CHARACTERIZATION OF FINE CRYSTALS IN EVAPORATIVE SALT CRYSTALLIZATION UNDER HIGH SUSPENSION CONDITIONS

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Abstract: Industrial crystallization should be carried out under high suspension conditions in order to obtain NaCl products efficiently. However, under such conditions, the nucleation rate becomes high. Therefore, it is necessary to control the excess number of fine crystals. This study focused on the characteristics of fine crystals generated under high suspension conditions. According to the experimental results, file crystals were classified and the generation mechanisms of fine crystals were discussed with undersaturation condition. Undersaturation condition in this study was carried out by injection of dissolution water. As the results, the following conclusions were obtained. (1) Under high suspension conditions, the influence of abrasion and breakage was greater than under low suspension conditions, and many fine crystals were generated. (2) The fine crystals could be classified into two types according to the shape of fine crystals. The effect of injection of dissolution water was different depending on the shape of fine crystals. (3) The dissolution water was effective for the preferential dissolution of the fine crystals and modification of the crystal surfaces directly related to the fine crystal generation.

1. Introduction

Salt crystals have been widely used in various industries, such as food and soda industry. Table 1 shows total demand and supply for salt in Japan [1]. The self-sufficiency ratio in Japanese salt supply is 15%. Japanese salt industries are handicapped by the absence of rock- salt. However, the maritime nation is surrounded by rich salt supplies in the form of sea water. In Japanese salt process, the saline content is increased to produce a highly saturated brine solution by using ion-exchange system. In the second stage, the large-scale vacuum-evaporation crystallization was carried out. Based on intensification of global competitiveness, the improvement of salt production is necessary. And it is necessary to carry out the crystallization process under much higher suspension conditions in order to make the production rate increase.

However, under such operating conditions, the nucleation rate in the crystallizer becomes high and the number of effective nuclei becomes excessive, so product crystal size distribution (CSD) does not become monodisperse. For these reasons, it is important to characterize the file crystals in evaporative crystallization under high suspension conditions.

Table 1: The yearly demand and supply for sodium chloride in Japan

	Division	2007 million tons
Yearly Demand	Food industry	0.85
	General industry	0.21
	Anti-icing	0.51
	Soda chemicals	7.19
	Other	0.34
	Total	9.10
Yearly Supply	Japanese Salt	1.14
	Imported Salt	8.00
	Total	9.14

There are some research papers for characterization of fine crystals and fine crystal removal [2, 3]. And there were a few methods of controlling the number of fine crystals [4, 5]. The common operation was "undersaturation operation" to dissolve file crystals. So the aim of this study is to understanding the generation mechanism and destruction behaviors of fine crystals by using undersaturation operation. Undersaturation operation of this study is the method of water injection as a solvent into the slurry and this water is called “dissolution water”.

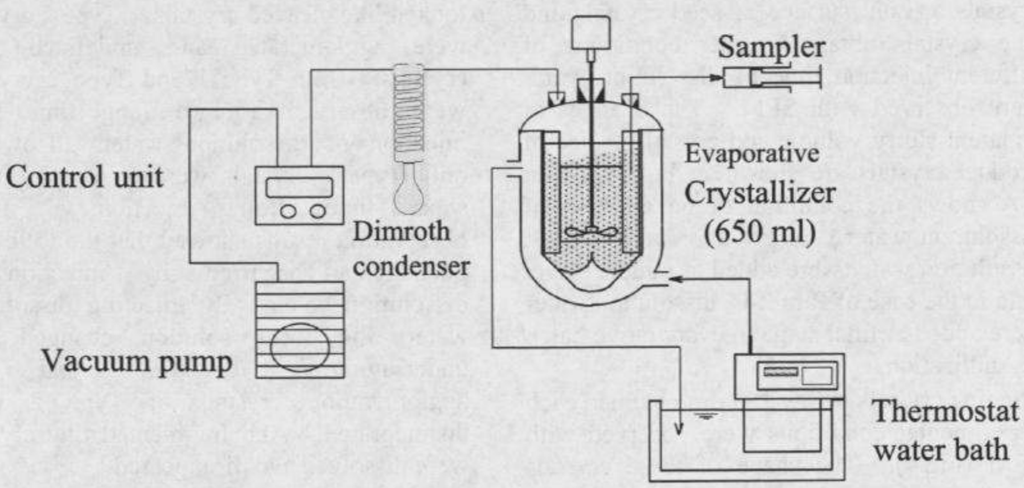


Fig. 1 Schematic diagram of experimental apparatus

2. Experiment

The vacuum type evaporative crystallizer is shown in Fig. 1. The experiment was carried out by batch operation. The crystallizer of 650 ml volume with a jacket was used and the internal pressure was controlled with a vacuum pump. The evaporation rate was controlled by temperature of the thermostat. The operation pressure was 13 KPa, and solution temperature was 58 degree C and agitating speed 600 rpm. The seed crystals (mean size was ca. 300 (m) were suspended in the solution and a predetermined initial suspension density could be achieved. After the experiment, solid liquid separation was carried out, the product crystals were dried, and CSD was measured by image analysis.

3. Experimental Results and Discussion

3.1 Effect of initial suspension density M_{T0}

Figure 2 shows the product crystal CSDs under the conditions of different initial suspension density M_{T0}. These results showed that the number of fine crystals increased under high M_{T0} conditions. The scanning electron microscope (SEM) photomicrographs of the product crystals obtained under these experiments were also shown in Fig.2. As M_{T0} increased, the crystal surface was damaged and the crystals had rounded corners.

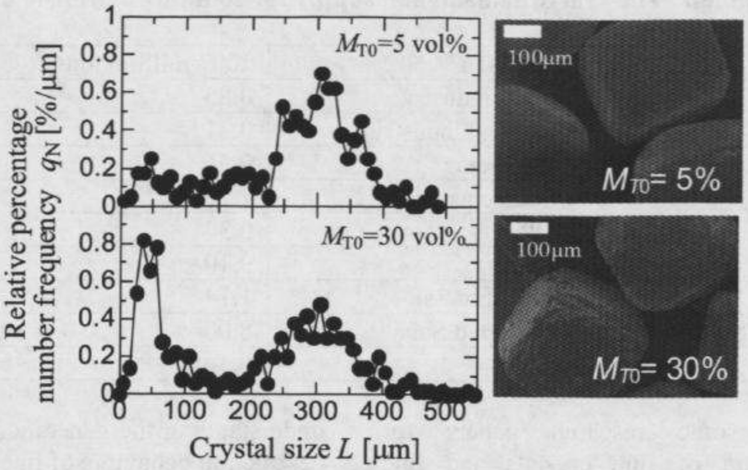


Fig. 2 Effects of suspension density M_{T0} on product CSDs and crystal surface

3.2 Characteristics of fine crystals generated under high suspension conditions

In order to discuss the characteristics of file crystals, crystal surface of seed crystals and fine crystals obtained under conditions of different injection time of dissolution water were observed with SEM. The changes in apparent slurry volume and crystal surface of product crystals are shown in Fig. 3. Run 2-A shows the condition of no addition of dissolution water. In the case of Run 2-B, dissolution water were added at middle stage. And in the case of Run 2-C, dissolution water were added at final stage in evaporative batch crystallization.

The fine crystals below 150 µm obtained each experimental conditions were observed with SEM (Fig.4). The shape of these crystals showed that the generated fine crystals could be classified into two types. Type 1 crystals have rectangular parallelepiped shape and looked like cleaved crystals. Type 2 crystals were agglomerated and undefined facet crystals. Both Type 1 and Type 2 crystals were observed after a long time from injection of dissolution water. However, only Type 1 crystals were observed after a short time from injection. These observation results showed that the following phenomena occurred by injection of dissolution water. By injecting dissolution water, the local solution changed into undersaturation condition and the agglomeration crystals of Type 2 were disintegrated. And fragmented tiny crystals were dissolved and disappeared.

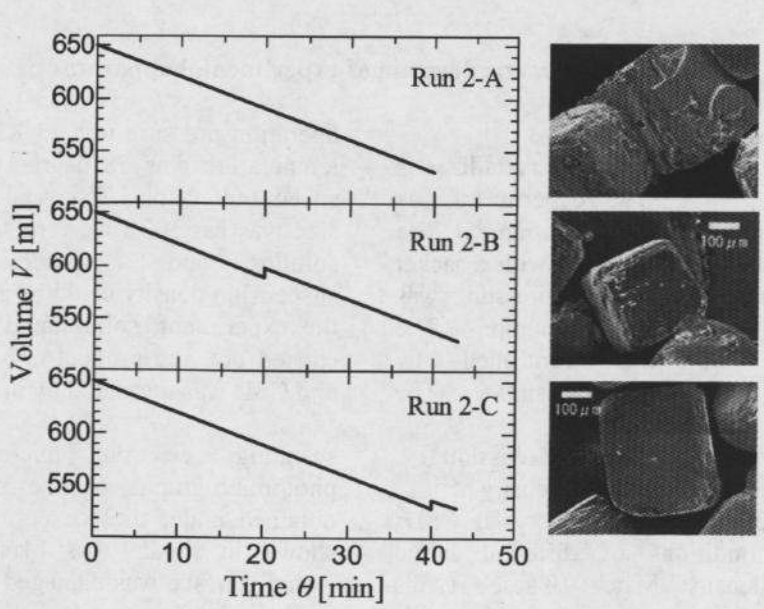


Fig. 3 Changes in apparent slurry volume and crystal surface of product crystals

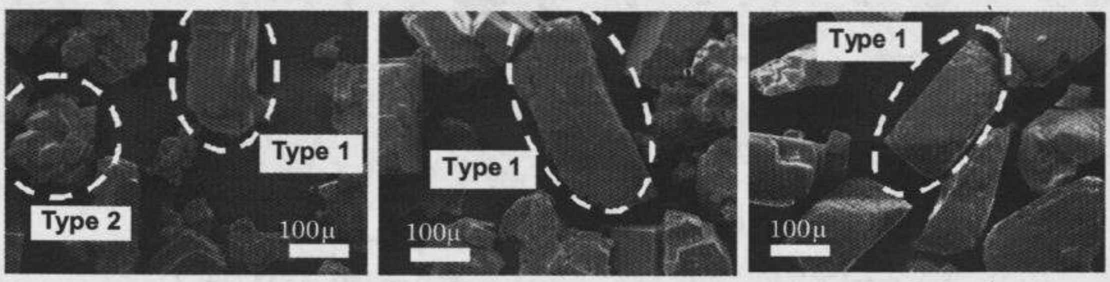


Fig. 4 SEM photomicrographs of generated fine crystals under high suspension conditions

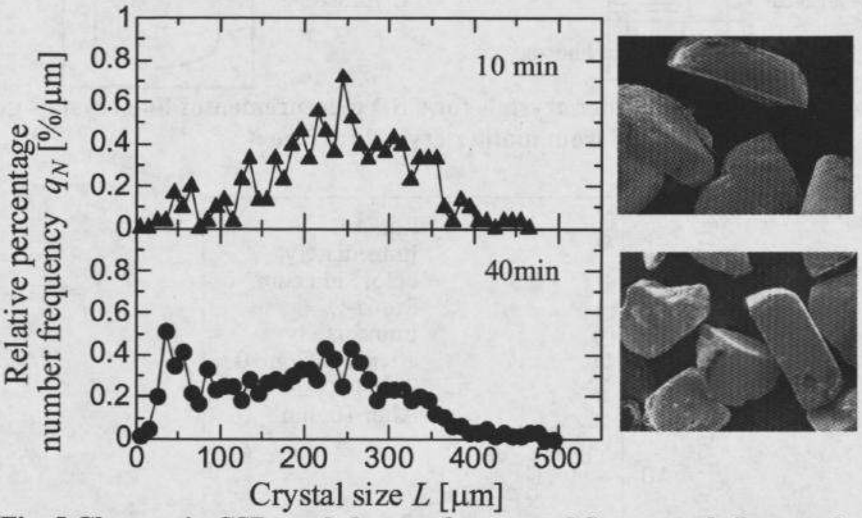


Fig. 5 Changes in CSDs and shapes of generated fine crystals in nonsolvent

In order to make clear the generation mechanisms of Type 1 crystals, the seed crystals were suspended in nonsolvent (acetone). Figure 5 shows the changes in CSDs and crystals shapes of generated fine crystals. It was clear that Type 1 crystals were generated by breakage of suspended seed crystals.

3.3 Characteristics of fine crystals generated from the suspended crystal surfaces

The following experiment was carried out in order to consider the characteristics of fine crystals generated from the suspended crystal surfaces. Two types of crystallizer were used (Fig. 6). The several millimeters single crystals fixed to the stainless steel wire (mother crystal) were set into a suspended solution in evaporative Crystallizer 1 (M_{T0} = 30 vol%). One of these mother crystals was sequentially taken out with predetermined time, and was moved into another clear supersaturated solution in Crystallizer 2. Schematic sampling timing chart is shown in Fig. 7. The number and CSD of the fine crystals generated from the surface of the mother crystal were measured with a coulter counter. The population density plot for fine crystals generated from the mother crystal is shown in Fig. 8. Immediately after injection of dissolution water, the number of fine crystals generated from the mother crystal surface decreased. However, this inhibitory effect becomes weak with the elapsed time from injection of dissolution water.

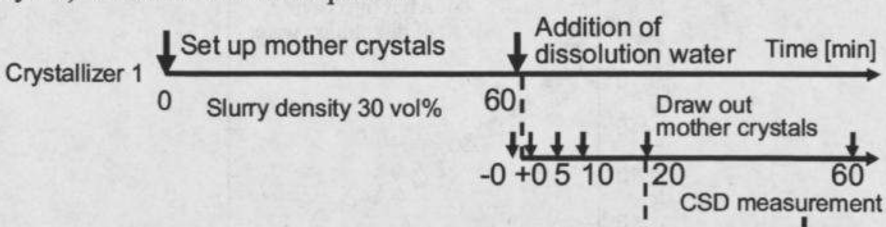


Fig. 6 Schematic diagram of experimental apparatus

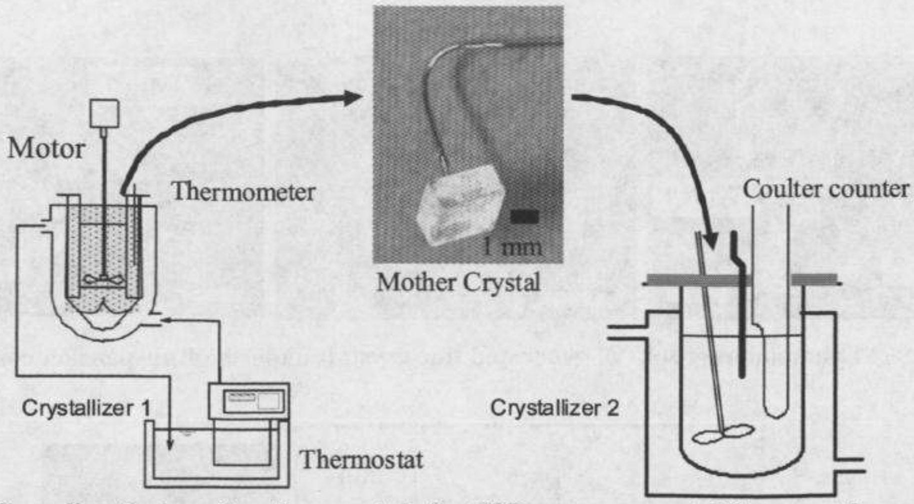


Fig. 7 Sampling timing of mother crystals for CSD measurementof fine crystals generated from mother crystal surface

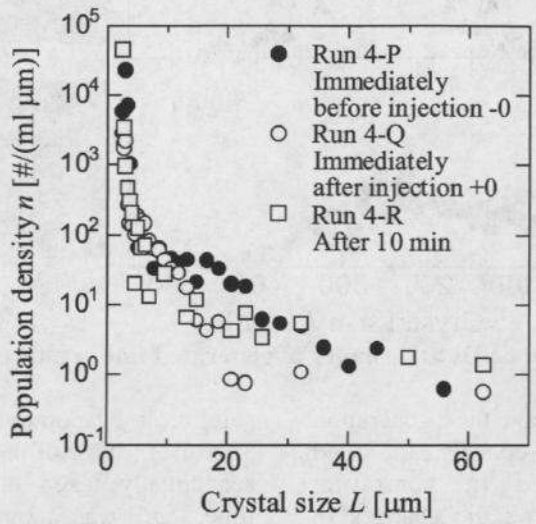
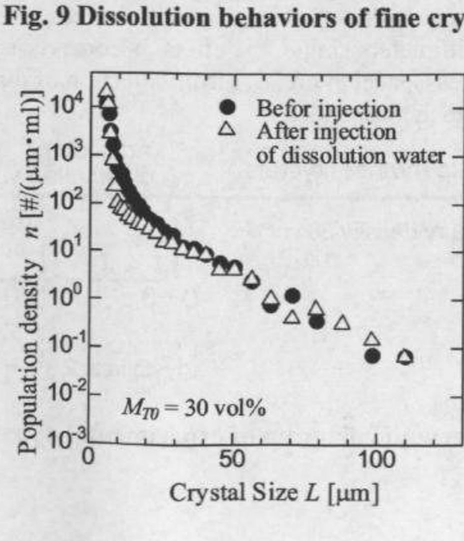


Fig. 8 Population density plot for fine crystals generated in Crystallizer 2

3.4 Dissolution behaviors of fine crystals

In order to discuss the dissolution behaviors of fine crystals, the number and CSD of fine crystals were measured with the coulter counter before and after injection of dissolution water in the suspended saturated solution. The results are shown in Fig. 9. The number of crystals below 40 μm was decreased by injection of dissolution water. On the other hand, differences in the number of crystals above 40 μm were not observed. These results confirmed the preferential dissolution of the fine crystals by injection of dissolution water

Fig. 9 Dissolution behaviors of fine crystals



4. Conclusion

In order to understand the characteristics of fine crystals generated under high suspension conditions, vacuum evaporative crystallization were carried out. And the generation mechanisms and destruction behaviors were discussed by using undersaturation operation. As the results, the following conclusions were obtained.

(1) Under high suspension conditions, the influence of abrasion and breakage was greater than under low suspension conditions, and many fine crystals were generated.

(2) The fine crystals could be classified into two types and the effect of injection of dissolution water was different depending on the shape of fine crystals.

(3) The dissolution water was effective for the preferential dissolution of fine crystals and modification on the crystal surfaces directly related to generation of fine crystals.

5. References

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