

Formation of Li Salts from Natural Brines during Isothermal Evaporation at 25°C

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Abstract: Li brines are the primary resources for Li salt industries. Evaporation is necessary to concentrate Li due to its low level of concentration in raw brines. The salt sequences during the evaporation of Li brines, especially the behavior of Li salts, represent key data for solar technologies. However, chemists cannot use any phase diagram to estimate Li salt sequences during evaporation at 25°C. The thermodynamic model proposed by us in 2003 represents the only tool for the prediction of equilibrium conditions during the evaporation of solutions containing Li^+ , Na^+ , K^+ , $\text{Mg}^{2+}/\text{Cl}^-$, SO_4^{2-} , and $-\text{H}_2\text{O}$ components at 25°C. In this paper, the predicted salt sequences of 20 brines are reported. The results indicate that (1) the first crystallized Li salt during evaporation of Li brine varies in brine composition; (2) lithium sulfate is crystallized in many cases initially for brines of magnesium sulfate subtype, while Db4 ($\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$) or Db3 ($2\text{Li}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$) appears first for sodium sulfate and magnesium sulfate subtypes with lower Mg/Li composition, and the final eutectic point is H + LiC + Lc + Ls + Car; (3) the final eutectic point is H + LiC + Lc + Car for brines of chloride type; and (4) Li content corresponding to the first crystallized Li salt is in the range of 0.43%–1%. These findings enhance our knowledge of Li chemistry and provide insights into solar pond technology of the Li-brine process.

Key words: Li-brine; Formation of Li salts; Isothermal evaporation of brine; Salt sequences from brine; Thermodynamic model for Li^+ , Na^+ , K^+ , $\text{Mg}^{2+}/\text{Cl}^-$, $\text{SO}_4^{2-} - \text{H}_2\text{O}$ system

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1 Introduction

Lithium and its compounds have significant industrial applications as new energy sources, materials, and information technology products. Lithium oc-

curs naturally in two forms: 1) hard rock, e. g., Spodumene ($\text{LiAlSi}_2\text{O}_6$), Petalite ($\text{LiAlSi}_4\text{O}_{10}$), Lepidolite ($\text{K}(\text{Li}, \text{Al})_3(\text{Si}, \text{Al})_4\text{O}_{10}(\text{F}, \text{OH})_2$); and 2) brines, e. g., salt lake brines, oil well brines, and underground brines. The Chile-based Sociedad Quimica y Minera (SQM) is the largest producer of

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Li commodities in the world. SQM produces Li compounds from brines of famous salt lake Atacama on the central Andes Mountains in Chile^[1].

Table 1 Chemical composition of various salt lake brines around the world (in mass percent)

Salt lake	Country	Li	Na	K	Mg	Ca	Cl	SO ₄	B	Density	Mg/Li
Atacama *	Chile	0.150	7.60	1.85	0.96	0.031	16.04	1.65	0.064	1.223	6.4
Cauchari	Arg.	0.051	9.33	0.42	0.145	0.033	14.86	1.57	0.112	1.215	2.84
Hombre Muerto	Arg.	0.062	9.79	0.617	0.085	0.053	15.80	0.853	0.035	1.205	1.37
Rincon	Arg.	0.033	9.46	0.656	0.303	0.059	16.06	1.015	0.040	1.220	9.29
Uyuni *	Bolivia	0.035	8.75	0.72	0.65	0.046	15.69	0.85	0.02	1.211	18.6
Great Salt Lake	USA	0.004	7.0	0.4	0.8	0.03	14.0	1.5	0.071	1.218	200
Bonneville *	USA	0.007	9.4	0.6	0.4	0.12	16.0	0.5	0.000 4	1.145	57.1
Searles Lake *	USA	0.008 3	15.20	2.30	0.034	—	12.39	4.56	0.350	1.30	4.1
Silver Peak	USA	0.023	6.20	0.53	0.03	0.02	10.06	0.71	0.008	1.14	1.43
Dead Sea	Isr., Jor.	0.002	3.0	0.6	4.0	0.3	16.0	0.05	0.003 3	1.232	2 000
Karabogaz	Turkm.	0.000 9	5.11	0.46	3.26	0.02	13.11	6.11	0.023	1.2 **	3 266
Bieletan *	China	0.01	1.882	1.87	5.172	0.035	19.34	0.54	0.012 4	1.240	517
Chaerhan	China	0.001 3	5.903	1.0	2.372	0.084	16.67	0.53	0.006	1.208 8	1 825
Dachaidan	China	0.02	10.6	0.4	1.3	0.04	18.7	2.25	0.040	1.174	65
Zabuye	China	0.097	10.81	2.64	0.001	0.007	12.16	5.24	0.286	1.297	0.01
Zacangchaca *	China	0.13	6.769	1.20	1.073	0.002	13.24	2.29	0.042	1.190	8.3
Xitaijinaier *	China	0.021	8.256	0.69	1.284	0.016	14.97	2.88	0.031 0	1.223 3	61
Yiliping *	China	0.022	6.694	0.91	2.0	0.031	16.17	1.14	0.018 4	1.215 2	91
Ocean water		0.000 017	1.08	0.039	0.13	0.04	1.94	0.27	0.000 4	1.023	7 647

* Interstitial brine; ** Estimated.

The Qinghai-Xizang (Tibet) Plateau of China is one of the areas carrying several salt lakes with high Li and B content in the world. They cover all three types of salt lakes. Table 1 displays the chemical composition of various salt lake brines around the world^[2].

However, the lithium content of the brines in the salt lakes is still too low to yield Li compounds, and even the highest Li concentration in the salt lake brine is approximately 0.15% in the Atacama salt lake brine. Therefore, evaporation of brines is neces-

sary to concentrate the Li content. Solar pond technologies are widely used for this purpose, because extreme dryness of the climate in the area is the most favorable factor for economical evaporation and concentration of brines. Furthermore, effective solar pond technologies are necessary for the comprehensive utilization of brine constituents. Meanwhile, they are environmentally friendly without any chemical residues.

2 Li brines and the formation of Li salts during their evaporation

Generally, salt lakes are of three types chemically: chloride, sulfate, and carbonate. The sulfate-type salt lakes are divided into two subtypes: magnesium sulfate and sodium sulfate. As shown in Table 1, Li brines mostly belong to the sulfate type. All brines contain cations such as Na^+ , K^+ , and Mg^{2+} (Ca^{2+}) except Li^+ , and the main anions are Cl^- and SO_4^{2-} but not HCO_3^- and CO_3^{2-} . We can list the main cations and anions under Janeck indices (Table 2) and display the composition of brines on the triangle phase of the $\text{Na}^+ - \text{K}^+ - \text{Mg}^{2+} / \text{Cl}^- - \text{SO}_4^{2-} - \text{H}_2\text{O}$ quinary system, as shown in Fig. 1.

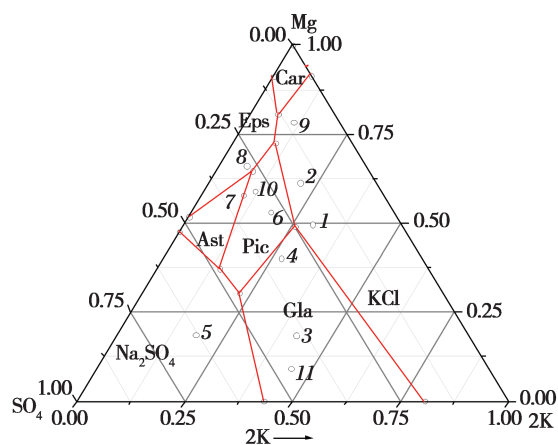


Fig. 1 Location of brines on the metastable phase diagram Na, K, Mg/Cl, SO_4 - H_2O system at 25°C

Note: Abbreviation: Car = $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$; Eps = $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; Ast = $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$; Pic = $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 6\text{H}_2\text{O}$; Gla = $3\text{K}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$

Table 2 Chemical types of brines and Janecke index on the phase diagram

Salt lake	Janecke Index of Brine Composition			Type of Brine	Points
	In Na, K, Mg/Cl, SO ₄ -H ₂ O System				
	K ₂	Mg	SO ₄		
Atacama *	0. 297 4	0. 496 5	0 . 206 1	Mg Sulfate	1
Uyuni	0. 210 9	0. 612 7	0. 176 4	Mg Sulfate	2
Hombre Muerto	0. 416 5	0. 184 6	0. 398 9	Na Sulfate	3
Rincon	0. 273 3	0. 400 2	0. 326 5	Mg Sulfate	4
Cauchari	0. 182 0	0. 187 4	0. 630 6	Na Sulfate	5
Zacangchaca *	0. 184 3	0. 530 1	0. 285 6	Mg Sulfate	6
Xitaijinaier *	0. 096 6	0. 579 0	0. 324 4	Mg Sulfate	7
Dachaidan	0. 063 1	0. 660 1	0. 276 8	Mg Sulfate	8
Yiliping*	0. 110 4	0. 784 1	0. 105 5	Mg Sulfate	9
Graet Salt Lake	0. 119 0	0. 588 8	0. 292 2	Mg Sulfate	10
Silver Peak	0. 451 0	0. 090 4	0. 458 6	Na Sulfate	11

As indicated above, the solar pond technology is key to the development and utilization of brine mineral resources. Therefore, the basic investigation involves isothermal evaporation. Many studies investigating the evaporation of brines in different types of salt lakes have been conducted since 1950s in

China. Scientists at Qinghai Institute of Salt Lakes (QISL) have already completed studies on the evaporation of brines in salt lakes, such as Dongtaijinaier, Xitaijinaier, Yiliping, Dachaidan, Xiaochaidan, Charhan, and Zacangchaka. The work covers isothermal evaporation at different temperatures and

natural evaporation as discussed below. Because salt lake brines in the Qinghai-Tibet Plateau are characterized by the high content of lithium and boron, the work focuses on the behavior of Li and B during evaporation and has already provided insight into salt formation.

SQM Corp. has also investigated the isothermal evaporation of Atacama brines and conducted studies in phase chemistry and solar pond technology for six years before manufacturing Li compounds from the brine^[3-4]. Chemists also completed the evaporation tests of Cauchari brine at 30°C recently in Argentina^[5]. They investigated the data using the metastable phase diagram developed by Jin Zuomei, a Chinese chemist, for the $\text{Na}^+ - \text{K}^+ - \text{Mg}^{2+} // \text{Cl}^- - \text{SO}_4^{2-} - \text{H}_2\text{O}$ quinary system at 25°C^[6].

The salt sequences during the evaporation of Li brines, especially exhibiting Li salt behavior, represent key data for solar technologies. They indicate the initial and final stages of salt precipitation and the chemical composition of salt mixtures and brines. Based on these data, a basic flow sheet can be established. Different salt mixtures need different technologies to generate the salt products. For example, the salt sequence of Atacama summer brine is listed in Table 2. LiKSO_4 is the main Li salt in the mixture. However, in winter, the salt mixture $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ is the main Li constituent, which explains the different processing technologies used by SQM Corp.^[3-4].

Table 3 Salt precipitation sequences of Atacama brine during evaporation in summer Salt precipitation sequences

Salt precipitation sequences
NaCl
NaCl + KCl
NaCl + KCl + LiKSO_4
NaCl + KCl + LiKSO_4 + $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
NaCl + KCl + LiKSO_4 + $\text{KCl} \cdot \text{MgSO}_4 \cdot 2.75\text{H}_2\text{O}$
NaCl + KCl + LiKSO_4
NaCl + $\text{KCl} \cdot \text{MgSO}_4 \cdot 2.75\text{H}_2\text{O}$ + $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
NaCl + KCl + $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ + $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

3 The salt lake brine system and its thermodynamic model

As reported in our previous studies, salt lakes on the Qinghai-Xizang Plateau are characterized by high concentrations of lithium and boron brines. These brines mostly belong to the $\text{Li}^+ - \text{Na}^+ - \text{K}^+ - \text{Mg}^{2+} / \text{Cl}^- - \text{SO}_4^{2-}$, borate- H_2O system. While the B species in brines are very complicated, the borate represents all forms of B species. Therefore, we can use the system to describe the physico-chemical behavior of brines in the salt lakes. This system differs from the classic seawater system, the soda lake system, and the nitrate system. It exhibits specific physico-chemical properties because of the strong hydration of the Li-ion and the coordination complexity of borate anions in aqueous solution. We designated the system as “Salt Lake Brine System.”

Salt lakes are natural and complex bodies of water and salts. Precipitation of salts during the evaporation of brine is a process entailing substantial multicomponent phase equilibrium. In order to calculate the thermodynamics and phase equilibrium of this system, the Pitzer ion interaction model of aqueous electrolyte was adopted. We fit all the 1090 data covering the measured osmotic coefficient and solubility data combined with data obtained from chemical literature to generate the parameterized model of Pitzer for the $\text{Li}^+ - \text{Na}^+ - \text{K}^+ - \text{Mg}^{2+} / \text{Cl}^- - \text{SO}_4^{2-} - \text{H}_2\text{O}$ system at 298.15 K^[7-9]. Our parameterized model can be used to calculate the thermodynamic properties of brines, predict the solubilities of the title system and its subsystems with Li salts, and predict the sequences of salt precipitation during the evaporation of brines at 298.15 K reported in our previous studies^[10-13].

We have provided a few comparative data^[8,12] to illustrate the accuracy of salt sequences predicted using our model. The prediction covered Dongtaijinar, Xitaijinar, Yiliping, and Atacama Silver Peak Li brines. The predicted sequences were completely simi-

lar to the experimental data. Here, a few data are listed to indicate the comparative findings (Tables 2–4).

Table 4 Calculated sequences of salt precipitation during isothermal evaporation of Xitaijinaier brine at 298.15K

Determined sequences ^[14]	Calculated sequences
Original brine	Original brine(undersaturated with NaCl)
H	H
H + Pic	H + Pic
H + Pic + Eps	H + Pic + Eps
H + Syl + Eps	H + Syl + Eps
Not observed	H + Syl + Eps + Hex
H + Syl + Hex	H + Syl + Hex
H + Hex + Syl + Kai + Car	H + Hex + Syl + Kai + Car (stable equil.)
H + Hex + Kai + Car	H + Hex + Kai + Car (stable equil.)
H + Car + Hex + Bis(exp. ended)	H + Car + Lh + Bis (stable equil.)
	H + Car + Lc + LiC + Ls(final eutonic point)

Table 5 Calculated sequences of salt precipitation during isothermal evaporation of Yiliping brine at 298.15K

Determined sequences ^[14]	Calculated sequences
Original brine	Original brine (undersaturated with NaCl)
H	H
H + Syl	H + Syl
H + Syl + Hex	H + Syl + Hex
H + Hex + Car	H + Hex + Car
H + Hex + Car + Kai	H + Hex + Car + Kai (stable equil.)
H + Hex + Car	
H + Car + Pt	H + Car + Pt (stable equil.)
H + Car + Pt + Lh	H + Car + Pt + Lh (stable equil.)
H + Car + Pt + Bir (exp. ended)	H + Car + Pt + Bis (stable equil.)
	H + Car + Lc + LiC + Ls (final eutonic point)

Table 6 Calculated sequences of salt precipitation during isothermal evaporation of Dongtaijinaier brine at 298.15K

Determined sequences ^[14]	Calculated sequences
Original brine	Original brine (undersaturated with NaCl)
H	H
H + Syl	H + Syl
H + Syl + Eps	H + Syl + Eps
H + Syl + Eps + Hex	H + Syl + Eps + Hex
H + Syl + Hex + Car	H + Syl + Hex + Car
H + Syl + Hex + Kai + Car	
H + Hex + Kai + Car	H + Hex + Kai + Car (stable equil.)
H + Hex + Car	H + Hex + Car (stable equil.)
H + Hex + Car + Pt	H + Hex + Car + Pt (stable equil.)
H + Car + Pt	H + Car + Pt (stable equil.)
H + Car + Pt + Lh	H + Car + Pt + Lh (stable equil.)
H + Car + Lh + Bis + Ls (exp. ended)	H + Car + Lh (stable equil.)
	H + Car + LiC + Lc + Ls (final eutonic point)

Based on the above tables, it can be seen that the evaporation experiments were not complete. The final eutonic point for evaporation of Li-bearing brines is the invariant point of $H + Car + LiC + Lc + Ls$. Also, the isothermal evaporation is characterized by a stable equilibrium path rather than a metastable condition, especially during the late phase of evaporation. We usually observe isothermal evaporation along the metastable path for other brines lacking Li, such as seawater brine. Perhaps, the high Li content in brine plays an important role during the process.

Prediction of salt sequences by our model can be also used to calculate the data necessary for the following process technology. For example, the changes in the composition and material balance of different

stages in salt precipitation during isothermal evaporation of Laguocuo salt lake brine at 25°C are discussed below.

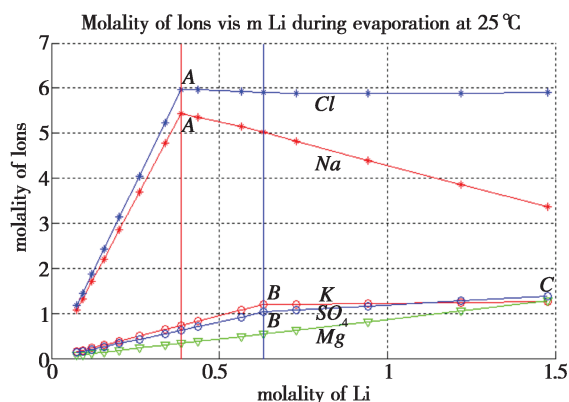


Fig. 2 Composition changes of Laguocuo salt lake brine during isothermal evaporation at 25°C

Table 7 Amounts of materials at saturation of K and Li salts for Laguocuo salt lake brine

A	B	C	D	E	F	Note
0.00	—	—	—	0.048 8	—	Original brine
73.83	—	—	26.17	0.186 4	3.82	To NaCl saturation
80.93	56.59	—	16.55	0.294 8	6.04	To KCl saturation
87.29	105.73 *	54.57	7.19	0.678 7	13.91	To Li salt saturation

Note: A—evaporated water%; B—precipitated NaCl%; C—precipitated KCl%; D—resulted bitter%; E—concentration of Li in the bitter (in mass%); F—concentration multiple of Li; *—conversion from KCl and Na_2SO_4 to additional NaCl

We applied our model of the $Li^+ - Na^+ - K^+ - Mg^{2+}/Cl^- - SO_4^{2-} - H_2O$ system to predict the salt sequences during isothermal evaporation at 298.15 K to more than 30 other Li brines. Here, we present the results of prediction along with the discussion.

4 Li salts and theoretical prediction of salt sequences

The highest content is represented by the total NaCl in all the natural brines. When brines were evaporated, the first crystallized salt is NaCl, and the following crystalline salts differed from each other. It can be predicted approximately based on the phase

diagram of the $Na^+ - K^+ - Mg^{2+}/Cl^- - SO_4^{2-} - H_2O$ quinary system at 25°C (Fig. 1).

The salt formation behavior of Li is complicated in the brine. Currently, chemists cannot use any phase diagram to estimate Li salt sequences during the evaporation at 25°C. Our 2003 thermodynamic model is the only tool available to chemists for the prediction of equilibrium conditions during evaporation of solutions containing Li^+ , Na^+ , K^+ , Mg^{2+}/Cl^- , SO_4^{2-} , and $-H_2O$ components at 25°C.

According to our model, the $Li^+ - Na^+ - K^+ - Mg^{2+}/Cl^- - SO_4^{2-} - H_2O$ quinary system contains solid phases of Li salt at 25°C as follows (Table 8).

Table 8 Lithium salts in the salt lake brine system at 25°C

Lithium salts	Abbreviation	Chemical formula
Lithium chloride	Lc	$\text{LiCl} \cdot \text{H}_2\text{O}$
Lithium sulfate	Ls	$\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$
Li – Carnallite	LiC	$\text{LiCl} \cdot \text{MgCl}_2 \cdot 7\text{H}_2\text{O}$
Double salt 1	Db1	$\text{Li}_2\text{SO}_4 \cdot 3\text{Na}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$
Double salt 2	Db2	$\text{Li}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4$
Double salt 3	Db3	$2\text{Li}_2\text{SO}_4 \cdot \text{Na}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$
Double salt 4	Db4	$\text{Li}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4$

As an original component of the system, LiCl and Li_2SO_4 contain several forms of hydrate: $\text{LiCl} \cdot \text{H}_2\text{O}$, $\text{LiCl} \cdot 2\text{H}_2\text{O}$, $\text{LiCl} \cdot 3\text{H}_2\text{O}$, $\text{LiCl} \cdot 5\text{H}_2\text{O}$, $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, and an uncertain salt $\text{Li}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$. They exist at 25°C as hydrated salts: $\text{LiCl} \cdot \text{H}_2\text{O}$ and $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$. The other Li salts shown in Table 8 are double salts derived from Li and other components in the system, especially sulfate double salts. Because the content of the other components is extremely higher than the Li content, these double salts are very easily

formed from brines during evaporation. This problem should be resolved, since it is related to the subsequent process technologies of the Li mixtures.

Results of predicted salt sequences for 20 brines are presented in Table 9 covering the first Li salt, Li concentration, a few properties of original brines, and types of brines. The ratios of Mg to Li and SO_4 to Li for original brines are counted as weight percentages.

Table 9 Results of predicted salt sequences for Li-brines

Salt Lake	First Li salt	Li%	Properties of original brines	Types
Dachaidam	Ls	0.464 5	$\text{Mg}/\text{Li} = 65$; $\text{SO}_4/\text{Li} = 112.5$	M
Dongtaijinaier	Ls	0.464 5	$\text{Mg}/\text{Li} = 31.2$; $\text{SO}_4/\text{Li} = 38.8$	M
Xitaijinaier	Ls	0.464 5	$\text{Mg}/\text{Li} = 61$; $\text{SO}_4/\text{Li} = 137$	M
Yiliping	Ls	0.464 5	$\text{Mg}/\text{Li} = 91$; $\text{SO}_4/\text{Li} = 51.8$	M
Jieze Chaka	Ls	0.464 5	$\text{Mg}/\text{Li} = 34.0$; $\text{SO}_4/\text{Li} = 27.4$	M
Sea Water	Ls	0.464 5	$\text{Mg}/\text{Li} = 37.14$; $\text{SO}_4/\text{Li} = 114.5$	M
Uyuni t	Ls	0.476 3	$\text{Mg}/\text{Li} = 23.4$; $\text{SO}_4/\text{Li} = 105.0$	M
Uyuni l	Ls	0.489 0	$\text{Mg}/\text{Li} = 22.1$; $\text{SO}_4/\text{Li} = 21.0$	M
Chabocuo	Ls	0.511 4	$\text{Mg}/\text{Li} = 27.4$; $\text{SO}_4/\text{Li} = 45.0$	N
Coipasa	Ls	0.534 0	$\text{Mg}/\text{Li} = 23.7$; $\text{SO}_4/\text{Li} = 52.4$	M
Baqiancuo	Ls	0.702 8	$\text{Mg}/\text{Li} = 6.50$; $\text{SO}_4/\text{Li} = 4.12$	M
Zacang Chaka	Db3	0.435 6	$\text{Mg}/\text{Li} = 11.6$; $\text{SO}_4/\text{Li} = 24.2$	M
Yibu Chaka	Db3	0.449 6	$\text{Mg}/\text{Li} = 1.96$; $\text{SO}_4/\text{Li} = 18.9$	M
Rincon	Db3	0.469 8	$\text{Mg}/\text{Li} = 8.61$; $\text{SO}_4/\text{Li} = 30.7$	M
Mariana	Db3	0.457 4	$\text{Mg}/\text{Li} = 10.4$; $\text{SO}_4/\text{Li} = 41.2$	M
Atacama	Db4	0.585 9	$\text{Mg}/\text{Li} = 6.40$; $\text{SO}_4/\text{Li} = 11.0$	M
Cauchari	Db4	0.669 8	$\text{Mg}/\text{Li} = 2.84$; $\text{SO}_4/\text{Li} = 30.8$	N

Continued from table 9:

Salt Lake	First Li salt	Li%	Properties of original brines	Types
Laguocuo	Db4	0.678 7	Mg/Li = 3.04; SO ₄ /Li = 22.6	N
Mamicuo	Db4	0.729 7	Mg/Li = 1.36; SO ₄ /Li = 7.28	M
Hombre Muerto	Db4	0.828 4	Mg/Li = 1.37; SO ₄ /Li = 13.8	N
Silver Peak	Db4	0.822 2	Mg/Li = 1.43; SO ₄ /Li = 30.9	N
Duomacuo	Db4	0.941 4	Mg/Li = 4.42; SO ₄ /Li = 3.57	N
Gaerkunsha	Db4	0.990 5	Mg/Li = 0.04; SO ₄ /Li = 9.64	N

Note: M-MgSO₄ subtype, N-Na₂SO₄ subtype

5 Formation of Li salts from brines during isothermal evaporation at 25°C

Based on the results of the predicted salt sequences for 20 brines listed in Table 9 and the experimental data, the general pattern underlying the formation of Li salts from brines during isothermal evaporation is as follows.

1) The phase equilibrium of the six-component system containing Li, Na, K, Mg/Cl, and SO₄ - H₂O is highly complex at 25°C. Our findings suggest that the system contains 30 chemical species including six ions, water, and 23 solid phases. The system contains 41 invariant eutectic points with five solid phases^[8]. Evaporation of the Li brine resulted in changes in brine composition via different solid phases, eutectic surfaces, eutectic lines, eutectic points, translation points, and the final eutectic point. Salt formation during evaporation is very complicated. However, the study of such a complex system deepens and widens our understanding of lithium salt chemistry.

2) The first crystallized Li salt during evaporation of Li brine has a varied brine composition. In brines of magnesium sulfate subtype, lithium sulfate is crystallized first in many cases, while Db4 (Li₂SO₄·K₂SO₄) or Db3 (2Li₂SO₄·Na₂SO₄·K₂SO₄) is formed first in case of sodium sulfate subtype and magnesium sulfate subtype with a lower Mg/Li composition. In a few cases, Db1 (Li₂SO₄·3Na₂SO₄·12H₂O) is formed first as a double sulfate salt of lithium without Mg. The type of initial Li crystal for-

mation depends on the ratios of SO₄²⁻ to Li⁺, Na⁺, and K⁺ of brine composition.

3) For brines of Mg-sulfate and Na-sulfate subtypes, the final eutectic point is the same as the unvariant eutectic point with five solid phases including H + LiC + Lc + Ls + Car, although they may have different initial crystals of Li salt. In fact, brines of Na-sulfate subtype transform to Mg-sulfate subtype in the late phase of evaporation. The above transformation of brines was observed frequently in experimental studies of isothermal evaporation of Na-sulfate subtype brines^[13]. The evaporation process reached the final eutectic point; that is, the unvariant eutectic point was H + LiC + Lc + Ls + Car in the six component system containing Li, Na, K, Mg/Cl, and SO₄ - H₂O at 25°C. Therefore, brines of both subtypes exhibit the same final eutectic point. At this point, Li exists as simple and double salts LiCl·H₂O, Li₂SO₄·H₂O, and LiCl·MgCl₂·7H₂O; K and Mg as double salt KCl·MgCl₂·6H₂O; and Na as NaCl in solid form. Notably, the only sulfate is Li₂SO₄·H₂O, and none of the sulfates of K, Mg, or Na exist at the point.

In case of a few brines, the evaporation process may reach other unvariant eutectic points, e. g., Dongtaijinaier brine reaches H + Car + Lh + Bis + Ls, Yiliping brine reaches H + Car + Lh + Bis + Ls, and Rincon brine reaches H + Car + Ls + Bis + LiC. However, these eutectic points are not final in the system, although they represent invariant points in the system. If evaporation processes continue, the phase transformation occurs and reaches the final eutectic point H + LiC + Lc + Ls + Car of the system.

4) For brines of chloride type, the final eutectic point is $H + LiC + Lc + Car$, which is the final invariant eutectic point of the five-component system comprising Li, Na, K, and $Mg/Cl - H_2O$. However, the foregoing brine of chloride type does not contain any sulfate totally. Brines of the chloride type cannot contain sulfate. Even a small amount of sulfate in chloride type brine is segregated to a component of the system. The brine type is changed to a sulfate subtype, and the final invariant eutectic point is $H + LiC + Lc + Ls + Car$ eventually.

5) Many experimental studies^[14] suggest that salt sequences during isothermal and natural evaporation of Li brine have a tendency to exhibit a stable equilibrium path rather than a metastable condition. For example, kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$) was detected during the isothermal evaporation of Dongtaijinaier, Xitaijinaier, and Yiliping brines, at 25°C, especially $MgSO_4 \cdot 4H_2O$ in the Dongtaijinaier and Yiliping brines. Our model is consistent with this conclusion. High Li content in brines may play an important role during the process.

6) Lithium content during the initial crystallization of the Li salt in the evaporation process is an important factor for solar pond technology, because it is the maximum theoretical limit that lithium can reach in brine. As shown in Table 6, the Li content ranges from 0.43% to 1%. The Li content during the initial crystallization of the Li salt as Db4 is obviously higher than that of $Li_2SO_4 \cdot H_2O$. These brines mostly belong to the Na-sulfate or Mg-sulfate subtype with a lower Mg/Li ratio. Undoubtedly, this conclusion facilitates the evaluation of potential lithium salt lake resources.

6 Conclusion

Currently, Li brines are the main sources for the extraction of basic Li salts industrially. Toward this end and for the comprehensive utilization of brine constituents, concentration of Li content via solar pond technologies is a necessary process. The salt se-

quence during evaporation of Li brines, especially the Li salt formation, provides important fundamental data for solar technologies. They represent the initial and final endpoints of salt precipitation, and chemical composition of salt mixtures and brines. Based on these data, the basic flow sheet can be established. Different salt mixtures can be processed into different salt products via specific technologies. In the present study, salt sequences during isothermal evaporation at 25°C for more than 30 Li brines were predicted using our thermodynamic model of the $Li - Na - K - Mg/Cl - SO_4 - H_2O$ quinary system. A few general conditions for the formation of Li salts during evaporation of Li brines have also been discussed. These findings extend our knowledge of Li chemistry and provide meaningful insight into the solar pond technology of the Li-brine process.

Salt Abbreviations

Ap	Aphthitalite	$NaK_3(SO_4)_2$
Ar	Arcanite	K_2SO_4
Bis	Bischofite	$MgCl_2 \cdot 6H_2O$
Blo	Bloedite	$Na_2Mg(SO_4)_2 \cdot 4H_2O$
Car	Carnallite	$KCl \cdot MgCl_2 \cdot 6H_2O$
Db1	Double Salt 1	$Li_2SO_4 \cdot 3Na_2SO_4 \cdot 12H_2O$
Db2	Double Salt 2	$Li_2SO_4 \cdot Na_2SO_4$
Db3	Double Salt 3	$2Li_2SO_4 \cdot Na_2SO_4 \cdot K_2SO_4$
Db4	Double Salt 4	$Li_2SO_4 \cdot K_2SO_4$
Eps	Epsomite	$MgSO_4 \cdot 7H_2O$
H	Halite	$NaCl$
Hex	Hexahydrate	$MgSO_4 \cdot 6H_2O$
Kai	Kainite	$KCl \cdot MgSO_4 \cdot 3H_2O$
Leo	Leonite	$K_2SO_4 \cdot MgSO_4 \cdot 4H_2O$
Lh	Leonhardtite	$MgSO_4 \cdot 4H_2O$
LiC	Lithium Carnallite	$LiCl \cdot MgCl_2 \cdot 7H_2O$
Lc	Lithium Chloride	$LiCl \cdot H_2O$
Ls	Lithium Sulfate	$Li_2SO_4 \cdot H_2O$
Mir	Mirabilite	$Na_2SO_4 \cdot 10H_2O$
Pt	Pentahydrate	$MgSO_4 \cdot 5H_2O$
Pic	Picromerite	$K_2SO_4 \cdot MgSO_4 \cdot 6H_2O$
Syl	Sylvite	KCl
Th	Thenardite	Na_2SO_4

References:

- [1] Song PS, Xiang RJ. Utilization and exploitation of lithium resources in salt lakes and some suggestions concerning development of Li industries in China[J]. Mineral Deposits, 2014, 33(5): 977 – 992.
- [2] Song PS, Li W, Sun B, *et al*, Recent Development on Comprehensive Utilization of Salt Lake Resources[J]. Chinese Journal of Inorganic Chemistry, 2011, 27(5): 801 – 815.
- [3] Pavlovic-Zuvic, P, Parada-Fredrick N, Vergara-Edwards, Recovery of potassium chloride, potassium sulfate and boric acid from the Salar de Atacama brines, Sixth International Symposium on Salt[M]. 1988, 2: 377 – 394.
- [4] Vergara-Edwards, L, Parada-Fredrick, N, Pavlovic-Zuvic P. Recovery of Lithium from crystallized salts in the solar evaporation of Salar de Atacama brines[M]//“Lithium, Current applications in science, medicine, and technology”, edited by Richardo Bach, 1985, 47 – 59.
- [5] King M, Amended Inferred Resource Estimation of Lithium and Potassium at Cauchari and Olaruz Salars, Jujuy Province, Argentina[R]//Groundwater Insight Inc, 2010: 75 – 83.
- [6] Jin Z, Xiao X, Liang S. Study of the Metastable Equilibrium for Pentanary System of $(\text{Na}^+, \text{K}^+, \text{Mg}^{2+})$, $(\text{Cl}^-, \text{SO}_4^{2-})$, H_2O [J], Acta Chimica Sinica, 1980, 38(4): 313 – 320
- [7] Song PS, Yao Y. Thermodynamics and Phase Diagram of the Salt Lake Brine System at 25°C [J]. CALPHAD, 2001, 25(3): 329 – 341.
- [8] Song PS, Yao Y. Thermodynamics and Phase Diagram of the Salt Lake Brine System at 298.15K, V. Model for the system $\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Mg}^{2+}/\text{Cl}^-, \text{SO}_4^{2-}/\text{H}_2\text{O}$ and its applications[J]. CALPHAD, 2003, 27(3): 343 – 352.
- [9] Song PS, Yao Y, Sun B. Pitzer model of thermodynamics for the Li, Na, K, Mg/Cl, $\text{SO}_4 - \text{H}_2\text{O}$ system [J]. Scientia Sinica Chimica, 2010, 40(9): 1286 – 1296.
- [10] Song PS, Yao Y. Parameters of Pitzer Model for the Salt Lake Brine System and their Applications, I. Applications in Physcal Chemistry for the system $\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Mg}^{2+}/\text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$ [J]. Journal of Salt Lake Reserch, 2003, 11(3): 1 – 8.
- [11] Song PS, Yao Y, Parameters of Pitzer Model for the Salt Lake Brine System and their Applications, II. Prediction of solubilities in the system $\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Mg}^{2+}/\text{Cl}^-, \text{SO}_4^{2-} - \text{H}_2\text{O}$ [J]. Journal of Salt Lake Reserch, 2003, 11(4): 1 – 12.
- [12] Song PS, Yao Y. Parameters of Pitzer Model for the Salt Lake Brine System and their Applications, III. Applications in Process technology in the system $\text{Li}^+, \text{Na}^+, \text{K}^+, \text{Mg}^{2+}/\text{Cl}^-, \text{SO}_4^{2-}/\text{H}_2\text{O}$ [J]. Journal of Salt Lake Reserch, 2004, 12(3): 1 – 10.
- [13] Bu L, Nie Z, Song PS. Computer simulation of 25°C – isothermal evaporation process of Li-Rich brines sodium sulfate subtype[J]. Acta Geologica Sinica, 2010, 84(11): 1708 – 1714.
- [14] Chen J, Liu Z, Fu T, *et al*//“Selected scientific work of Liu Dagang (Ta-Kong Liu)” [M], Ed Hu Keyuan (Khu Keyuan), Beijing: Science Press, 1997: 109, 117 – 124.