Effects of K+, Na+, Mg2+ And B4O72- Coexistence Impurities on Crystalline Characteristics of Lithium Carbonate

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Abstract. Crystallization of lithium carbonate was performed in the presence of mixture analogous to those of Salt Lakes. Lithium carbonate exists in a crystalline system containing K+, Na+, Mg2+ and B4O72- impurities and the solubility decreases with the composition of impurities increases. In addition, effects of impurity composition on Li2CO3 crystal morphology, crystal size and purity were also thoroughly examined.

1. Introduction

With the rapid development of new energy industries [1], ore and salt lakes are two primary resources for lithium production; the latter contains 69% of the total reserves [2]. With the wide application of lithium salt products in high-tech fields, lithium carbonate has the potential for significant applicability in this industry [3]. Lithium carbonate is the most basic and a critical step in the process of lithium extraction from salt lakes. Therefore, the crystallization processes of lithium carbonate from Salt Lake solutions were studied in depth.

China's Salt Lake resources are rich. Among them, lithium salt lakes which are suitable for development have provided viable process pathways after years of research and are currently utilized in industrial production. However, low utilization of Salt Lake resources and substandard impurity removal rate in the purification process have severely restricted the development of the Salt Lake lithium industry.

The most significant problems facing the development of this industry include low yield, low product purity and poor crystal morphology. Specifically, the production of battery-grade lithium carbonate requires multiple re-pulping washing to meet production requirements; this results in higher production costs of lithium carbonate and complicates the production process. Research on lithium resources from salt lakes by groups at home and abroad have primarily focused on the purification process (deep impurity removal); research on the mechanism of lithium carbonate crystallization is limited. The actual solution of precipitation of a solution containing lithium carbonate which coexists with a variety of impurities determines the crystallization mechanism and the complexity of the process. Regardless of the physical and chemical methods used, the impurity problem still poses significant challenges. For example, the chemical properties of sodium and lithium are similar and it is
difficult to completely separate those two elements. Furthermore, the separation of magnesium and lithium is also difficult; lithium ion-rich solutions generally are required for the addition of soda ash to obtain the precipitation of lithium carbonate crystals. The products obtained by the interaction of lithium carbonate with a variety of impurities (such as (K⁺, Na⁺, Mg²⁺ and B₄O₇²⁻) are the core problems in obtaining battery-grade lithium carbonate crystals. Because impurities have an important effect on the super saturation of solution, morphology, particle size, the thermodynamics and kinetics of the lithium carbonate crystal is clearly merited. Impurities also lead to problems such as complex production issues, high costs and low yields.

The experimental and theoretical morphologies of lithium carbonate are needed [4]. Control over the morphology and crystal forms of minerals is significant for crystal engineering [5]. Synthesis of advanced inorganic materials with controllable morphology, size and crystallographic structure is often driven by industry requirements in diverse areas such as electronics, cosmetics, pigments, ceramics and medicine [6, 7]. Up to now, the size, morphology, crystallization and growth of lithium carbonate crystals have been widely studied using organic templates, biomacromoleculars, or polymers [8-11]. The process of obtaining Li₂CO₃ using LiCl and Na₂CO₃ has been studied in order to investigate the effects of temperature, stirring speed, and the Na₂CO₃ feed rate on the supersolubility of Li₂CO₃ [12, 13]. Crystal properties are important because they influence the reactivity, fluidity and wettability of the crystals, as well as the subsequent processes to which the crystals are subjected [14,15]. The desired properties for a crystalline product vary depending on the application; e.g. needle-shaped crystals are undesirable in pharmaceutical applications because of its difficult processing [16]. Size and shape distributions impact various solid properties, including end-use efficacy such as bioavailability for pharmaceuticals [17], catalyst reactivity [18], flowability, wettability, and adhesion [19-22].

The mechanism of action involving impurities such K⁺, Na⁺, Mg²⁺ and B₄O₇²⁻ in the crystallization process of lithium carbonate reaction were examined. This provided basic theoretical support for process control and equipment design for lithium carbonate crystallization.

To study the influence of impurities on the crystallization characteristics of lithium carbonate, it is very important to provide basic theoretical support for process control and equipment design for lithium carbonate crystallization.

2. Experimental

2.1. Materials
LiCl·H₂O (analytical grade) and MgCl₂·6H₂O were obtained from Sinopharm Chemical Reagent Co. Analytical grade Na₂CO₃ (AR) was purchased from Macklin. NaCl and Na₃B₄O₇·10H₂O were obtained from Tianjin Damao Chemical Reagent Co., Ltd.

All solutions were prepared using deionized water. The concentration of Li⁺ was determined using inductively coupled plasma mass spectrometer.

2.2. Set up
The experimental set up for measuring solubility is shown in Fig. 1. The crystallizer is a 500 mL jacketed glass vessel with a 100 mm internal diameter; its temperature was controlled with a thermostatic reaction bath whose temperature was controlled by a water-bath with an accuracy of ± 0.5 °C. A magnetic stirrer (450 rpm) ensured rapid mixing. Na₂CO₃ solution was added by a peristaltic pump, the addition velocity was 0.2 mL/min.

2.3. Procedures
This study was carried out as follows. Initially, 50 mL of a LiCl solution (3.215 mol/L) was introduced into the crystallizer; the water bath and stirring were then started (except for those experiments to investigate the impact of stirring speed). When the solution temperature stabilized, the laser apparatus and peristaltic pump to feed the Na₂CO₃ solution (2.0 mol/L) were turned on. When the solution
temperature stabilized, turned the peristaltic pump to feed Na₂CO₃ solution (1.037 mol/L) was turned on; this time was recorded as the start time. Time intervals were set to 0, 2, 5, 10, 15, 20, 40 and 60 min.

The experimental procedures for determining Li₂CO₃ solubilities in the presence of impurities or additives are described below. These studies focus on effects of impurities on its morphology and the mechanism of its action.

3. Results and Discussion

3.1. Effect of Na⁺, K⁺, Mg²⁺, B₄O₇²⁻ on the solubility of lithium carbonate

In a Salt Lake system, the existence of Na⁺, K⁺, Mg²⁺ and B₄O₇²⁻ impurities significantly alter crystallization processes; those effects are shown in Figure 2. Lithium chloride was treated with a variety of impurities in ratios from 0.76-3.79. These results showed that the solubility of lithium carbonate decreases to different degrees due to the presence KCl, NaCl, MgCl₂ or Na₂B₄O₇•10H₂O; this decrease stems from the changes the equilibrium of dissolved lithium carbonate. The metals all possess similar chemical properties (Na⁺, K⁺, Mg²⁺) and enhance both the ionic strength and the opportunity to combine with CO₃²⁻. They ultimately reduce the solubility of lithium carbonate. Mg²⁺ not only accelerates ionic motion and collisions between Li⁺ and CO₃²⁻, but also promotes the solute transfer process; both of which are favorable for nucleation. The presence of Na⁺, K⁺, Mg²⁺ and B₄O₇²⁻ in the system has salting-out effect on lithium carbonate.

In the Salt Lake system, however, several impurities often act together during the crystallization of lithium carbonate. In this study we plan to use a systematic approach for the addition of salt impurities (KCl, NaCl, MgCl₂, Na₂B₄O₇•10H₂O) to solutions of lithium chloride and study effects of solubility, morphology and particle size of lithium carbonate.

![Fig 1. Schematic diagram of experimental](image1)

![Fig 2. Solubility effects of Li₂CO₃ based on impurity](image2)
Setup. 1-stirrer, 2-thermometer, (a1) Effects of a single impurity; 3-crystallizer, 4-thermostatic waterbath. (a2) Effects of group impurity.

3.2. Effects of Na+, K+, Mg2+ and B4O72- on lithium carbonate crystal shape

The surface of the crystal is smooth and neat in the absence of impurities. The lithium carbonate crystal plane adhered to crystal granules, identified as Mg (OH)2. In the presence of KCl, however, the lithium carbonate crystal plane is rough and has a narrow width. In the presence of sodium chloride, the lithium carbonate width and length of the crystal vary greatly. Facial growth rates have been developed [12]. The lithium carbonate toward the thin and long direction to develop if B. Scanning electron micrograph (SEM) images Li2CO3 crystals obtained in the presence of several impurities are shown in Figure 3.

Fig 3. SEM micrographs of Li2CO3 particles. a-No impurity; b-MgCl2; c-KCl; d-NaCl; e-Na2B4O7•10H2O.

Fig.4. X-ray micrographs of Li2CO3 particles
X-ray diffraction patterns of synthesized crystals were measured for a qualitative analysis study and those results are shown in Fig. 4. X-ray micrographs of pure Li$_2$CO$_3$ were smooth and sharp with fine crystal shape.

Several impurity systems were examined (MgCl$_2$, KCl, NaCl and Na$_2$B$_4$O$_7$•10H$_2$O); all peaks of Li$_2$CO$_3$ appeared and obtained crystals were referenced to Li$_2$CO$_3$ and NaCl. The intensity of some faces increased; this effect was most pronounced for the pure crystal relative to crystals that contained impurities (MgCl$_2$, KCl, NaCl and Na$_2$B$_4$O$_7$•10H$_2$O). Different crystal shapes and XRD peaks were observed due to facial growth alteration; only NaCl peaks appear in the XRD patterns which implies that Na$^+$ has great influence for Li$_2$CO$_3$ crystal. Impact of pH alteration on crystal formation.

The pH of mother liquor without an impurity was greater than mother liquors containing of impurities. Table 1 shows the impurity composition/purity of Li$_2$CO$_3$:

### Table 1. Impurity content and purity of Li$_2$CO$_3$

| Types of杂志es | No impurity | K$^+$ | Na$^+$ | Mg$^{2+}$ | B$_2$O$_7^{2-}$ | Combination of impurities |
|----------------|-------------|-------|--------|-----------|----------------|-------------------------|
| Li$^+$/%        | 17.79       | 16.74 | 16.50  | 16.02     | 16.67          | 15.51                   |
| purity of Li$_2$CO$_3$/% | 98.83       | 93.00 | 91.67  | 89.00     | 92.61          | 86.17                   |

3.3. Effects of Na$^+$, K$^+$, Mg$^{2+}$ and B$_4$O$_7^{2-}$ on crystal size

In order to examine the impact of impurity on crystal size, Li$_2$CO$_3$ crystals were sieved in a distribution from 4.3% to 9.0%. Those results are seen in Fig. 5. As the concentration of impurity increased, the particle size decreased. The interaction of the impurity with Li$_2$CO$_3$ crystals is a superficial phenomenon like morphology and particle size.

In the mass transfer process, the total surface area of particles and the active spots of the reaction will change; this results in an alteration of the size and shape of the Li$_2$CO$_3$ crystals.

4. Conclusion

It was confirmed that solids precipitated in salt systems which combined lithium chloride and sodium carbonate which mimic those of Salt Lake systems. Impurity composition is the main influence of Li$_2$CO$_3$ crystallization in salt lakes.

The impacts of impurity identity and composition on the solubility, particle size and morphology were determined. Li$_2$CO$_3$ crystals obtained in the presence of Na$^+$, K$^+$, Mg$^{2+}$ and B$_4$O$_7^{2-}$ were obtained; those results showed a decrease in solubility and particle size.

Additional work will need to be performed to determine the mechanism of activation for these Salt Lake systems with Na$^+$, K$^+$, Mg$^{2+}$ and B$_4$O$_7^{2-}$ impurities.
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