# Crystallization behavior and kinetics of calcium carbonate in highly alkaline and supersaturated system

Ganyu Zhu [a,b], Huiquan Li [a,*], Shaopeng Li [a], Xinjuan Hou [a], Dehua Xu [a,b], Rongyi Lin [a], Qing Tang [a]

[a] Key Laboratory of Green Process and Engineering, National Engineering Laboratory for Hydrometallurgical Cleaner Production Technology, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China
[b] University of Chinese Academy of Sciences, Beijing 100049, China

## A B S T R A C T

In causticization process of $Na_2CO_3$–$Ca(OH)_2$, which is a liquid–solid system with high alkalinity and supersaturation, agglomeration and morphology instability of $CaCO_3$ crystal have greatly limited its application. To deeply investigate the internal relations between crystallization process and condition control in this system, crystallization kinetics was conducted in a continuously operated crystallizer. The kinetic equations of growth rate, nucleation rate and agglomeration kernel were correlated in terms of power law kinetic expressions based on the agglomeration population balance equation. Magma density and mean residence time exert a considerable effect on crystal growth, nucleation, and agglomeration. Crystal growth and nucleation are surface-integration-limited and size-limited, respectively. Agglomeration increases with increasing mean residence time, but the increase in magma density break down the agglomerates by frequent and energetic collisions. Through the study, crystallization behavior of $CaCO_3$ in causticization system was revealed, and the particle size and morphology were efficiently predicted and controlled. These results can provide a basis for understanding the design of the reactor.

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## 1. Introduction

Causticization is an important fundamental process to regenerate caustic alkali with sodium carbonate. This process, which can be seen in Scheme 1, has been widely used in alkali recycling in chemical industries such as papermaking [1–3], solid wastes utilization [4], and so on.

Till the beginning of last century, a number of systematic studies to the system have been focused on equilibrium of the reaction [5,6] and the settling rate of calcium carbonate ($CaCO_3$) [7]. Due to difficulties of the phase and morphology control in the process, utilization of $CaCO_3$ has been greatly limited [8]. The large amount of solid by-product leads to serious environmental problems, and restricts the development of industries which contain causticization process. Recently, numerous efforts have been exerted toward exploring process development to control the crystallization of $CaCO_3$ in the highly alkaline and supersaturated system [9–11]. However, the lack of crystallization behavior

research and kinetic calculations lead to a lot of problems such as agglomeration, instability of morphology, and the design of reactor in the engineering scale-up. Therefore, crystallization kinetics, which concludes nucleation, crystal growth, and agglomeration kinetics, is critical to the $CaCO_3$ properties control and reactor design.

In crystallization researches of $CaCO_3$, the growth behavior [12–14] and kinetics [15–17] have been widely investigated with various methods. Tai et al. [17] investigated the synthetic effects of temperature and magnetic field on aragonite and calcite growth, and explain the growth rate data using the cluster-transformation mechanism. Rosa et al. [18] studied growth kinetics of calcium carbonate at 25, 30, and 37 °C, and determined the edge free energies from the slopes of linearized graphs. However, the agglomeration kinetics, which is essential to $CaCO_3$ properties control, was rarely considered except the investigation for $Na_2CO_3$–$CaCl_2$ reaction system [19]. On the other hand, crystallization of $CaCO_3$ of these studies was mainly conducted from liquid solutions, which systems were mainly liquid–liquid, at low supersaturation, and nearly neutral. These systems are different from causticization system, which is characterized by liquid–solid system, high supersaturation, and alkalinity. The existence of $OH^-$ in

* Corresponding author. Tel.: +86 10 82544825; fax: +86 10 82544830.
 E-mail address: hqli@ipe.ac.cn (H. Li).

**Notations**

| | |
|---|---|
| $a$ | activity of the solute, $kmol/m^3$ |
| $B_a - D_a$ | agglomeration term |
| $B_0$ | nucleation rate, $1/m^3 \, s$ |
| $C$ | initial concentration of $Ca(OH)_2$, $kmol/m^3$ |
| $G_v$ | volume growth rate, $m^3/s$ |
| $k_B$ | nucleation rate constant |
| $k_G$ | volume growth rate constant |
| $k_\beta$ | agglomeration kernel constant |
| $K_{sp}$ | solubility product of $CaCO_3$ |
| $L$ | crystal size, m |
| $M_T$ | magma density, $kg/m^3$ |

| | |
|---|---|
| $n$ | volume population density, $1/m^3$ |
| $T$ | absolute temperature, K |
| $\Delta t$ | reaction time range, s |
| $V$ | crystallizer volume, $m^3$ |
| $v$ | crystal volume, $m^3$ |
| $\Delta v$ | volume interval between $v^i$ and $v^{i+1}$ $(m^3)$ |
| $\overline{v}$ | mean crystal volume between $v^i$ and $v^{i+1}$ $(m^3)$ |
| $\Delta w$ | weight fraction between $v^i$ and $v^{i+1}$ |
| $\sigma$ | relative supersaturation |
| $\beta$ | agglomeration kernel, $m^3/s$ |
| $\tau$ | mean residence time, s |
| $\mu_i$ | $i$th moment of distribution, $m^{3i}/m^3$ |
| $\rho_c$ | crystal density $(kg/m^3)$ |

causticization system, which can be combined with $Ca^{2+}$, has a competitive effect to $CO_3^{2-}$. Meanwhile, the dissolution of $Ca(OH)_2$ may make the parameters of nucleation, growth and agglomeration different with those in above systems. Thus, the presented kinetic results are unsuitable for causticization process.

In this work, a study on the crystallization behavior and kinetics of nucleation, crystal growth, and agglomeration in complicated causticization system has been conducted at different concentrations of $Ca(OH)_2$ with an mixed suspension, mixed product removal (MSMPR) crystallizer, which has been proposed and applied extensively [20–22]. Kinetic equations of growth rates, nucleation rates, and agglomeration kernels of $CaCO_3$ were correlated in terms of power law kinetic expressions based on the agglomeration population balance equation. Influences of magma density, mean residence time, the alkaline solution, and $Ca(OH)_2$ concentration were also discussed. These crystallization kinetic researches in causticization are highly necessary for the $CaCO_3$ properties control and reactor design.

## 2. Material and methods

### 2.1. Materials

The chemicals used in this study possessed the following purities: CaO, AR, 98.0%, supplied by Beijing Yili Chemical Reagent Co. and $Na_2CO_3$, AR, 99.8%, supplied by Xilong Chemical Reagent Co. To prepare a series of calcium hydroxide suspensions with concentration ranging from 0.011 mol/L to 0.75 mol/L, CaO was slaked in double-distilled water at 343.15 K for 0.5 h after calcinations. Sodium carbonate solutions of the same concentration with calcium hydroxide suspensions were prepared.

### 2.2. Experimental system

A laboratory-scale continuous MSMPR system is used for kinetic crystallization study (Fig. 1S). The main equipment of the system includes the crystallizer with a volume of 2 L. A two-paddle propeller mixer of standard geometric proportions was located in the crystallizer to maintain a stable and intensive enough circulation of suspension. To keep the temperature stable, the crystallizer was heated by the water outside from water bath with a thermoelectric controller. The temperature inside the crystallizer was measured using a thermometer. The experiments were conducted at 303.15 K with an agitation speed of 300 rpm. The reactants of $Ca(OH)_2$ suspension and $Na_2CO_3$ solution with the temperature of 298.15 K

$$Na_2CO_3 + Ca(OH)_2 \rightleftharpoons CaCO_3(S) + 2NaOH$$

**Scheme 1.** Causticizing reaction.

were pumped into the crystallizer, respectively. The products were withdrawn with a peristaltic pump simultaneously to the product storage tank.

### 2.3. Experimental procedure of $CaCO_3$ crystallization kinetics

Initial concentration of the reactants and the mean residence time ($\tau$) were changed in different runs, and the mean residence time ranged from 30 min to 120 min. In a typical run, $Na_2CO_3$ solutions and $Ca(OH)_2$ suspensions were continuously and simultaneously fed into the crystallizer at the same speed. The specific working volume of the suspensions was 1.2 L, and isometric suspensions with the inlet liquids were extracted to maintain a stable volume in the crystallizer. Mean residence time was calculated according to feeding speed and suspension volume in the crystallizer. The crystallizer was operated to reach steady state after $5\tau$ to $8\tau$ (Fig. 2S). In order to achieve high withdrawal velocities and no crystal classification, the sample of a certain volume was rapidly and intermittently withdrawn at steady state. Part of the sample suspension was instantaneously analyzed to obtain the particle size distribution (PSD) using Malvern Mastersizer Hydro 2000MU. The shape factor was obtained with PSD data and calculated to be 0.752. The other part of the sample was filtered with a 0.22 μm filter. The filtration was also divided into two parts to get its composition. The concentrations of $CO_3^{2-}$ and $OH^-$ were determined by titration with standardized HCl, and $Ca^{2+}$ and $Na^+$ contents were analyzed using inductively coupled plasma optical emission spectrometer (ICP-OES, Thermal Scientific iCAP 6300). Then the relative supersaturation ($\sigma$) was calculated with concentrations of $Ca^{2+}$, $Na^+$, $CO_3^{2-}$, and $OH^-$ in filtration.

Finally, a sample of certain volume was withdrawn and then filtered. A crystal sample of the whole cake was washed with anhydrous ethanol and air-desiccated at 80 °C for 12 h to determine the magma density ($M_T$). Morphology and phase of the

**Table 1**
Crystallization conditions of calcium carbonate.

| | |
|---|---|
| Temperature (K) | 303.15 |
| Agitation speed (rpm) | 300 |
| Initial concentration of calcium hydroxide (mol/L) | 0.011–0.750 |
| Initial concentration of sodium carbonate (mol/L) | 0.011–0.750 |
| Crystallization volume (L) | 1.2 |
| Magma density $(kg/m^3)$ | 0.210–35.208 |
| Mean residence time (min) | 30–120 |
| Shape factor | 0.752 |