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Phase Equilibria of Salt-water Systems Containing Magnesium and Borate Ions

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1 Introduction

A salt lake is a naturally occurring complex body of water and salt interaction. More than 700 salt lakes are widely distributed in the area of the Qinghai-Tibet Plateau. Most of the salt lakes are famous for their abundance of lithium, potassium, magnesium, and boron resources. It is well known that salt-water phase equilibria play an important role in exploiting brine resources and describing the geochemical behavior of brine minerals. Investigating solubility phenomena of salt-water systems containing magnesium and borate ions is of great importance for exploitation and comprehensive utilization of such kind of salt resources such as extracting lithium, boron and potassium.

2 Stable Phase Equilibrium Containing magnesium and borate

The Ternary Systems: In order to exploit and utilize the borate type of salt lake brines, a few related salt-water systems had been studied. The solubility and thermodynamic properties of the system K^+, Mg^{2+}//$B_4O_7^{2-}$–H_2O at 298 K (Jin et al., 2004) and 348 K (Jing et al., 2013), Mg^{2+}//Cl^-, $B_4O_7^{2-}$–H_2O at 298 K (Du et al., 2000), Mg^{2+}// SO_4^{2-}, $B_4O_7^{2-}$–H_2O at 298 K (Song et al, 1987), Na^+, Mg^{2+}// $B_4O_7^{2-}$–H_2O at 288 K (Peng, 2008), Mg^{2+}//Cl^-, $B_6O_{10}^{2-}$–H_2O at 298 K (Bei et al., 1997), Mg^{2+}//SO_4^{2-}, $B_6O_{10}^{2-}$–H_2O at 298 K (Sun et al., 2000) had been researched. It is dedicated that none of double salts, solid solutions, hydration phenomena can be found and the crystallization forms of magnesium-borate were $MgB_4O_7{\cdot}9H_2O$ and $MgB_6O_{10}{\cdot}7.5H_2O$. $MgB_4O_7{\cdot}9H_2O$ and $MgB_6O_{10}{\cdot}7.5\ H_2O$ were disproportionate dissolved solids and could be transformed each other. It is worthwhile to note that $K_2B_4O_7$ had salting-out effect to MgB_4O_7 when the system is at 298 K, but two salts appeared a mutual solubilizing at 348 K strongly. The phase equilibria of systems MgO–B_2O_3–H_2O at a series of temperature (Пельша А.Д, 1973) had been investigated by Soviet Union scientists in 50s and 60s of last century. It is indicated that the crystallization forms of magnesium-borate were $MgO{\cdot}3B_2O_3{\cdot}7.5H_2O$, $2MgO{\cdot}3B_2O_3{\cdot}15H_2O$, $MgO{\cdot}B_2O_3{\cdot}3H_2O$ and $MgO{\cdot}2B_2O_3{\cdot}9H_2O$. The crystallization forms of magnesium-borate were relevant to temperature.

The Quaternary Systems: The salt-water systems Mg^{2+}//Cl^-, SO_4^{2-}, $B_4O_7^{2-}$–H_2O at 288 K (Li, 2009), Li^+, K^+, Mg^{2+}//$B_4O_7^{2-}$–H_2O at 288 K (Xiao et al., 2010), Na^+, K^+, Mg^{2+}//$B_4O_7^{2-}$–H_2O at 288 K (Peng, 2008) were presented and neither double salt nor solid solution was formed at investigated temperatures in these systems. In the system Li^+, Mg^{2+}//SO_4^{2-}, $B_4O_7^{2-}$–H_2O at 288 K (Sang et al., 2010) and 298 K (Song et al., 1991), there was also no double salt or solid solution. When compared the two experimental data, it was found that the solubility of Li_2SO_4, $MgSO_4$ and $Li_2B_4O_7$ at 288 K was smaller than that at 298 K, while the solubility of MgB_4O_7 has almost no change. The salting-out effect of $Li_2SO_4{\cdot}H_2O$ to $MgSO_4{\cdot}7H_2O$ at 288 K was weaker than that at 298 K. In the system K^+, Mg^{2+}//SO_4^{2-}, $B_4O_7^{2-}$–H_2O at 288 K (Sang et al., 2011), K^+, Mg^{2+}//Cl^-, $B_4O_7^{2-}$–H_2O at 288 K (Sang et al., 2009) and Na^+, Mg^{2+}//SO_4^{2-}, $B_4O_7^{2-}$–H_2O at 288 K (Sang et al., 2010), double salts $K_2SO_4{\cdot}MgSO_4{\cdot}6H_2O$, $KCl{\cdot}MgCl_2{\cdot}6H_2O$ and $Na_2SO_4{\cdot}MgSO_4{\cdot}4H_2O$ can be found respectively.

The Quinary Systems: The system Li^+, K^+, Mg^{2+}//SO_4^{2-}, $B_4O_7^{2-}$–H_2O at 288 K (Xiao, 2010), Na^+, Mg^{2+}, K^+//SO_4^{2-}, $B_4O_7^{2-}$–H_2O at 288 K (Peng, 2008), Na^+ (K^+), Mg^{2+}//Cl^-, SO_4^{2-}, $B_4O_7^{2-}$–H_2O at 288 K (Zhao, 2010), and Li^+, Mg^{2+}//Cl^-, SO_4^{2-}, $B_4O_7^{2-}$–H_2O at 288 K (Li, 2009) had been reported. The results showed that double salts $K_2SO_4{\cdot}MgSO_4{\cdot}6H_2O$, $Na_2SO_4{\cdot}MgSO_4{\cdot}4H_2O$, $Li_2SO_4{\cdot}K_2SO_4$, $Na_2SO_4{\cdot}3K_2SO_4$, $KCl{\cdot}MgCl_2{\cdot}6H_2O$ and $LiCl{\cdot}MgCl_2{\cdot}7H_2O$ can be formed in corresponding quinary systems. Tetraborate is in form of $B_4O_5(OH)^{2-}$ in saturated solution and it was difficult for this complex layered structure to be combined with other ions and to form double salts.

$B_4O_7^{2-}$ was the comprehensive statistics form of boron

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in brine. $MgSO_4$ could retardant transformation of hungchsaoite to inderite because of its common ion effect to magnesium borate. While the salt of $MgCl_2$ has strong hydroscopicity, hungchsaoite could be transformed into inderite when the solution contains magnesium chloride.

3 Metastable Phase Equilibria of Containing magnesium and borate

The phenomenon of super-saturation of brines containing magnesium borate is often found both in natural salt lakes and in solar ponds. Therefore, in order to separate and purify the salts effectively, knowledge of the metastable phase equilibrium is essential to objectively demonstrate the interaction of brine mineral and reveal the crystallized path of salts. The system Li^+, Na^+, K^+, Mg^{2+}// $B_4O_7^{2-}$–H_2O at 288 K (Wei, 2008) and its subsystems such as ternary systems (Na^+, Mg^{2+}//$B_4O_7^{2-}$–H_2O, K^+, Mg^{2+}// $B_4O_7^{2-}$–H_2O, Li^+, Mg^{2+}//$B_4O_7^{2-}$–H_2O), quaternary systems (Li^+, Na^+, Mg^{2+}//$B_4O_7^{2-}$–H_2O, Li^+, K^+, Mg^{2+}//$B_4O_7^{2-}$–H_2O, Na^+, K^+, Mg^{2+}//$B_4O_7^{2-}$–H_2O) had been investigated. Results showed that these metastable phase equilibria of the quinary system and its subsystems were all simple eutectic type, and no double salt or solid solution was formed at 288 K. The salt of $Na_2B_4O_7$ had the salting-out effect to $Li_2B_4O_7$, while the salt of $Na_2B_4O_7$ had the solubilizing effect to MgB_4O_7.

Compared with stable phase diagram, the solubility of MgB_4O_7 increased obviously in metastable phase diagram. The reason may be that low polymerization degree of polyborate anions can form higher polymerization degree through polycondensation under metastable conditions. Variety of polyborate anions can exist in the same solution at the same time and are in dynamic equilibrium of interactions and transformation. Therefore, boron-oxygen acid salts can easily form supersaturated solution.

Key word: salt-water system, phase equilibrium, magnesium, borate

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