chemical and will need to be managed as part of any geothermal lithium process [129,277,284,292–296]. In most cases considering geothermal lithium, silica control is presumed to be precipitation, but electrocoagulation to remove silica has been proposed [297].

Silica removal by sorption and precipitation prior to direct lithium extraction was investigated in the laboratory by Simbol, Inc. as part of a US Department of Energy (DOE) funded study [129,130]. The sorbent used to remove silica from test solutions was not named in the reports, but may have been activated alumina [129,130,162]. Versions of the sorbent were tested for sorption of silica from laboratory solutions and was regenerated by alkaline extraction with sodium hydroxide and a regeneration treatment with acid [130]. In some experiments, the silica could not be stripped off the sorbent and in many cases the amount of chemical required for stripping and regeneration was high enough that it was concluded there was no practical way to regenerate the sorbent or recover the silica once it was adsorbed [129,130].

There is also some interest in creating a marketable product out of silica precipitated during geothermal power production and geothermal lithium production process [130,287,298]. Harrison and coworkers investigated the conversion of ion-silicate solids to a more valuable product [129,130]. A process to produce iron phosphate, which is used in the production of lithium-ion battery cathodes and pesticides, was developed [129,130]. The iron-silicate filter cake was washed with water to remove sodium chloride and other soluble salts, then the filter cake was dissolved in hydrochloric acid or sulfuric acid to produce ferric chloride or ferric phosphate [130]. The soluble ferric solution was then reacted with phosphoric acid and neutralized with caustic soda to precipitate iron phosphate that was reported to meet cathode powder purity specifications [130]. It was recognized that the process may not be economical [129,130].

Boron

Boron is a commonly co-occurring metalloid that must be separated from lithium for most lithium applications (Tables 2 and 12) [59,117,119,299–303]. Most boron removal processes involve precipitation. Brown et al. [61] treated a 3% lithium chloride solar-concentrated brine with lime and calcium chloride to convert boron to calcium borate hydrate. The calcium borate hydrate was separated by precipitation, along with magnesium hydroxide and calcium sulfate dehydrate, which are formed in the same process [61]. Precipitation treatment is used as part of process trains to produce high-purity lithium carbonate and chloride [55,61,304].

Perez et al. [273] extracted boron from a solar-concentrated salar brine from Argentina via solvent extraction with aliphatic alcohols in a hydrocarbon solvent solution, where isooctyl alcohol and 5% to 20% by volume tributylphosphate was dissolved in petroleum distillates (Escaid 100). Boron was collected as calcium borate ($CaB_2O_4.6H_2O$), thereby eliminating both boron and calcium from the remaining brine [273].

Arsenic

Park et al. [263] showed that the presence of arsenic negatively impacts the adsorption of lithium onto a MnOx. They conducted experiments with geothermal brines from Hatchobaru, Kyushu, Japan and found sorption interference by arsenic at a concentration of approximately 3 mg/L. Their solution to deal with the interference of As^{3+} was to apply a two-part adsorption process. In the first step, the brine was reacted with magnetite (Fe_3O_4), which has a strong adsorption affinity for As^{3+} but not for lithium [263]. Subsequently, the lithium was adsorbed onto λ-MnO_2. Removing the As prevented the decomposition of λ-MnO_2 [263].

As discussed above, Harrison and coworkers investigated the potential commercial value of ion-silicate solids from a geothermal power plant in the Salton Sea KGRA [129,130]. The iron-silicate precipitate they produced was found to contain arsenic, which reduced any possible value from the iron-silicate, so methods to remove arsenic before precipitation of silica were investigated [130]. Arsenic removal by sulfide precipitation and partial oxidation were both investigated [130]. Sulfide precipitation worked for arsenic removal in test solutions, but not with real brines from the Elmore power plant [130]. Partial oxidation by air sparging was considered more effective, removing approximately 90% of the arsenic from solution, which resulted in less arsenic in the iron-silica filter cake [130]. It was noted that adding ferric hydroxide was also effective at removing arsenic from brines [130].

Phosphates and Fluorides

Other elements such as phosphates and fluorides could interfere with lithium adsorption from geothermal brines [302]. Although these compounds have not been investigated extensively in the context of geothermal lithium, they have been considered in the context of battery recycling [305]. Recycling companies use staged pH adjustment and solvent stripping with D2EHPA to separate lithium from contaminants such as phosphorus and fluorine [290,305].

In summary, the selectivity of the sorbent, the tolerance of the sorbent to interfering ions, and the purity of the lithium extracted from the sorbent will be major cost drivers for real-world applications [47]. How the sorbents perform in the presence of any number of co-occurring chemical elements, including magnesium, calcium, manganese, and base metals, will determine the level of pretreatment required before the lithium extraction step. If the sorbent is not sufficiently selective, high concentrations of competing ions may render it ineffective for lithium extraction. The ability of the sorbent to tolerate scaling, coating, or poisoning by minerals and other chemicals found in geothermal brines may also prove an important limiting factor to full-scale application. In addition, the presence of even trace contaminants and other impurities in the lithium solution extracted from the sorbent during regeneration could affect the value of the final lithium product derived from geothermal fluids (i.e., lithium chloride, lithium hydroxide). The level of pretreatment of geothermal brines that will be required before sorbent extraction of lithium will depend on the sorbent process being used, the available options for post-extraction purification and the purity specifications for the produced lithium chloride, lithium carbonate, or lithium hydroxide, that vary by application and the buyer's requirements.

4. Mineral Recovery from Salton Sea Geothermal Brines

Hypersaline Salton Sea geothermal brines are considered the most promising sources of brine lithium in the United States. Salton Sea geothermal brines also have high concentrations of other minerals and there is a long history of geothermal mineral extraction and recovery operations in the region (Table 13). Lessons learned from earlier mineral extraction projects will be valuable to improving the success of future efforts.

Table 13. Timeline of pilot-scale or larger geothermal mineral extraction projects in the Salton Trough geothermal resource area in California and Mexico.

Approximate Dates or Decade	Mineral Resource Extracted from Geothermal Brine	Organizations Involved	Reference
1932–1954	Carbon dioxide	Cardex Western Company	[306–308]
1964–1965	Unspecified minerals	Earth Energy Co., Union-Pure Oil Co.	[29,309]
1965–1967	Sodium chloride Potassium chloride Calcium chloride	Imperial Thermal Products, Inc., Morton International	[29,306,309]
1966–1970s	Calcium chloride	Chloride Products Company, Inc., Western Geothermal, Inc., Hills Brothers, Lee Chemical.	[29]
1970s	Calcium chloride	Geothermal Energy and Mineral Corporation	[29]
1970s	Calcium chloride	Morton Salt Company	[29]
1970s	Potassium chloride Lithium carbonate	Comisión Federal de Electricidad (CFE) (Cerro Prieto, Mexico)	[29]
1970s	Mixed metal hydroxides (iron, manganese, zinc)	Hazen International and Department of the Interior US Bureau of Mines	[31,275]
1980s	Mixed hydroxides of iron, manganese, lead, zinc	Department of the Interior US Bureau of Mines	[310]
1990s	Mixed iron, silica, silver, copper, antimony, arsenic	Unocal Corporation	[311]
2001–2004	Zinc metal	CalEnergy Minerals, LLC, MidAmerican Energy Holdings Co.	[287,312–314]
2014–2015	Lithium, silica, manganese, zinc, potassium	Simbol Materials	[129,130,314]

4.1. Dry Ice Production

The earliest commercial project identified was the production of dry ice from the Imperial carbon dioxide field. Shallow sands 60 to 220 m below the surface in this field produced 98% pure carbon dioxide, which was used commercially from 1933 to 1954 by the Cardex Western Company to manufacture dry ice for the refrigeration of boxcars. Production was abandoned after the development of modern refrigerated transport [306–308].

4.2. Calcium Chloride

Several companies extracted salts from Salton Sea geothermal brines during the 1960s and 1970s (Table 13). Salts that were collected commercially included sodium chloride, potassium chloride, and calcium chloride [29,306]. Calcium chloride production appeared to be profitable, in that several plants were operated over a number of years and in some cases, plants were sold to a series of owner-operators (Table 13) [29]. The demand for calcium chloride is expected to grow by over 5% annually between 2020 and 2025 to reach a market value of $1.92 billion by 2025 [315]. Since calcium must be managed as part of any lithium extraction process, it should be considered if there may be a market for calcium products.

4.3. Base Metals

In the 1970s and 1980s, the US Bureau of Mines extensively investigated the potential for base metal recovery from Salton Sea geothermal brines [31,65,274,285,309,310,316].

Some of these projects advanced to pilot-scale testing [31], but many were tested at the bench scale only.

Hazen International was commissioned by the US Bureau of Mines to design metal recovery processes for Salton Sea geothermal brines [31,274,275,309]. The proposed processes included a primary step applying lime to precipitate iron hydroxides and then a second step where lime was used to precipitate mixed hydroxides of zinc, manganese, and lead [275]. Hazen International reportedly designed and operated a 15-gpm pilot plant, using post-flash brine from the San Diego Gas and Electric power plant at the Magmamax No. 1 well [31]. While their complete design included steps for silica, iron, manganese, and lithium recovery (Figure 22), the actual pilot plant used just one lime-precipitation step in which a co-mingled precipitate containing iron, manganese and zinc was obtained [31].

In the early 1980s, the US Bureau of Mines operated a pilot-scale metals recovery unit using post-flash geothermal brines from the Salton Sea KGRA [310]. The brine source was treated with lime to precipitate iron, manganese, lead, and zinc before reinjection of brine [310]. The process used 27 pounds of lime per 1000 gallons of brine and achieved a 95% to 99% removal of iron, manganese, zinc, and lead. It was observed that lower doses of lime were insufficient for complete precipitation of manganese, whereas higher doses of lime caused re-dissolution of precipitated lead [310]. The use of air oxidation was investigated and found to have either no effect or a negative effect on metals recovery [310]. The investigators concluded that the quality of the hydroxide precipitate was poor in terms of metal content and value and suggested that precipitation of metal-bearing sulfides would be a better approach to recover metals [310].

Subsequent studies by the US Bureau of Mines investigated sulfide precipitation using real brines [285]. Sulfide precipitation with H_2S was able to remove over 99% of the zinc and lead in the brine so long as the pH was controlled with lime. Recycling the sulfide precipitates increased crystal size, resulting in a product that was easier to filter [285]. A typical sulfide precipitate contained 53% ZnS, 8% PbS, 24% MnS, and 15% FeS. Adding sulfide as FeS or CaS was not effective in precipitating zinc and lead, but zinc in the brine could be selectively removed with a strongly basic ion-exchange resin [285]. A proposed flowsheet for metals recovery included steps for silica removal, sulfide precipitation of metals, lime treatment, and lithium precipitation with aluminum (see discussion below) [285]. However, to our knowledge, sulfide precipitation was not applied or tested at the pilot scale.

In the 1990s, Unocal developed a "Line Mine" process that was used to capture scaling minerals from brines prior to reinjection [311]. The process was operated at full-scale for several years and the potential to monetize the mineral deposits collected by the Line Mine process was investigated [272,311,317]. Although the collected mineral scales did contain precious and semi-precious metals, including silver, metal concentrations and amounts recovered were insufficient to support an economic commercial mineral recovery process [272,311,317].

CalEnergy Minerals operated a zinc metal manufacturing facility at its Elmore power plant in the early 2000s [287,313]. The demonstration plant produced 41,000 lbs. of high-grade zinc using an ion-exchange process [312]. After recovery of the zinc from the ion-exchange resin, the zinc was placed in electrolytic cells and the zinc was deposited on cathodes as zinc metal in a batch process over a 24 h period [312]. High-purity zinc deposits, reported to be a quarter of an inch thick, were scraped off of the electrodes and melted into ingots [312,314]. The facility was expected to produce an estimated 30,000 metric tons per year of zinc and had sales contracts with Cominco, a major zinc producer and broker [312,318]. The facility operated commercially for several years, but the venture was abandoned in 2004 as a result of not meeting production goals and a drop in commodity prices [313].

4.4. US Bureau of Mines: Lithium Recovery by Precipitation Process

The US Bureau of Mines developed a process for recovering lithium from Salton Sea geothermal brines using precipitation of lithium with aluminum chloride [65]. The aluminum chloride precipitation process was applied to brine solutions that had been treated with lime to remove metals (as described above). The lithium extraction process consisted of adding a solution of $AlCl_3$ and increasing the pH to 7.5 with lime slurry. This process removed more than 99% of the lithium from solution [65]. The recovered lithium-aluminum precipitate was dissolved in hydrochloric acid and sparged with hydrogen chloride gas to separate out aluminum (as $AlCl_3$). The remaining solution, containing lithium chloride and calcium chloride, was evaporated at 100 °C. The dried chlorides were extracted with tetrahydrofuran to leach out the calcium, allowing 97% of the lithium to be recovered [65]. After evaporation of the tetrahydrofuran, the lithium chloride was dissolved in water and treated with oxalic acid to remove impurities, resulting in 99.9% pure lithium chloride product that represented a recovery of 89% of the lithium present in the original brine [65]. This method of lithium recovery was apparently never tested at the pilot scale [65]. It can be seen from this example that although lithium recovery is clearly possible, a technology or process must be both economically and environmentally sustainable to be practical.

4.5. Simbol, Inc.: Integrated System for Lithium Recovery and Purification

Starting in approximately 2008, Simbol Inc. conducted a series of projects to develop processes for the extraction and recovery of mineral resources from geothermal brines in the Salton Sea KGRA [129,130,314,319]. Mineral management, extraction, and recovery targets included silica, potassium, manganese, zinc, lead, lithium carbonate, lithium hydroxide, and hydrochloric acid (Figure 23) [129,130,314]. Simbol conducted research and planned the development of commercial-scale facilities [129,130,314,320]. From these efforts, Simbol, Inc. and related persons and companies developed a substantial body of intellectual property (Table 7).

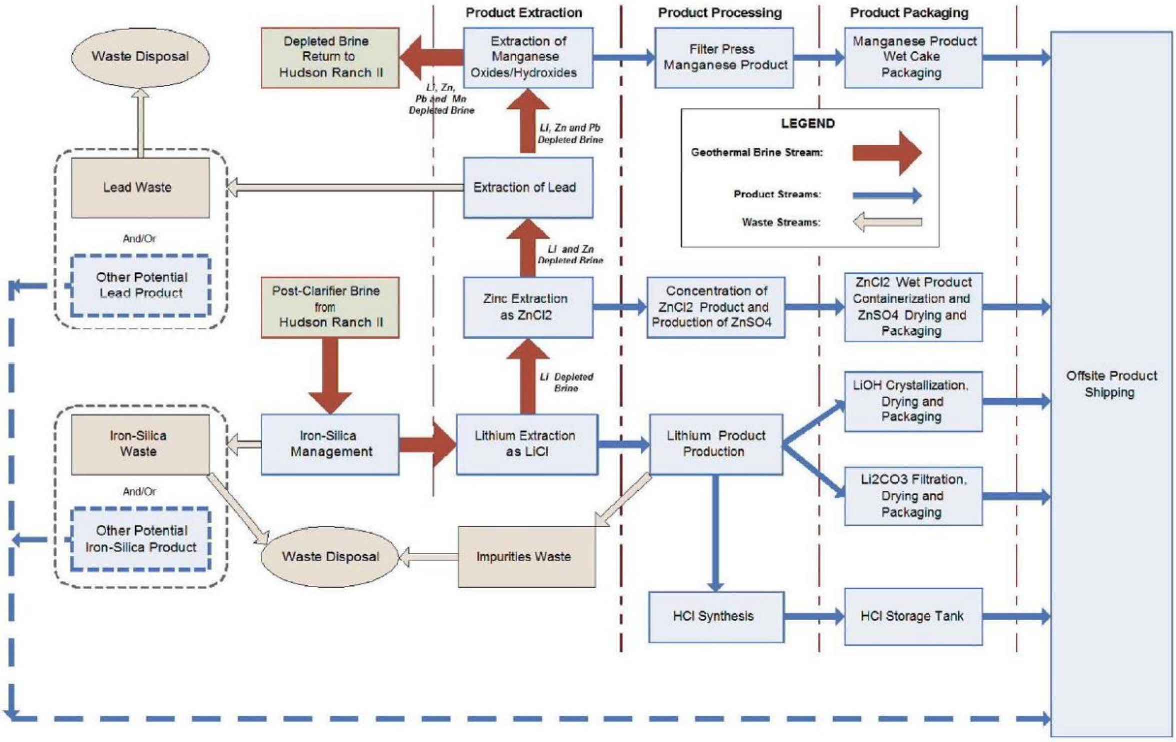

Figure 23. Simbol Hudson Ranch mineral management and recovery process [314].

Simbol conducted a major research project examining the extraction and recovery of minerals from geothermal brines that was funded by the US Department of Energy and the California Energy Commission [129,130]. The project was a wide-ranging investigation of multiple processes directly and indirectly related to extraction of lithium from geothermal brine [129,130]. Since the objective of the investigators was to develop intellectual property, including patents (Table 7), some key information is missing from the technical reports and one report is partially redacted [129,130]; however, the major activities of the project are described.

Simbol, Inc. operated research and development (R&D) facilities in California, including (1) a laboratory and manufacturing facility in Pleasanton, where a pilot lithium extraction plant was tested against synthetic brines; (2) a skid-mounted pilot plant that was used to test lithium extraction from geothermal brines at the CalEnergy Elmore geothermal power plant and the EnergySource Hudson Ranch (John Featherstone) power plant; and (3) a pilot facility for lithium hydroxide and lithium carbonate production in Brawley, CA [129,130]. Activities conducted at these facilities are described below.

Simbol also planned a larger R&D pilot plant facility at the EnergySource Hudson Ranch I geothermal power plant (Figure 23) [314]. This R&D facility was designed to receive brine flows of between 6 and 10 gallons per minute from the operating geothermal power plant and discharge treated brine that was depleted in silica, iron, lithium, zinc and manganese to an adjacent brine waste pond [320]. The facility planned to use scale inhibitors, flocculants, potable water, salt (sodium chloride), calcium hydroxide, soda ash (sodium carbonate), hydrochloric acid and sodium hydroxide [320]. The intention was for this facility to be operated as a commercial business [321,322].

Field pilot tests of a direct lithium extraction process were conducted by Simbol at two geothermal power plants in the Salton Sea KGRA [129,130]. A skid-mounted pilot plant was initially built and tested using synthetic solutions at the Pleasanton facility and then transported to the power plants for testing against real Salton Sea geothermal brines. Schematics and detailed descriptions of the pilot units were not included in the reports [129,130].

The pilot plant, initially consisting of a silica pretreatment process followed by a lithium extraction process, was first tested at the CalEnergy Elmore power plant over an approximately 125 day period [129,130]. At the Elmore test-site, the pilot was operated with Sorbent-P (see description in AlOH section) and possibly other sorbents at a temperature of 105 °C and a flow of 5 gallons per minute. Each test run was operated for approximately two weeks, but data from the Elmore pilot tests are not included in published reports [129,130]. It was reported that the results of the pilot testing at Elmore showed that initial testing with surrogate brines at the Pleasanton facility was not sufficient to predict operations using actual geothermal brines [130]. The test solutions used at Pleasanton did not contain manganese, which occurs in high concentrations in Salton Sea brines (Table 2), and during pilot tests with geothermal brines, manganese interfered with lithium extraction [323].

The pilot at the Elmore location used the Simbol sorptive silica removal process and it was reported that both iron and silica were removed to below measurable detection in the treated brine [130]. However, the sorption process was not considered economical and pilot tests at the Featherstone facility apparently used a precipitation process for silica control (see discussion above) [129,130].

The skid-mounted pilot plant was moved to the EnergySource John L. Featherstone power plant at Hudson Ranch and modified by the addition of unit processes for the purification and concentration of recovered lithium chloride [129,130]. Purification included removing divalent and trivalent cations and boron from the recovered lithium chloride solution stripped from the sorbent [129,130]. How manganese or other constituents of the geothermal brine were managed was not specifically reported, but the purification step implies manganese was adsorbed with the lithium and removed during purification of the lithium chloride stream. The concentration step was not described, but the overall process was reported to produce a 35 to 40 weight-percent lithium chloride solution [130].

At the Hudson Ranch facility, two lithium sorbents were tested and Sorbent-A was determined to have a higher sorption capacity than Sorbent-P and apparently produced the same purity of lithium chloride concentrate [130]. The pilot plant received a brine stream piped directly from the power plant and operated for over 9000 h from November 2012 through 2013 and produced a purified lithium chloride product. Lithium extraction efficiencies as high as 95% were reported [130]. Parameters monitored during pilot testing included efficiency of lithium extraction and iron-silica removal, weight percent of lithium chloride in the product solution, impurities in the lithium chloride product solution, masses of process chemicals and water consumption; unfortunately, none of these data were reported [129,130]. These data were used by Simbol to identify operating costs and plan scale-up to a commercial facility [129,130]. It was reported that Sorbent-A was easier to manufacture and this sorbent was presumably intended for use in the commercial facility.

The lithium chloride purification process used for separating multivalent cations and boron from lithium chloride during the Hudson Ranch pilot test was not described, except that it was originally a three-step process that was reduced to two steps with the goal of lowering costs [129,130]. They tested the purification process against almost approximately 25,000 L of stripped lithium chloride and found the overall process had a yield of between 75% and 86%, with some batches having yields as high as 94% [130]. The concentration process, which occurred after purification, was not described, except to say that initial equipment purchased for the process was inadequate [130]. The final concentration process took the 1.7% lithium chloride solution discharged from the purification process and concentrated it to a 36% solution [129,130].

At Brawley, CA, Simbol established pilot facilities for converting lithium chloride to lithium carbonate and lithium hydroxide [129,130]. A pilot plant was operated for over 125 days in three periods, using both synthetic and real geothermal brines [130]. The real brine used was lithium chloride concentrated from the Hudson Ranch pilot plant, which was shipped to Brawley in totes. The geothermal lithium brine was converted to lithium carbonate by addition of soda ash (Na_2CO_3), which reacts with LiCl to produce Li_2CO_3. After washing and drying, a battery-grade lithium carbonate (99.9% purity) was produced [130]. Sodium and magnesium concentrations were reported to be 13 and 1 mg/kg, respectively, in the final product. The particle size of the precipitated carbonate was not within battery specifications, but this was resolved by further grinding in a laboratory mill [130]. The amount of lithium carbonate produced from geothermal brine was not reported.

Simbol investigated production of battery-grade lithium products from lithium chloride brines generally, with the objective of eventually establishing a production facility. One process that was evaluated involved reacting Li_2CO_3 from the soda ash method (described above) with lime (CaO) to produce LiOH solutions, which once evaporated, yields $LiOH{\cdot}H_2O$ [130]. The soda ash method is essentially the conventional approach for making lithium chloride into Li_2CO_3 and $LiOH{\cdot}H_2O$ products and this method is practiced commercially. However, the process has drawbacks, including requiring the mixing of slurries, rather than aqueous solutions. The maximum concentration Simbol achieved using this method was approximately 3.5 weight percent LiOH, which would need to be further evaporated, washed, and purified to produce a saleable grade of $LiOH{\cdot}H_2O$ [130].

Simbol also conducted laboratory tests on a patented processes for converting lithium chloride (LiCl) to lithium hydroxide ($LiOH{\cdot}H_2O$) and lithium hydroxide to lithium carbonate (Li_2CO_3) [129,130]. The patented Simbol process used for conversion of lithium chloride to lithium hydroxide was not specified in technical reports [129,130], but Simbol has a number of patents concerning lithium chloride processing (Table 7), including patents related to the electrochemical conversion of lithium chloride to lithium hydroxide [324–326]. The patented processes involve reacting lithium chloride in an electrochemical cell to make lithium hydroxide and then reacting lithium hydroxide with carbon dioxide to produce lithium carbonate [324–326]. The process used at Brawley involved the electrochemical conversion of LiCl to LiOH, followed either by concentration to give $LiOH{\cdot}H_2O$, or direct carbonation of the LiOH using carbon dioxide (CO_2) to give Li_2CO_3 [130].

It is apparent that many of the processes investigated as part of state and federal sponsored research studies (described above) were incorporated in the design of a commercial-scale lithium extraction and recovery facility that was to be located at the EnergySource Hudson Ranch power plant [314,319]. According to planning documents submitted to California state agencies, post-flash brines were to be piped from the power plant to adjacent facilities for silica and iron removal, lithium extraction, lithium purification, and lithium product production [314]. Silica and iron were to be removed and lithium extraction was to be accomplished with one of the proprietary lithium extraction media discussed above [314]. The product of the lithium extraction process, a lithium chloride stream, was to be transported via pipeline to the lithium purification process area, where impurities were to be removed from the lithium chloride product stream, but specific impurities removed and processes to be used were not specified in public documents [314]. The purified lithium chloride was to be concentrated in an evaporator or equivalent process and then to be converted to lithium carbonate solids or lithium hydroxide crystals in the lithium product production facility [314]. The lithium carbonate solids and lithium hydroxide crystals were to be transported, apparently as a slurry, to a lithium product handling, production and warehouse building [314]. The lithium carbonate was to be dewatered on a belt filter and the resulting filter cake was to be washed multiple times with hot condensate water and then dewatered, washed again, and fed to a dryer. The lithium carbonate product was then to be cooled and size classified [314]. The lithium hydroxide ($LiOH{\cdot}H_2O$) crystals were to be separated from the lithium-rich process fluid in a filtration system, dried, and cooled [314]. The dried lithium products were to be packaged, palletized, staged, bagged, and loaded into trucks for distribution [314]. However, this facility was never completed and Simbol only operated as a commercial business for a short period of time after completing the pilot studies [321,322].

In addition to lithium recovery, the Simbol facility planned on recovering other potentially valuable materials from geothermal brines (Figure 23) [314,319,327]. Recovered iron-silicate was considered for use as a concrete additive and other purposes and approximate annual iron-silicate production rates were estimated to be 64,800 metric tons for a commercial facility [129,130,161,314]. Existing technology was proposed to synthesize hydrochloric (HCl) gas from hydrogen gas (H_2) and chlorine gas (Cl_2) that was produced during the conversion of lithium chloride to lithium products. The HCl gas would be dissolved in water to produce an approximately 31% HCl product that could be sold or used on site [314]. The lithium-depleted brine from the extraction process would be treated to recover zinc chloride ($ZnCl_2$), which would be purified or converted to zinc sulfate ($ZnSO_4$) for sale to off-site customers [314]. After zinc removal, the resulting brine would be further processed to produce an estimated 4250 metric tons of lead sulfide (PbS) wet cake, which was also slated to be sold [314]. Following lead removal, manganese would be recovered as mixed manganese oxides and hydroxides by precipitation, followed by dewatering on a filter press to produce a wet cake for an off-site market [314]. To our knowledge, the proposed resource recovery processes were not implemented and products were not sold to off-site customers.

Simbol ceased commercial operations in the Salton Sea KGRA in approximately 2016 [322]; however, people associated with Simbol continue to produce intellectual property related to the extraction, recovery, and purification of lithium (Table 7).

4.6. EnergySource: Integrated System for Lithium Recovery and Purification

EnergySource has continued developing their own lithium resources under a project referred to as ATLiS [40]. Project ATLiS is a initiative by EnergySource to build and operate a new facility to extract and produce commercial quantities of battery-specification lithium products utilizing geothermal brines from California's Salton Sea geothermal resource area [40]. The project is slated to produce up to 16,500 metric tons per year of LCE at the current brine flows of 1574 m^3 per h (7000 gallons per min). Construction is on target to start in 2022, with commercial lithium production expected to begin in 2024 [40].

EnergySource has continued to develop lithium extraction processes specifically targeted for geothermal brines from the Salton Sea KGRA and is currently marketing a process technology named "Integrated Lithium Adsorption Desorption" (ILiAD) [279]. The ILiAD process has been patented and includes pretreatment, lithium extraction, purification and lithium product production steps (Figure 24) [133–135,279]. Unlike the Simbol process (Figure 23), in the ILiAD process, removal of zinc and manganese precedes the lithium extraction process (Figure 24). Iron, silica, zinc and manganese are removed and recovered in sequential steps before lithium extraction (Figure 24) [133–135,279]. Lithium is removed with AlOH or AlOx sorbents using a continuous bed process [133–135,279]. According to the patent, the lithium chloride selective adsorbent may be a resin-based alumina imbibed adsorbent, a lithium alumina intercalate adsorbent, an alumina imbibed ion-exchange resin, or an alumina-based adsorbent [133–135]. Iron and silica are removed by precipitation and zinc and manganese are removed by solvent extraction with Cyanex 272 or similar solvents using a counter-current contactor [133–135]. Post-extraction purification and processing include processes for removal of calcium and magnesium by ion exchange and further purification of the lithium chloride stream by precipitation and solvent stripping reactions (Figure 24) [133–135]. Lithium hydroxide is produced by electrolysis and lithium carbonate is produced by the addition of sodium carbonate and purified by cycles of crystallization and dissolution (Figure 24) [133–135]. The process is designed to be modular, with each process module sized for production of approximately 3000 metric tons LCE per year, depending on brine lithium concentrations [133–135]. Pilot trials demonstrated the ability to produce high-purity lithium products (>99.9% pure) at a 90% lithium recovery rate [133–135].

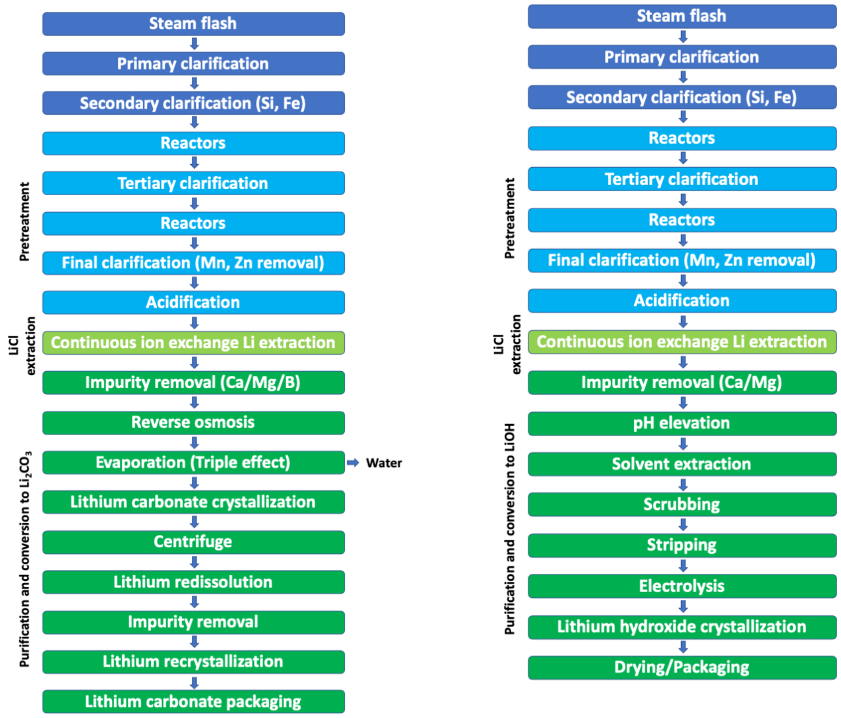

Figure 24. EnergySource patented process for extraction of lithium and other valuable materials from geothermal brines from [133–135]. The process train includes pretreatment, lithium chloride extraction and recovery by continuous counter-current ion exchange, followed by purification and conversion of lithium chloride to saleable products, either lithium carbonate or lithium hydroxide. See Featherstone et al. [133–135] for a complete description of the process flow diagrams. This process is marketed as the ILiAD Process [279].

5. Results and Conclusions

Technology for the direct extraction and recovery of lithium from brines will be very important for the development of new lithium resources to meet the rising demand for lithium-dependent energy storage. Geothermal brines could become a major new source of lithium both in the United States and elsewhere. In this paper, we expanded our paper that was presented at the 46th Workshop on Geothermal Reservoir Engineering at Stanford University [328], providing more details on direct lithium extraction technologies and discussing in depth the potential application of these technologies to the extraction of lithium from geothermal brines.

The most well-investigated and technologically advanced method for direct lithium extraction from brines is adsorption by metal oxides and hydroxides. Solvent extraction of lithium from brines using lithium-selective solvents and sorption using organic polymer sorbents, including metal-imprinted polymers, are early-stage technologies that show promise. Membrane-based processes are largely used for removing water or interfering ions, rather than for the direct extraction of lithium. Processes based on precipitation and common ion-exchange resins can extract lithium from brines, but are not specific to lithium and therefore are not considered practical for economical lithium extraction from geothermal brines, which have very complex chemistry.

Metal oxide and hydroxide sorbents are selective for lithium due to crystalline or layered properties that act like molecular sieves that allow lithium to enter ion-exchange sites, whereas larger ions are sterically excluded. These materials adsorb lithium ions while releasing hydrogen ions in high and neutral pH solutions and release lithium ions while adsorbing hydrogen ions in acidic solutions. The molecular sieve ion-exchange sorbents have been used to extract lithium ions from brines to produce concentrated lithium-ion solutions. The concentrated lithium-ion solution can be further processed into chemicals for the battery industry or other industries.

General properties concerning metal oxide and hydroxide sorbents are provided above. The specific details concerning the chemistry and crystalline properties that determine the capacity and specificity of lithium sorption by metal oxides and hydroxides can be found in the cited primary references and in review papers. Currently, MnOx and TiOx derivatives are believed to be promising sorbent materials for the extraction of lithium from geothermal fluids and other brines; however, the full-scale application of MnOx and TiOx sorbents still need to be demonstrated. Aluminum sorbents, which are relatively less expensive, are being used economically to produce lithium chloride from salar brines in South America and continue to be investigated for the extraction of lithium from geothermal brines.

Sorption of lithium with inorganic molecular sieve ion-exchange sorbents is widely believed to offer the most likely pathway for the development of economic lithium extraction and recovery from Salton Sea geothermal brines. All currently proposed lithium recovery processes for Salton Sea geothermal fluids are based on using molecular sieve ion-exchange sorbents for the extraction of lithium. Although many solid sorbents are entering commercial application against a variety of brines, there is still a need to conduct laboratory and pilot-scale testing of many lithium sorbents against Salton Sea geothermal brines to determine the performance of the sorbents against these complex brines and under real-world conditions.

Solvent extraction with crown ethers is a promising area for developing a direct lithium extraction technology, but both fundamental and applied research is needed to advance and validate this technology. Crown ether technology has not been proven using geothermal brines. Other promising low technology readiness level methods include ion-imprinted polymers and cyclic siloxanes. If these technologies can be validated, they have the potential to reduce the need for extensive pretreatment and simplify extraction processes. These early-stage technologies may one day offer second-generation technologies for direct lithium extraction from geothermal fluids.

It is apparent that lithium extraction and recovery from geothermal brines are becoming technically possible, but challenges still remain in developing economically and environmentally sustainable processes at scale that can serve as a foundation for the lithium-dependent low-carbon economy. For many technologies, laboratory studies can no longer address major questions concerning the development of direct lithium extraction processes, and more expensive and risky field studies at larger scales, using actual brines, are needed to advance commercial-scale geothermal lithium resource extraction.

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