THINK SIMULATION! Getting the chemistry right.

Breakthrough chemistry simulations for lithium processes

Using simulation to maximize your investment return in lithium extraction and processing

May 2018

INSIDE

OLI Systems' MSE databank
has parameters to simulate lithium & potash chemistry
in the OLI v9.6 platform

For leaching studies, evaporation studies, or
for simulation of any phase of lithium extraction
from either mineral ore or from evaporation of lithium-bearing brines, this software can:

- Save time and effort on engineering analysis
- Dramatically improve accuracy of simulation modeling
- Accelerate new project design
- Improve the quality of operations

Introduction

The worldwide demand for lithium continues to increase and this presents significant opportunity for the lithium industry, as companies race to get lithium production to market. Traditional lithium extraction from mineral ores such as spodumene, and evaporation of lithium compounds from the lithium-rich brines such as those found in the Andean salars have been the basis for most production schemes. Profitability and competitive edge for companies comes from some way to make lithium production either faster or less expensive, or devise a way to rely on greater yield, purity, and production efficiency. As with other industries, working engineering design schemes through mathematics and chemistry principles is one way to gain this competitive edge.

Photo taken at the edge of the largest salt plain in the world, the Salar the Uyuni, in the Bolivian Andes.

Process simulation deficiencies

Unfortunately for the industry until now, process simulation of lithium schemes has been able to address some, but not all aspects of optimizing lithium production schemes. What has been lacking is the rigorous chemistry calculations that are critical for yield and purity optimization of this highly reactive and complex lithium chemistry. What is needed are accurate solubility calculations at high salinity, and also the simulation of the complex chemistry of double-salts. These missing features have made any chemistry predictions out of reach of all major flowsheet simulator systems. The industry has been satisfied with "bucket chemistry," or empirical approaches that roughly and imprecisely characterize the behavior of lithium processes.

OLI Systems electrolyte thermodynamics

OLI Systems, Inc., a global electrolyte chemical technology leader located in New Jersey, USA, is uniquely positioned to move beyond bucket chemistry for lithium processes and can supply the missing mission-critical aspect of rigorous chemistry simulation for lithium.

OLI Systems has made electrolyte thermodynamics the focus of its research and development for the past 47 years, and has a proven framework for predicting the properties and solubilities at extreme salinities, temperatures, and pressures. A few examples of past areas of study and "flagship" chemistries in OLI's simulation roster includes, but is not limited to: calcite, barite and halite solubility up to 1500 bar / 300 C; monoethylene glycol (MEG) and the complex behavior of its mixtures; sulfur-iodine thermochemical cycle at high temperatures; and amines and hydrochlorides commonly found in oil and gas refining.

The bottom line is that OLI Systems' framework is sufficiently robust and extendible to deliver rigorous and accurate chemistry simulation for any complex and interactive chemistry of interest.

The OLI Systems lithium chemistry initiative

Lithium and the components usually found with lithium is an example of one such complex and interactive chemistry. OLI Systems first looked at the lithium + potash chemistry in 2012 and quickly understood that a comprehensive model for this chemistry would be a 'mega' system that would encompass – to begin – Li-Mg-Na-K-Ca-SO_4-CO_3-Cl-OH. OLI Systems assessed that this system would require literally years of study and would need a team of thermophysical modelers to collaborate on developing all the required parameters.

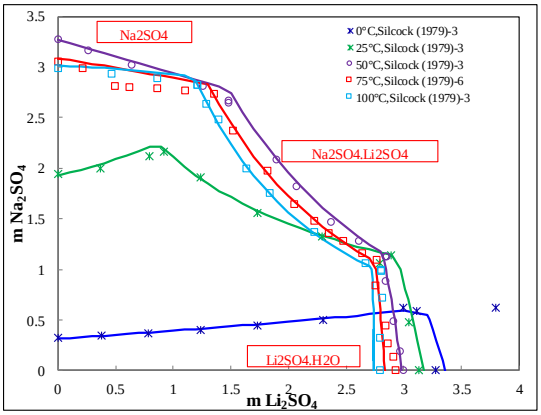
Lithium phase 1 and potash chemistry is complete

As of 2018 with the release of OLI V9.6, a major subset of OLI Systems' lithium chemistry initiative is complete. OLI's simulation capabilities include:

Fundamental sulfate – chloride systems

Parameters for these binary systems:

- Lithium sulfate & water $Li_2SO_4 – H_2O$
- Lithium chloride & water $LiCl – H_2O$



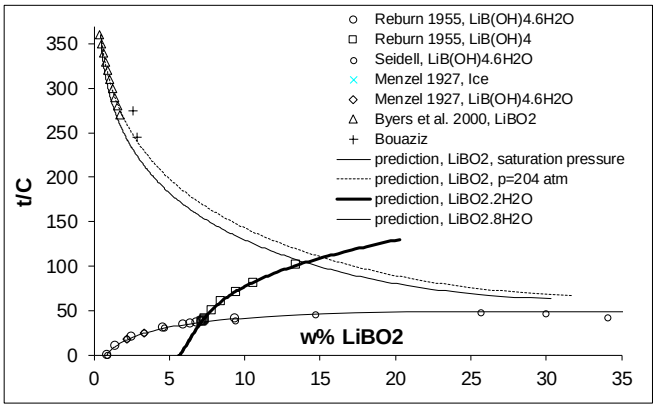
Parameters for these ternary systems:

- Lithium sulfate, potassium sulfate & water $Li_2SO_4 – K_2SO_4 – H_2O$
- Lithium chloride, potassium chloride & water $LiCl – KCl – H_2O$
- Lithium sulfate, sodium sulfate & water $Li_2SO_4 – Na_2SO_4 – H_2O$
- Lithium chloride, sodium chloride & water $LiCl – NaCl – H_2O$
- Lithium chloride, magnesium chloride & water $LiCl – MgCl_2 – H_2O$
- Lithium chloride, calcium chloride & water $LiCl – CaCl_2 – H_2O$

Lithium borate systems

Parameters for these binary systems:

- Lithium metaborate & water $LiBO_2 – H_2O$
- Lithium borate & water $Li_2B_4O_7 – H_2O$
- $LiB_5O_8{\cdot}5H_2O$ & water $LiB_5O_8{\cdot}5H_2O – H_2O$
- Lithium hydroxide & water $LiOH – H_2O$



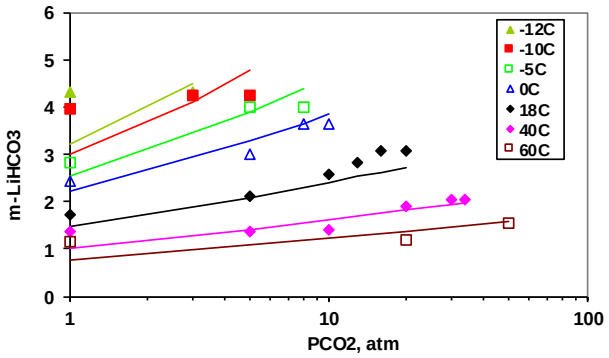
Parameters for these ternary systems:

- Lithium hydroxide, H_3BO_3 and various lithium borate phases & water
- Li borates, lithium chloride, sodium chloride & water
- Lithium chloride, H_3BO_3 & water
  potassium sulfate & water $Li_2SO_4 – K_2SO_4 – H_2O$

Various systems related to Li processing

Parameters for these binary systems

- Lithium fluoride & water $LiF – H_2O$
- Lithium carbonate & water $Li_2CO_3 – H_2O$



Parameters for these ternary systems

- Lithium carbonate, lithium hydroxide & water
- Lithium carbonate, carbon dioxide & water
- Lithium chloride, carbon dioxide & water
- Lithium chloride, zinc chloride & water
- $SiO_{2(am)}$, lithium chloride & water
- Lithium chloride and methanol, ethanol, formic acid & water

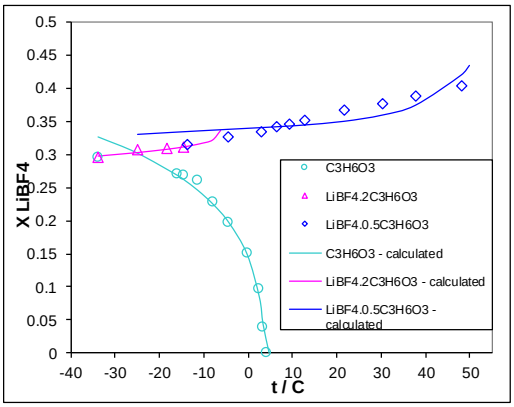
Systems related to battery electrolytes

Solutes include:

- Lithium hexafluorophosphate $LiPF_6$
- Lithium tetrafluoroborate $LiBF_4$
- Lithium perchlorate $LiClO_4$

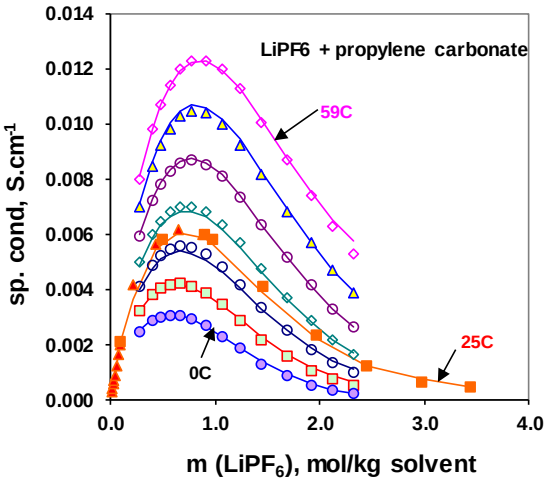
Solvents include selected pure and mixed carbonates

- Dimethylcarbonate
- Diethylcarbonate
- Ethylenecarbonate
- Propylenecarbonate



Electrical conductivity

The OLI Systems framework also has the ability to model transport properties. Here is an example of the electrical conductivity of lithium hexafluorophosphate and propylene carbonate. The model is predictive and built in this case on underlying experimental data.



Battery simulation studies

Why is electrical conductivity important in battery studies?

In a battery, the electrolyte should have sufficiently high electrical conductivity and, at the same time, it should remain thermodynamically stable in the liquid phase in a wide temperature range in which the battery is expected to be used in practice. This can be achieved by creating appropriate formulations containing a lithium salt such as $LiPF_6$ and highly polar organic solvents such as various alkyl carbonates.

OLI System's MSE model makes it possible to predict both the electrical conductivity and phase equilibria in such mixtures, thus helping to optimize the composition and performance of the battery electrolyte. The model is calibrated by reproducing selected experimental data in binary systems within their experimental uncertainty (as shown in the diagrams on the right-hand side) and then it can predict the behavior of more complex battery systems.

Other studies OLI Systems' simulation enables

The implementation of these major aspects of the complete lithium chemistry system now provides all engineers with the ability to design more efficient processes, and to predict more closely than ever before the yield and purity of their products. Measurable quantities like pH, conductivity, concentrations, and TDS, now are firmly rooted in a fundamental physico-chemical basis.

To assist clients in deploying this data, OLI Systems' simulation packages include:

- **OLI Studio** where clients can use the survey capability to calculate the effect of evaporation or leaching on lithium processes.
- **OLI Flowsheet: ESP** where clients can design entire processes, such as an evaporation pond process
- **OLI Engine in <Alliance Partner Products>** where clients can use OLI in an existing Alliance Partner flowsheet to obtain rigorous chemistry analysis of process streams

Looking ahead: Partnering with OLI Systems to extend the lithium chemistry initiative

More remains to be done, building on this current capability. As we move into the lithium-based transportation economy, new sources of lithium ore, spodumene, clays, recyclables will become cost-competitive alternatives. To meet these chemistry demands, OLI will continue to focus its scientific energy and move deeper into these chemistries.

We have plans to pursue this chemistry further, and we are seeking industry partners to help steer and specify this work. A one-time investment can reap years of benefit, and using the OLI framework as a proven delivery vehicle is a low-risk investment. You have the assurance that OLI will work with you to "get the chemistry right." And, there is no other simulation company who is positioned to finish this work.

Partnering with OLI can increase your competitive edge and bring your process ideas early to market. You can selectively help us co-fund chemistry that is mission-critical to your operation. As an additional feature, the selected graphs in this technical brief are part of OLI's validation spreadsheet system which will be open for the lithium chemistry only to OLI's lithium chemistry initiative partners.

Some of the possible chemistries that we will be tackling include:

- Remaining borate chemistry
  to completely model the behavior of borates in brines associated with Li production
- Improvement of chemistry of lithium in brines
  beyond the fundamental lithium chemistry that has been recently completed
- Modeling production of lithium nitrate
  from caliche sources and thermal energy storage systems
- Chemistry required for modeling lithium recycling processes
  *lithium with nickel, calcium, magnesium and ammonium sulfate*s
- Chemistry required for modeling lithium-based working fluids
  lithium with bromides and molybdates

Take action now!

To find out more about how your business can gain the intelligence you need in understanding your lithium processes through accessing the OLI software, or to find out how to partner with OLI on the lithium chemistry initiative, please contact us at sales@olisystems.com and mention this technical brief to arrange a free Application Assessment for your lithium chemistry challenges.

For more Information

Authors: Anthony J. (AJ) Gerbino, PhD, OLI Systems, Inc.
Andre Anderko, PhD, OLI Systems, Inc.
Pat McKenzie, OLI Systems, Inc.

www.olisystems.com

Related Paper: "Aqueous chemistry of lithium production," by Mike Dry and AJ Gerbino, given at ALTA 2018