

Refining of crude Li_2CO_3 via slurry phase dissolution using CO_2

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Abstract

Refining of crude Li_2CO_3 produced from salt lake brines of Qinghai, China, by direct carbonation with CO_2 –water solutions under different conditions was studied. The process is based on the reaction of Li_2CO_3 with CO_2 –water solutions to convert the former to the more soluble lithium bicarbonate. The carbonation experiments were carried out in a three-phase mechanically agitated slurry-bed reactor. The parameters that may affect the dissolution of Li_2CO_3 in CO_2 –water solution such as CO_2 pressure, temperature, CO_2 flow rate, solid concentration, particle size of Li_2CO_3 , slurry filling degree, agitator shape and agitation speed were investigated. The effects of immersion time of Li_2CO_3 in the slurry before carbonation as well as multiple carbonation cycles were also examined.

It was found that the rate of dissolution of Li_2CO_3 increased with increasing CO_2 pressure inside the reactor, agitation speed or CO_2 flow rate. Furthermore, it increased with decreasing Li_2CO_3 particle size, slurry filling degree, reaction temperature or solid concentration. The immersion time had almost no effect on the carbonation ratio of Li_2CO_3 . By multiple carbonations, it was possible to convert all of the insoluble Li_2CO_3 to lithium bicarbonate. The kinetics of the carbonation process in determined time intervals can be properly represented by $1 - (1 - X)^{1/3} = kt$. Finally, the Arrhenius activation energy of the carbonation reaction was obtained by calculation.

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1. Introduction

High purity Li_2CO_3 can be used for pharmaceutical applications, production of electronic grade crystals (e.g. LiNbO_3 and LiTaO_3 crystals), or to prepare battery-grade lithium metal, etc. With the development of battery and single crystal industries in the world, the demand for it is dramatically growing in recent years, whereas its supply is in some degree lacking. Consequently, promoting production of high purity Li_2CO_3 has become extremely necessary in nowadays. There exist abundant in lithium resources with large reserves in China, from which relatively low-cost crude Li_2CO_3 can be obtained. The present work aimed at realizing preparing high purity Li_2CO_3 from such feedstocks.

Some special methods, such as the Zintal–Harder–Dauth method, the re-crystallization method, the precipitation method and the carbonation method, can be used to prepare high purity Li_2CO_3 , depending on the properties of the feedstock [1]. In

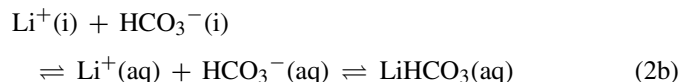
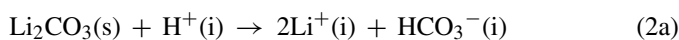
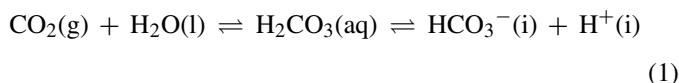
order to decrease the presence of impurities, LiOH and crude Li_2CO_3 are used as main feedstocks for preparing high purity Li_2CO_3 , the latter being the primary industrial raw material of lithium. The advantages and drawbacks of the two routes to produce high purity Li_2CO_3 can be found elsewhere [2]. In fact, most of the LiOH is converted from crude Li_2CO_3 by a causticization step, and then reacts with CO_2 to precipitate pure Li_2CO_3 . This route was tested by Brown and Patrick, et al., but the results were unsatisfactory [3,4]. It is obvious that using crude Li_2CO_3 extracted from lithium resources as the feedstock is cheaper and more efficient, hence a better choice. Commercial crude Li_2CO_3 produced from lithium-containing minerals, brines or sea water carries considerable amounts of impurities, such as calcium, magnesium and other multivalent ions as well as acid insoluble residues and so on. In order to eliminate them, the slight-soluble Li_2CO_3 should be first converted to a water-soluble compound.

Direct carbonation of Li_2CO_3 by pure CO_2 will not introduce other impurities, and water-soluble lithium bicarbonate (LiHCO_3) can be obtained; secondly, and no less important, CO_2 as a leaching agent has no appreciable environmental impact because the residues generated do not need any subsequent

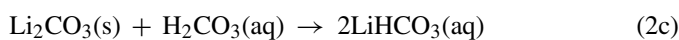
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treatment. Impurities in the crude Li_2CO_3 are either solubilized or precipitated out. The dissolved impurities are separated from LiHCO_3 by means of ion exchange, or liquid–liquid extraction. Purified Li_2CO_3 is then precipitated [5–8]. Clearly, the carbonation stage is very important in controlling production rate of high purity Li_2CO_3 . Therefore, it is very necessary to know the carbonation mechanism and its kinetics. The mechanisms and kinetics of carbonation of CaO and MgO with similar process have been reported previously [9,10]. However, the carbonation process of Li_2CO_3 , and the kinetics of this stage in particular has never been reported till now. In this work, extensive investigations have been carried out so as to better understand the mechanism of carbonation of Li_2CO_3 slurries.

The main reactions involved in the process are as follows:



or, by summation



where $\text{HCO}_3^-(\text{i})$, $\text{H}^+(\text{i})$ and $\text{Li}^+(\text{i})$ are the products formed and/or adsorbed at the interface.

The recovery of CO_2 and production of pure Li_2CO_3 precipitate can be accomplished by heating the purified lithium bicarbonate solution under vacuum conditions. The precipitation process (see Eq. (3)) is conducted at 353 K and 0.035 MPa, which will not be further covered in this paper.



The dissolution rate of any mineral is dependent upon the transport rate of reactants and products between the mineral surface and the bulk solution, the rate of heterogeneous reaction at the mineral surface, and, possibly, on the rates of homogeneous reactions within the solution [11].

The reaction rate constants of the first part of Eq. (1), i.e. $\text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$ at 1 atm and 298 K as found by Loewenthal and Mariaare are 0.037 s^{-1} for the forward reaction and 13.7 s^{-1} for the backward reaction [12]. This means that the forward reaction is slow while the backward reaction is much faster. On the other hand, the reaction rate constants for the second part of Eq. (1), i.e. $\text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{HCO}_3^-(\text{i}) + \text{H}^+(\text{i})$ are far larger than those of other reactions involved in Eq. (1) [13]. As a result, for the hydration of CO_2 in plain water, the whole reaction (1) is in equilibrium. But in this process, the hydrogen ions formed in Eq. (1) react with the $\text{Li}_2\text{CO}_3(\text{s})$ in the slurry, thus the reaction moves forward and more bicarbonate ions are formed.

The reaction between CO_2 and water can be promoted by the increase of CO_2 partial pressure or decrease of temperature [14]. Generally, the rate constant of a reaction increases with increasing temperature. Thus, temperature has contradictory effects in

Table 1

The solubility of Li_2CO_3 in water at different temperatures (solubility: g/100 g H_2O) [15]

Temperature (K)	Solubility
273	1.54
283	1.43
293	1.33
298	1.27
303	1.25
313	1.17
323	1.08
333	1.01
353	0.85
373	0.72

these reactions. However, high temperature is not recommended because it would result in the decomposition of both carbonic acid and lithium bicarbonate.

Small amounts of $\text{Li}_2\text{CO}_3(\text{s})$ can dissolve in water as shown in Table 1, but it takes a long time to reach the solubility equilibrium. Therefore, it is necessary to immerse $\text{Li}_2\text{CO}_3(\text{s})$ in water before reaction so as to reduce the mass transfer resistance of the reactants between the reaction interface and bulk. At the beginning of the reaction, the pH value of the solution is high. With progress of the reaction, the pH gets low. In the end, the carbonic acid buffer is formed, i.e., H_2CO_3 and HCO_3^- are in equilibrium.

In this work, the parameters influencing the dissolution of Li_2CO_3 in the CO_2 –water solution including CO_2 pressure, temperature, CO_2 flow rate, solid concentration in the slurry, particle size of Li_2CO_3 , agitator shape, agitation speed, immersion time and slurry filling degree in the reactor were investigated. The kinetic equation and the Arrhenius activation energy were obtained.

2. Experimental work

2.1. Experimental setup

A 5 L gas–liquid–solid three-phase mechanically agitated slurry-bed reactor was used for the carbonation experiments. The reactor has a feed hopper at the top and also a discharge port in which the liquid can be forced out under pressure. A steel pipe with a gas bubbler extends to the bottom of the reactor, from which the CO_2 is bubbled to the system. The pressure is adjusted through a safety valve and a pressure gauge. The temperature and agitation speed are controlled by a control box. The reactor is attached to a high pressure CO_2 gas cylinder equipped with CO_2 flow and pressure regulators. The CO_2 flow rate is measured with a calibrated rotameter connected between the cylinder and the reactor as shown in Fig. 1.

2.2. Materials and chemicals

The crude Li_2CO_3 used in this work was extracted from salt lakes brines and supplied by the Qinghai Lithium Co. Ltd. China. The physical and chemical analyses of the feedstock

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