



The Challenges of Predictive Numerical Calculation within Hypersaline Brines: Examples from Lithium Brines

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Abstract

Lithium brines, today's main lithium source have been increasingly studied in recent years. Geochemical modelling can be used to predict the operational or underground brine lithium concentrations, but it can also be applied to ground stability prediction. However hypersaline systems are challenging to model due to the inaccuracies introduced by elevated ionic strength when using the extended Debye-Hückel theory. A different approach, such as Pitzer is required. However, while generally internally consistent, this database is limited in the number of phases and elements it contains and therefore has limited predictive power. To overcome this issue, a literature review was undertaken.

Keywords: Numerical Modelling, Pitzer, PHREEQC, Lithium, Brines

Introduction

Lithium is understood by many to be the “fuel of the future”, as it is at the core of a post-fossil fuel economy. Along with several niche applications, such as technical grease, medication, lithium is now used essentially within batteries for electric vehicles and smart technologies, smartphone and wearable devices of all kinds. Lithium can be considered a fuel in the sense that, while electric car batteries will eventually be recycled, it is unlikely that the lithium contained in most wearables will be.

Lithium can be mined conventionally or extracted from naturally-enriched continental brines hosted within endorheic lakes (e.g. Evans 2014). It is currently understood that 60% of the global lithium resource is hosted in continental brines in South America (Bolivia, Chile and Argentina) with some appreciable lithium brine in the southwest USA, Australia and Israel. Owing to their preponderance as a source of lithium, brine formation has been increasingly studied in recent years (e.g. Evans 2014).

Numerical predictive calculations applied to lithium brines are mostly used to predict the operational concentrations or grade, of lithium being produced. However, it can be used as an optimisation tool for the lithium extraction process, and it can also be applied

to the prediction of ground stability caused by changes in hydrogeological conditions or to the modelling of the lithium concentration within the underground brine. The high salinity of the brines produces a high ionic strength, generally above 3 compared to 0.72 for seawater (Nordstrom et al 1979) is a source of challenges for both the laboratory analysis and predictive numerical calculations. Many analytical methods are impacted by salt effects which can cause interferences with the analyses being carried out. Generally diluting the sample will allow reduce the salt effects and for the analysis to be carried out. However, dilution and *a fortiori* repeated dilution of the same sample introduces errors in the analysis and can cause matrix effects. Owing to the critical nature of lithium brine, efforts have been undertaken globally to determine thermodynamical parameters allowing its modelling.

The aim of this paper is to provide the readers with published lithium parameters to use within the Pitzer framework, including the reproduction of endorheic lake chemistry from the literature and an example of numerical modelling of lithium processing from brine via evapoconcentration.



Methods

Thermodynamic equilibrium calculations are based on the law of mass action to calculate mineral solubility and saturation indexes. However, the ionic strength of a solution has a significant effect on the thermodynamic properties of ions. For instance, with increasing ionic strength aqueous complexing will lower the activity of free ions. Illustrating the importance of aqueous complexing and activity corrections Appelo and Postma (2005) calculated the difference between activity and concentration for a 3.5% seawater at pH 8.22 and found differences of 30% for Na^+ , 40% for Cl^- , 50% for SO_4^{2-} , 60% for Mg^{2+} and Ca^{2+} , and 15% for HCO_3^- . Using the extended Debye-Hückel theory to adjust the standard Gibbs energy and enthalpy to the desired ionic strength will perform well for solutions of ionic strength up to 0.7 mol/L or 2 mol/L if HCO_3^- and SO_4^{2-} are low (Parkhurst 1990). Brine and *a fortiori* lithium brine are far more concentrated, and to provide a semblance of approximation would require a different calculation method. The Pitzer equations (e.g. Pitzer 1981) have been developed for these ionic strengths.

These equations were first described by Pitzer to understand the behaviour of ions in high ionic strength. The parameters of the Pitzer equations, such as the osmotic coefficient, mixed ion activity coefficients, and salt solubility are derived from various experimental data. They are more rigorous than the equations of specific ion interaction theory, but also more numerous and difficult to determine experimentally.

Sets of those parameters have been measured and compiled since the 1970s, first by Kim and Frederick (1988) for single salts in aqueous solutions at 298.15 K. Then for some complex electrolytes, Ge et al. (2007) obtained a new set of Pitzer parameters. The Pitzer database for PHREEQC (Parkhurst and Appelo 1999), is built upon the formalism defined by Pitzer and derived from the database developed for the program PHRQPITZ (Plummer et al 1988). This database is built and extended on the compilations of Harvie et al. (1984), updated by the data for minerals from Deer et al. (1997), a temperature and pressure dependent volume of aqueous species, using pa-

rameters obtained from Johnson et al., 1992 and data compiled by Laliberté (2009).

Despite these efforts the Pitzer database for PHREEQC is extremely limited with 14 elements and 54 mineralogical phases compared to 29 elements and 71 different minerals for the PHREEQC database, by comparison the LLNL database has over 1000 phases described. This status signifies that the Pitzer database is internally consistent but has limited predictive power outside of the few elements and phases covered. In the context of lithium brine, only a few mixing parameters are defined, and no Li bearing phases are defined. To overcome this issue, a literature review must be undertaken to integrate lithium and lithium phases in the database.

Parameters and values from Monnin et al., 2002 and Meng et al., 2014, can be used to integrate lithium within the Pitzer database. Values for lithium bearing species can be found in other studies, e.g. Rard et al. (2007) and the entire work on the Yucca Mountain Project “data0.ypf.R2” (BSC 2007). While numerous Li bearing mineralogical phases are summarised in other Debye-Hückel databases these phases are not described with the Pitzer formalism and analogue phases have to be used. This method introduces errors that are difficult to quantify. The parameters summarised (Table 1) in Song et al 2017 were used in this study.

In addition, oxygen was defined as a species and several phases were recalculated from other databases distributed with PHREEQC version 3.4.0-12927. H_2O and $\text{O}_2(\text{g})$ was recalculated from Minteq v4 database, distributed with PHREEQC while Li_2CO_3 , LiCl , Lime and Hydrophilite (CaCl_2) were ported from the Lawrence Livermore National Laboratory (LLNL) database. It is understood that adding elements and phases in this manner reduces the degree of internal consistency of the database and introduces error that can only be corrected by recalculating all the parameters existing within the database.

Case Study

A brine is a solution containing high amount of dissolved salts of higher concentration than seawater (> 3.5%). Solutions of lower concentrations are defined as saline water (1-3.5%), Brackish water (0.1-1%) and fresh-



Table 1 Compilation of Pitzer parameters used in this study.

-B0			-PSI			
Li+	Cl-	0.20818	Cl-	SO4-2	Li+	-0.0124
Li+	SO4-2	0.14396	Cl-	SO4-2	Na+	0.0014
-B1			Cl-	SO4-2	Mg+2	-0.048
Li+	Cl-	-0.0726	Cl-	SO4-2	K+	-0.022
Li+	SO4-2	1.17736	Na+	Li+	Cl-	0.0057
-C0			Na+	Li+	SO4-2	-0.006
Li+	Cl-	-0.0042	Na+	K+	Cl-	-0.0074
Li+	SO4-2	-0.0571	Na+	Mg+2	Cl-	-0.0078
-THETA			Na+	Mg+2	SO4-2	-0.01
Na+	Li+	0.02016	K+	Li+	SO4-2	-0.0018
Na+	Mg+2	0.07	K+	Li+	Cl-	-0.012
Na+	K+	-0.012	K+	Mg+2	SO4-2	-0.015
K+	Li+	-0.0508	K+	Mg+2	Cl-	-0.008
K+	Mg+2	0	Mg+2	Li+	Cl-	-0.0059
Mg+2	Li+	0.0102	Mg+2	Li+	SO4-2	-0.0006
Cl-	SO4-2	0.02				

water (< 0.1%). Lithium brine are typically defined as hypersaline, with salinity ranging between 1.7 and 24 times that of seawater, with the Atacama high lithium brine reaching up to 3.1 g/L. Typical examples of brine chemistry are defined in Table 2. The ocean concentration is consistent with the chemistry defined by Nordstrom et al 1979.

The commercial production of lithium from brine, despite local differences in elemental composition, concentrations and physical parameters, follow generally the same processing methodology (Garrett, 2004). This methodology is used because they

face the same issues of low concentrations and presence of potentially fouling components (such as magnesium). Most commercially exploited brine deposits are located in endorheic basins that are favourable to evapoconcentration. As a low-cost method, it is generally adopted and is represented in our idealized process route illustrated in Figure 1.

The first step in the process is to preconcentrate the brine via solar evaporation. Ideally up to 90% of evaporation occurs and the resulting brine is used in lithium production. This degree of evaporation corresponds to an ideal concentration of 6 wt.% of lithium in

Table 2 Typical lithium brine chemistry (e.g. Evans 2014; Song 2017).

Elements	Ocean	Clayton valley, USA		Salar de Atacama, Chile		Qarhan Salt Lake, China		Zhabuye Salt Lake, China	
		min	max	min	Max	Min	Max	min	max
g/L									
Li	0.0001	0.2	0.4	1.1	3.1	0.10	12.25	0.5	1
K	0.038	5.3	10	18	29.7	-	-	26.4	38.3
Mg	0.12	0.3	0.6	8.2	15.3	8	119	0	0.01
Ca	0.04	0.2	0.5	0.2	0.4	-	-	0	0.1
B	0.0004	0	0.1	0.6	0.7	-	-	2.9	14.6
Na	1.05	62	75	10.3	91.0	-	-	106.6	108.1
Cl	1.9	101	117	20.3	189.5	-	-	121.6	123.1



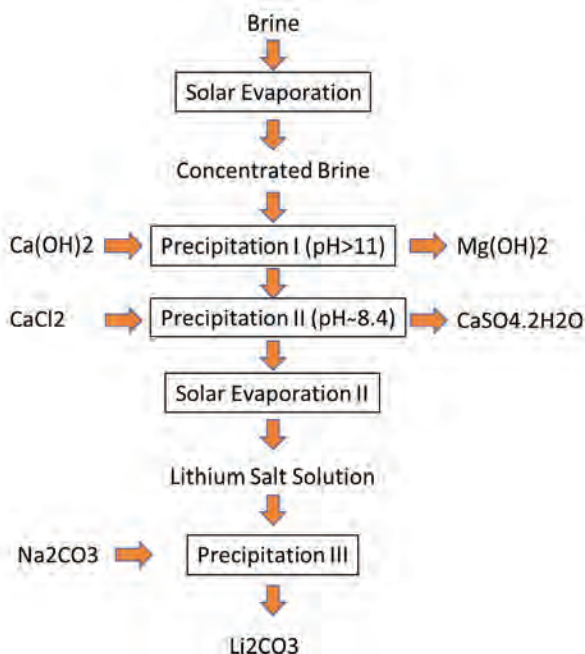


Figure 1 Generalized Process for Lithium Bearing Brines (modified from Garrett, 2004)

solution. This concentration has been defined as the “end point” or “drying-up point” (e.g. Galli et al. 2014).

The development of an increasingly saturated brine solution through evapoconcentration forces saturation with respect to lower solubility salts (e.g. anhydrite, halite) and a resulting brine solution that contains a progressively higher concentration of more soluble components such as lithium and boron. Lithium concentrations of 0.32 g/L to 2.75 g/L can be reached in such systems, however in carbonate rich brines lithium can settle as Li_2CO_3 crystals (Yu et al. 2015). While this allow for the recovery of some lithium, optimisation procedures consisting of removal of fouling elements (e.g. Mg , SO_4) will allow for an increase in efficiency. The formation of battery grade LiCl and Li_2CO_3 using an evaporation-precipitation-crystallization route requires the initial separation and precipitation of magnesium and calcium carbonates from the pre-concentrated brine (e.g. Boryta 2011; Galli et al. 2014). Although variations exist they typically use low cost reagents to precipitate calcium and magnesium as sulfate or carbonate salts at high alkalinity concentrations. Typically, solar evaporation has a recovery of

approximately 50%, however the lithium carbonate process has a demonstrated recovery of above 80% (Pistilli 2013)

Calculations

The parameters defined in Table 1 were used to calculate elemental speciation, saturation indexes for different brines and reproducing the lithium extraction process described in Fig. 1.

The example of the Atacama brine, using maximum concentrations is illustrated in Fig. 2 and 3. Those figures illustrate the increase in concentration from the brine as evaporation occurs, from 0.16 g/L to 1.44 g/L. The addition of CaCl_2 and Ca(OH)_2 allows the precipitation of Mg and SO_4 through the precipitation of brucite and gypsum. The ultimate step, addition of Na_2CO_3 allows the precipitation of LiCO_3 with a modelled recovery of 87.5%. Allowing LiCO_3 to precipitate without addition of Na_2CO_3 yield a predicted recovery rate of 39.6%. These values, are broadly in line with operating brine operations and indicate the validity of this numerical approach.

The use of less concentrated solutions, such as seawater and Zhabuye Salt Lake requires the second evapoconcentration step to allow suf-



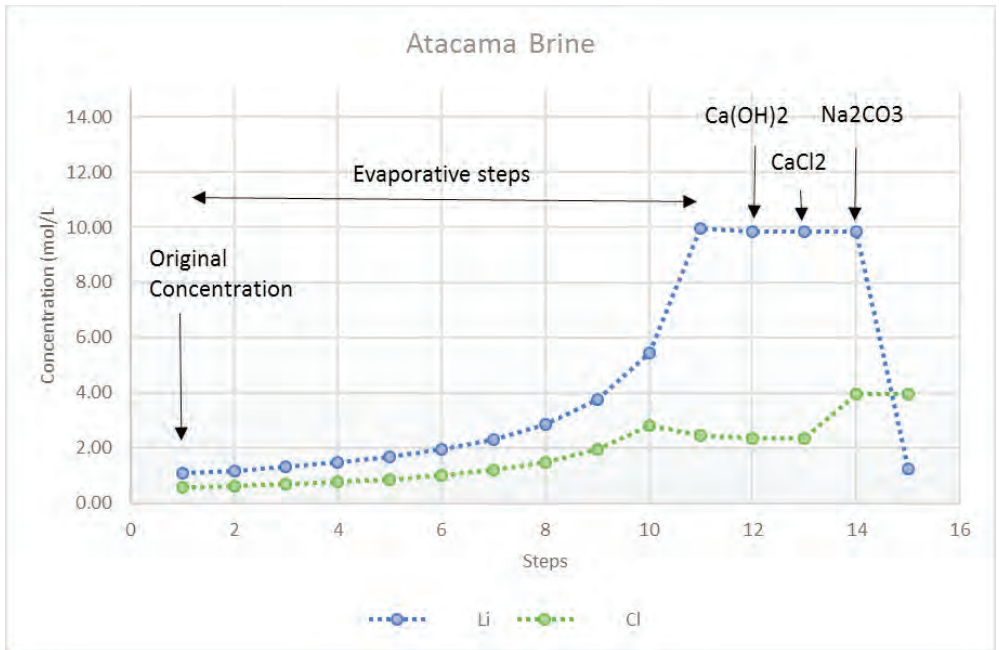


Figure 2 Evolution of the Li and Cl concentrations in the Atacama brine as a function of the progress of the process

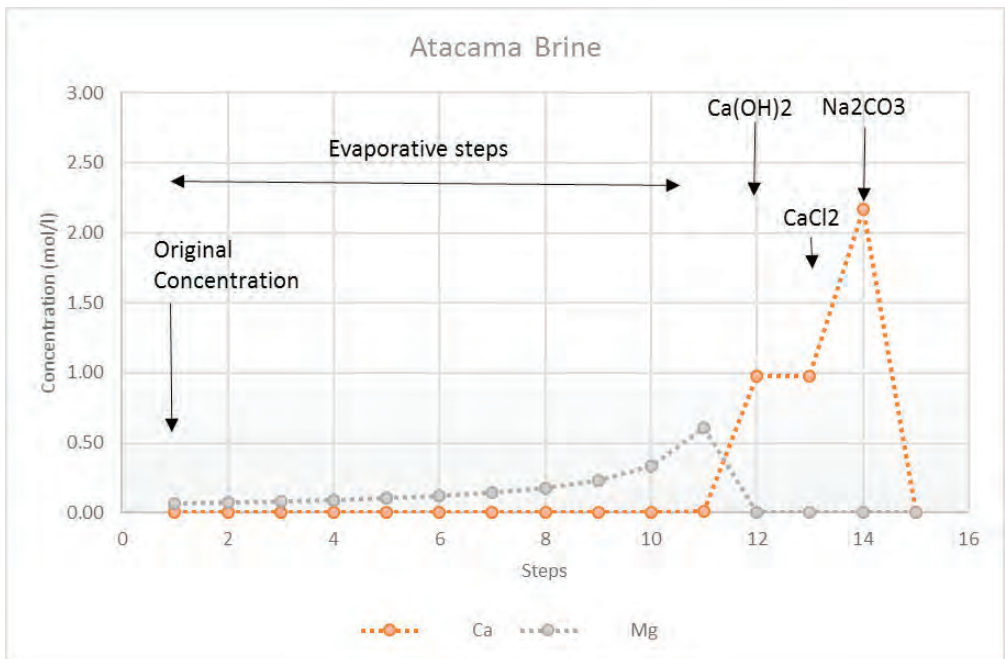


Figure 3 Evolution of the Ca and Mg concentrations in the Atacama brine as a function of the progress of the process



ficient for a sufficient increase in Li concentration to make this process economical.

Conclusions

The literature review and addition of Pitzer parameters of importance for the accurate modelling of lithium brine using the Pitzer formalism should allow for more accurate geochemical modelling of both lithium concentration within the brine, such as isopach calculations, but also, as exemplified in this study the calculation of lithium extraction processes. The predictions of Atacama brine showed therein illustrates the capacity of the model to reproduce the recovery rates of mentioned by Pistilli. While this result is encouraging, using the Pitzer formalism for more general predictions would still require a massive overall and update of the existing databases.

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