

Supporting Information

Recovery of Lithium Carbonate from Dilute Li-Rich Brine via Homogenous and Heterogeneous Precipitation

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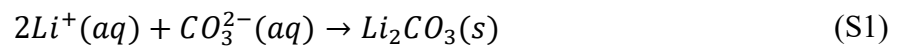
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S.1 Fundamentals of $\text{Li}_2\text{CO}_3(\text{s})$ precipitation routes by Na_2CO_3 or NaOH/CO_2 addition

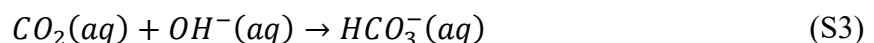
In the present work, the reactive crystallisation of $\text{Li}_2\text{CO}_3(\text{s})$ from relatively Li-concentrated solutions was analysed studying two different separation routes: (i) addition of Na_2CO_3 solution and (ii) addition of NaOH solution and CO_2 insufflation.

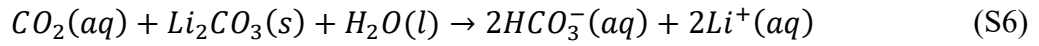
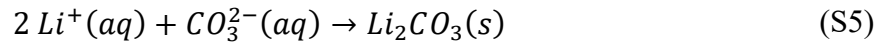
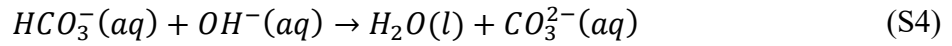
In the first case, Li^+ and CO_3^{2-} ions react yielding the poorly soluble $\text{Li}_2\text{CO}_3(\text{s})$, according to Eq. (S1).



Li_2CO_3 precipitation using Na_2CO_3 has been widely investigated in the literature and various parameters affecting Li_2CO_3 recovery were studied: the reaction temperature, the solution pH, the initial Li^+ concentration, the presence of dissolved salts, the Na_2CO_3 addition flow rate and the stirring speed¹.

On the other hand, the NaOH solution and CO_2 insufflation precipitation route has been less studied in the literature. In the process, first, CO_2 has to dissolve in the Li^+ solution, Eq. (S2). Then, the dissolved $\text{CO}_2(\text{aq})$ reacts with OH^- ions to form bicarbonates (HCO_3^-), Eq. (S3). Bicarbonates further react with OH^- ions leading to carbonates, Eq. (S4). Finally carbonates and lithium ions precipitate as Li_2CO_3 , Eq. (S5). A continuous CO_2 insufflation, however, can decrease solution pH affecting the $\text{CO}_2/\text{HCO}_3^-$ equilibrium causing the re-dissolution of the precipitated Li_2CO_3 in the form of the soluble LiHCO_3 , Eq. (S6).





The complex set of simultaneous reactions, taking place during the $Li_2CO_3(s)$ precipitation process in a gas-liquid reaction system, makes the process more difficult to be analysed and controlled with respect to the classical use of Na_2CO_3 separation route². In the precipitation gas-liquid system, several parameters have to be carefully controlled, e.g. the reaction temperature, the solution pH, the $CO_2(g)$ volume flow rate and the bubble size³. The reaction temperature does not only influence the solubility of Li_2CO_3 , but also the $CO_2(g)$ dissolution velocity. Increasing temperature decreases Li_2CO_3 solubility that, in turn, induces a faster $CO_2(g)$ consumption pushing the $CO_2(g)$ dissolution due to the lower $CO_2(g)$ bulk concentration in the solution. On the other hand, it has also to note that $CO_2(g)$ solubility decreases. A critical parameter is the solution pH. As shown from Eq. (S6), the final pH affects the re-carbonation equilibrium of Li_2CO_3 , thus the time point when CO_2 is stopped must be properly controlled to avoid excessive re-carbonation of Li_2CO_3 , which causes excessive product loss. Bubbles' size is also an important parameters: small bubbles enhances $CO_2(g)$ mass transport, thanks to large specific surface area, accelerating the process⁴.

S.1.1 $Li_2CO_3(s)$ solubility in pure water system

In comparison to most salts, the solubility of $Li_2CO_3(s)$ decreases increasing temperature. The solubility constant (K_{sp}) at 20 °C is $5.3 \cdot 10^{-4}$ and $8.9 \cdot 10^{-5}$ at 90 °C according to the HSC data of Metso-Outotec. In the present work, an initial Li^+ concentration of about 4000 ppm was employed in all experiments in accordance with expectation of the SEArcularMINE project chain. At such initial Li^+ concentration, the maximum theoretical Li^+ recovery can vary from

59 % at 50 °C to 69 % at 80 °C⁵, when using reactants stoichiometric amounts. It should be noted that, at an initial Li⁺ concentration of 4000 ppm, only Li₂CO₃ could be studied as a viable route for Li⁺ recovery due to the high solubility of LiOH(s) in water, i.e. ~127,000 ppm at 20 °C⁶ with respect to that of Li₂CO₃ (~13,000 ppm at 20 °C).

S.1.2 Influence of Inorganic Solution Components on Li₂CO₃(s) solubility

The presence of dissolved ions in Li⁺ solutions has been found to influence Li₂CO₃ solubility. Sun et al.¹ reported a Li₂CO₃ solubility decrease after the dissolution of NaCl and KCl salts (salt-out effects), while Li₂CO₃ solubility increased dissolving Na₂SO₄ salts (salt-in effect). Cheng et al.⁵ studied the Li₂CO₃(s) solubility in Na⁺, K⁺, Li⁺, Cl⁻ brines in a temperature range between 20 and 90 °C by the isothermal dissolution method. Li₂CO₃ was found to be more soluble in NaCl and KCl single added salt systems and even more soluble in mixtures of dissolved NaCl and KCl solutions. Wang et al.⁷ measured the solubility, the super solubility, and the metastable zone width of Li₂CO₃ in mixed LiCl–NaCl–KCl–Na₂SO₄ solutions in a temperature range from 20 to 80 °C employing the isothermal dissolution method and the turbidity technology. Results were in accordance with those reported by Sun et al.¹. Ma et al.⁸ studied the crystallization of lithium carbonate in LiCl solutions containing other salts mimicking China's Salt Lakes ones. It was observed that lithium carbonate solubility decreased increasing composition of K⁺, Na⁺, Mg²⁺ and B₄O₇²⁻ ions. At the same time, as salts concentration increased, Li₂CO₃(s) particle sizes and purity decreased. King et al.⁹ investigated the Li₂CO₃(s) precipitation process also in the presence of divalent cations, i.e. Mg²⁺ and Ca²⁺, in LiBr solutions. Even at low Mg²⁺ concentration, Li⁺ precipitation was found to be considerably hindered. Furthermore, the presence of divalent ions reduced Li₂CO₃(s) crystals growth and purity.

S.2 Supporting tables

Tables listing additional information about the experimental tests discussed in the manuscript.

Table S1 Chemical reagents characteristics employed for Li⁺ precipitation analysis.

Compound	Formula	Manufacturer	Purity
Lithium chloride	LiCl	Carl Roth	≥99 %
Sodium carbonate	Na ₂ CO ₃	VWR	99.7 %
Strontium chloride hexahydrate	SrCl ₂ *6H ₂ O	Carl Roth	≥99 %
Potassium chloride	KCl	Carl Roth	≥99 %
Sodium chloride	NaCl	Merck	≥99 %
Nitric acid	HNO ₃	Carl Roth	69 %
Rubidium chloride	RbCl	Carl Roth	≥99 %
Sodium hydroxide	NaOH	Carl Roth	≥99 %
Magnesium chloride	MgCl ₂	Carl Roth	≥98.5 %
Calcium chloride	CaCl ₂	Carl Roth	≥94 %
Ethanol	CH ₃ CH ₂ OH	Carl Roth	≥70 %
Carbon dioxide	CO ₂	Linde	99.9 %

Table S2 Reacting quantities for Li_2CO_3 precipitation tests at different $[\text{CO}_3^{2-}]/[\text{Li}^+]$.

$\text{CO}_3^{2-}/$ Ratio	Li^+	Li^+ concentration in the feed solution [ppm]	LiCl feed solution volume [mL]	2.0 Na_2CO_3 M volume [mL]	Li^+ concentration in the total volume [ppm]
0.25		4330	115	9	4010
0.5		4780	105	18	4080
0.75		5280	95	28	4080
1		5820	86	36	4100
2		10100	50	72	4140

Table S3 Calculated ionic strength for 0.70 M LiCl solutions, before Na_2CO_3 solution addition, with and without NaCl and KCl salts.

Investigated solutions	Ionic strength I [M]
0.70 M LiCl	0.70
0.70 M LiCl and 1.5 M KCl	2.20
0.70 M LiCl and 2.0 M NaCl	2.70
0.70 M LiCl and 1.5 M KCl + 2.0 M NaCl	4.20

Table S4 Divalent cations concentration in LiCl solutions with 2.0 M NaCl and 1.5 M KCl (before addition of Na₂CO₃ solution). In each solution, Li⁺ concentration after carbonate dosing was ~4000 ppm.

Investigated solutions before Na ₂ CO ₃ addition	Ionic strength <i>I</i> [mol/L]
0.70 M LiCl, 1.5 M KCl, 2.0 M NaCl	4.20
0.70 M LiCl, 1.5 M KCl, 2.0 M NaCl + 0.17 M CaCl ₂	4.70
0.70 M LiCl, 1.5 M KCl, 2.0 M NaCl + 0.25 M MgCl ₂	4.95
0.70 M LiCl, 1.5 M KCl, 2.0 M NaCl + 0.17 M SrCl ₂	4.70
0.70 M LiCl, 1.5 M KCl, 2.0 M NaCl + 0.17 M CaCl ₂ + 0.25 M MgCl ₂ + 0.17 M SrCl ₂	5.95

Table S5 Reacting solutions at different OH⁻/Li⁺ ratios.

OH ⁻ /Li ⁺ Ratio	LiCl volume [mL]	NaOH volume [mL]	Li ⁺ concentration after NaOH addition [ppm]
1	110	9.0	4290
1.5	110	13	4180
2	110	18	3900
4	110	47	4165

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