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Phase Equilibria of the Aqueous Systems Containing Lithium and Carbonate Ions

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1 Introduction

Alkaline lakes are widely distributed in the area of the Qinghai-Tibet Plateau. Most of the salt lakes are famous for their high concentration of lithium, potassium, magnesium, boron (Ma, 2000). In recent years, as a new energy material, lithium and its compounds are widely used in the new area, such as aerospace industry, nuclear energy, battery industry and optics industry. Due to low cost and simple chemical process extracting lithium from salt lake brine, the brine has replaced mine and became the main raw material production of lithium carbonate. It is well known that solid-liquid phase equilibrium plays an important role in exploiting salt lake brine resources and describing the geochemical evolution of brine minerals. At present most of extracting lithium from brine use sodium carbonate as precipitant to product primary products, lithium carbonate (Cao et al, 2009). In this paper, some progresses on the phase chemistry of brine systems containing lithium and carbonate at present years were summarized.

2 Stable Phase Equilibrium Containing Lithium and Carbonate

Ternary Systems: Using the method of isothermal equilibrium, the stable system $Li^+//CO_3^{2-}$, $B_4O_7^{2-}$–H_2O at 298 K and 288 K were reported (Zeng et al, 2000; Sang et al, 2002). Based on the solubility data, the phase diagram of the system was plotted, which consists of one invariant point, two univariant curves and two single salt crystallized zones corresponding to Li_2CO_3, $Li_2B_4O_7{\cdot}3H_2O$ in the system at 298 K and 288 K. This system at both temperatures belongs to a simple eutectic type, and neither double salts nor solid solutions were found. A comparison of the phase diagrams for the ternary system at 288 K and 298 K shows that the crystallized area of Li_2CO_3 is increased whereas $Li_2B_4O_7{\cdot}3H_2O$ is decreased obviously.

Quaternary Systems: Solubilities and physicochemical properties in the quaternary system Li^+, $K^+//CO_3^{2-}$, $B_4O_7^{2-}$–H_2O at 288 K and 298 K were experimentally studied with the isothermal equilibrium method, respectively (Yin et al, 2004; Zeng et al, 2002). The phase diagrams of the system at 288 K and 298 K consist of two invariant points, saturated with Li_2CO_3 + $K_2CO_3{\cdot}1.5H_2O$ + $Li_2B_4O_7{\cdot}3H_2O$ and Li_2CO_3+ $Li_2B_4O_7{\cdot}3H_2O$ + $K_2B_4O_7{\cdot}4H_2O$, respectively. The salt of K_2CO_3 had a strong salting out effect to tetraborates ($K_2B_4O_7$ and $Li_2B_4O_7$). On the basis of solubility data of ternary subsystem, Pitzer's theory of aqueous electrolyte solutions was used for solubility calculating at 298 K, and the calculated solubilities basically are agreed with the experimental values.

Quinary Systems: The complex quinary system Li^+, Na^+, $K^+//CO_3^{2-}$, $B_4O_7^{2-}$–H_2O was constructed (Sang, 2005). According to the experimental data, the phase diagram was filled with the six crystallization fields corresponding to $K_2CO_3{\cdot}3/2H_2O$, $K_2B_4O_7{\cdot}4H_2O$, $Na_2B_4O_7{\cdot}10H_2O$, $Na_2CO_3{\cdot}10H_2O$, $NaKCO_3{\cdot}6H_2O$ and $Li_2B_4O_7{\cdot}3H_2O$. The crystallized area of $K_2CO_3{\cdot}3/2H_2O$ was the smallest, while the borates ($K_2B_4O_7{\cdot}4H_2O$, $Li_2B_4O_7{\cdot}3H_2O$, and $Na_2B_4O_7{\cdot}10H_2O$) have larger crystallization fields than the others. In addition, the double salt $NaKCO_3{\cdot}6H_2O$ was found in this quinary system, and K_2CO_3 has the highest concentration and strong salting-out effect to other salts.

3 Metastable Phase Equilibria of Containing Lithium and Carbonate

Sulfate-type brine systems: Using the isothermal evaporation method, the metastable equilibria of the quaternary system Li^+, $K^+//CO_3^{2-}$, SO_4^{2-}, $B_4O_7^{2-}$–H_2O at 288 K and 273 K (Sang et al, 2010; Zhou, 2009), and its subsystems Li^+, $K^+//CO_3^{2-}$, SO_4^{2-}–H_2O were presented (Sang et al, 2007; Sang et al, 2011). Compared the quaternary systems at 288 K and 273 K, the solid phase

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numbers and the minerals existed are the same at different temperatures, while the area of crystallized zones are different. The crystallization forms of lithium-borate were $LiBO_2·8H_2O$ at 273 K, and $Li_2B_4O_7·3H_2O$ at 288 K. It means that the crystallization form of lithium-borate were relevant to temperature. The quaternary system at 273 K has crystallized zones of double salt $Li_2SO_4·K_2SO_4$, which can be formed in the quaternary system Li^+, K^+//SO_4^{2-}, $B_4O_7^{2-}$–H_2O and Li^+, K^+, Mg^{2+}//SO_4^{2-}–H_2O at 298 K. The double salts $Li_2SO_4·K_2SO_4$ are easily crystallized from room temperature to low temperature at stable or metastable phase equilibrium system.

Chloride-type brine systems: Compared with stable phase diagram at 298 K, the solid phase number and the mineral form in the quinary system Li^+ , K^+ //Cl^- , CO_3^{2-} , $B_4O_7^{2-}$ –H_2O at 288 K (Wang et al, 2001; Zeng et al, 2006) were changed. These changes between phase diagrams at different temperature will be very useful for separation and purification of salts. In addition, the results of quaternary system Li^+, K^+//Cl^-, CO_3^{2-}–H_2O at 298 K demonstrated that the isotherm diagram consists of two invariant points, five univariant curves and four crystallization fields corresponding to $K_2CO_3·3/2H_2O$, KCl, Li_2CO_3 and $LiCl·H_2O$. Compared with the stable phase diagram, the crystallized area of potassium chloride is increased obviously, and the reason may be that ions of bittern are easy to form a supersaturated interface state in the process of evaporation. The salt of K_2CO_3 has a strong salting out effect to LiCl and K_2CO_3 (Deng et al, 2000; Yan et al, 2008).

Borate-type brine systems: The quaternary system Li^+, K^+//CO_3^{2-}, $B_4O_7^{2-}$–H_2O at 273 K and 288 K shows that the solubility of the lithium carbonate has a negative temperature effect, and the crystallization field of lithium carbonate at 273 K is smaller than that at 288 K, while the crystallization fields of potassium carbonate, lithium borate at 273 K are larger than those at 288K (Yin, 2004; Zeng et al, 2008).

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