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Valorization of Geothermal Waters: the Development and Testing of a Supercritical Fluid Extraction Process for the Recovery of Lithium

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ABSTRACT

Many geothermal waters are enriched in a range of metals and minerals. Lithium has been identified as one of the more attractive metals for extraction and has also been defined by the U.S. Department of Energy as a critical material because of its use in batteries for electric vehicles and portable electronics. Extraction of lithium from geothermal brines has been attempted with a range of different methods, most depending on adsorption or ion exchange on a surface. Because of the dependence on surfaces, scaling can be severely detrimental to the recovery of lithium and silica removal is required for the processes to operate. Additionally, there has been a lack of focus on the concentration process necessary to make geothermal waters feasible for the production of lithium chemicals, which are generally made from brines that have been concentrated to about 4,000-6,000 mg/L.

Compared to conventional lithium extraction and concentration methods, a supercritical fluid extraction process is faster, more environmentally friendly and not sensitive to silica scaling. By using a lithium selective crown ether extractant dissolved in supercritical carbon dioxide the extraction process takes about an hour and results in significant concentration of lithium into an aqueous solution. It takes place across a fluid interface at pressures and temperatures sufficient to both prevent silica scaling and limit the effect of scaling if it happens. The overall extraction efficiency of lithium from a 10 mg/L synthetic geothermal water solution is 30% in a batch operated process, at 60°C and 250 bars. In this paper we present both the development and synthesis of the lithium selective crown ether extractants, and the application of those extractants in the novel supercritical fluid extraction of lithium from synthetic geothermal brines.

1. INTRODUCTION

Geothermal brines can be highly enriched in selected dissolved metals and minerals compared to seawater and groundwater and a number of geothermal brines are enriched in lithium. This is the result of continuous interactions of geothermal fluids with lithium-bearing rocks at depth and under elevated temperatures typical of a geothermal system.

Mining lithium from geothermal brines unlocks a new revenue stream for geothermal operations. In Table 1 the concentration of lithium in geothermal brines pumped out of the ground in select geothermal areas is presented. To understand the scale of potential lithium production from geothermal brines, in the generation of 250 MW_e from a liquid-dominated geothermal steam flash plant, up to 175,000 m^3 of brine may be processed per day (Gallup, 1998). The lithium production on a yearly basis from geothermal power plants could therefore be on the order of 300-900 tons, or 1600-4800 tons of lithium carbonate which is the most commonly traded form of lithium for battery production. The price of battery grade lithium carbonate is about 15,000 USD/ton at the moment (Metalary, 2019), giving an estimated total value of 24-72 million USD in the brine of a 250 MW_e geothermal power plant.

Table 1: A comparison of the lithium concentration in brines in geothermal areas with the lithium concentration in lithium brines mined for lithium.

Geothermal Area	Li [mg/L]
Salton Sea, CA	132
East Mesa, CA	4.3
Coso Hot Springs, CA	25
Dixie Valley, NV	2
Yellowstone, WY	0.1-3.5
Fenton Hill, NM (EGS)	6-250
Valles Caldera, NM	3-25
Reykjanes, Iceland*****	4.18
Seawater	0.17
Salar de Atacama, Chile	1000-4000
Salar del Hombre Muerto, Argentina	220-1000
Salar de Uyuni, Bolivia	500-3000
Silver Peak, NV	230

Despite the elevated concentration of lithium in geothermal brines, the concentrations tend to be at least an order of magnitude lower than the concentrations in salt lakes where lithium is currently extracted in commercial operations. The concentrations in geothermal brines range from 4 – 130 mg/L whereas the concentrations in traditional lithium extraction from salt lake brines are in the range of 200 – 4000 mg/L (Fowler & Zierenberg, 2015; Gallup, 1998; Grigsby & Tester, 1989; Harrar & Raber, 1983; Legers, 2008; Stauffer, Jenne, & Ball, 1980). These relatively low concentrations demand the development of new and alternative methods for lithium extraction. Extraction of lithium from geothermal brines has been attempted with a range of different methods, most depending on adsorption or ion exchange on a surface. Because of the dependence on surfaces, scaling can be severely detrimental to lithium extraction and silica removal is required for the processes to operate. Additionally, there has been a lack of focus on the concentration process necessary to make geothermal brines feasible for the production of lithium chemicals, which are generally made from brines that have been concentrated to about 4,000-6,000 mg/L.

We have developed an alternative method that does not rely on solid extraction surfaces or membranes, making it less susceptible to surface scaling and more tunable to varying concentrations of dissolved species found in different geothermal systems. The supercritical fluid extraction process avoids this limitation as it involves transferring extracted components across a fluid interface rather than onto a solid surface or through a solid membrane. A supercritical fluid extraction process is also suited for operation at or above the temperatures and pressures typically present in geothermal applications (120 - 320°C and 0 - 23 bars (Eliasson, Thorhallsson, & Steingrimsson, 2011)). The absence of solid surfaces minimizes precipitation problems commonly encountered when temperatures and pressures are reduced for geothermal brines during energy extraction. The supercritical fluid extraction process also concentrated lithium in the geothermal brine from 10 mg/L to 5,000 mg/L in about an hour, a process that takes 12-18 months in traditional lithium recovery from salt lake brines through solar evaporation (Grosjean, Miranda, Perrin, & Poggi, 2012).

1.1 Supercritical Fluid Extraction Process

Supercritical fluids are substances that have exceeded their critical temperature and pressure. In the near critical region, their properties are highly tunable and scale with changes in density that are easily specified by fixing temperature and pressure. We have taken advantage of the solubility changes of selective extractants in supercritical carbon dioxide ($ScCO_2$), when developing a lithium extraction process with $ScCO_2$ as a solvent. The low viscosity and high diffusivity of $ScCO_2$ also allow for the operation of a fast process and the strong dependence of the solubility of compounds in $ScCO_2$ on pressure is a key feature in enabling a quick increase in the concentration of lithium in the fluid produced from the extraction (Gupta & Shim, 2006). The high compound solubility at high pressures enables the operation of an extraction process that is carried out at a specific supercritical pressure. After separation of the supercritical phase from the original host phase, the extracted material is precipitated out by lowering the pressure to a specific level, often near or below the critical pressure of the solvent, where the solubility of the extracted material is significantly reduced. The substantial change in solubility that results with changing pressure enables rapid concentration of lithium in the produced fluid.

Figure 1 schematically depicts a supercritical extraction process for the extraction of lithium from a lithium-containing brine on an industrial scale. A lithium-containing brine is pumped through an extraction reactor where it comes into contact with a supercritical fluid phase with a dissolved extractant. Lithium transfers from the brine phase into the supercritical phase by selective capture of lithium ions in the extractant. The supercritical phase flows out of the extraction reactor through a pressure reducing valve and into a condenser. The lithium removed from the brine in the extraction reactor is precipitated out of solution in the condenser and concentrated in an organic solvent. In this way the lithium is extracted from the brine and concentrated in a single process. After being captured in an organic solvent in the condenser, the lithium is washed out of the organic solvent in a stripping process with a mineral acid, and subsequently can be made into lithium products.

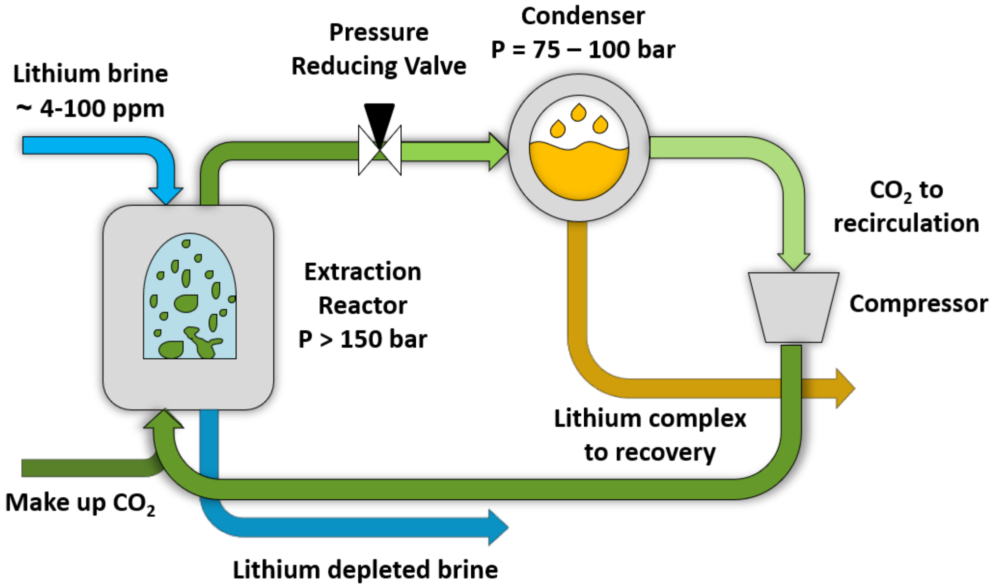

Figure 1: A schematic depiction of the supercritical fluid extraction of lithium from a lithium brine on an industrial scale.

1.2 Crown Ether Extractants

In our supercritical fluid extraction process we use strategically designed crown ether extractants, developed and synthesized in our research group, paired with a commercially available cation exchanger. The crown ethers and cation exchanger used in this research are depicted in Figure 2.

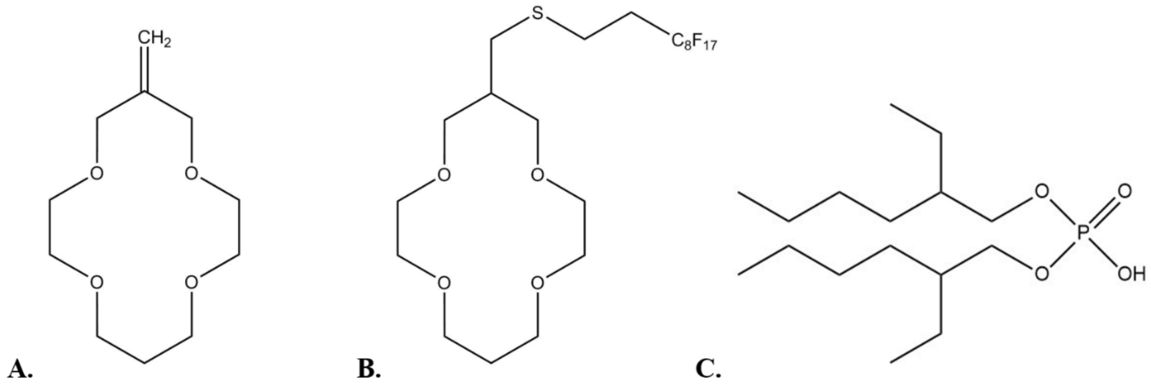

Figure 2: The crown ether extractants and cation exchanger used in the extractions performed in this research. A. M14C4 (methylene-14-crown-4), B. F14C4 (fluorinated 14-crown-4), and C. HDEHP (bis(2-ethylhexyl) phosphate).

A key feature for the development of a supercritical fluid extraction process for the extraction of lithium is the selection and development of a lithium extractant. Previous research has shown 14-crown-4 ethers to be effective lithium extractants (Czech, Babb, Son, & Bartsch, 1984; Inoue, Hakushi, Liu, & Tong, 1993; Suzuki et al., 1993) but the research on crown ether solubility in supercritical carbon dioxide, which is critical to the effectiveness of a supercritical fluid extraction process, is not encouraging (Wang, Elshani, & Wai, 1995). We therefore selected two different crown ether extractants for our development of a supercritical fluid extraction process for lithium; 3-methylene-14-crown-4 and a novel fluorinated 14-crown-4, first synthesized in our laboratory. We developed the fluorinated 14-crown-4 to make a highly ScCO$_2$ soluble lithium extractant building upon previous work that has shown fluorination to be an effective way to increase the solubility of metal extractants in ScCO$_2$ (Laintz, Wai, Yonker, & Smith, 1991).

2. EXPERIMENTAL PROCEDURE

2.1 Crown Ether Extractant Synthesis

The procedure for the synthesis of 3-methylene-14-crown-4 (M14C4) was adopted from published literature procedures (Czech et al., 1984, 1992; Tomoi, Abe, Ikeda, Kihara, & Kakiuchi, 1978)). A fluorinated side chain was attached at the methylene attachment point through thiol-ene click chemistry to make the novel fluorinated 14-crown-4 ether (F14C4).

^{1}H NMR and ^{13}C NMR spectra were obtained with a Mercury 300 MHz spectrometer while ^{19}F NMR measurements used an INOVA 400 MHz spectrometer. All spectra were taken in deuterated chloroform and chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane (TMS). Direct analysis in real time – high resolution mass spectrometry (DART-HRMS) was obtained with IonSense DART coupled with HRMS and is reported in g/mol with the molecular formula. All of the compounds subjected to DART-HRMS were detected as $[M+H]^+$, which is consistent with gas-phase ionization processes presented in the literature (Gross, 2014). Chemicals were purchased from MilliporeSigma, Oakwood Chemicals, and Santa Cruz Biotechnology, and were used without further purification.

2.1.1 3-methylene-14-crown-4 (M14C4)

M14C4 was synthesized and purified according to the following procedure that was adapted from the literature (Czech et al., 1992):

5.0 g of 3,7-dioxa-1,9-nonanediol (30 mmol) and 3.8 g of 3-chloro-2-chloromethyl-1-propene (30 mmol) were each dissolved in separate vials in 17 mL of dry tetrahydrofuran (THF). 4.6 g of sodium hydride (192 mmol) were dissolved in 68 mL of dry THF and allowed to equilibrate at reflux conditions for 1 hour. The previously prepared mixtures of the reactants and THF were slowly added to the refluxing solution (~1 mL/min). The reaction was allowed to proceed for 72 hours at which point the excess sodium hydride was destroyed with 20 mL of methanol. The solvents were dried off under reduced pressure and the resulting mixture was resuspended in 50 mL of methylene chloride and washed with 50 mL of deionized water. The water was subsequently washed with 2x50 mL of methylene chloride. The resulting combined methylene chloride solution was dried over sodium sulfate and filtered. Note that the solution was not filtered through celite because the ethers in the solution are not stable in contact with celite. The solution was then dried under reduced pressure to collect the crude product. The crude product was distilled under reduced pressure (at about 5 torr) to give 1.3 g of a purified product. The leftover crude after the distillation was further purified by column chromatography. The solid phase was basic alumina and the solvent system was hexanes/ethyl acetate (0-30% ethyl acetate). The chromatography provided an additional 0.13 g of purified product. The combined yield on a mass basis was 22%. The NMR spectra and DART-HRMS can be seen in the SI; the data is as follows: ^{1}H NMR: δ 1.77 (pentet, 2H), 3.59-3.67 (multiplet, 12H), 4.13 (singlet, 4H) and 5.14 (singlet, 2H); ^{13}C NMR: δ 28.65 (CH$_2$), 65.61, 68.41, 69.71, 70.56 (CH$_2$O), 113.77 (=CH$_2$), 142.62 (=C); DART-HRMS: 216.14 g/mol (C$_{11}$H$_{20}$O$_4$, as [C$_{11}$H$_{20}$O$_4$ + H]).

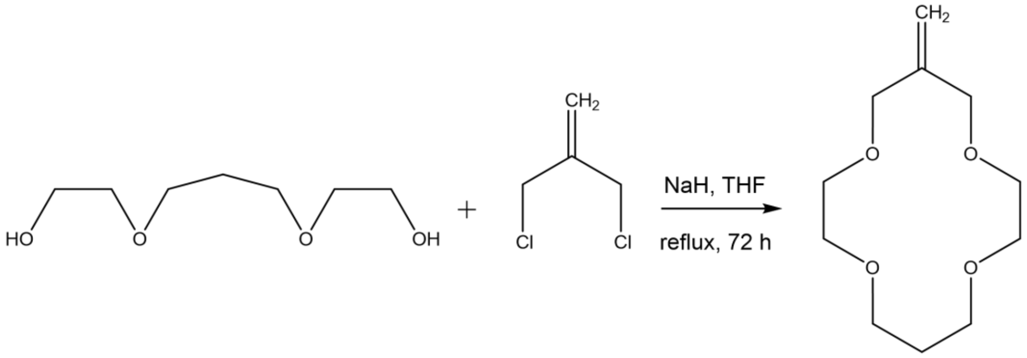

Figure 3: Synthetic pathway for making M14C4.

2.1.2 (6-(((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)thio)methyl)-14-crown-4 (F14C4)

The fluorinated crown ether F14C4 (6-(((3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl)thio)methyl)-1,4,8,11-tetraoxacyclotetradecane) was synthesized and purified according to the following procedure:

164 mg of M14C4 (0.76 mmol) and 182 mg of 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (0.38 mmol) were dissolved in 250 µl of ethyl acetate. 80 µl of a 70 mg/mL solution of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) in ethyl acetate (0.02 mmol) was added and the mixture was exposed to UV/visual light for 270 seconds. The ethyl acetate was dried off under reduced pressure and the resulting dried mixture was dissolved in 200 µl of methanol. 50 µl of deionized water were added and the solution was loaded onto a fluorous column, that had been prepared with 1 mL of deionized water, to separate the mixture with a fluorous solid phase extraction (FSPE). The column was washed with 80:20 methanol:water, methanol, and ethyl acetate. Each solvent fraction was collected separately. The fractions were dried under reduced pressure and analyzed with ^{1}H NMR, ^{19}F NMR and DART-HRMS. The F14C4 was in the methanol fraction, 233 mg or a yield of 88%. The unreacted M14C4 was in the 80:20 methanol:water fraction and the unreacted fluorinated thiol was in the ethyl acetate fraction. The NMR spectra and DART-HRMS can be seen in the SI; the data is as follows: ^{1}H NMR: δ 1.74 (pentet, 2H), 1.94 (septet, 1H), 2.36 (multiplet, 2H), 2.52 (doublet, 2H), 2.66 (multiplet, 2H), 3.54-3.66 (multiplet, 16H); ^{19}F NMR: δ-80.78 (triplet, 3F), -114.38 (quintet, 2F), -122.00 (doublet, 6F), -122.77 (singlet, 2F), -123.42 (singlet, 2F), -126.16 (singlet, 2F); DART-HRMS: 696.12 g/mol ($C_{21}H_{25}O_4F_{17}S$, as [$C_{21}H_{25}O_4F_{17}S$ + H]).

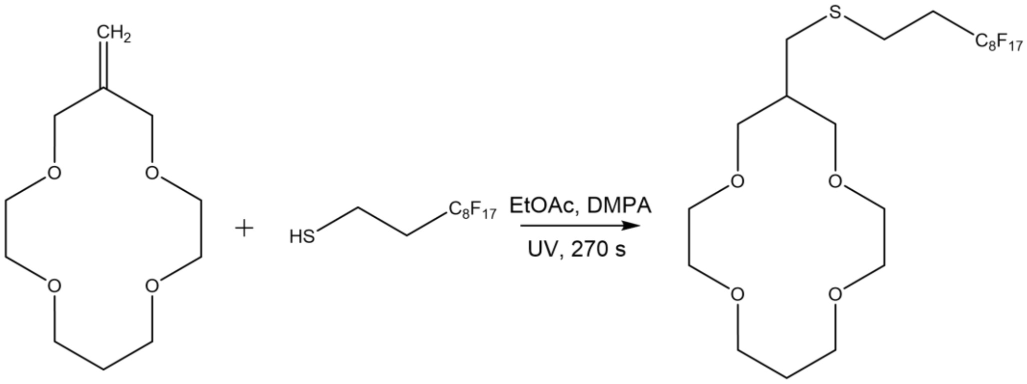

Figure 4: Synthetic pathway for making F14C4.

2.2. Supercritical Fluid Extraction Procedure

ScCO$_2$ extraction experiments were performed in a high pressure and high temperature experimental system that was fabricated in the lab at Cornell University. A flow diagram of the system can be seen in Figure 5. In a typical ScCO$_2$ extraction experiment, a 25 ml reactor was loaded with a measured amount of crown ether, cation exchanger, and 15 ml of a synthetic geothermal brine. The reactor was connected to the rest of the high pressure and high temperature system and wrapped in heating tape.

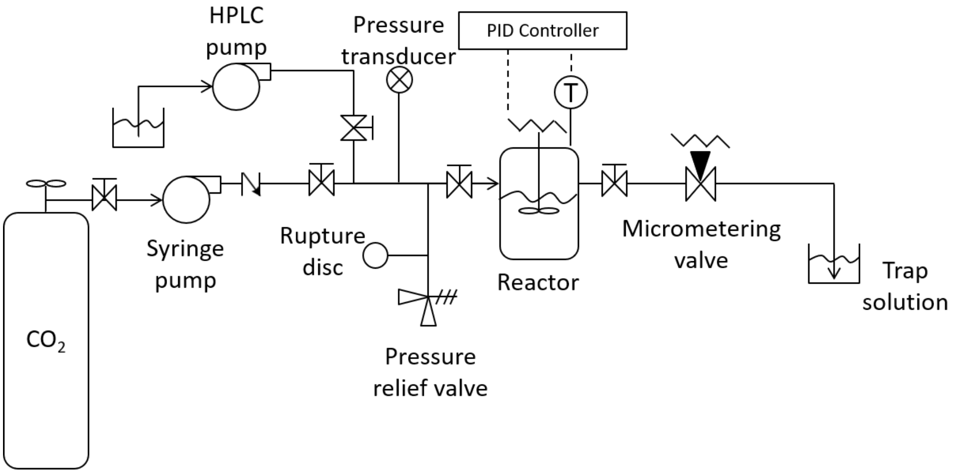

Figure 5: A schematic figure of the high pressure and high temperature experimental system used in the performance of supercritical fluid extraction experiments in this research.

When the reactor reached the desired experimental temperature, T = 60°C or T = 85°C, the reactor was pressurized to the planned pressure, 200 bars or 250 bars, and the mixture inside the reactor was stirred with a magnetic stir bar. A static extraction was performed for 30 min. After the static extraction stage, a dynamic extraction was performed by flowing $ScCO_2$ through the synthetic geothermal brine. 100 mL of $ScCO_2$ at the operational temperature and pressure were flowed through the reactor at about 3 mL/min. The outlet stream of $ScCO_2$ was bubbled through chloroform in a graduated cylinder to capture extracted materials. Finally, the system was flushed with $ScCO_2$ for an additional 45 min at a flow rate of about 2-3 mL/min.

At the conclusion of an experiment, the reactor was detached from the system and opened. The synthetic geothermal brine that was subjected to the $ScCO_2$ extraction process was sampled and analyzed for lithium and sodium content by ICP-OES.

3. RESULTS AND DISCUSSION

The purified crown ethers were used as extractants in all the experiments performed in this research. It is worth noting that the extractants were recovered and reused following the extraction experiments with 1) an FSPE process similar to the one applied in the synthetic process for F14C4 when recovering F14C4 from the extraction mixture, and 2) an aluminum silica column separation when recovering M14C4 from the extraction mixture. Both crown ethers were reused with fully retained activity in further experiments. For a more detailed discussion on the recovery process and confirmation of retained activity refer to a paper on the crown ether synthesis and characterization published by our research group (Palsdottir, Alabi, Park, Sakanaka, & Tester, 2019).

The two synthesized extractants, paired with the commercially available HDEHP, were studied in this research (see Figure 2). These extraction systems were researched at several different conditions, where the temperature, pressure, and cation exchanger excess were modified. In each extraction the selectivity of the extraction system towards lithium over sodium and magnesium was also evaluated. The extraction efficiency for each of these cations was defined by

$$Extraction\ \% = \frac{[metal\ ion]_{initial} - [metal\ ion]_{residual}}{[metal\ ion]_{initial}} \qquad (1)$$

where $[metal\ ion]_{initial}$ is the initial concentration of each metal ion in the aqueous phase, and $[metal\ ion]_{residual}$ is the residual concentration of each metal ion in the aqueous phase following the extraction. The concentration of lithium, magnesium, and sodium in the synthetic geothermal brine subjected to extraction in this research is presented in Table 1.

Table 2: The concentration of Li^+, Na^+, and Mg^{2+} ions in the synthetic geothermal brine subjected to $ScCO_2$ extraction in this research.

Metal ion	Concentration [mg/L]
Li^+	10
Na^+	500
Mg^{2+}	40

The results of the extractions performed can be seen in Figure 6. The first extraction case was performed at 60°C and 250 bars, with a 300-fold excess of HDEHP and a 50-fold excess of the crown ethers, with respect to the lithium concentration in the aqueous phase. In the second extraction case the temperature was 85°C and the pressure 250 bars, with a 300-fold excess of HDEHP and a 50-fold excess of the crown ethers. In the third case the conditions were 60°C and 200 bars, with a 300-fold excess of HDEHP and a 50-fold excess of the crown ethers. In the fourth and last case the temperature was 60°C and the pressure 250 bars but the excess of HDEHP was modified to be 50-fold. The excess of the crown ethers was kept constant; at 50-fold.

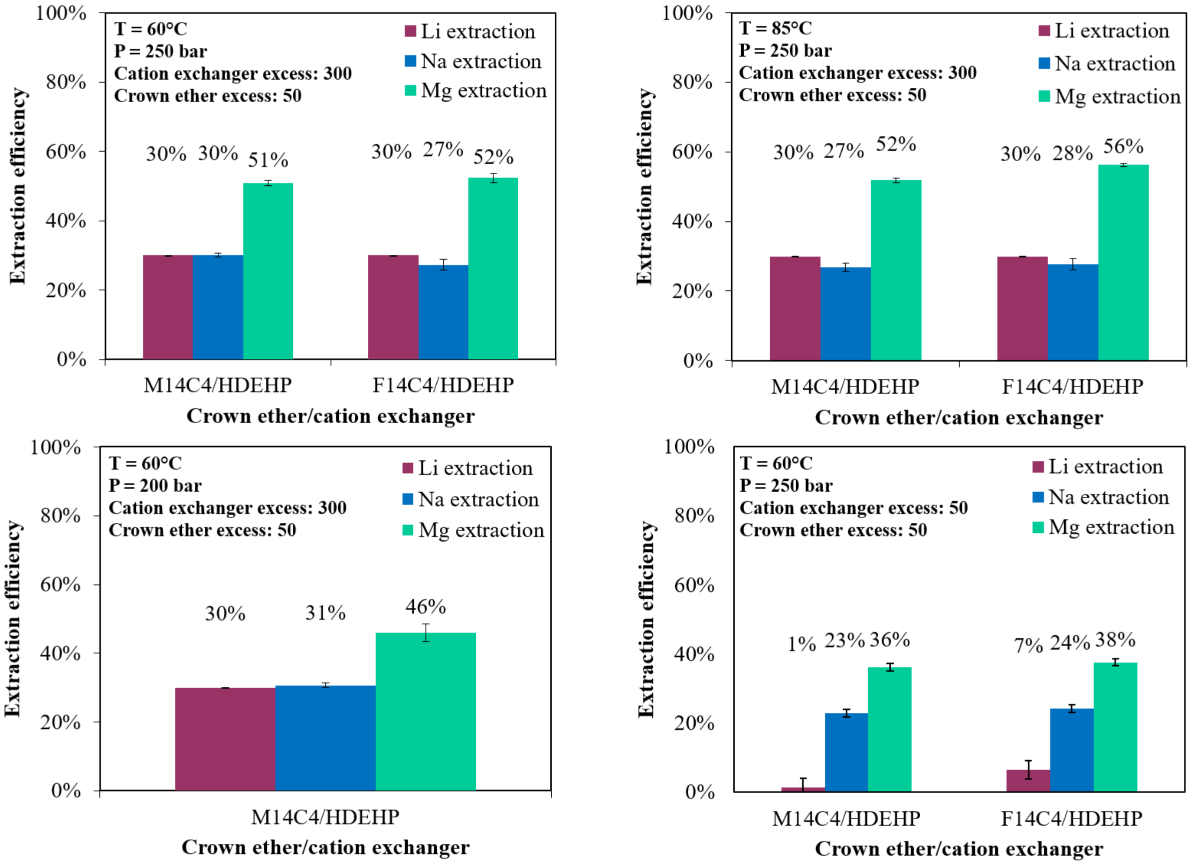

Figure 6: The results of the extraction experiments performed in this research. Variables include temperature, pressure, and cation exchanger excess.

From Figure 6 we see that modifying the pressure and temperature in the extraction system between 60°C and 85°C and 200 bars and 250 bars has little effect on the extraction of lithium or on the selectivity in the extraction towards lithium over sodium and magnesium. Modifying the cation exchanger excess however has a much larger effect. Such a huge excess of HDEHP and the effect lowering the excess has might indicate that the crown ether is not very important in the extraction process. To test this a simple liquid-liquid extraction process between an aqueous lithium and sodium chloride solution and chloroform phase containing HDEHP was performed. This test showed no extraction of lithium or sodium. For more details on this experiment see Ruttinger et al. (2019).

There is a significant co-extraction of both magnesium and sodium in every case. This is because the process developed is a size-selective extraction process and magnesium and sodium are the alkali and earth alkaline metal ions closest to lithium in size. This co-extraction may not be of concern because in practical applications sodium and magnesium concentrations can be lowered with post-processing before the production of lithium products. In spite of the co-extraction of other compounds we have developed a very fast and effective concentration process for lithium in geothermal brines. If better selectivity towards lithium over other compounds is necessary, a process like this one could be coupled with other more selective processes that have been developed and function as a pre-concentration process.

4. CONCLUSIONS AND RECOMMENDATIONS

This research for the first time reports on the effectiveness of the selective extraction of lithium using crown ethers in supercritical carbon dioxide ($ScCO_2$). We demonstrated that with properly selected crown ether and cation exchanger pairs, $ScCO_2$ extraction of lithium is achievable. In addition, feasible selective extraction was also shown from solutions with high concentration of other cations such as sodium and magnesium. Over the ranges of pressure and temperature examined from 200 bars to 250 bars and from 60°C to 85°C we did not observe a measurable effect on the extraction process, as long as the solubility of extractants and cation exchangers in the $ScCO_2$ phase is maintained. Changing the ratio between the cation exchanger, crown ether extractant, and lithium can however greatly affect the extraction efficiency of lithium and the selectivity towards lithium over other metals. Further optimization of this process in future work should look more closely at these ratios to determine if a more efficient and selective process can be designed.

A very minimal difference is observed in our experiments between using the fluorinated 14-crown-4 (F14C4/HDEHP) and methylene-14-crown-4 (M14C4/HDEHP) in the extraction. The difference is most pronounced in the case of extraction at 60°C and 250 bars with a 50-fold crown ether and cation exchanger excess, with respect to lithium. In this case the lithium extraction efficiency is higher for the F14C4/HDEHP system than the M14C4/HDEHP system; 7% versus 1% extraction efficiency.

The best results in terms of overall lithium extraction efficiency and lithium selectivity in this research were achieved with the extraction system with either F14C4 or M14C4, at 60°C and 250 bars, with a 300-fold excess of HDEHP and a 50-fold excess of F14C4 or M14C4. For F14C4 the extraction efficiency of lithium was 30%, the sodium extraction efficiency was 27%, and the magnesium extraction efficiency was 52%. For M14C4 the extraction efficiency of lithium was 30%, the sodium extraction efficiency was 30%, and the magnesium extraction efficiency was 51%.

Although others have evaluated lithium recovery from geothermal brines, there are no commercial operations anywhere in the world at the present time. Direct comparison with industrial operations was therefore not possible. Nonetheless, we did compare the results of this research to traditional lithium extraction from brines found in salt lakes or salars. The overall recovery of lithium in traditional salt lake lithium operations is generally about 40% or lower (Tahil, 2007). This recovery is the result of a process that utilizes solar evaporation for brine concentration and may take up to two years. Our extraction process, operated on a synthetic geothermal brine with a 10 mg/L lithium concentration, had a maximum lithium extraction efficiency of 30%. In addition to the similar levels of lithium recovery, in our process we concentrate lithium from 10 mg/L in the geothermal brine to 5,000 mg/L in the produced fluid from the extraction process. These results are encouraging for our process both for geothermal fluids and other lithium-rich brines.

Further research on this process will involve converting it from a batch process to a continuous process. Additionally, the cation exchanger and crown ether excess should be optimized further, and the possibility of using other commercially available cation exchanger should be studied.

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REFERENCES

Czech, B. P., Babb, D. A., Son, B., & Bartsch, R. A. (1984). Functionalized 13-crown-4, 14-crown-4, 15-crown-4, and 16-crown-4 compounds: synthesis and lithium ion complexation. *The Journal of Organic Chemistry*, *49*(25), 4805–4810. Retrieved from http://pubs.acs.org/doi/abs/10.1021/jo00199a011

Czech, B. P., Zazulak, W., Kumar, A., Olsher, U., Feinberg, H., Cohen, S., … Bartsch, R. a. (1992). Synthesis of substituted 14-crown-4 compounds. *Journal of Heterocyclic Chemistry*, *29*(Oct-Nov), 1389–1400.

Eliasson, E. T., Thorhallsson, S., & Steingrimsson, B. (2011). Geothermal Power Plants. In *Short Course on Geothermal Drilling, Resource Development and Power Plants* (pp. 1–23).

Fowler, A. P. G., & Zierenberg, R. A. (2015). Rare Earth Element Concentrations in Geothermal Fluids and Epidote from the Reykjanes Geothermal System, Iceland. In *Proceedings of the World Geothermal Congress 2015* (pp. 1–9). Melbourne, Australia.

Gallup, D. L. (1998). Geochemistry of geothermal fluids and well scales, and potential for mineral recovery. *Ore Geology Reviews*, *12*(4), 225–236. https://doi.org/10.1016/S0169-1368(98)00004-3

Grigsby, C. O., & Tester, J. W. (1989). Rock-water interactions in the Fenton Hill, New Mexico, hot dry rock geothermal systems. II. Modeling geochemical behavior. *Geothermics*, *18*(5–6), 657–676. https://doi.org/10.1016/0375-6505(89)90099-0

Grosjean, C., Miranda, P. H., Perrin, M., & Poggi, P. (2012). Assessment of world lithium resources and consequences of their geographic distribution on the expected development of the electric vehicle industry. *Renewable and Sustainable Energy Reviews*, *16*(3), 1735–1744. https://doi.org/10.1016/j.rser.2011.11.023

Gross, J. H. (2014). Direct analysis in real time — a critical review on DART-MS. *Anal Bioanal Chem*, *406*(1), 63–80. https://doi.org/10.1007/s00216-013-7316-0

Gupta, R. B., & Shim, J. J. (2006). *Solubility in Supercritical Carbon Dioxide*. CRC Press.

Harrar, J. E., & Raber, E. (1983). *Chemical Analyses of Geothermal Waters and Strategic Petroleum Reserve Brines for Strategic and Precious Metals*. *Journal of Geochemical Exploration*. Livermore, CA.

Inoue, Y., Hakushi, T., Liu, Y., & Tong, L. H. (1993). Molecular Design of Crown Ethers. 12. Complexation Thermodynamics of 12- to 16-Crown-4: Thermodynamic Origin of High Lithium Selectivity of 14-Crown-4. *Journal of Organic Chemistry*, *58*(20), 5411–5413. https://doi.org/10.1021/jo00072a024

Laintz, K. E., Wai, C. M., Yonker, C. R., & Smith, R. D. (1991). Solubility of fluorinated metal diethyldithiocarbamates in supercritical carbon dioxide. *The Journal of Supercritical Fluids*, *4*(3), 194–198. Retrieved from http://www.sciencedirect.com/science/article/pii/089684469190008T

Legers, L. (2008). The Trouble with Lithium 2 Under the Microscope. *Meridian International Research*, (May), 1–54.

Metalary. (2019). Retrieved January 1, 2019, from https://www.metalary.com/lithium-price/

Pálsdóttir, A., Alabi, C. A., Park, E. R., Sakanaka, M. G., & Tester, J. W. (2019). Solubility characterization of 14-crown-4 ethers for the supercritical extraction of lithium from natural brines: Synthesis, solubility studies and thermodynamic solubility modeling. *Industrial & Engineering Chemistry Research*. (Submitted)

Ruttinger, A., Pálsdóttir, A., Tester, J. W., & Clancy, P. (2019). A quantitative metric for the design of selective supercritical CO_2 extraction of lithium from geothermal brine. *ChemSusChem*, *12*. doi:10.1002/cssc.201901200.

Stauffer, R. E., Jenne, E. A., & Ball, J. W. (1980). *Chemical studies of selected trace elements in hot-spring drainages of Yellowstone national park*. Washington DC.

Suzuki, K., Yamada, H., Sato, K., Watanabe, K., Hisamotoj, H., Tobe, Y., & Kobiro, K. (1993). Design and Synthesis of Highly Selective Ionophores for Lithium Ion Based on 14-Crown-4 Derivatives for an Ion-Selective Electrode. *Anal. Chem.*, *65*(12), 3404–3410. https://doi.org/10.1021/ac00071a012

Tahil, W. (2007). *The Trouble with Lithium*. Retrieved from https://dev.px4.io/en/concept/architecture.html

Tomoi, M., Abe, O., Ikeda, M., Kihara, K., & Kakiuchi, H. (1978). Syntheses of hydroxy group-containing crown ethers and polymer-supported crown ethers. *Tetrahedron Letters*, *33*, 3031–3034.

Wang, S., Elshani, S., & Wai, C. M. (1995). Selective Extraction of Mercury with Ionizable Crown Ethers in Supercritical Carbon Dioxide. *Analytical Chemistry*, *67*(5), 919–923.