Impurity in Sodium Chloride Crystals from a Continuous MSMPR Crystallizer

Kouji MAEDA *, Koichi TOJO *, Hideo MIKI *, Yusuke ASAKUMA * and Keisuke FUKUI *

Abstract

We performed a continuous industrial MSMPR crystallization of sodium chloride (NaCl) by means of evaporation at different impurity concentrations in a liquor solution such as seawater. We sieved the suspended crystals in the crystallizer, and determined the growth and nucleation rates using the population balance of the crystal size distribution (CSD). We observed the crystals at each stage in the sieves with a microscope, and measured the degrees of roundness and agglomeration. We also measured the impurity concentration represented by potassium ions in the crystals. The suspension density was useful for correlating the growth and nucleation rates. The impurity concentration in the crystals increased as that in the solution increased. We described the impurity concentration as a function of the crystal size, and it was larger at a size range of less than 300 μm and had minimum values and increased slightly by again increasing crystal size. The degrees of roundness and the aggregation of the crystals were significant factors for correlating the impurity concentration in the crystals. We propose modeling by operative variables for the growth rate, nucleation rate, suspension density, degrees of roundness, and aggregation, and the distribution coefficient of impurity as a function of crystal size for NaCl industrial crystallization.

Key Words: Sodium Chloride, MSMPR crystallizer, Impurity, Crystal size distribution

1. Introduction

In the Japanese salt industry, sodium chloride (NaCl) is mainly recovered from seawater through ion-exchange and evaporative crystallization processes. This methodology has been established as a traditional process. Properties such as crystal size distribution (CSD), morphology, and the purity of the NaCl crystal products are still satisfactory for industrial uses. However, the traditional crystallization methodology could still be improved or altered. Currently, energy efficiency may not be optimized in multi effect evaporative crystallizers. The CSD of suspension crystallization has been studied and modeled in many papers on industrial crystallization, and it seems that the population balance model is the most successful theory 1-9. A few studies have reported on impurity inclusion in the suspended crystals 10-12. So far, studies have avoided considering the impurity of suspended crystals because of the complicated mechanism in the crystallizer. Several factors affect the purity of crystals in a suspension crystallizer even if the pure solute crystallizes thermodynamically, including (a) the kinetic distribution or adsorption of impurity into the crystals and (b) mechanical inclusion and the adhesion of mother liquor to the crystals.

The significant factors of impurity inclusion in suspension crystallization are: (a) the agglomeration of the crystals and (b) the attrition of the crystals. Those factors are complexly correlated with each other in suspension crystallization. The operative variables influencing crystal size, agglomeration, attrition, and purity have not been qualitatively considered when designing a crystallizer for the desired purity of the crystals. We have systematically studied several mechanisms of impurity inclusion 13-15. The attrition growth and agglomeration of small crystals decreases the purity of the suspended crystals 13-16. On the other hand, the growth rate of suspended crystals (secondary growth) may differ from the growth rate (primary growth) of a single crystal. The growth rate of the suspended crystals may be promoted by fine crystals and agglomeration, and might also be reduced by attrition. When the contribution of fine crystals (surface roughness), agglomeration, and attrition to the growth rate of suspended crystals can be distinguished from one another, the impurity inclusion may be correlated only by examining each growth rate 16-18.

In this study, we will investigate the CSD, impurity distribution, degrees of roundness, and agglomeration for continuous MSMPR crystallization. We will consider the relative mechanism of impurity inclusion as a function of
2. Experimental

2.1. Experimental procedures

We used NaCl as a crystal solute, and KCl, MgCl₂·6H₂O, and CaCl₂ as impurity components. The purity of each of the salts was more than 99%. We purchased these extra pure grade salts from the Kanto Chemical Company. Table 1 shows the compositions of salt in the solutions (Run 1-8).

Fig. 1 shows the experimental apparatus of a vaporizing type continuous MSMPR crystallizer. This apparatus consisted of two vessels. We used one vessel as the crystallizer and the other vessel for the dissolution of crystals. Their volumes were 2 and 5 L, respectively. We kept the feed solution of the NaCl saturated at 303 K at 323 K in the dissolving tank using a temperature controller. First, we moved 2 L of the saturated solution from the dissolving tank to the crystallizer, and concentrated the solution by evaporating it with a vacuum pump until we had removed 500 ml of water. We returned the slurry in the crystallizer to the dissolving tank after a certain interval that was controlled by an optical level sensor, and we also continuously returned the evaporated water to the dissolving tank. The saturated solution was continuously fed from the dissolving tank. We carried out this continuous operation for a period ten times longer than the residence time of the solution, which was sufficient for achieving a steady state. Table 2 shows the operative conditions at different runs. The operative variables in our experiments were the impurity concentration in the solution (Run 1-5), and the residence time (Run 6-8).

2.2. Analysis of NaCl crystals

We sampled the slurry in the crystallizer, and the crystals were separated by centrifugal filtration. We washed the crystals with an acetone solvent in a centrifugal filtration, and dried the crystals at 100°C for 24 hours. We measured the CSD using a sieving method.

<table>
<thead>
<tr>
<th>Run</th>
<th>Impurity concentration in the solution, Ci [-]</th>
<th>KCl [wt %]</th>
<th>MgCl₂ [wt %]</th>
<th>CaCl₂ [wt %]</th>
<th>NaCl [wt %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>0.03</td>
<td>1</td>
<td>0.5</td>
<td>1</td>
<td>97</td>
</tr>
<tr>
<td>3</td>
<td>0.10</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>0.15</td>
<td>2</td>
<td>5</td>
<td>3</td>
<td>85</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
<td>3</td>
<td>7</td>
<td>4</td>
<td>80</td>
</tr>
<tr>
<td>6-8</td>
<td>0.51</td>
<td>13.78</td>
<td>30</td>
<td>5.26</td>
<td>48.79</td>
</tr>
</tbody>
</table>

![Fig. 1 Experimental apparatus of MSMPR crystallizer](image-url)
The size from sieving is based on the weight, and we converted it to this size based on the crystals number. We defined the size of crystals sieved as the size of each sieve net. We determined the growth rates and nucleation rates by the population balance of CSD at different operative conditions. We then measured the degree of roundness using the crystal images to investigate the attrition and shape of the crystals at different crystal sizes. We defined the degree of roundness \((Rd)\) using the following equation\(^{(1)}\):

\[
Rd = \frac{r_1 + r_2 + r_3 + \cdots}{RN},
\]

where, \(r_1, r_2, \text{ and } r_3\ldots\) are the curvature radii of the corners of the crystals, \(R\) is the maximum inscribed radius of a crystal, and \(N\) is the number of corners in a crystal, respectively.

We measured the degree of agglomeration using images of the crystals to investigate the effect of agglomeration on the impurity concentration at different crystal sizes. The degree of agglomeration \((\text{Agg})\) was defined using the following equation\(^{(2)}\):

\[
\text{Agg} \times 100 = \left[ P_b^2 + \frac{4}{3} P_b^{LA} + \frac{5}{3} P_b^{MA} + 2 P_b^{HA} - 1 \right].
\]

where, \(P_b^S\) is the probability of the aggregated crystals at four different categories \((i)\) determined by sampling 50 crystals under a microscope. The superscripts show the following categories: \(S\) is a single crystal; \(LA\) stands for low agglomeration; \(MA\) stands for medium agglomeration; and \(HA\) means high agglomeration.

We weighed the crystals at each stage of the sieves and dissolved them in pure water. We measured the contents of K ion, Mg ion, and Ca ion in NaCl crystals using atomic adsorption analysis (Shimadzu AA470). K ion was used as the representative impurity. The other ions were relatively smaller than the K ion, and they were omitted in this paper.

### 3. Results and discussion

We plotted the sieved crystals at different operative conditions according to the population balance equation\(^{(3)}\) defined as

\[
\ln [nL] = \ln \left( \frac{B}{G} \right) - \frac{L}{Gr}.
\]

The typical CSD is shown in Fig. 2. The growth rate of the suspended crystals should be influenced by agglomeration and attrition, as mentioned later. We were not able to distinguish the growth rate of the suspended crystals from the growth rate of the single crystals\(^{(16-18)}\). However, we consequently got a linear relationship, and determined the growth rates and nucleation rates as overall values.

#### 3.1. Growth rate and nucleation rate as functions of suspension density

In general, the growth rate and nucleation rate depend on the supersaturation, agitation, and suspension densities in the continuous crystallizer\(^{(1)}\). The agitation or specific power input was fixed, and the supersaturation was very small and was not a useful variable in our experiments. The impurity concentration and residence time were changed as the operative variables. Consequently, the two variables controlled suspension density in the continuous crystallizer. When the impurity concentration increased in the solution, the suspension density decreased according to the solubility property. When the residence time increased, the suspension density increased. Therefore, it is useful for us to consider...
Fig. 4 Growth rate as a function of suspension density

Fig. 5 Nucleation rate as a function of suspension density

the function of the impurity concentration, $C_i$, and the residence time, $\tau$, to present the suspension density, $M_T$. The empirical function in our experiments is given by the following equation:

$$G = 9 \times 10^{-10} M_T^{1.2}$$

$$B = 2 \times 10^{-8} M_T^{0.07}$$

$$M_{Tm} = 0.375 \left( \frac{C_i + 2}{\tau} \right) + 0.28$$

Fig. 3 shows the comparison of experimental suspension density with the modeled suspension density of Equation (4). All experiments readily converged to the diagonal. The correlated function might be only valid for more than 3,600 [s] residence time.

We obtained the growth rates and nucleation rates in all experiments using Equation (3). The impurity concentration in the solution reduced the nucleation rate and suspension density, and then increased the growth rate slightly. The nucleation rate increased inevitably with the residence time, and consequently, the suspension density also increased. The suspension density representing the nucleation rate directly influenced the crystal growth rates even at different operative conditions. The suspension density was an effective variable for correlating both the growth rate and nucleation rate, as shown in Fig. 4 and Fig. 5. We obtained the correlation functions of suspension density, $M_T$, for the growth rate, $G$, and the nucleation rate, $B$.

$$G = 9 \times 10^{-10} (M_T)^{1.2}.$$  (5)

$$B = 2 \times 10^{-8} (M_T)^{0.07}.$$  (6)

Fig. 6 Typical NaCl crystals at different sizes
(A) 500 $\mu$m, (B) 300 $\mu$m, (C) 120 $\mu$m
3.2. Degrees of roundness and agglomeration of NaCl crystals as functions of crystal size

Controlling CSD might be achieved by estimating the growth rate and nucleation rate in the crystallizer according to Equations (3-6). However, we could not predict the purity of the crystals only using the population balance theory. We have studied the impurity inclusion in the suspended crystals and found that the attrition and aggregation properties of the crystals are significant factors, and that the kinetic distribution of impurity is often important mechanism. The kinetic distribution of impurity is an inevitable problem in any crystallization method, and it is a function only of the growth rate. The attrition and aggregation properties depend on the hardness of crystals and they change with crystal size. Fig. 6 shows typical crystals at different sizes. Agglomeration was observed in small crystals, and attrition was also observed in large crystals. The degree of roundness, Rd, was a function of the crystal size, L and the residence time, τ, as shown in Fig. 7 and Fig. 8. A larger crystal size and a larger residence time made the crystals rounder. The degree of roundness is given by the following function:

\[
Rd = \exp\left(-0.72/\tau (L - 0.00012)\right).
\]

The degree of agglomeration, Agg, was a function of crystal size, L, only, as shown in Fig. 9. The smaller crystals caused more agglomerated crystals. The impurity concentration and residence time were not related to the agglomeration process. The degree of agglomeration is given by the following function.

\[
A_{gg} = 100 \exp \left[-1600L\right].
\]

This function means that all fine crystals have nucleus sizes that agglomerate with one another. The nuclei form a pure crystalline phase, but the agglomeration of the nuclei causes impurity inclusions between nuclei. The fine agglomerated crystals continue growing by reconstructing the interface between nuclei, and are then purified by increasing the crystal size.

The degrees of roundness and agglomeration are conventional functions of crystal size, and we expect to correlate these with the impurity concentration of the suspended crystals.

3.3. Impurity distribution as a function of crystal size

The essential property is the purity of the crystals for NaCl crystallization as well as the CSD. The relationship between the impurity concentration and crystal size is useful when considering the optimal operation of crystallization. Unfortunately, purity as a crystal property in suspension crystallization has largely been ignored. Most papers have been satisfied with the successful representation of CSD property. We have systematically...
considered several factors related to impurity inclusion in suspension crystallization. The impurity concentration as a function of crystal size is the most important description for all crystallization processes. Fig. 10 shows the K ion in the NaCl crystals as a function of the crystal size at different impurity concentrations in the solutions. We first noticed that the crystals having different sizes contained different concentrations of impurity. The K ion as an impurity was very large at a small size. The concentration of impurity in crystals had a minimum at 300 μm, and increased slightly with crystal size. When the impurity concentration in the solution increased, the impurity in the crystals also increased. Fig. 11 shows the distribution coefficient of the K ion between the solution and crystals. We converged the distribution coefficient with different impurity concentrations in the solutions. Fig. 12 shows the impurity concentration in the crystals as a function of the crystal size at different residence times. The impurity concentration was very large when compared with Fig. 10 because the impurity concentration in the solution was the maximum possible value for NaCl crystallization. However, the distribution coefficient shown in Fig. 13 was close to Fig. 11. The purity was also the highest at 300 μm. The residence time, meaning the growth rate, did not strongly influence the impurity concentration in the crystals.

We should express the essential kinetic distribution of impurity, $K_i$, by the growth rate with the thermodynamic distribution coefficient, $K_o$. We have also proposed the impurity distribution model from melt crystallization as follows:

$$K_i = 1 - \exp(-12500 \times G) + 0.005 \times R_d + (A_{gg}/100)^{31}$$

$$[dC_e/dC] = \frac{[dC_i/dC]}{[dC_e/dC]}$$

We could also model it as a function of the growth rate, $G$. In this case, the NaCl crystal thermodynamically forms a pure phase, and $K_o = 0$. Equation (9) can be simplified as

$$K_i = 1 - \frac{dC_i}{dC}$$

In this experiment, we also modeled the concentration...
The constant, -12500, is related to the mass and heat transfer properties in the suspension system. The effect of attrition and agglomeration on inclusion of impurity in the crystals is added to Equation (11) in our experiments. Empirically, we suggested the following equation:

\[ K_i = 1 - \exp(-12500 \cdot G) . \]  

The calculated distribution coefficients in Fig. 11 and Fig. 13 were described by Equation (12) as a function of crystal size. The proposed function can qualitatively represent the impurity distribution for suspended crystals. In terms of NaCl crystallization, the agglomeration of small crystals was most effective for the impurity distribution, but the kinetic distribution was very low, and the attrition of large crystals defines the average impurity distribution of large crystals. The crystal properties, CSD, agglomeration, attrition and distribution of impurity were related to one another, and they were predicted by impurity concentration and residence time only in our experiments. We expect that the derived functions will also be useful for many industrial suspending crystallization processes.

4. Conclusion

We carried out the continuous MSMPR crystallization of NaCl crystals by evaporation to consider the following crystal properties: CSD, agglomeration, attrition, impurity, and the distribution of the suspended crystals. The suspension density was a very good variable for correlating both the growth and nucleation rates, and we modeled the suspension density as a function of impurity concentration and residence time. The degree of roundness and degree of agglomeration were functions of crystal size. The impurity distribution coefficient was large at a small crystal size and increased slightly with crystal size. The behavior of impurity distribution coefficient was correlated by the proposed distribution coefficient model containing the kinetic distribution term, the attrition term, and the agglomeration term.

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Nomenclature

- \( K_i \): effective distribution of impurity [-]
- \( L \): crystal size [m]
- \( M_T \): experimental suspension density [-]
- \( M_{Tm} \): modeled suspension density [-]
- \( n \): population density [1/mm/m³]
- \( N \): the number of corners in the crystal [-]
- \( P_{\text{agg}} \): probability of aggregated crystals of groups(i) [-]
- \( r \): curvature radiuses of the crystal’s corner [m]
- \( R \): maximum inscribed radius of the crystal [m]
- \( R_d \): degree of roundness [-]
- \( x_K \): impurity concentration in the crystal [-]
- \( \tau \): residence time [s]

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**連続晶析槽から得られる食塩結晶中の不純物**

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**要 領**

海水を想定した不純物濃度で食塩の連続工業晶析操作を蒸発法で行った。晶析槽の懸濁結晶をふるい分けし、成長速度と核発生速度を結晶粒子群の粒度分布から求めた。各々のサイズの結晶粒子を顕微鏡で観察し、結晶粒子の丸み度と凝集率を測定した。カリウムイオンを不純物成分の代表として結晶中の不純物濃度を測定した。連続晶析操作における懸濁密度は成長速度と核発生速度の相間に有効であった。結晶中の不純物濃度は小粒径で高くなり、300μm程度で最小値となり粒径とともに顕著に高くなった。結晶粒子の丸み度と凝集率は結晶中の不純物濃度の相関において重要な因子ととなった。最後に、食塩工業晶析操作に対して懸濁密度、成長速度、核発生速度、結晶粒子の丸み度と凝集率、不純物の分配係数と操作因子の関係のモデルを提案した。

**キーワード**: 食塩, 連続晶析操作, 不純物分布, 粒度分布

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