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Preparation of lithium carbonate from spodumene by a sodium carbonate autoclave process

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ABSTRACT

Preparation of lithium carbonate from spodumene concentrate was carried out by a sodium carbonate autoclave process. The effects of different operation conditions including liquid-to-solid ratio, Na/Li ratio, agitation speed, reaction temperature and reaction time on the lithium carbonate conversion efficiencies were initially investigated. The results show that the conversion efficiency is not less than 94% under the optimal conditions. The purity of the obtained lithium carbonate can reaches up to 99.6%, which is higher than that obtained by sulfuric acid method.

1. Introduction

As the lightest metal, lithium is now widely used in battery, alloy, and nuclear power fields. Although this metal element occurs in a wide variety of minerals and ores, there are only a relatively few ores that are sufficiently available and contain a sufficient amount of lithium to make them attractive as a commercially practicable source of lithium. Among these commercially practicable sources of lithium, spodumene is the mineral that attracts the most interest and various processes for recovering the lithium values from spodumene ore have been proposed. In a number of these processes, only two processes have been practiced: sintering method and sulfuric acid process (Kondás et al., 2006; Shin et al., 2005; Tu et al., 2003; Yang, 2004), and sulfuric acid process has become the main method for production of lithium carbonate from spodumene due to its high efficiency. However, this process has its intrinsic drawbacks, such as high levels of sulfate and heavy metal ions in the product, sophisticated process for recovering sodium sulfate, etc.

In order to overcome these drawbacks, an autoclave method for production of lithium carbonate from spodumene has been suggested as the alternative (Amouzegar et al., 2000; Olivier et al., 1978). During this process, owing to its low reactivity, the α-spodumene was first roasted and transformed into β-spodumene at high temperature. Then the β-spodumene reacted with sodium carbonate solution to form lithium carbonate and analcime slurry in an autoclave according to the following reaction:

$$\beta - Li_2O \cdot Al_2O_3 \cdot 4SiO_2 + Na_2CO_3 + nH_2O = Li_2CO_3 + Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot nH_2O \quad (1)$$

The slurry was then leached with carbon dioxide and the resulting bicarbonate solution was heated to derive lithium carbonate (Jandová et al., 2010; Yi et al., 2007).

$$Li_2CO_3 + CO_2 + H_2O = 2LiHCO_3 \quad (2)$$

$$2LiHCO_3 = Li_2CO_3 + CO_2 + H_2O \quad (3)$$

Although the sodium carbonate autoclave method was proposed as an alternative method for production of lithium carbonate from spodumene many years ago, few detail investigation and evaluation on this method were reported. In this paper, a sodium carbonate autoclave process for production of lithium carbonate from spodumene is proposed and the results of investigation on this process are presented. The main objective is to determinate the optimal conditions to prepare high purity lithium carbonate from spodumene concentrate.

2. Experimental work

2.1. Materials

The spodumene concentrate used in this experiment was collected from a company in Jiangsu Province, China. Elemental analysis results

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of the spodumene concentrate is presented in Table 1. The purity of spodumene in the concentrate is about 75%. Analytical grade reagents were purchased in the local market, including sulfuric acid (AR, Hengyang Kaixin Chemical Co., Ltd), sodium carbonate (AR, Guangdong Xilong Chemical Co., Ltd). All aqueous solutions were prepared using distilled water.

2.2. Experimental method

α-spodumene is a monoclinic aluminium silicate, which has compact structure and hardly reacts with acid or base except hydrofluoric acid. So it is difficult to extract lithium from α-spodumene. As a result, the α-spodumene must be roasted and converted to its beta form before autoclaving carbonation. The effects of roasting conditions on the conversion ratio have been investigated in our previous work [Tian, et al. 2011]. In this study, the α-spodumene concentrate was roasted in an electrical muffle furnace (Hangzhou Zhuochi Co.,Ltd) at 1050 °C for 30 min for crystal transformation. The obtained β-spodumene was then used for autoclave process. The sodium carbonate autoclave process was carried out in a 1 L stainless steel autoclave which was equipped with a heating system, an internal cooling coil and a variable speed stirrer (WDF-1, Weihai Automatically-controlled Reactor Co., Ltd). 20 steel balls (ϕ10 mm) were put into the autoclave to enhance the agitation in this experiment.

The autoclave was charged with Na_2CO_3 solution and β-spodumene, and then sealed and heated at 5 °C/min to the temperature specified for the test. The system was allowed to react under constant temperature for the specified time. At the end of the experiment, the autoclave was cooled by circulating cold water through the cooling coil and the slurry in the reactor was discharged.

The reacted slurry was then put into a 2 L reactor equipped with an agitator, and water was added into the slurry to adjust the liquid-to-solid ratio to 8. For carbonation reaction, carbon dioxide gas was sparged into the slurry at a flow rate of 0.5 l/min for 120 min to ensure that almost all lithium carbonate in the slurry converted to lithium bicarbonate. After the carbonation reaction, the slurry was filtered. The residue on the filter was washed with dilute sulfuric acid solution and distilled water, and finally analyzed by atomic absorption spectroscopy (AAS, Beijin Puxi General Instrument Co., Ltd., TAS990F) and X-ray diffraction (XRD, Rigaku, D/max-7500). Because the β-spodumene is inactive to sulfuric acid at room temperature, the residue was washed with a dilute sulfuric acid solution and water for many times before analysis, which should not remove lithium from the un-reacted β-spodumene in the residue. Thus the lithium carbonate conversion efficiency was calculated according to the lithium content in the washed residue.

The lithium bicarbonate rich filtrate was heated to 90 °C in a 2 L reactor equipped with an agitator and maintained at this temperature for 120 min to drive off CO_2. The resulting slurry was filtered and lithium carbonate was obtained. The contents of impurities in the lithium carbonate were determined by atomic absorption spectroscopy and inductively coupled plasma (ICP, Perkin Elmer, Optima 3000) analysis. The test work flowsheet is shown in Fig. 1.

Table 1
Elemental analysis results of spodumene concentrate.

Element	Content, %	Element	Content, %
Li	2.81	Na	0.395
K	0.255	Ca	0.112
Mg	0.063	Al	13.4
Fe	0.358	P	0.057
S	0.111	Ba	0.001

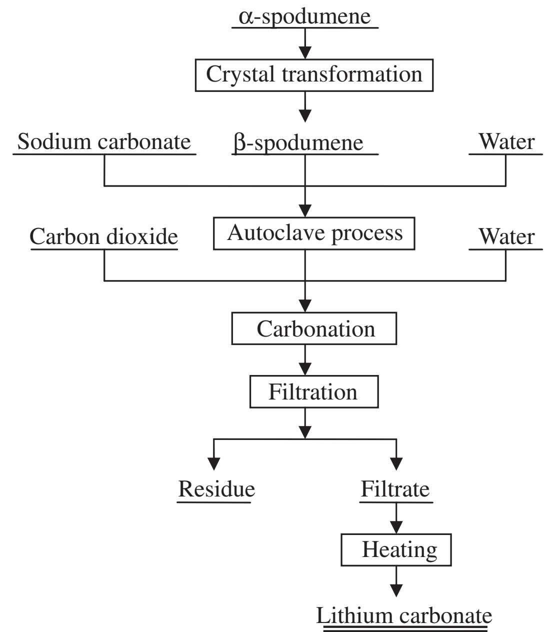

Fig. 1. Schematic of laboratory process for preparation of lithium carbonate from spodumene.

3. Results and discussion

3.1. Autoclaving carbonation

In order to obtain the optimal conditions for preparation of lithium carbonate from spodumene, the effects of different variables on the lithium carbonate conversion efficiencies were evaluated. The main variables studied were ratio of liquid to solid, ratio of lithium to sodium, agitation, temperature and time of reaction. The results obtained are summarized as the follows.

3.1.1. Effect of liquid-to-solid ratio

The effect of liquid-to-solid ratio on the lithium carbonate conversion efficiency was studied in the range from 2 to 5 (milliliter of solution per gram of solid), maintaining the sodium-to-lithium ratio at 1.5, stirring speed at 350 rpm, reaction temperature 230 °C and reaction time 90 min.

In order to evaluate the experimental error, each experiment was replicated for five times. The average conversion efficiency and standard deviation was calculated and the results are presented in Fig. 2, where it can be seen from the error bars that the largest standard deviation is about ±1.6%.

As can be seen in Fig. 2, increasing the liquid-to-solid ratio from 2 to 4, an obvious increase in the lithium carbonate conversion efficiency is obtained. The efficiency reaches up to about 96% when the liquid-to-solid ratio of 4 is used. Since lithium carbonate is slightly soluble in water at high temperature (Somers, et al., 1971), this may be partially explained by the fact that more lithium carbonate layer covering the spodumene particles in the slurry can dissolve with increasing liquid-to-solid ratio. As a result, the mass transfer between the spodumene particles and sodium carbonate solution is strengthened and thus the reaction (1) can proceed more smoothly.

However, a further increase in the ratio from 4 to 5 does not lead to a substantial increase in the efficiency. Consequently, according to these data, the autoclave process should be carried out at the liquid-to-solid ratio of 4.