Phase Equilibria of the Brine Systems Containing Strontium and Calcium Ions

Xia Wang¹, Kaiyu Zhao¹, Long Li¹, Yafei Guo¹, Lingzong Meng¹,² and Tianlong Deng¹,*

¹Tianjin Key Laboratory of Marine Resources and Chemistry, College of Marine and Environmental Sciences, Tianjin University of Sciences & Technology, Tianjin, China
²School of Chemistry and Chemical Engineering, Linyi University, Shandong China

*Corresponding author e-mail: tldeng@tust.edu.cn

Abstract. It is well known that the comprehensive utilization of the Salt Lake resources successfully must be guided corresponding to the aqueous phase equilibria and phase diagrams. Researches on the phase relationships of brine systems containing calcium and strontium ions are essential to promote the development for the relative resources discovered in China at recent years. In this paper, the phase equilibria of calcium-containing systems, strontium-containing systems and calcium-strontium coexisted brine systems around the world were reviewed. The problems existed recently and new trends in future were point out.

1. Introduction
Inorganic liquid mineral resources are abundant in seawater, Salt Lake brines and oil-field brines. Comparing to seawater and Salt Lake brines, the valuable resources of oil-field brines have not been fully developed. The oil-field brines in the Nanyishan District of the Qaidam Basin in China are rich in various elements such as calcium, lithium, boron, strontium, rubidium and cesium. Especially the concentration of calcium is extremely high. The brines are classified as calcium chloride type according to the Sunlin classification [1]. In addition to calcium chloride, the concentration of strontium in the oil-field brine is up to 4450 mg/L [2]. Due to the extremely similar chemical properties between strontium and calcium, there is a challenge to separate calcium and strontium in the coexistence of calcium and strontium brines [3]. The results are essential for strontium and calcium separation from the brines. Therefore, researching on the phase equilibria for the systems containing strontium and calcium are so significant. The research on this aspect has become a hot topic of widespread concerns amongst domestic and foreign scholars [4, 5]. The phase diagram can be used to judge the precipitation sequence and conversion rules of various salts in the system, exploring the chemical production process, determining the optimum production conditions and formulating the optimal technological process [6]. In this article, progresses on phase equilibria of the brine systems containing strontium and calcium are summarized.
2. Study on Phase Equilibrium of Calcium-containing System

2.1. Study on stable phase equilibrium of calcium-containing system

With the development of the society and economy, solid mineral resources were increasingly reduced. Hence, the effective development and utilization of seawater and brine resources will grow in importance and these were inseparable from theoretical guidance of water and salt system phase diagram. Application of the principles and methods which obtained in phase diagram, may determine the route for some chemical products, improved and optimized existing production processes and production conditions, explored and acquired new technology, new process and new products.

As early as the 18th century, a great deal of research has been done on the phase equilibrium of calcium-containing brine system at our country and abroad [7]. In 1905, Van't Hoff et al. studied the phase relationships of Na+, K+, Mg2+, Ca2+ // Cl− ─ H2O systems at 25°C and 83°C in synthetic brines. The solubility of this system was measured and the solubility at 25°C was studied more comprehensively, eventually, nineteen quinary co-saturation points and five solubility parameters about quinary co-saturation points at 83°C of calcium-containing system were given. D’Ans et al. studied the phase relationships of this system at 0°C, 25°C, 55°C and 83°C, and measured the solubility of this system, respectively, the solubility data of quinary co-saturation points at 0°C, 25°C, 55°C and 83°C were given. It was worth pointing out that the three quinary co-saturation points at 25°C are both the crystallization phase areas of carnallite, and a quinary co-saturation point at 83°C was also a co-saturated zone of glauberite and potassium, which had not mentioned in Van't Hoff’s study.

W. T. Han [8] and S. Q. Gu [9] et al. studied the forming conditions of polyhalite (K2SO4·MgSO4·2CaSO4·2H2O) in Na+, K+, Mg2+, Ca2+ // Cl−, SO42− ─ H2O system, reported the precipitation area of polyhalite at 15°C, 25°C and 35°C, and found the calcium salts after balance, containing glauberite (Na2SO4·CaSO4), polyhalite (K2SO4·MgSO4·2CaSO4·2H2O), syngenite (K2SO4·CaSO4·H2O) and gypsum (CaSO4·2H2O), which provided a new basis for discussing the formation conditions of carnallite in salt deposits. Y. W. Li et al. [10] got a further study on precipitation area of calcium-rich syngenite in unsaturated region of this system, found twenty-five co-saturation points containing calcium at 55°C, and identified the solid phase, which contain K2Ca3(SO4)2+H2O and K2SO4·CaSO4·6H2O.

Csetenyi et al. in Hungary studied the phase equilibrium relationships of two different systems CaO ─ Na2O ─ B2O3 ─ H2O [11] and CaO ─ K2O ─ B2O3 ─ H2O [12] at 25°C and 50°C, especially the phase area of CaO. According to the experiment data and thermodynamics prediction, the phase diagram was drawn, and the experimental values were in good agreement with the predicted values. In addition, the relationships of two quaternary systems above and their sub-systems at 25°C were studied, and the solubility of KB2O3·4H2O, K2B2O3·(OH)4·2H2O, KBO2·1.25H2O, K2CaB2O7·12H2O and KB2O3(3OH)·2H2O was measured by isothermal dissolution method.

S. Q. Wang et al. [13] studied the phase equilibria in the aqueous ternary system LiBO2·CaB2O7·H2O at 288.15 K and 298.15 K, and the solubilities and physicochemical properties, including pH and density were investigated. Lianying Lei et al. [14] did some research of solid-liquid phase equilibria about ternary system CaCl2·CaB2O7·H2O at 308.15 K and 323.15 K at 0.1 Mpa, the phase diagram and the diagram of physicochemical properties versus of the composition of CaCl2 in the system 308.15 and 323.15 K were plotted.

2.2. Study on metastable phase equilibrium of calcium-containing system

Dan Li [15] studied the metastable phase equilibrium of the quaternary system Li+, Na+, Ca2+ // Cl− ─ H2O and its three subsystems Na+, Ca2+ // Cl− ─ H2O, Li+, Ca2+ // Cl− ─ H2O and Li+, Na+ // Cl− ─ H2O at 15°C using isothermal evaporation method, the solubility and physicochemical properties in all studied systems were measured. As to the diagram of quaternary system, there are two invariant points, five co-saturated curves and four co-saturated crystallizing zones, and it is desirable to point that in the
study of the ternary system Li⁺, Ca²⁺ // Cl⁻ — H₂O, a kind of hydrous double salt LiCl·CaCl₂·5H₂O was found, and first reported its optical properties.

Dongchan Li [16] studied the metastable phase equilibria of the quaternary system Na⁺, K⁺, Ca²⁺ // Cl⁻ — H₂O at 15°C and 35°C, and found a invariant point, three co-saturated curves and three co-saturated crystallizing zones. It is highly desirable that the balance solid phase in crystallizing zones containing KCl, NaCl and CaCl₂·6H₂O at 15°C, KCl, NaCl and CaCl₂·4H₂O at 35°C. The author first fitting the parameters of this quaternary system, and successfully predict the metastable equilibrium solubility of quaternary and ternary systems at 15°C and 35°C, respectively.

3. Study on Phase Equilibrium of Strontium-containing System

As a rare alkaline-earth metal, strontium was mainly in the form of sulfates and carbonates in nature. The strontium salts in the oil-field brine were presented in the form of soluble mineral, their solubility are similar to that of calcium salts and barium salts, and their carbonate and sulphate solubility in water were so small. This factor determines the chemical classification of rich-strontium brines in salt lake, which could only be the type of chloride, not carbonate and sulfate [17]. Due to the high economic value of the main elements of oil-field brine, the research on strontium in brine had become an advanced research focus [18–20].

G. O. Assarsson [21] studied the solubility of the binary system SrCl₂ — H₂O at 18–114°C in 1953. The author obtained the liquid phase composition and equilibrium solid phase of invariant points. And pointed out that the corresponding solid phase by SrCl₂·6H₂O into SrCl₂·2H₂O at 60°C. In 1969, M. Kylvynov [22] reported the solubility of this system at 25°C, and found two invariant points, the corresponding equilibrium solid phases respectively SrCl₂·2H₂O, NaCl and SrCl₂·2H₂O, SrCl₂·6H₂O. X. P. Ding et al [23] studied the solubility of the ternary system NaCl — SrCl₂ — H₂O at 25°C based on which the inconsistency of invariant point corresponds to the composition of the liquid phase and equilibrium solid phase by predecessors. An invariant point was determined, the corresponding solid phase was NaCl, SrCl₂·6H₂O. At the same time, the author makes inferences about the causes of SrCl₂·2H₂O in reference [21], indicating that SrCl₂·2H₂O can be found on the recrystallization or drying of the original material chlorinated strontium.

D. W. Li [24] studied the phase equilibria in the quinary system NaCl — KCl — MgCl₂ — SrCl₂ — H₂O at 75°C and some subsystems by isothermal solution saturation method according to the composition of the strontium-rich brines resources in the Sichuan Basin. The quinary system had a double salt and no solid solution was found. In the phase diagram, the system at 75°C had two invariant points, five co-saturated curves and four co-saturated crystallizing zones corresponding to SrCl₂·2H₂O, KCl, MgCl₂·6H₂O and KCl·MgCl₂·6H₂O. Besides, the author [25] respectively finished the ternary system MgCl₂ — SrCl₂ — H₂O at 50°C and 75°C. The phase diagrams both 50°C and 75°C belonged to a simple type, and without double salt and solid solution. The result was consistent with the study of the system by G.O. Assarsson in 1954 [26].

B. P. Blidin [27] in 1952 and Kvdynov [28] in 1954 respectively on the ternary system LiCl — SrCl₂ — H₂O at 25°C were studied. They all pointed out that the system at 25°C and at the same time there were two kinds of strontium chloride hydrate (SrCl₂·2H₂O, SrCl₂·6H₂O). However, the former did not have the solubility data of lithium hydrate. As LiCl·H₂O was highly absorbent, it was difficult to precipitate in solution. In brief, it could not be exactly determined.

4. Study on Phase Equilibrium of Calcium-strontium Coexisted Brine System

Due to the extremely similar chemical properties between strontium and calcium, a conclusion of calcium strontium coexistence system was found. The solid solution (Ca, Sr)Cl₂·6H₂O forms in the coexistence system containing strontium and calcium at low temperatures, but the solid solution did not form at high temperatures [29]. For ternary system CaCl₂ — SrCl₂ — H₂O, G. O. Assarsson [30] researched the solubility of 22 temperatures in 18–114°C. Y. J. Bi et al [31] researched the phase equilibrium of quaternary system LiCl — CaCl₂ — SrCl₂ — H₂O and its subsystem at 25°C, and found two invariant points and nine invariant points of the quaternary system. The author studied the
solubility of ternary system CaCl$_2$ – SrCl$_2$ – H$_2$O at 25°C in detail. The four phase zones of the system were obtained by analyzed wet residue, X-ray spectroscopy and polarizing microscope. These phase zones corresponding to CaCl$_2$·6H$_2$O, solid solution that rich in calcium, solid solution that rich in strontium and SrCl$_2$·6H$_2$O.

5. Conclusion
In this paper, those aspects are discussed in the following base on summarizing progress in domestic and foreign related researches: Firstly, because of strontium calcium is extremely similar; the interference of the measurement is obvious. It is necessary to develop an analysis method which is suitable for coexistence system containing strontium and calcium ions. Secondly, reported phase system of brine containing strontium calcium phase equilibrium mainly focused on the stable phase equilibrium of simple system. Nevertheless, the multi-temperature stability and metastable phase equilibrium for complex brine system Li$^+$, Na$^+$, K$^+$, Ca$^{2+}$, Sr$^{2+}$ // Cl$^-$ – H$_2$O are not reported. Thirdly, for the phenomenon of low temperature formation (Ca, Sr) Cl$_2$·6H$_2$O solid solution in strontium calcium coexistence system, existing research reports are the solubility data of the ternary system CaCl$_2$ – SrCl$_2$ – H$_2$O, the crystallization of solid solution in complex system is still needs further study.

Acknowledgments
Financial supports from the National Natural Science Foundation of China (U1507112, 21406104, U1406113 and U1607123), the Postdoctoral Science Foundation (2015M581303 and 2016M592827) and the Innovative Research Team of Tianjin Municipal Education Commission, China (TD12-5004) are acknowledged.

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