Supercritical fluid extraction of lithium from geothermal waters using strategically engineered crown ether extractants

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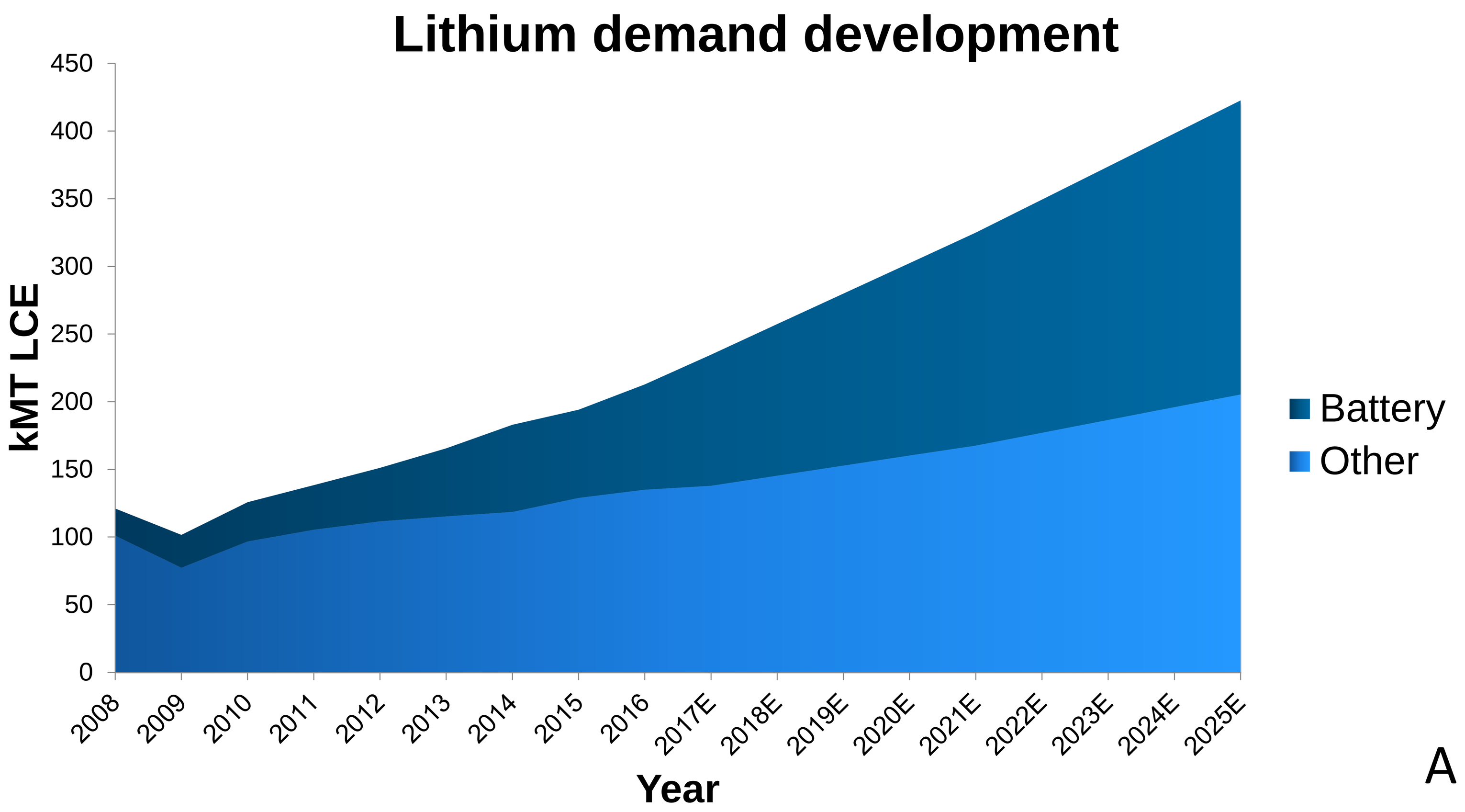
Lithium demand has risen steadily in the last years, mainly due to the increased use of rechargeable batteries for applications such as portable electronics and electronic vehicles . Geothermal waters have been suggested as an alternative resource to meet the increased lithium demand. Below we present a method for the recovery of lithium from geothermal waters; a supercritical fluid extraction of lithium using strategically designed and synthesized lithium selective crown ethers

Motivation

Rising lithium demand



Sources: Stormcrow Capital, Goldman Sachs Global Investment Research, USGS Mineral Commodity Reports - Lithium

Lithium demand has risen steadily in the last couple of decades due to the increased use of rechargeable batteries.

The Resource

Geothermal waters are an attractive resource for lithium, some having concentrations in the same range as traditional lithium brine resources.

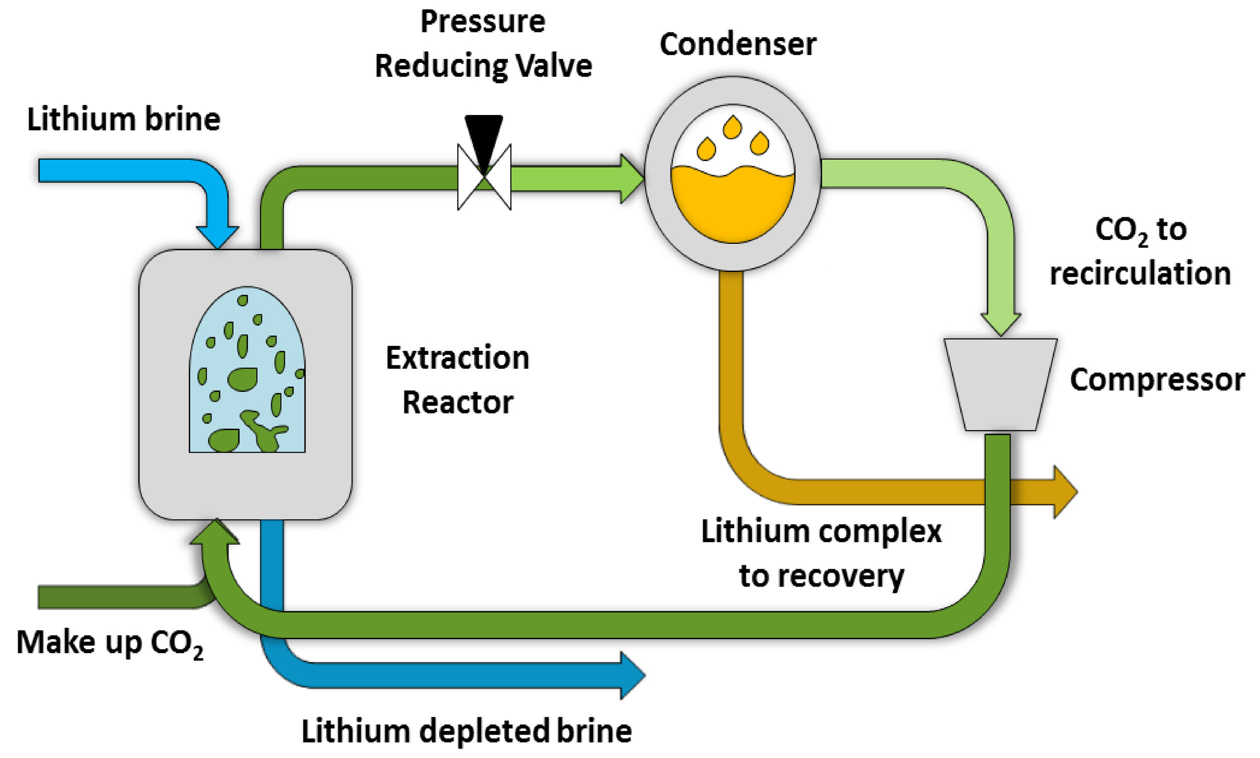
Geothermal Area	Li, ppm
Salton Sea, CA[1]	132
Coso Hot Springs, CA[1]	25
Fenton Hill, NM (EGS)[2]	6-250
Reykjanes, Iceland	4.18

Lithium Resource	Li, ppm
Salar de Atacama, Chile[3]	1000-4000
Salar del Hombre Muerto[3]	220-1000
Salar de Uyuni, Bolivia[3]	500-3000
Silver Peak, NV[3]	160

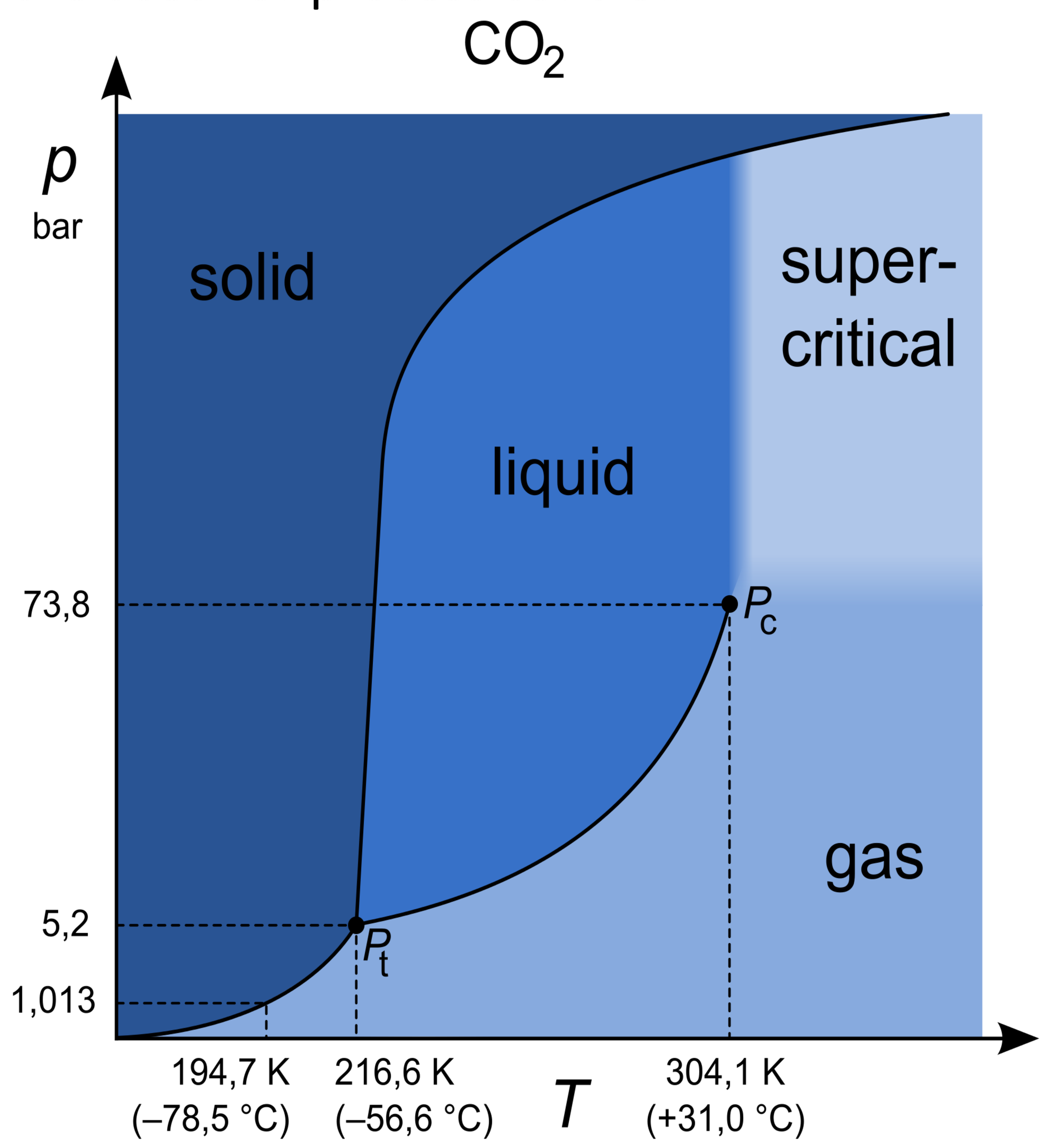
[1]Harrar, J. E. & Raber, E. *Geothermics* **13,** 349–360 (1984).
[2]Grigsby, C. O., Tester, J. W., Trujillo, P. E. J. & Counce, D. A. *Geothermics* **18,** 629–656 (1989).
[3]Legers, L. *Meridian Int. Res.* 1–54 (2008).

Process Design

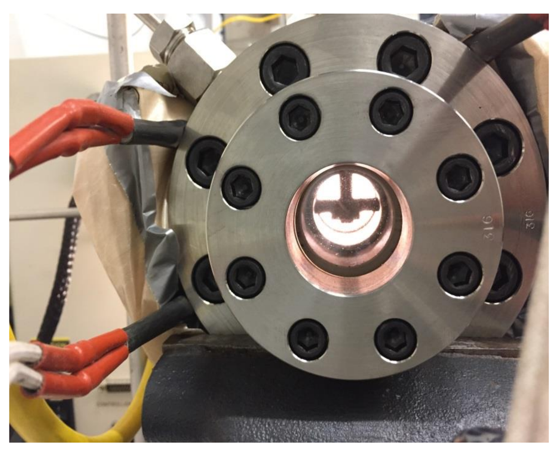
Supercritical fluid extraction of lithium



A fast and effective extraction process where the chemistry of the extractants and the pressure in the system are used for process control.



Carbon dioxide is the most commonly used supercritical solvent and the solvent of choice for the supercritical fluid extraction of lithium. Above is a phase diagram for carbon dioxide, showing the pressures and temperatures needed to reach a supercritical state. Below are pictures of the lab set up.



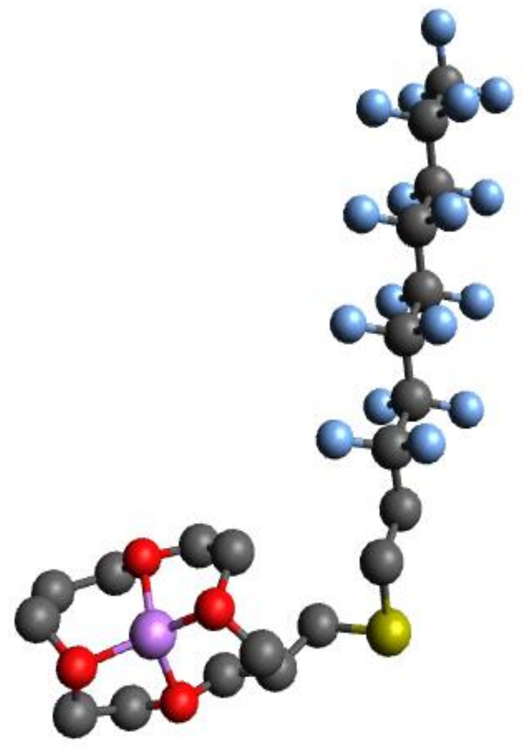
Extractant Design

Fluorinated crown ethers

The design and synthesis of the lithium extractant was guided by two key goals:

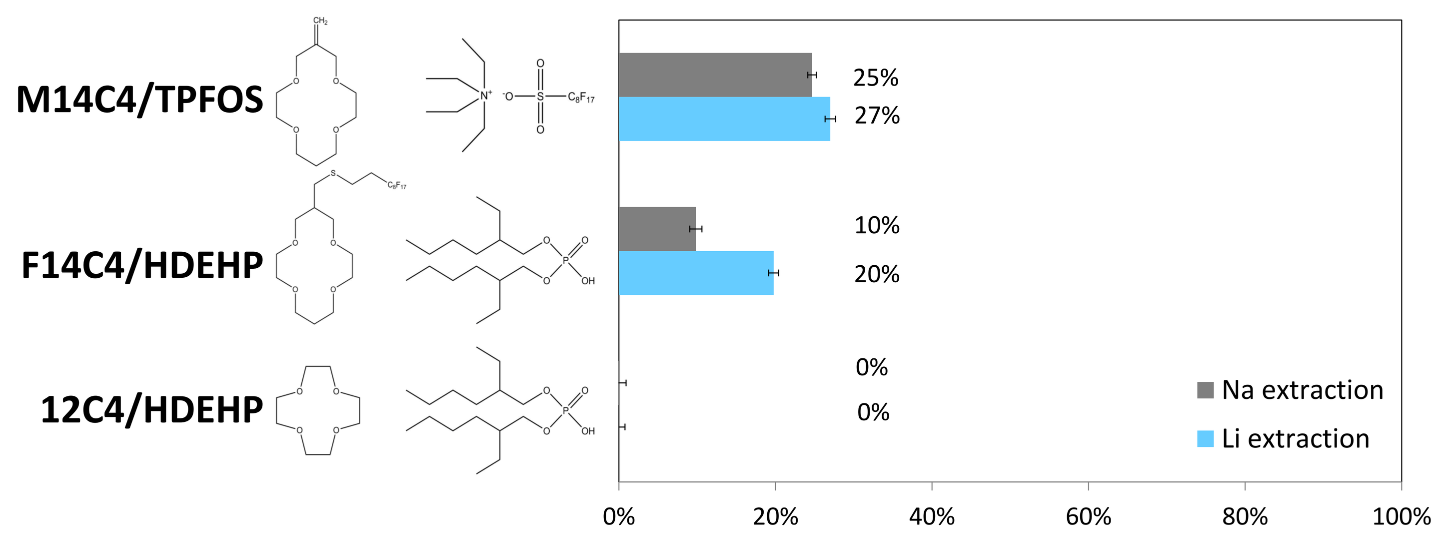
1) lithium selectivity
2) solubility in supercritical carbon dioxide.

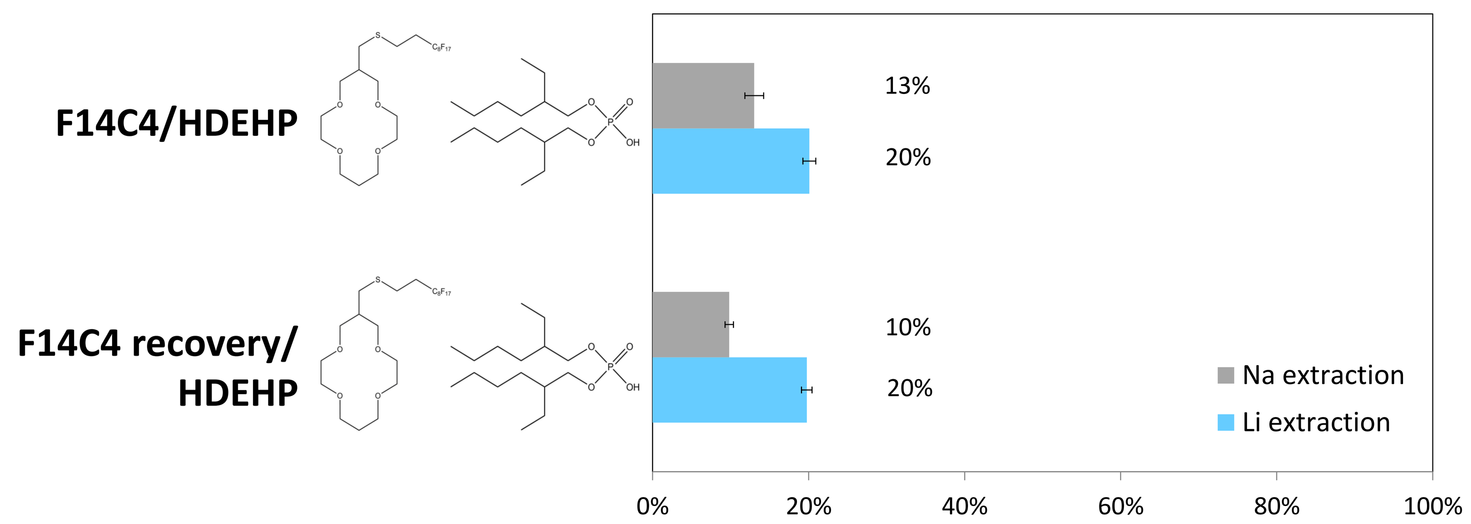
The size of the crown ether cavity ensures a selective extraction and the fluorinated side chain enables high solubility in supercritical carbon dioxide.



Preliminary Testing

Liquid-liquid lithium extraction





Preliminary results suggest a very reasonable extraction efficiency for the synthesized crown ethers in a batch process of liquid-liquid extraction with chloroform as a solvent. They also show a better selectivity for a fluorinated crown ether over a non-fluorinated crown ether. A commercially available lithium crown ether extractant showed no activity. The fluorinated crown ether is recoverable with 75% recovery.