Supporting Information (SI)

Reactive Crystallization of Li_2CO_3 in LiOH/KOH Solutions: Solubility, Nucleation and Carbonization

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The concentration of OH^- and CO_3^{2-} in the solution was determined by titration, according to the *Geology and Minerals Industry Standard* (DZ/T 0064.49-1993) in China. The solution to be measured and 4 drops of phenolphthalein solution (10g/L) were added to a conical flask, and a titration with hydrochloric acid (0.05 mol/L) was implemented until the red color just disappeared. 4 drops of methyl orange solution (0.5 g/L) was then added to the solution, and a repeated titration was implemented until the solution changed from yellow to orange. Table S1 demonstrates the calculation of the relevant ion concentrations.

Table S1. Concentration calculation of OH^-, CO_3^{2-} and HCO_3^- in solution

Conditions	Contained ions	Concentration calculation
$V_1 > V_2$	OH^- CO_3^{2-}	$OH^-\ (mg/L) = \frac{c \times (V_1 - V_2) \times 17.01}{V} \times 1000$ $CO_3^{2-}\ (mg/L) = \frac{c \times 2V_2 \times 30.01}{V} \times 1000$
$V_1 = V_2$	CO_3^{2-}	$CO_3^{2-}\ (mg/L) = \frac{c \times 2V_1 \times 30.01}{V} \times 1000$
$V_1 < V_2$	CO_3^{2-} HCO_3^-	$CO_3^{2-}\ (mg/L) = \frac{c \times 2V_1 \times 30.01}{V} \times 1000$ $HCO_3^-\ (mg/L) = \frac{c \times (V_2 - V_1) \times 61.02}{V} \times 1000$
$V_1 = 0$	HCO_3^-	$HCO_3^-\ (mg/L) = \frac{c \times V_2 \times 61.02}{V} \times 1000$
$V_2 = 0$	OH^-	$OH^-\ (mg/L) = \frac{c \times V_1 \times 17.01}{V} \times 1000$

where c represents the concentration of hydrochloric acid, mol/L; V_1 represents the volume of hydrochloric acid consumed in the titration when phenolphthalein is used as indicator, mL; V_2 represents the volume of hydrochloric acid consumed in the titration when orange solution is used as indicator, mL; V represents the volume of the solution to be measured.

The Raman spectra (DRX, Thermo Fisher, USA) of the crystallization mother liquor at different times were shown in Figure S2. With the introduction of CO_2, peak 1 appeared at Raman shift of 1065 cm^{-1}, and its intensity gradually increased, corresponding to the CO symmetric stretching vibration of CO_3^{2-}. Peak 2 appeared at Raman shifts of 1016 cm^{-1} and peak 3 appeared at 1364 cm^{-1}, corresponding to the C-OH stretching vibration and the CO symmetric stretching vibration of HCO_3^-, respectively, which also confirmed the formation of HCO_3^- in reaction (d). The intensities of these peaks gradually increased with the continuous introduction of CO_2.

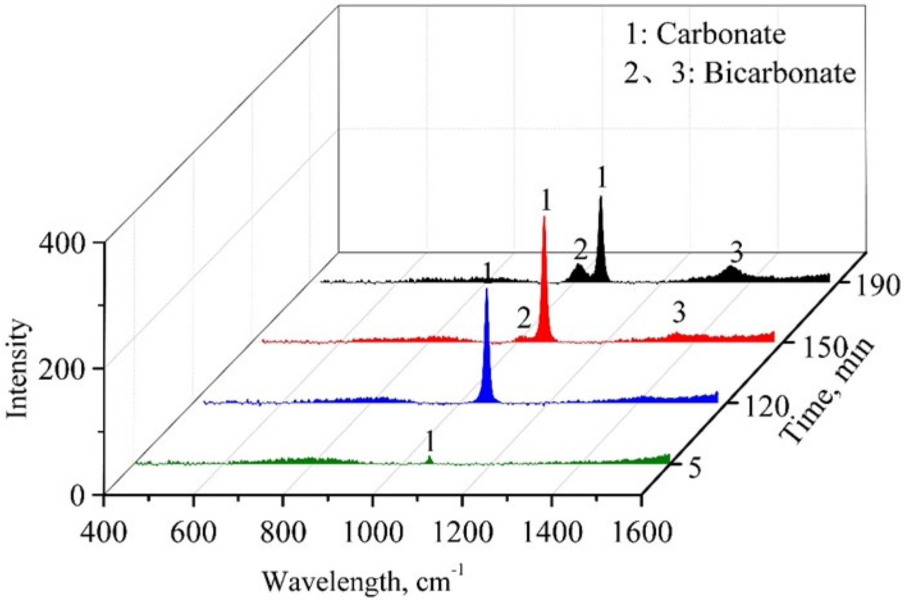

Figure S1. Evolution of Raman spectra of the mother liquors in carbonation of LiOH/KOH solutions

Figure S3 demonstrates the variation in the concentration of CO_3^{2-} versus time at different temperatures, which shows a trend of first increasing and then decreasing.

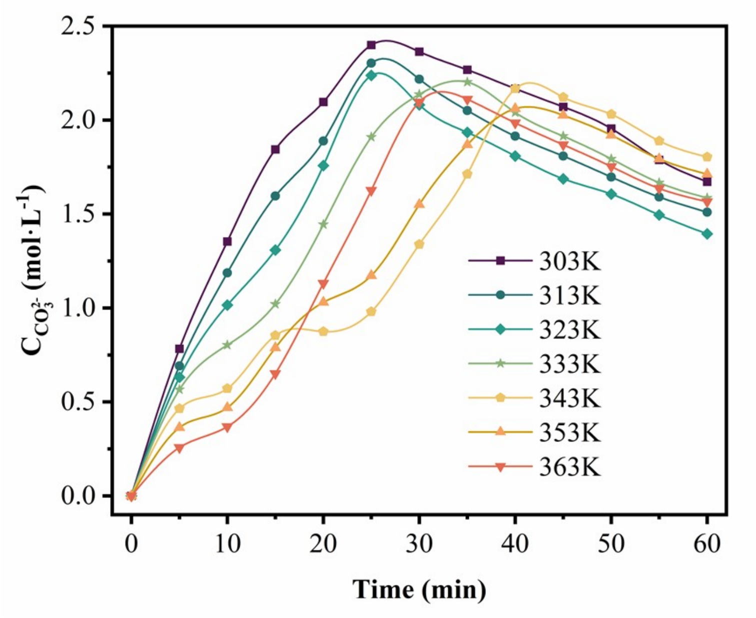

Figure S2. Concentration of carbonate ion versus time at different temperatures