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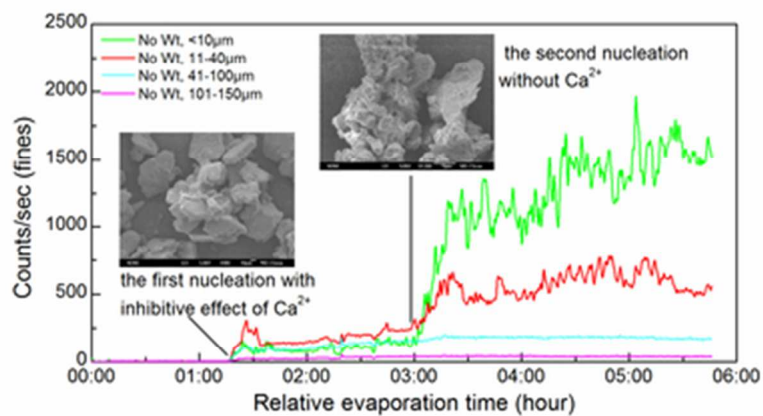


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ARTICLE TYPE

# Inhibitive Effect of Calcium on the Primary Nucleation of Sodium Carbonate in the Evaporation Process of the Caustic Liquor

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The primary nucleation of sodium carbonate in the caustic liquor was monitored using a focused beam reflectance measurement (FBRM) during the evaporation in a batch evaporator. The results obtained by the FBRM system showed that there were two abrupt increases, and the crystals obtained from the two increases exhibited different morphologies. The content of calcium in the first abrupt crystal was much higher than that in the stock solution. Calcium ions were found to have inhibitive effect on sodium carbonate nucleation.

## Introduction

In the Bayer process for alumina production, the caustic liquor remaining after precipitation and hydrate separation is recycled back to the extraction step after concentration by evaporation.<sup>1</sup> Thus, evaporation of caustic liquor is a vital procedure and a high-energy consumption unit in the Bayer process, taking nearly 27% energy of the overall energy intensity of alumina.<sup>2</sup> Additionally, the cost of evaporation accounts for 10% to 12% of the total production cost. Many evaporators suffer from scaling of their heat transfer surfaces and the type of scaling varies for different industries.<sup>3-7</sup> In the alumina industry, the scale of sodium carbonate is the major problem due to its high content in caustic liquor. The presence of sodium carbonate in caustic liquor is unavoidable and originates from three main sources: 1) transformation of calcium and magnesium compounds in bauxite during alumina extraction; 2) absorption of CO<sub>2</sub> in the air by caustic liquor, especially during the precipitation process; 3) undecomposed lime after lime is added to the caustic liquor.<sup>8</sup>

Along with concentration by evaporation, crystals of the impurity salts (mainly sodium carbonate, sodium sulfate, sodium aluminosilicate hydrate) tend to form scale on the surface of multiple-effect evaporators. This process decreases heat exchange efficiency and restricts liquor flow, which in turn increases operation costs along with other adverse effects. It was believed that the condition of solutions used for generating primary nuclei were more likely to contribute to scaling.<sup>9</sup> In order to gain a better understanding of the scaling process, it is necessary to determine the crystallization mechanisms of the scales that lead to scale precipitation, including supersaturation, nucleation, crystal growth and agglomeration.<sup>10</sup> It is known that the presence of impurities in a system can considerably affect nucleation behavior. Baynton *et al.* have demonstrated that phosphonate additives show inhibitory effects on calcite precipitation while promoting crystallization on barium sulfate.<sup>11</sup> Yang *et al.*<sup>12</sup> reported the influence of magnesium ions and amino

acids on the nucleation and growth of hydroxyapatite. Shi *et al.* reported the inhibitive effect of calcium on burkeite crystallization.<sup>9</sup> The inhibitive effect of calcium on the primary nucleation of sodium carbonate in the evaporation process of the caustic liquor has not yet been reported in the literature.

This paper focuses on the primary nucleation of sodium carbonate and the effects of calcium ions on nucleation during the evaporation process. In the present research, we use a stock solution with similar contents to simulate caustic liquor. In this manner, the effects of unidentified constituents in the precipitation can be avoided. The stock solution was monitored online to observe the nucleation during the evaporation.

## Experimental Equipment and Procedures

The chemicals used in the experiments were all AR grade. The stock solution was prepared in a nickel vessel by heating sodium hydroxide, aluminum hydroxide and sodium carbonate at proper proportions in deionized water. The solution was allowed to fully react and form a clear solution. The clear solution was decanted into a crystallizer after further filtration through a PTFE membrane with 0.22 μm pore-size. The stock solution's molar ratio (MR) was 3.08, having the same MR with the caustic liquor after precipitation in the Bayer process. The content of sodium hydroxide and sodium carbonate were both in conversion to that of sodium oxide, expressed as N<sub>k</sub> and N<sub>c</sub>, respectively. The initial N<sub>k</sub> of the stock solution was between 175 and 280 g L<sup>-1</sup> while the initial N<sub>c</sub> was between 12 and 30 g L<sup>-1</sup>. These values of N<sub>k</sub> and N<sub>c</sub> were used to match the concentration ranges typically encountered in the 1st and 5th effects evaporators of a Bayer alumina refining plant.

The evaporation crystallizations were carried out in a 0.7-L Parr crystallizer (Fig. 1). The evaporation crystallizer was heated to in a thermostatically controlled oil bath. The temperature of the system was kept 383K by adjusting the lift on the valve plate to obtain appropriate vacuum. The evaporated water was forced to a glass condenser by a water ring vacuum pump, which was cooled

by water.

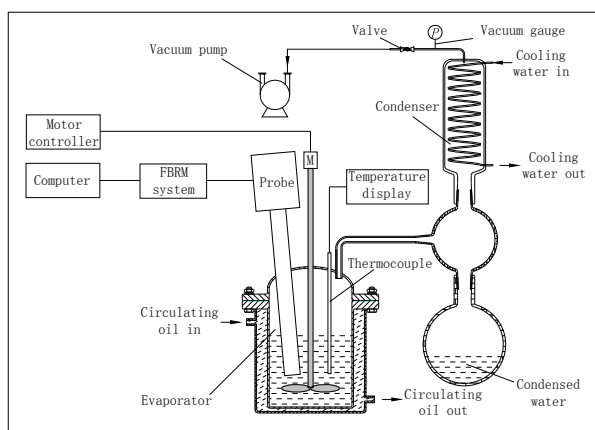


Fig. 1 The schematic diagram of the experimental apparatus.

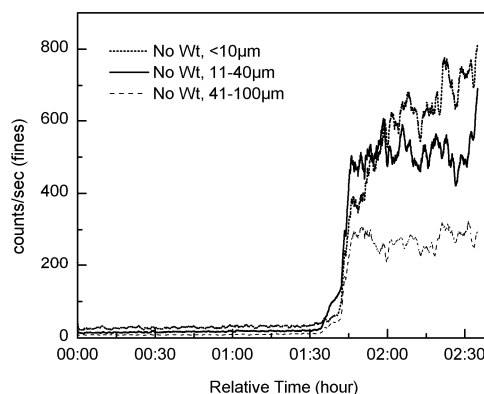


Fig. 2 The FBRM data during the evaporation of a stock solution (30g sodium carbonate added): initial  $N_k=201.2 \text{ g L}^{-1}$ ,  $N_c=13.5 \text{ g L}^{-1}$ ; critical  $N_k=291.1 \text{ g L}^{-1}$ ,  $N_c=19.5 \text{ g L}^{-1}$ .

The crystallizer and the impeller were made with PTFE material. A thermocouple covered with PTFE was used to measure the solution temperature. The solution sampling was performed by a vertical sampling tube near the probe of a focused beam reflectance measurement (FBRM) D600L system. FBRM system can directly monitor the chord length distribution (CLD) online at 2s intervals. It is a promising apparatus that is valuable for the determination of the metastable zone width. The applications of FBRM technology can be found elsewhere.<sup>13</sup>

The content of sodium and aluminum was analyzed using inductively coupled plasma atomic emission spectrometry (ICP-AES, Optima 5300DV, Perkin-Elmer). Sodium hydroxide and sodium carbonate were determined by a titrimetric method. The crystal phase analysis was done by X-ray diffraction (XRD, Phillips PW223/30). Crystal morphologies were identified by field-emission scanning electron microscopy (FESEM, JSM-6700F, JEOL).

## Results and Discussion

### Metastable Zone of Sodium Carbonate.

A series of batch evaporation experiments with varying initial  $N_c$  were performed at 383K with a fixed stirring rate. The experiments were stopped when abrupt increases in chord counts were indicated by the FBRM system (Fig. 2), which indicates the beginning of nucleation. The critical  $N_c$  was defined as the supersolubility of sodium carbonate.

The solubility of sodium carbonate was determined by placing a series of supersaturated model solutions in airtight stainless steel autoclaves with polytetrafluoroethylene linings inside of a thermostatic shaker. The liquid in each autoclave was sampled and examined every three days. The thermodynamic equilibrium state was considered to be achieved when the relative deviations between pre and post samplings were less than  $\pm 1.0 \%$ .

The metastable zone of sodium carbonate in the stock solution is shown in Fig. 3. Although the supersolubility curve is ill-defined, the diagram above is divided into three zones: the stable, metastable, and labile zones. Experimental values for determining the metastable zone width depend very strongly on the method of detecting the onset of nucleation. However, it is still possible to extract kinetic information on the nucleation process as well as on the growth behavior of very small crystals.<sup>14</sup>

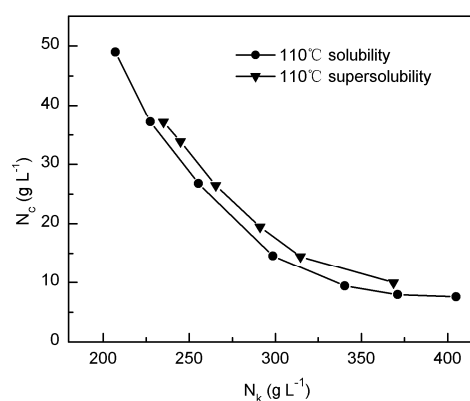


Fig. 3 The metastable zone of sodium carbonate at 383K.

### Batch Evaporation Experiments.

Results obtained by the FBRM system during an evaporation experiment with an initial sodium carbonate  $20 \text{ g L}^{-1}$  and under the same conditions for the metastable zone of sodium carbonate are shown in Fig. 4. The first abrupt increase in chord counts occurred when  $N_k$  reached  $314.7 \text{ g L}^{-1}$ . When  $N_k$  reached  $384.5 \text{ g L}^{-1}$ , the second abrupt increase in chord counts occurred. Both of the crystallization stages had the same phase of sodium carbonate, while the morphologies were differed, as shown in Fig. 5 and Fig. 6. The morphology of the crystal obtained from the first abrupt increase was flat polyhedron, while the second was irregular porosity.

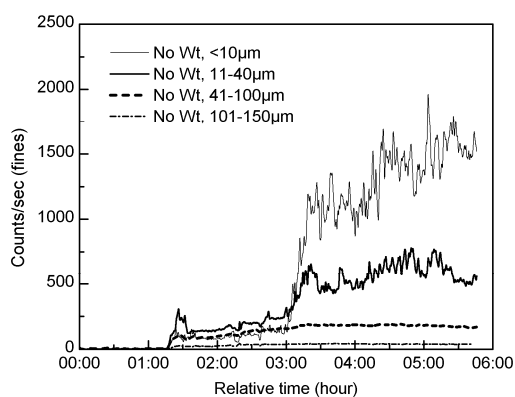


Fig. 4 FBRM data during evaporation of the stock solution (20g sodium carbonate added): initial  $N_k=255.2 \text{ g L}^{-1}$ ,  $N_c=11.7 \text{ g L}^{-1}$ ; critical  $N_k=314.7 \text{ g L}^{-1}$ ,  $N_c=14.4 \text{ g L}^{-1}$ .

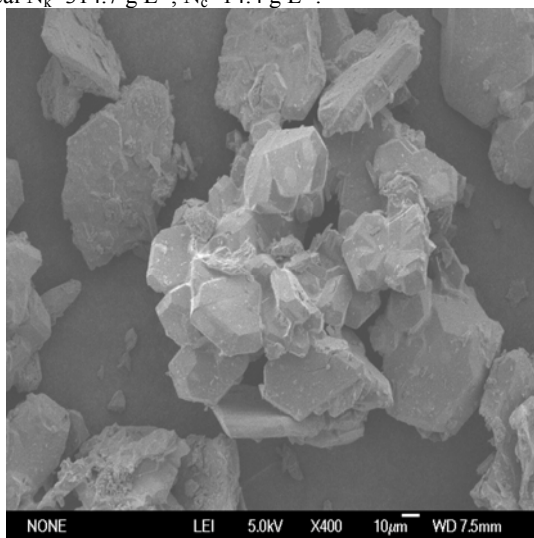


Fig. 5 SEM image of crystal obtained after the first abrupt increase.

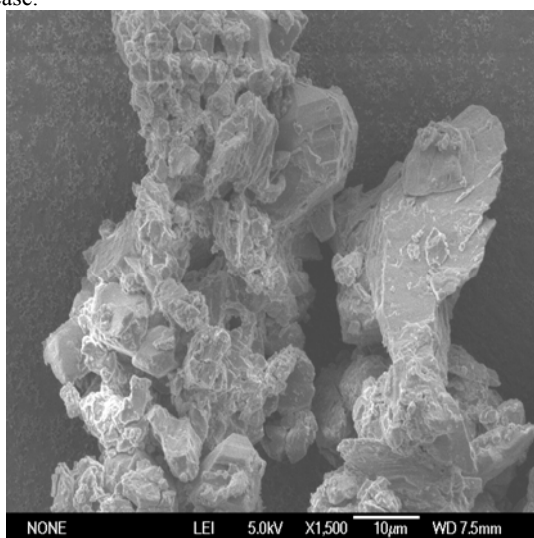


Fig. 6 SEM image of crystals obtained after the second abrupt increase.

The content of calcium in the first crystals was determined to be 157 ppm, which is much higher than that of the stock solution

which is beyond the detection limit of the ICP–AES. The structure of the first crystals was sodium carbonate, identified by X-ray diffraction. Shi et al. have reported that calcium ions are enriched by burkeite crystals during evaporation and inhibit the primary nucleation of burkeite.<sup>9</sup> The unusually high content of calcium in the first crystals appears to be the reason for the two abrupt changes in chord counts.

#### Crystallization without Calcium.

Calcium could come from the sodium carbonate or sodium hydroxide reagents. EDTA was added to the stock solution to remove any trace calcium. EDTA is a common complexing agent because it can form complexes with most metal ions. When 100 ppm EDTA was added to the stock solution, only one abrupt increase in chord counts occurred. Also, the content of calcium in the sodium carbonate crystal was beyond the detection limit of the ICP–AES. The morphology of the crystal (Fig. 7) was irregular porosity; the crystal with flat polyhedron morphology was no longer present.

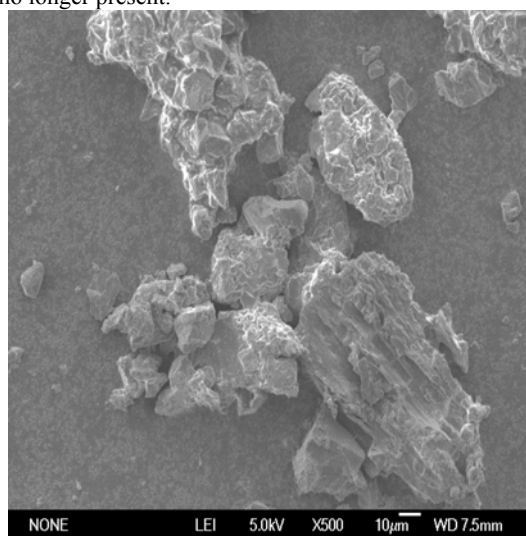


Fig. 7 SEM image of the crystal obtained when 100ppm EDTA added to solution.

The results of the previous experiments can be used to reduce the trace calcium content in the evaporation solution. Calcium ions can be enriched in the sodium carbonate crystal of the first stage. This enrichment makes the calcium content beyond the detection limit of the ICP–AES at the end of the first abrupt increase. Two-stage crystallization can be introduced, where the goal of the first stage is to deplete calcium brought in as contaminants by the reagents so that the second-stage crystallization can start without calcium present in the solution after filtration.

The experiments were carried out as follows: The first stage was conducted in the same manner as the batch evaporation experiments except that the quantity of sodium carbonate was enhanced to ensure that second stage solution had the same content of sodium carbonate after filtration. As expected, the crystal behavior was the same as in experiments with EDTA added. Only one abrupt increase in chord counts occurred, and the calcium content in sodium carbonate crystal was beyond the detection limit of the ICP–AES.

#### The Effects of Additives on the Supersolubility of Sodium Carbonate.

A set of batch evaporation experiments was performed to determine the effects of additives on the nucleation of  $\text{Na}_2\text{CO}_3$ . The stock solution mixed together with certain excess calcium salt (100ppm calcium) was filtrated through a PTFE membrane with 0.22  $\mu\text{m}$  pore-size. Due to the low solubility of  $\text{Ca}^{2+}$  in the caustic liquor with high content of sodium carbonate, minimal calcium salts were dissolved and the contents of calcium in the stock solution with additives were beyond the detection limit of the ICP-AES. In each run, the initial stock solution had the same  $N_k$  and  $N_c$  with varied initial additives. The critical  $N_k$  obtained from each experiment is shown in Fig. 8. The difference between the pure stock solution and that with additives was significant. The critical  $N_k$  of the pure stock solution's nucleation was 9  $\text{g L}^{-1}$  lower than that of the solution with saturated calcium salt, excluding calcium carbonate. The difference in critical  $N_k$  values demonstrates the inhibitive effect of calcium. When 100 ppm EDTA was added to the stock solution, the calcium ion was chelated and the critical  $N_k$  was 302.1  $\text{g L}^{-1}$ . This value is almost 30  $\text{g L}^{-1}$  lower than that of the solution with calcium chloride. The results demonstrate that calcium can inhibit sodium carbonate nucleation.

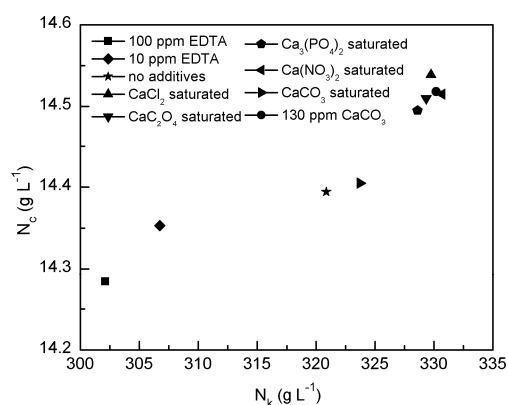


Fig. 8 The critical  $N_k$  of whose nucleation with additives.

Fig. 9 shows the FBRM results obtained during the evaporation when 130 ppm calcium carbonate powder was added to the stock solution. Fig. 10 shows the CLD of the crystals at certain time. As is shown in Fig. 9 and Fig. 10, from 0 to 50 min, the peak goes down non-significant, indicating that the small particles were dissolved slowly in this period; after 50 min, the peak and the number of chord counts both increase sharply, suggesting the nucleation of  $\text{Na}_2\text{CO}_3$  has occurred. The critical  $N_k$  is 330.2  $\text{g L}^{-1}$ , which is higher than that with saturated  $\text{CaCO}_3$ . It suggests that the existence of small  $\text{CaCO}_3$  powder does not accelerate the nucleation. Conversely, it can be further dissolved to the solution, providing more  $\text{Ca}^{2+}$  for the inhibitive effect.

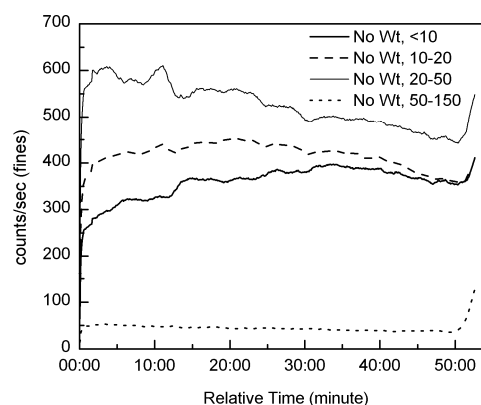


Fig.9 FBRM results during the evaporation when 130 ppm  $\text{CaCO}_3$  powder was added.

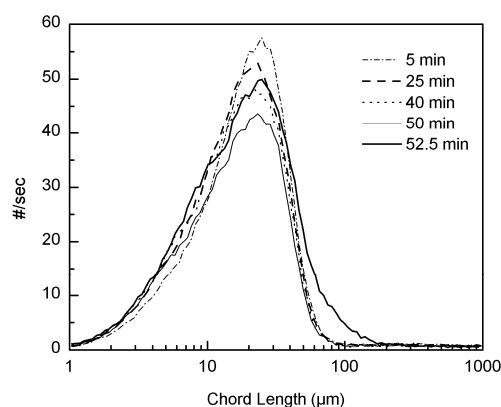


Fig. 10 CLD of the crystals during the evaporation when 130 ppm  $\text{CaCO}_3$  powder was added.

#### The Inhibitive Mechanisms of Calcium Ions.

The experiments above showed that calcium ions inhibit the nucleation of sodium carbonate. In this section, the mechanism of the inhibitive effects is discussed. The presence of impurities in a system can affect nucleation behavior considerably. It has long been known that traces of foreign ions, especially  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$ , have a similar action on inorganic salts. It would be unwise to attempt a general explanation of the phenomenon of nucleation suppression by added impurities with so little quantitative evidence available, but certain patterns of behavior are beginning to emerge. For example, the higher the charge on the cation, the more powerful the inhibiting effect. Cations may act as structure-breakers in the solution phase. Botsaris, Denk and Chua (1972) suggested that if the impurity suppressed primary nucleation, secondary nucleation could occur if the uptake of the impurity concentration gradient about itself. In this case, the concentration of impurities near the crystal surface becomes lower than in the bulk solution. If the concentration is reduced enough, nucleation can occur.<sup>14</sup> It is common that crystal behavior can be changed when trace impurities are added. Berry *et al.* claim that substitution of one element for another is common in minerals and that the relative size of atoms or ions is the primary factor governing such substitution. Shi *et al.* claim that the substitution of calcium ions for sodium ion inhibits burkeite nucleation.<sup>9</sup>

Vacancies caused by impurity ions of different charges from the host ions have been detected in the crystal lattice of NaCl.<sup>15</sup>

The ionic radius of calcium is similar to that of sodium, which means that calcium could substitute for sodium ions in sodium carbonate crystals. Substituting a calcium ion (Ca<sup>2+</sup>) for a sodium ion (Na<sup>+</sup>) could change the electrical neutrality of the crystal embryos, hence collisions among the embryos could be prevented and the subsequent formation of nuclei will be inhibited.

Another possibility is that Ca<sup>2+</sup> can suppress nucleation by adsorbing at defects on existing sodium carbonate crystal surfaces and thus make the crystals prone to crack propagation and disintegration. If Ca<sup>2+</sup> is adsorbed on the surface of sodium carbonate crystal, the disorder of the crystal lattice will inhibit the latter growth of embryos. Through either of the two mechanisms above, calcium ions can inhibit the sodium carbonate nucleation and be enriched in the crystal.

## Conclusions

A set of batch evaporation experiments with varied additives were performed to determine the nucleation of Na<sub>2</sub>CO<sub>3</sub>, monitored using the FBRM system. The results showed that there were two abrupt increases and the crystals obtained from the two increases exhibited different morphologies. The content of calcium in the first abrupt crystal was much higher than that in the bulk solution. Calcium ions showed an inhibitive effect on sodium carbonate nucleation. The inhibitive mechanism was supported by the crystallization without calcium and the critical N<sub>k</sub> of the experiments with different additives. It is a significant exploration to reveal the scaling mechanism of sodium carbonate during evaporation. The falling film evaporators could be optimized to produce higher concentrated caustic liquor, which was pumped to forced circulation evaporators for further concentration. The evaporation efficiency could be improved by avoiding the potential scale of sodium carbonate in falling film evaporators.

## Acknowledgment

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## Notes and references

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