

Technology for Lithium Extraction in the Context of Hybrid Geothermal Power

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Keywords: Lithium, critical materials, hybrid systems, resource extraction and recovery

ABSTRACT

The U.S. Department of Energy's Geothermal Technologies Office (GTO) has been in the forefront of sponsoring research investigating the potential recovery of lithium, rare earth elements, and other critical minerals from geothermal brines. It has been proposed that the future of geothermal energy should include "hybrid systems" that combine electricity generation with other revenue-generating activities, such as recovery of valuable and critical minerals, including lithium.

Lawrence Berkeley National Laboratory is reviewing technology and processes for the recovery and purification of lithium from geothermal brines for GTO, with the objective of enabling the integration of critical materials recovery with geothermal energy production. The purpose of this study is to provide a summary of knowledge, technology, and techniques for extraction and purification of lithium and associated critical materials. Both existing and emerging technologies are examined and evaluated in the context of the unique challenges presented by the extraction of critical materials from geothermal fluids. The study aims to synthesize complex and disparate information in a format that will assist future process development and the advancement of hybrid geothermal power production.

1. INTRODUCTION

Lithium is a light and highly reactive metal that is the principal component in one of the most promising forms of high energy-density batteries (Grosjean et al., 2012; Ambrose and Kendall, 2020). As electric vehicles (EV) gain a significant share of the car market, lithium production must grow proportionately with vehicle demand (Grosjean et al., 2012). In addition to use for EV batteries, lithium is a critical material for ceramics, glass, metallurgy, air treatment, pharmaceuticals, and polymers (Bradley et al., 2017). Due to this variety of uses, lithium is on the list of critical materials necessary for the economy and security of the United States (Department of the Interior, 2018).

Between 1975 and 2005, world lithium production increased by a factor of about five (Bradley et al., 2017). Average lithium demand rose by 6% annually between 2000 and 2008, driven by demand in both the battery and aluminum applications (Grosjean et al., 2012). The current increased demand for lithium is driven by two types of battery demands: 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. A 2020 World Bank study predicts that this will result in an increase in lithium production from 85 ktons lithium in 2018 to 415 ktons lithium in 2050, representing an increase of 488% (Hund et al., 2020). 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 kilotons lithium carbonate equivalent (LCE) to 1790 kilotons LCE in 2030 (Khan, 2020). The US is currently dependent on foreign sources of lithium and it is anticipated that there will be significant growth in US lithium production as part of this market shift.

The DOE Geothermal Technologies Office has funded studies to assess the distribution and abundance of lithium within geothermal brines throughout the western US (Neupane and Wendt, 2017; Simmons et al., 2018; Simmons, 2019). Most geothermal brines were found to have lithium concentrations less than 1 ppm, and only 35 samples had lithium concentrations greater than 20 ppm (Neupane and Wendt, 2017; Simmons et al., 2018; Simmons, 2019). All of the samples with higher lithium concentrations were from within the Imperial Valley (CA), where the Salton Sea known geothermal resource area (KGRA) is located (Neupane and Wendt, 2017; Simmons, 2019). It was determined that the Salton Sea field represents by far the largest potential lithium geothermal brine resource in the US, with potential production levels at existing brine flow rates estimated to be 34 to 168 kilotons lithium carbonate equivalent (LCE) per annum (Neupane and Wendt, 2017).

The lithium production rate for the Salton Sea geothermal field calculated by Neupane and Wendt (2017) is based on a wide range of measured lithium contents from these brines (90-440 ppm) and assumes a capacity factor of 90% and recovery of lithium at an 80% efficiency from the current geothermal power capacity of just under 400 MWe produced by the power plants operated by CalEnergy and EnergySource. CalEnergy, which currently operates 10 power plants at the Salton Sea, estimates a potential annual lithium production of 90 kilotons LCE from their existing operations and estimates that an additional 210 kilotons LCE could be produced if their current leases were fully exploited (Besseling, 2018). McKibben et al. (2020) estimate that the proven lithium reserves from the Salton Sea geothermal field are on the order of 10,600 metric kilotons of LCE.

Clearly, the Salton Sea KGRA has the potential to become a significant source of domestic lithium production (Alston et al., 2020). Technology for the extraction of lithium from saline solutions has been developed and are being commercialized. These technologies, discussed in this paper, offer great promise for the development of a domestic lithium economy; however, geothermal brines from the

Salton Sea KGRA are very saline and highly complex (Table 1). In Salton Sea geothermal brines, lithium is not the most abundant element (Table 1), and many of the other more abundant elements may need to be removed or controlled before lithium can be extracted and recovered. In this paper, we discuss the status of lithium extraction technology and the potential for current and future technology to enable lithium resource development in the Salton Sea region.

Table 1. Salton Sea geothermal brine chemical composition. Average values calculated from values reported in the literature representing post-flash geothermal brines (Skinner et al., 1967; Blake, 1974; Palmer et al., 1975; Featherstone and Powell, 1981; Maimoni, 1982; Zukin et al., 1987; Williams and McKibben, 1989; Duyvesteyn, 1992; McKibben and Hardie, 1997).

Element or Analyte	Mean (mg/L)	SD	%RSD	N
Cl	142,015	18,853	13	13
Na	49,249	5,578	11	13
Ca	25,684	3,050	12	13
K	14,467	3,370	23	13
Fe	1,347	653	48	13
Mn	1,201	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

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

2. LITHIUM EXTRACTION AND RECOVERY FROM BRINES: CURRENT AND FUTURE PRACTICE

2.1 Current Practice: Evaporative Concentration

Under current practices, lithium carbonate (Li_2CO_3) and lithium chloride (LiCl) are produced from salar brines by evaporative concentration followed by further refining (e.g., Brown et al., 1981; Meshram et al., 2014; Bradley et al., 2017; Albemarle Corporation, 2020). Wells are drilled to access the underground salar brine deposits and the 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 (Bradley et al., 2017; Samco, 2018). The brine is concentrated by solar evaporation to crystallize sodium, potassium and magnesium chlorides, leaving a concentrated solution of lithium chloride (Meshram et al., 2014). This lithium chloride solution is further refined at an adjacent facility to remove both bulk and trace impurities and, in some cases, to convert lithium chloride to lithium carbonate or lithium hydroxide (Munk et al., 2016; Samco, 2018; Albemarle Corporation, 2020).

Although production of lithium using solar evaporation followed by refining is nominally inexpensive, the solar process is time consuming, land intensive and wasteful of water (Wall, 2019). It would be an impractical approach for harvesting lithium from geothermal brines in the US, due to the need to reinject brine to maintain power production and the negative environmental impacts associated with large evaporation ponds.

2.2 Future Practice: Direct Lithium Extraction

For both geothermal and conventional lithium resources, the future of lithium production is the application of 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. The ideal technology would be one that can specifically pluck lithium ions out of complex geochemical soup, while leaving all other salts and metals in solution. In reality, it is recognized that direct lithium extraction will not be ideal and that direct lithium extraction will involve the development of engineered processes that contain multiple steps to manage interfering co-occurring chemicals (Perez et al., 2014; Munk et al., 2016). Major elements and compounds found in geothermal brines that can interfere in lithium extraction include other alkali metals (Na, K), alkaline earth metals (Mg, Ca, Sr, Ba), so-called heavy metals (Mn, Fe, Zn, Pb), and metalloids (B, Si, As) (Abe and Chitrakar, 1987).

3. TECHNOLOGY FOR DIRECT LITHIUM EXTRACTION

Although there are numerous potential approaches to the extraction and recovery of lithium from brines, the most well investigated approaches include adsorption of lithium to inorganic mineral sorbents and the extraction of lithium from brines using solvents. Other separation processes include precipitation, organic resin and polymer sorbents, and membrane-dependent processes. Sorption of lithium

with inorganic molecular sieve ion-exchange sorbents is the most developed technology and is widely believed to offer the most likely pathway for the development of economic lithium extraction and recovery from Salton Sea brines. However, other technologies that are still in early development may one day offer a second generation of technologies for direct, selective lithium extraction.

3.1 Precipitation

It is possible to use simple and well understood chemical precipitation reactions to recover lithium from brine. Some of the precipitation processes used for lithium recovery from seawater and brines include alkaline pH adjustment and addition of sodium carbonate, sodium oxalate, or other precipitation agents (Meshram et al., 2014). Lithium can be recovered by lime precipitation, but aluminum salts are reported to show the best performance for lithium recovery from geothermal water (Meshram et al., 2014; Schultze and Bauer, 1984). The US Bureau of Mines developed technology for the precipitation and recovery of lithium from geothermal brines (Schultze and Bauer, 1984), but it is not apparent the process was ever applied for commercial purposes. The process involved precipitation with aluminum chloride (AlCl_3) and lime at pH 7.5 and leaching the resulting filter-cake with hydrochloric acid and tetrahydrofuran (Schultze and Bauer, 1984). The process recovered 89% of the available lithium and produced a 99.9% pure lithium chloride (Schultze and Bauer, 1984). Meshram et al. (2014) reported that the appropriate pH for lithium recovery is 10–13 and use of NaAlO_2 produced better recoveries than AlCl_3 . With a high purity NaAlO_2 solution as precipitating agent, about 98–99% Li recovery was achieved at pH 11.5 from a silica (SiO_2) and calcium-free geothermal water (Meshram et al., 2014).

Precipitation reactions are routinely used in geothermal power production, especially for the control of silica (von Hirtz, 2016), 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, iron hydroxides, etc.) 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.

3.2 Organic Sorbents

3.2.1 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 (Dupont, 2019, 2020; Lee and Bauman, 1979; Li et al., 2018; Meshram et al., 2014). However, early studies showed that organic ion-exchange resins exhibited low selectivity for lithium ions (Dupont, 2020; Meshram et al., 2014). Ion-exchange resins only become effective for selective lithium extraction when impregnated with inorganic, lithium-selective sorbents (Burba, 1984; Lee and Bauman, 1980a, 1982; Lee and Bauman, 1979; Lee and Bauman, 1978).

3.2.2 Ion-imprinted polymers and other organic sorbents

Several researchers 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 lithium, and not competing ions, to enter. For example, Ventura and others created a nanocomposite sorbent comprised of lithium-ion sieve nanoparticles and lithium-imprinted polymeric resins for the selective recovery of lithium from geothermal brines (Ventura et al., 2018; Ventura et al., 2016). Lu et al. (2018) developed lithium-imprinted polymers that contained crown ether structures that selectively adsorbed lithium over sodium and potassium. Crown ether moieties are also used in other ion-imprinted polymers designed for lithium adsorption (Zhang et al., 2017). Ueda (2015) used cyclic siloxane to remove and concentrate lithium ions as cyclic siloxane-lithium complexes. The cyclic siloxane-lithium complexes are extracted using liquid-liquid extraction and then recovered from the organic phase by filtering (Ueda, 2015).

The use of synthesized organic polymers to selectively extract lithium seems a very promising approach. As discussed below, smaller crown ether structures have been shown to selectively bind lithium, even in complex solutions. Cyclic siloxanes appear to function in a similar manner to crown ethers, but to our knowledge have not been investigated to any significant extent in the context of geothermal lithium recovery. Lithium-imprinted polymers are in development by startup companies, but are still at a very low technology readiness level.

3.3 Inorganic Sorbents

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 (Li et al., 2018). Many of the lithium sorbents under investigation for use in direct lithium extraction from brines are used as cathode materials in lithium-ion batteries (Meshram et al., 2014). Dow Chemical Company first proposed using microcrystalline AlOH embedded in anion-exchange resins for the selective removal of lithium from brines (Lee and Bauman, 1979). Ooi, Miyai and co-workers first proposed the use of manganese oxides (MnOx) as sorbents for the recovery of lithium from seawater (Ooi et al., 1986; Miyai et al., 1988). TiOx materials are used in lithium-ion batteries and their application to recovery of lithium from brines has been proposed more recently (Zhu et al., 2012; Chaban et al., 2016; Wang et al., 2017; Li et al., 2018; Chaban et al., 2019). The properties of inorganic crystalline sorbents have been scientifically investigated and efforts are underway to apply these solid sorbents in engineered systems for the selective recovery of lithium from natural and industrial fluids, including geothermal brines.

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 et al., 1992; Feng et al., 1993; Chitrakar et al., 2001; Zhang

et al., 2007; Liu et al., 2015; Li et al., 2018). Adsorbed lithium is typically recovered by use of an acid stripping solution, such as hydrochloric acid, and the sorbent is regenerated or cycled for repeated use.

3.3.1 Aluminum hydroxides

Sorbents made from aluminum hydroxides (AlOH) have been shown to preferentially adsorb lithium (Lee and Bauman, 1978, 1979, 1980, 1982). Lithium ions lie in the octahedral voids of the AlOH layers (Besserguenev et al., 1997; Isupov, 1999; Wang et al., 2013). Crystalline aluminum trihydroxides ($\text{Al}(\text{OH})_3$), such as gibbsite, bayerite, and nordstrandite, can form layered intercalation matrices with lithium (Bauman and Burba, 1997; Besserguenev et al., 1997; Isupov, 1999; Wang et al., 2013). Amorphous $\text{Al}(\text{OH})_3$ can be reacted with lithium chloride at elevated temperature to form crystalline $\text{LiCl}\cdot 2\text{Al}(\text{OH})_3$, which can adsorb lithium ion from lithium-containing brines (Lee and Bauman, 1982; Burba, 1984). One effective variant of AlOH sorbents are layered lithium-aluminum double hydroxides, which have been demonstrated as effective for removal of lithium for complex solutions including geothermal brines (Fogg and O'Hare, 1999; Fogg et al., 2002; Menzheres et al., 2004; Wang et al., 2013; Yu et al., 2015; Qu et al., 2016; Paranthaman et al., 2017; Li et al., 2018; Wu et al., 2019; Hu et al., 2020; Jiang et al., 2020).

Challenges to full-scale implementation of AlOH sorbents in Salton Sea geothermal brines include the need to control interference from co-occurring metals and the stability of the sorbent over time, especially during extraction of the sorbed lithium and regeneration of the sorbent (Harrison, 2014; Harrison et al., 2014; Featherstone et al., 2019; Wu et al., 2019). Modifications of the AlOH sorbents include approaches to improve sorbent stability and robustness (Burba et al., 2014; Burba et al., 2015). Ion-exchange resins can be used to stabilize AlOH sorbents (Lee and Bauman, 1978, 1979, 1980, 1982; Jiang et al., 2020). Burba et al. (2015) 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. (2019) included iron in the formulation of layered aluminum double hydroxide chloride sorbents to improve sorbent stability.

AlOH-based sorbents have been in development for many years and have served as the lithium extraction technology for a number of pilot and proposed full-scale direct lithium extraction ventures (EnergySource, 2012; Harrison et al., 2014; Featherstone et al., 2019; EnergySource Minerals, 2021). Numerous studies have shown that AlOH-based sorbents are effective at extracting lithium from geothermal brines, but full-scale commercial application of these sorbents still has not been proven.

3.3.2 Manganese oxides

Manganese oxides (MnOx) have been demonstrated to preferentially adsorb lithium from seawater (Ooi et al., 1986; Miyai et al., 1988). In the case of MnOx sorbents, the sorbents are often spinel structures and are usually cubic close-packed oxides (Feng et al., 1992; Feng et al., 1999; Zhang et al., 2017; Liu et al., 2019; Xu et al., 2021). For the preparation of manganese oxide porous crystals, metal ions can be used as templates to control the pore dimensions in various synthesis processes (Figure 1) (Feng et al., 1999). Manganese oxides show ion sieve properties and the spinel-type ion sieves have effective pore radii of 0.07 nm, which makes them selective for the adsorption of lithium (Feng et al., 1999). Materials that are commonly used as templates (Figure 1) for MnOx designed for lithium adsorption include lithium and magnesium; however, other metals may be added (Feng et al., 1993; Tian et al., 2010; Chaban et al., 2016; Levy et al., 2017; Chaban et al., 2019).

Studies have shown that MnOx sorbents are very selective for lithium over manganese, calcium, strontium, barium, sodium, and potassium (Feng et al., 1999; Xu et al., 2021). It has been established that MnOx crystals made with magnesium or lithium as the template metal (Figure 1) offer the best selectivity for lithium over monovalent and divalent cations (e.g., Feng et al., 1992; Feng et al., 1993; Chitrakar et al., 2002; Özgür, 2010; Zhang et al., 2010). Recepoglu et al. (2017) investigated the adsorption of lithium from geothermal water using both powdery and granulated forms of $\lambda\text{-MnO}_2$ derived from spinel-type lithium manganese dioxide and found that intra-particle diffusion was the kinetic rate-controlling step. Renew and Hansen (2017) used a MnOx sorbent as part of a process train for the extraction of lithium from geothermal brines. Pretreatment for removal of silica and divalent cations was considered critical to prevent coating of the MnOx sorbent, which would prevent lithium sorption.

Many variations of MnOx have been synthesized, characterized, and tested for lithium adsorption under a variety of conditions. For example, Liu et al. (2015) synthesized $\text{Li}_{1.6}\text{Mn}_{1.6}\text{O}_4$ and $\text{MnO}_2\cdot 0.5\text{H}_2\text{O}$. Other formulations include lithium antimony manganese oxides ($\text{MnO}_2\cdot 0.10\text{Sb}_2\text{O}_5$ hydrates) and iron-doped MnOx (Chitrakar et al., 2000; Chitrakar et al., 2014). Li et al. (2018) conducted a review of MnOx sorbents and identified maximum capacities of MnOx as approximately 55 mg/g, but more typically in the range of 20 to 40 mg/g.

Sorbed lithium can be recovered with dilute acid solutions; however, in some cases the adsorptive capacity for lithium ions decreased through repeated adsorption/elution cycles (Ooi et al., 1986; Miyai et al., 1988; Liu et al., 2019; Xu et al., 2021). Li et al. (2018) 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 using acid degrades the ion-exchange capacity and results in a poor cycling stability. This key issue limits MnOx potential for upscaling (Li et al., 2018).

Industrial application of MnOx (and other inorganic sorbents) frequently focuses on improving the stability of the sorbents and several different approaches to stabilizing sorbents have been proposed. Snyder (2018) proposed 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. Other suggested coatings include polymers, such as polystyrene and polydivinylbenzene, fluorides, fluoride polymers, and nitrides (Snyder, 2018). Ryu et al. (2017) successfully combined silica (SiO_2) with a lithium MnOx ($\text{Li}_{1.33}\text{Mn}_{1.67}\text{O}_4$) by a high-energy milling technique and calcination to impart improved stability to the spinel MnOx and reduced the level of Mn dissolution during the acid extraction of sorbed lithium. 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 (Chung et al., 2008; Park et al., 2012; Xiao et

al., 2012). Polymer nanofibers were used to stabilize MnOx sorbent and resulted in enhanced lithium sorption attributed to reduced interference for alkaline earth metals (Park et al., 2016; Chung et al., 2017). Other suggested stabilizing approaches include using chitosan, polystyrene, polydivinylbenzene, fluoride polymers, and sulfonate polymers (Chung et al., 2016; Ryu et al., 2016; Chung et al., 2017; Snyder, 2018; Snyder et al., 2019b, a).

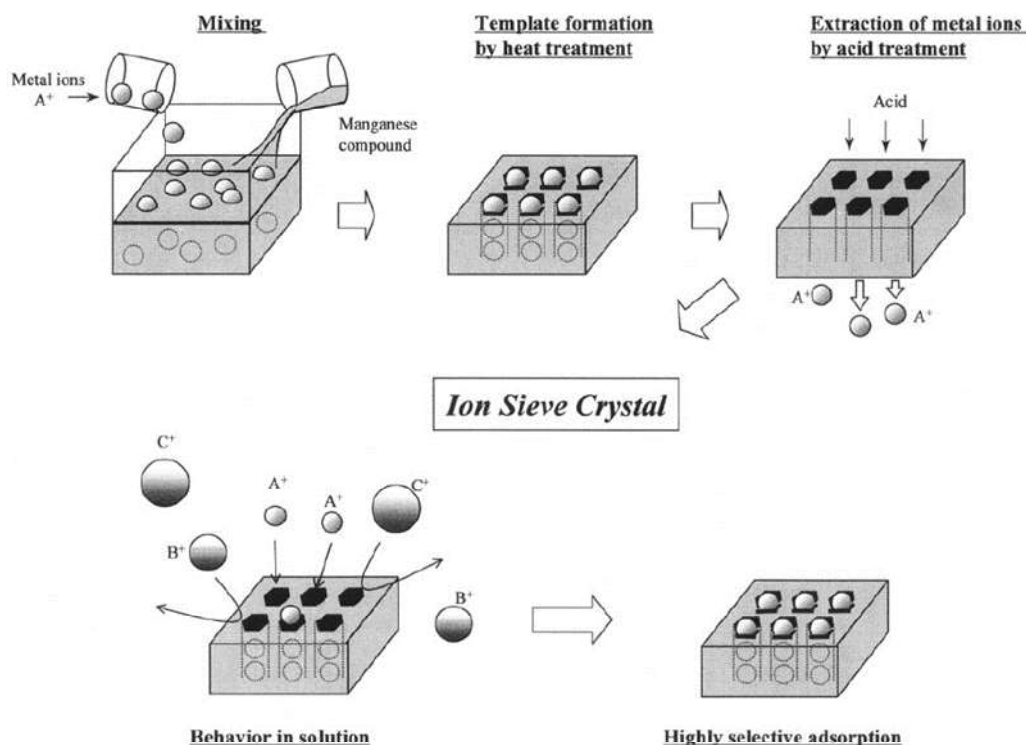


Figure 1. Schematic representation of the synthesis of manganese oxide ion sieve and ion-exchange behavior (Feng et al., 1999).

MnOx sorbents are widely considered very promising sorbents for full-scale application and new projects being developed for the extraction of lithium from Salton Sea geothermal brines may use MnOx sorbents in their lithium sorption processes (Chao, 2020). Other metal oxides, such as titanium oxides, have been shown to selectively adsorb lithium and may be utilized in the future, but currently these materials are still being investigated at a fundamental level in the laboratory and are not yet developed for commercial application (Li et al., 2018; Chaban et al., 2019).

3.3.3 Titanium oxides

Crystal TiOx that have been used in batteries have also generated interest as molecular sieve ion-exchange adsorbents for lithium (Li et al., 2018; Zhang et al., 2017; Zhu et al., 2012). Studies have demonstrated that TiOx were at least as effective as MnOx for the sorption of lithium ions from solution (Chaban et al., 2016; Li et al., 2018; Wang et al., 2017; Zhang et al., 2017). Spinel TiOx are more acid stable, potentially conferring robustness during cycling between sorption and stripping processes (Li et al., 2018). TiOx may have some advantages over MnOx, including being considered more environmentally friendly, but TiOx is still being investigated at a fundamental level in the laboratory (Chaban et al., 2019; Li et al., 2018). Few studies have examined the efficacy of TiOx in complex brines, but H₂TiO₃ was found to have high selectivity for lithium over other monovalent or divalent cations; however, sorption kinetics may be slow (Chitrakar et al., 2014a; Wang et al., 2017).

3.3.4 Other inorganic sorbents

Other metal oxides have been proposed for use as lithium adsorbents. Activated alumina, an aluminum oxide (AlOx), has been proposed as a sorbent for lithium extraction from brines (Burba et al., 2015; Burba et al., 2014; Fujii, 1994a, b; Harrison, 2015, 2013; Harrison et al., 2017; Harrison et al., 2019; Luo et al., 2008). Snyder et al. (2018) applied high-throughput density functional theory and specific ion interaction theory to identify candidate lithium metal oxide compounds and identified numerous compounds as potential lithium extractants, including LiAlO₂, LiCuO₂, Li₂MnO₃, Li₄Mn₅O₁₂, Li₂SnO₃, Li₄TiO₄, Li₄Ti₅O₁₂, Li₇Ti₁₁O₂₄, and Li₃VO₄ (Snyder et al., 2018). Titanium(IV) antimonate has been proposed as a cation-exchange sorbent for extracting lithium from seawater and hydrothermal brines (Abe and Chitrakar, 1987; Abe and Hayashi, 1984). Spinel-type lithium antimony manganese oxide has also been shown to be an effective variant of MnOx for the sorption of lithium (Chitrakar et al., 2000). Ho et al. (1978) filled the macropores of activated carbon

with a tin oxide and hydrous tin oxide and found high selectivity for lithium over other alkali metals. They also tested a number of other hydrous oxides, including Al(III), Fe(III), Zr(IV), and Nb(V), but did not find these metal oxides to be effective for lithium adsorption (Ho et al., 1978).

Other inorganic materials that have been proposed for sorption of lithium include thorium arsenate and natural or synthetic clays (Alberti and Massucci, 1970; Belova, 2010; Belova, 2017; Wisniewska et al., 2018). Crystalline $\text{Th}(\text{HAsO}_4)_2 \cdot \text{H}_2\text{O}$ was used to separate lithium from other alkali metal ions (Alberti and Massucci, 1970). Clay such as zeolite can be modified with AlOH and other chemicals to make lithium sorbates (Belova, 2010; Belova, 2017; Wisniewska et al., 2018). Belova (2017) found AlOH-modified zeolite showed selectivity with regard to lithium ions. Wisniewska et al. (2018) investigated the possibility of extracting lithium from geothermal water using natural and synthetic zeolites and zeolites treated with poly-acrylic acid.

3.4 Organic Solvent Separations

Solvent extraction is a well established technology for the separation of metals from aqueous solutions. Solvent extraction is economically used in industry for the extraction and concentration of metals, particularly valuable or semi-valuable metals, such as copper and uranium (Rotuska and Chmielewski, 2008; Fleitlikh et al., 2018; McKinley and Ghahreman, 2018; Perez et al., 2019; Nguyen et al., 2020; Solvay, 2020; Spasic et al., 2020). Solvent extraction is economical for the extraction of metals from aqueous solutions due to the simplicity of the equipment and operation, but chemical costs may be significant (Fleitlikh et al., 2018; McKinley and Ghahreman, 2018; Perez et al., 2019; Nguyen et al., 2020; Pramanik et al., 2020; Spasic et al., 2020). It has been shown that solvent extraction techniques may be used to separate lithium quantitatively and selectively from aqueous solutions (e.g., Lee et al., 1968; Hano et al., 1992; Swain, 2016; Li et al., 2017; Liu et al., 2019; Zhou et al., 2020; Xu et al., 2021). Metals extracted into an organic, nonpolar phase are typically recovered by use of an aqueous stripping agent, commonly an acidic solution, such as hydrochloric acid. The most lithium-selective solvents are in the family of crown ethers (Swain, 2016; Liu et al., 2019; Xu et al., 2021).

3.4.1 Crown ethers

Crown ethers and aza crown ethers have been shown to have selective reactivity with lithium (Swain, 2016). Cation extraction by the polydentate structure of crown ether is governed by the structure (steric properties) of the ether and electrostatic interactions between lithium and oxygens in the crown ether (Figure 2) (Swain, 2016). The selectivity order for alkali metals by crown ether is dependent on the cavity size and the bonding of lithium decreases as the crown ring size increases (Bartsch et al., 1985; Swain, 2016). Crown ethers and aza crown ethers of the structure 15-crown-5 or smaller have lithium selectivity (Figure 2), with 12-crown-4 and possibly 14-crown-4, with or without pendant arms, appear to have the greatest selectivity toward lithium over competing alkaline metals (Bartsch et al., 1985; Swain, 2016; Liu et al., 2019; Xu et al., 2021).

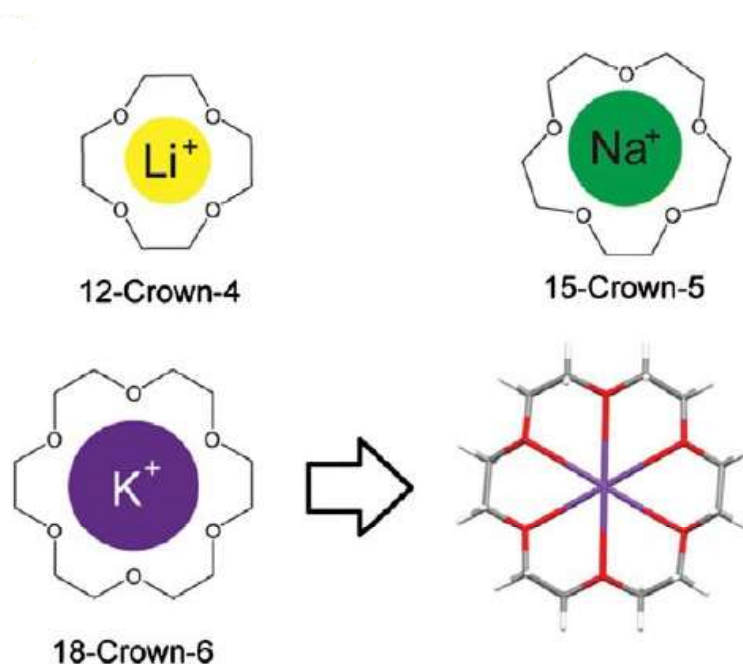


Figure 2. Crown ether ring size determines affinity for lithium ion, with smaller ring structures being more selective for lithium. (Swain, 2016).

Modifications of crown ether extractions include attaching crown ethers to carbon nanotubes, and combining crown ethers with ionic liquid extraction or supercritical fluid extraction (Abbott et al., 2011; Swain, 2016; Torrejos et al., 2016; Liu et al., 2019; Ruttinger et al., 2019; Zhu et al., 2019; Pálsdóttir et al., 2020; Xu et al., 2021). Crown ethers having pendant side arms with functional groups such as carboxylic acids, aromatic carboxylic acids, phosphoric acids, phenolic moieties, alcohols, and amines form strong bonds with lithium

(Swain, 2016; Liu et al., 2019; Xu et al., 2021). Several studies have investigated polymerized crown ethers for lithium extraction (Huang et al., 2018; Li et al., 2019; Xu et al., 2019; Bai et al., 2020; Li et al., 2020; Wang et al., 2020). All of these approaches have shown some degree of success for selective extraction of lithium from simple solutions.

Although crown ethers and aza crown ethers have been successful in the laboratory, there are significant barriers to commercial application of crown ethers for the 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 (Swain, 2016; Liu et al., 2019; Xu et al., 2021). 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 on fundamental and applied properties of crown ethers in the context of geothermal lithium is needed (Swain, 2016; Liu et al., 2019; Xu et al., 2021).

3.4.2 Multicomponent solvent systems

Organic solvent processes for metal extraction and purification frequently use a mixture of chemicals that include: 1) an extractant, such as a metal chelating or binding reagent; 2) a co-extractant, such as an adduct-forming synergistic reagent; and 3) a diluent or bulk solvent. Example diluents are kerosene, xylene, and alkanes, such as dodecane (Fleitlikh et al., 2018; Lee et al., 1968; Nguyen and Lee, 2018; Spasic et al., 2020; Zante et al., 2020a). Extractants include neutral species, such as ketones, beta-diketones, or organophosphates and ionizable species, such as carboxylic or phosphoric acids and amines and other ionizable functional groups (Fleitlikh et al., 2018; Liu et al., 2019; Nguyen and Lee, 2018; Nguyen et al., 2020). A variety of organic and inorganic compounds, such tri-n-octyl phosphine oxide (TOPO) or ferric chloride, serve as synergistic adducts. In some cases, extractants such as di-2-ethylhexylphosphoric acid (D2EHPA) are used alone (Nguyen and Lee, 2018; Spasic et al., 2020). More frequently, synergistic mixtures, such as D2EHPA and TOPO, are applied together to enhance selectivity or recovery efficiency (Spasic et al., 2020).

Solvent extraction was proposed for the extraction of lithium from aqueous solutions of alkali metal salts as early as 1954 (Fernelius and Vanuiter, 1954). Lee et al. (1968) extracted lithium from a solution of alkali metal salts using an adduct between dibenzoylmethane (DBM) and TOPO. The resulting product had the form $\text{LiDBM}\cdot 2\text{TOPO}$ or $\text{Li}_2(\text{DBM})_2\cdot 2\text{HDBM}\cdot 4\text{TOPO}$, depending on the original solution composition. The chelated lithium was extracted with dodecane or p-xylene (Lee et al., 1968). Other investigators have used a variety of combinations of co-extractants to recover lithium from solution (e.g., Ghorbanzadeh et al., 2018; Granata et al., 2012; Guo et al., 2013; Hano et al., 1992; Yang et al., 2020; Zhang et al., 2020a). Individual organophosphorus compounds have also been investigated for the direct extraction of lithium from solution (El-Eswed et al., 2014; Nguyen and Lee, 2018). Neutral extraction systems containing tributyl phosphate (TBP), FeCl_3 , and kerosene have been extensively investigated (Liu et al., 2019; Nguyen and Lee, 2018; Su et al., 2020a; Su et al., 2020b; Zhou et al., 2020).

Generally, the combination of beta-diketone and neutral ligand has an excellent performance for the lithium extraction and separation from other alkali metal ions (Liu et al., 2019; Swain, 2016; Pranolo et al., 2015). However, experience in the lithium battery recycling industry specifically and mining applications generally show that solvent extraction systems favor the complexation of transition metals, such as cobalt and copper, and divalent alkaline earth metals over lithium (e.g. Hano et al., 1992; Xu et al., 2021). It can be concluded that ketone, beta-diketone and organophosphorus solvents 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, particularly for the removal of the divalent cations and interfering or valuable metals (e.g., Boukraa, 2020; Featherstone et al., 2019; Nguyen and Lee, 2018; Torkaman et al., 2017; Virolainen et al., 2016; Xu et al., 2021; Yang et al., 2020).

3.4.3 Alternative diluents: Ionic liquids and supercritical carbon dioxide

Ionic liquids and supercritical carbon dioxide have been used as diluents for solvent extraction systems. Ionic liquids are frequently employed as the diluent with ketones, beta-diketones, or organophosphates (Liu et al., 2019; Shi et al., 2014; Shi et al., 2015; Shi et al., 2016, 2017a; Shi et al., 2017b; Shi et al., 2020a; Zante et al., 2020b; Zhou et al., 2020). Supercritical carbon dioxide has been used as a diluent for crown ethers (Pálsdóttir et al., 2020; Palsdottir and Tester, 2019; Ruttinger et al., 2019).

Ionic liquids can have properties as an extractant or as co-extractants and ionic liquids have also been investigated for the separation of lithium isotopes (Abbott et al., 2011; Liu et al., 2019; Swain, 2016; Xu et al., 2013). Imidazole ionic liquids were shown to have properties for the direct extraction of lithium ions, even in the absence of a co-extractant or chelating agent (Shi et al., 2017b; Shi et al., 2020a; Wang et al., 2018). However, the selectivity of ionic liquids has not been fully demonstrated. For example, it was shown that tetrabutylammonium 2-ethylhexyl hydrogen-2-ethylhexylphosphonate was effective for the separation of lithium from other alkaline metals, but the ability of this ionic liquid to separate lithium from alkaline earth or other cations was not investigated (Shi et al., 2020a).

Although ionic liquids show promise for use in the selective extraction of lithium from geothermal brines, their application may be problematic. (Abbott et al., 2011). Loss of the ionic liquids into the extracted solution is a common problem (Liu et al., 2019; Shi et al., 2015; Wang et al., 2018). Physical properties (such as viscosity) and solubilities with water will limit the choice of ionic liquids that can be used (Abbott et al., 2011). The high cost of these solvents also suggests that ionic liquids are better suited to small volume applications for extraction of high value metals (Abbott et al., 2011). 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 (e.g., Abbott et al., 2011; Liu et al., 2019; Masmoudi et al., 2020; Zhou et al., 2020).

3.4.4 Modification on solvent extraction: Supported liquid membranes and other surfaces

Supported liquid membranes (SLM) are a variant of multicomponent solvent systems (Misra and Gill, 1996; Parhi, 2013; Parhi and Sarangi, 2008). 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 a bulk liquid membrane, where a flat membrane separates a solvent phase from the aqueous phase and an emulsion liquid membrane, where surfactants are added to form emulsions that can be separated by a membrane (Misra and Gill, 1996). Other modifications on solvent extraction include impregnation of resins or solid supports with extractants or extractant mixtures (Guo et al., 2013; Nishihama et al., 2011).

Stability of SLM is a key issue for the application of these solvent membrane systems (Song et al., 2014; Swain, 2016; Zante et al., 2020a). For example, Ma and Chen (2000) reported the extraction of lithium from geothermal water with the SLM technique using a mixture of extractants, including TOPO, immobilized in a porous membrane. This SLM showed 95% extraction of lithium ions in just 2 hours; however, it exhibited stable performance for only up to 72 hours before the flux dropped drastically (Ma and Chen, 2000). Membranes have been observed to lose capacity quickly (Paredes and de San Miguel, 2020; Zante et al., 2020a). Some systems appear to be more stable than other systems and several investigators concluded that SLM is suitable for the extraction of lithium from brines (Song et al., 2014; Zante et al., 2020a).

3.5 Membrane Separations Technology

Research on membrane separations for direct lithium extraction is predominantly focused on filtration membranes that allow permeation of the lithium ion and reject other ions (Zhang et al., 2020b). 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 (Zhang et al., 2020b). In the context of lithium recovery from brines, membranes are predominately used to pretreat brines for the removal of divalent cations, metals, and other interfering substances before the process of concentrating, precipitating or otherwise extracting lithium (Li et al., 2019b; Liu et al., 2019; Zhang et al., 2020b). Membranes that are designed to retain lithium are typically not rejecting lithium, per se, but rather are adsorbing lithium preferentially and allowing other ions to pass (e.g., Lu et al., 2018). Polymer membranes that adsorb lithium are discussed under adsorbents.

Reverse osmosis (RO) could potentially be applied to pretreatment of geothermal brines; however, the application would be for water removal to concentrate brines before precipitation, sorption, or other concentration steps (e.g., Somrani et al., 2013; Wang et al., 2020a). RO is not selective for lithium or other specific ions and serves the same function as evaporation or distillation in lithium processing (i.e., water removal). It is not apparent that RO will ever be economical to apply to treatment of geothermal brines.

Nanofiltration has been investigated extensively for the separation of lithium from magnesium and other interfering divalent cations (Bi et al., 2014; Li et al., 2017; Somrani et al., 2013; Sun et al., 2015; Tian et al., 2010; Wang et al., 2020a; Wen et al., 2006; Yang et al., 2011; Zhang et al., 2020b; Zhongwei and Xuheng, 2015). Since 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 (e.g., Eramet, 2020b; Featherstone et al., 2019; PurLucid Treatment Solutions Inc., 2020; Renew and Hansen, 2017; Wang et al., 2020a).

3.6 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 (Duyvesteyn, 1992; Duyvesteyn and Sabacky, 1995; McKinley and Ghahreman, 2018). 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 (Ball and Boateng, 1987; Yang and Hou, 2012; Zhang et al., 2020b). Electrodialysis for lithium extraction can be used with SLM and potentially other modifications of solvent extraction technology (e.g., Hoshino, 2013; Liu et al., 2020). 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 (Ammundsen and Paulsen, 2001; Liu et al., 2015b; Liu et al., 2014; Xu et al., 2012; Zhongwei and Xuheng, 2015; Zhu et al., 2018).

In systems for the separation and recovery of lithium, electrical potential is applied to improve selectivity or process kinetics in combination with membrane and sorbent technology discussed above. Ball and Boateng (1987) used electrodialysis with lithium-selective membranes and lime precipitation to separate lithium from magnesium and other multivalent cations. Itoh et al. (1999) proposed an electrodialysis method using a lithium-selective “partition” composed of TiO_x crystals that would allow the selective passage of lithium. Chang et al. (2004) proposed combining adsorption and electrodialysis to enrich lithium ions in brine from a level of several ppm to about 1.5% in a process that uses electrodialysis as a post-extraction concentration step. Zhongwei and Xuheng (2015) 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 (Zhongwei and Xuheng, 2015).

Mroczek et al. (2015) applied electrodialysis to geothermal brines from the Wairakei (NZ) geothermal power station. The geothermal fluid was first desilicated using electrocoagulation with aluminum electrodes and then lithium was extracted with electrodialysis. The influence that the voltage, current, fluid temperature, and acidification had on lithium extraction was measured in a laboratory electrodialysis unit (Mroczek et al., 2015). 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 about 2-4, and the highest extraction rate achieved

was 0.28 mg/hour·cm² of active membrane using a three-membrane stack. Increased current increased the extraction rate, but had a negative effect on membrane lifetime (Mroczek et al., 2015).

Li et al. (2019b) reviewed selective electrodialysis in the context of lithium extraction from water. They noted that the extraction of lithium ion from salt lake brines can be achieved by electrodialysis using commercially available anion-exchange membranes and lithium iron phosphate (LiFePO₄)/iron(III) phosphate (FePO₄) electrodes. Parameters such as pH and salt content influenced lithium extraction and that lithium adsorption as high as 38.9 mg/g could be achieved (Li et al., 2019b). The applied voltage, feed velocity, feed lithium to magnesium ratio and pH significantly influenced the lithium to magnesium separation factor (Li et al., 2019b). It was concluded that selective electrodialysis was superior to nanofiltration for the fractionation of lithium to magnesium in solutions with a high initial mass ratio (Li et al., 2019b). However, it was suggested that the poor durability of ionic membranes is a major issue preventing electrodialysis becoming a practical technology for the recovery of lithium from brines (Li et al., 2019b).

4. PRETREATMENT BEFORE DIRECT LITHIUM EXTRACTION

For all direct lithium extraction technologies, the presence of interfering substances will require that the technology for lithium extraction be applied in conjunction with other processes, as part of a process “train” consisting of multiple stages. For inorganic ion sieve ion-exchange sorbents, the selectivity of the sorbent, the tolerance of the sorbent for interfering ions, and the purity of the lithium extracted from the sorbent will be major cost drivers for real-world applications (Kay, 2020). How the direct lithium extraction technology performs in the presence of any number of co-occurring chemical elements, including magnesium, calcium, manganese, and heavy metals, will determine the level of pretreatment required before the lithium extraction step. The level of pretreatment needed for a geothermal brine will also depend on available options for post-extraction purification and the purity requirements, which vary by application and buyer, for the lithium chloride, lithium carbonate, or lithium hydroxide product.

Geothermal fluids are complex solutions (Table 1) and even the most selective molecular sieves adsorb undesirable minerals from lithium leachates or brines (Jiang et al., 2020; Mceachern et al., 2020; Perez et al., 2014; Xu et al., 2021). The initial brine composition determines the production process, which typically includes: 1) one or more pretreatment steps, to prepare the brine for lithium extraction; 2) the lithium extraction and recovery process, to concentrate the lithium from the brine, typically as a lithium chloride; and 3) post-extraction processing, to remove impurities from the recovered lithium and convert lithium chloride to other products (e.g., Munk et al., 2016; Perez et al., 2014). For geothermal brines, typical materials that must be removed or reduced in concentration before lithium extraction include silica, magnesium, calcium and other metals (Mceachern et al., 2020). Major elements and compounds found in geothermal brines that can interfere in lithium extraction include other alkali metals (Na, K), alkaline earth metals (Mg, Ca, Sr, Ba), so-called heavy metals (Mn, Fe, Zn, Pb), and metalloids (B, Si, As) (Abe and Chitrakar, 1987). In Salton Sea brines, lithium is not the most abundant element (Table 1), and many other more abundant elements may need to be removed or controlled before lithium can be adsorbed using currently available technology.

4.1 Alkali Metals

Alkali metals other than lithium often occur in brines at concentrations many times greater than lithium concentrations (Table 1) and even though most inorganic metal oxide sorbents are preferentially selective for lithium over sodium or potassium, due to the much higher concentrations of sodium and potassium than lithium in typical brines, it is still possible for these elements to reduce the efficiency of lithium sorption (Chitrakar et al., 2014a; Shi et al., 2011; Snyder et al., 2018; Xiao et al., 2012). For maximum economic value, the final lithium product, such as lithium carbonate, lithium chloride, or lithium hydroxide, must be essentially free of sodium and potassium (Perez et al., 2014). The separation of lithium from sodium and potassium can be accomplished using solvents, precipitation, selective filtration and other methods that are typically applied after other pretreatment steps (e.g., Chitrakar et al., 2014a; Harrison and Burba, 2017a; Meshram et al., 2014; Nishihama et al., 2011; Samco, 2018). Potassium is also removed and recovered as potentially valuable potash (Harrison, 2014; Harrison et al., 2014; Samco, 2018).

4.2 Alkaline Earth Metals

Pretreatment for the removal of alkaline earth metals, particularly calcium and magnesium, is an important anticipated cost for commercial deployment of molecular sieve sorbents (EnergySource Minerals, 2020; Key, 2020; Mceachern et al., 2020; Samco, 2018). Separation of lithium from magnesium is critical to achieving high recovery efficiency and purity of the final lithium product (Jiang et al., 2020; Mceachern et al., 2020; Perez et al., 2014; Xu et al., 2021). 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.

Xu et al. (2021) 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 (Xu et al., 2021). Ion-exchange resins are often applied for the separation of alkaline earth metals from alkaline metals (Lee and Bauman, 1980b; Shi et al., 2020b). Nishihama et al. (2011) purified the recovered lithium 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 the recovery of lithium as precipitates of Li₂CO₃ using (NH₄)₂CO₃ saturated solution. The yield of recovered Li₂CO₃ with this process was 56% with more than 99.9% purity (Nishihama et al., 2011). Bukowsky et al. (1991) demonstrated that precipitation followed by ion-exchange can be effectively used for separation and recovery of lithium from a synthetic solution of calcium and magnesium chlorides. Laitala et al. (2017) proposed using precipitation with sodium carbonate or calcium hydroxide for bulk precipitation of magnesium and calcium, followed by liquid-liquid extraction with organophosphates to remove residual calcium and magnesium. Perez et al. (2014) used two-stage precipitation of magnesium with calcium hydroxide to recover virtually all magnesium precipitated in the form of magnesium hydroxide, but also significant quantities of calcium in the form of gypsum (CaSO₄·2H₂O) and

boron in the form of calcium borate ($\text{CaB}_2\text{O}_4 \cdot 6\text{H}_2\text{O}$). Magnesium can also be removed from lithium brines by using oxalic acid precipitation (Meshram et al., 2014).

Many other approaches for removing or controlling alkaline earth metals have been proposed as part of direct lithium extraction processes including nanofiltration and modified nanofiltration using chemical reagents (e.g., Li et al., 2017; Li and Binnemans, 2020; Renew and Hansen, 2017). Xu et al. (2021) 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 (Xu et al., 2021).

4.3 Heavy Metals

Numerous transition and post-transition metals co-occur with lithium in geothermal brines. Of particular concern are iron and the so-called heavy metals, which may occur in high concentration, may form scales or precipitates (e.g., iron), 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 could potentially benefit the economics of lithium recovery (Bakane, 2013; Millot et al., 2020).

The US Department of the Interior, Bureau of Mines extensively investigated the potential for mineral recovery from Salton Sea geothermal brines (Blake, 1974; Berthold et al., 1975; Christopher et al., 1975; Crane, 1982; Maimoni, 1982; Schultze and Bauer, 1982a,b, 1984, 1985). One process that was developed involved the precipitation of mixed hydroxides of iron, zinc, manganese, and lead (Christopher et al., 1975; Maimoni, 1982). The hydroxide precipitation process was investigated and developed for a number of years, and included variations such as partial oxidation, but eventually the investigators concluded that the quality of the hydroxide precipitate was poor in terms of metal content and value and suggested that sulfide precipitation would be a better approach for metals recovery (Schultze and Bauer, 1982a). Subsequent studies by the Bureau of Mines investigated sulfide precipitation using real brines, but it was not apparent that sulfide precipitation was applied or tested at the pilot scale (Schultze and Bauer, 1985).

CalEnergy Minerals operated a zinc metal manufacturing facility at its Elmore power plant in the Salton Sea KGRA (Clutter, 2000; Geothermal Resources Council, 2004; MidAmerican Energy Holding Co., 2003). The demonstration plant produced 41,000 lbs. of high-grade zinc using an ion-exchange process (Clutter, 2000). 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 and then recovered and melted into ingots (Clutter, 2000; EnergySource, 2012). The facility operated commercially for a number of years, but the venture was ultimately abandoned (Bloomberg, 1999; Clutter, 2000; Geothermal Resources Council, 2004).

Maimoni (1982) 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. Manganese and zinc have been identified as attractive targets for economic metals recovery (Bakane, 2013; Cetiner et al., 2015; Christopher et al., 1975; Harrison et al., 2014; Schultze and Bauer, 1985). MidAmerican Energy Holding Co. (2003) conducted laboratory-scale studies using solvent extraction for manganese pretreatment and recovery. Solvent-extracted manganese was converted to manganese dioxide by electrolytic oxidation, however co-extracted iron and calcium affected the value of the process (MidAmerican Energy Holding Co., 2003).

4.4 Metalloids & Other Elements

High concentrations of silica occur in geothermal brines and geothermal power plants have silica control processes as part of their normal operations (Brown, 2011; MidAmerican Energy Holding Co., 2003; von Hirtz, 2016). 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 (MidAmerican Energy Holding Co., 2003; von Hirtz, 2016). It is recognized that silica is a major scale-forming chemical and will need to be managed as part of any geothermal lithium process (Bakane, 2013; Bourcier et al., 2005; Harrison, 2014; Harrison and Burba III, 2014; Harrison and Burba, 2017a, b, 2019; Rothbaum and Middendorf, 1986). In most cases considering geothermal lithium, silica control is presumed to be precipitation, but other processes such as ultrafiltration and electrocoagulation to remove silica have been proposed (Iwanaga et al., 2007; Bourcier et al., 2009; Sato et al., 2020). There is also some interest in creating a marketable product out of silica precipitated during geothermal power production and geothermal lithium production process (Bloomquist and Povarov, 2008; Harrison et al., 2014; MidAmerican Energy Holding Co., 2003).

Boron is a commonly co-occurring metalloid that must be separated from lithium for most lithium applications (Bell, 2020; Belova, 2010; Bunani et al., 2017; Kesler et al., 2012; Recepoglu et al., 2018; Steinmetz, 2017; Tan et al., 2018; Wisniewska et al., 2018). Most boron removal processes involve precipitation, but solvent extraction is also applied (Brown et al., 1981; Perez et al., 2014). Precipitation treatment was used as part of a process train to produce to produce high purity lithium carbonate and chloride (Brown and Boryta, 1981, 1993; Brown et al., 1981).

Other elements such as arsenic, phosphates and fluorides can interfere with lithium adsorption from geothermal brines or reduce the value of recovered lithium (Park et al., 2012; Recepoglu et al., 2018). Although these compounds have not been investigated extensively in the context of geothermal lithium, they have been considered in the context of battery recycling (e.g., Asano et al., 2017; Park et al., 2012). Recycling companies use staged pH adjustment and solvent stripping to separate lithium from contaminants such as phosphorus and fluorine (Asano et al., 2017; Ishida and Asano, 2015). During chemical treatment of Salton Sea brines with acids or reducing agents to inhibit the formation of ferric silicate scales in well casings and brine pipelines, the deposition of silver-rich scales was observed (Gallup, 1992).

4.5 Integrated Systems for Commercial Direct Lithium Extraction

There are numerous examples of process trains for lithium recovery from geothermal brines and most, in not all, include steps for removing alkaline and alkaline earth metals and many include processes for heavy metal removal or recovery. Most processes for geothermal brines were applied in the laboratory or proposed on paper, but some direct lithium extraction processes have been pilot tested at geothermal facilities in the Salton Sea KGRA (EnergySource Minerals, 2021, 2020; Featherstone et al., 2019; Harrison, 2014; Harrison et al., 2014; Schultze and Bauer, 1984). New geothermal lithium projects are under commercial development in the Salton Sea KGRA and there is also interest in extraction of lithium from geothermal brines in Europe (Chao, 2020; EnergySource Minerals, 2021, 2020; Eramet, 2020a). As discussed above, the most advanced technologies are in the realm of solid adsorbents and most, if not all, current commercial lithium recovery process are based on using molecular sieve ion-exchange sorbents for the extraction of lithium.

5. CONCLUSIONS

There are a number of different approaches being investigated for the direct extraction of lithium from geothermal brines. The most advanced technologies are in the realm of solid adsorbents and most commercialized lithium recovery process are based on using molecular sieve ion-exchange sorbents for the extraction of lithium. Although many solid sorbents are entering commercial application, 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 under real-world conditions. The full-scale application of more advanced AIOH and MnOx sorbents still needs to be demonstrated.

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 is still at a very low technology readiness level and has not been proven against geothermal brines. However, if this technology can be validated, it has the potential to reduce the need for extensive pretreatment and simplify extraction processes. Other promising low technology readiness level technologies include ion-imprinted polymers and cyclic siloxanes.

It is apparent that lithium extraction and recovery from geothermal brines is becoming technically possible, but challenges still remain in developing a sustainable process 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 geothermal lithium resource extraction.

6. ACKNOWLEDGMENTS

This work is supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE), Office of Technology Development, Geothermal Technologies Office, under Award Number DE-AC02-05CH11231 with LBNL. We would like to thank Ji Yeon Lee (LBNL) for her assistance on this project.

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