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# Control of Crystal Size Distribution in Industrial Crystallization of Sodium Chloride

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ABSTRACT

**To try to prevent cyclic changes of size distribution of product crystals in an industrial crystallizer, experiments concerning the supply of seed crystals were carried out. The cyclic change was prevented by controlling the supply of seeds, but it was thought that agglomeration occurred in the case of small seeds. A manufacturing method for product crystals of 400 μm under various operating conditions was discussed. An evaluation of the quality of product crystals was attempted using measurements of hardness and moisture. The measurement of hardness was taken as an effective evaluation of the quality of product crystals.**

## INTRODUCTION

The crystal size distribution of sodium chloride produced by a continuous crystallizer varies cyclically (Hasegawa, 1990). Therefore, product crystals of a desired size are difficult to obtain. The main reason is considered to be that the nucleation rate varies with changes in operating conditions and the size distribution of crystals suspended in the crystallizer.

The authors discuss a method of supplying seed crystals needed to maintain a constant nucleation rate, and a method of manufacturing product crystals of mean size of 400 μm under various operating conditions. The efficiency of seed crystals is discussed by comparing the numbers of seed crystals and product crystals. An evaluation of the quality of product crystals was attempted using measurements of hardness and moisture.

## APPARATUS AND EXPERIMENTAL METHODS

### Apparatus

The evaporating jet-mixing crystallizer (shown in Fig. 1) used in this study was similar to a mixed suspension mixed product removal crystallizer. It had 3 $m^2$ of heat exchange area and was 0.5 $m^3$ in volume. This crystallizer was characterized by the use of a suspension which was mixed while being injected through a nozzle, and coarse crystals could be obtained.

### Experimental methods

Brine was prepared to 25 wt% with reagent grade sodium chloride. The seed crystals of 100, 200 or 270 μm were prepared by the sieving of reagent grade sodium chloride. Half a cubic meter of brine fed into the crystallizer was circulated at 15, 20 or 25 $m^3/h$. The brine heated by the steam in the heat exchanger was evaporated at 90°C in the crystallizer. The evaporation rate, taken as the weight of condensed vapor drained off, was measured every 30 min and was adjusted to 50, 75 or 100 kg/h by altering the flow rate of steam. The brine was supplemented to replace amounts lost through evaporation, so that a constant level of brine in the crystallizer was maintained.

When the brine had been concentrated to supersaturation, the nucleation could be observed through a port in the side wall of the crystallizer. The initial seed crystals, 45 kg of mean size 270 μm, were quickly introduced to the crystallizer. After 30 min had elapsed, a fixed amount of seed crystals of 100, 200 or 270 μm were introduced successively to the crystallizer at 15 min intervals.

The product crystals were neither removed nor sampled until a desired suspension density of 0.04, 0.07 or 0.10 had been reached. Once the desired suspension density had been obtained, sufficient crystals were taken out to keep a constant amount of crystals in the crystallizer.

The product crystals were dehydrated by centrifuge, and their weight was measured. Two hundred grams of product crystals were washed with ethanol and dried at 60°C for 1 h. The size distribution of this sample was measured by sieve analysis. When the accumulated amount of the product crystals became five times that of the suspended crystals in the crystallizer, the operation of crystallizer was regarded as having reached a steady state. The hardness and moisture of these samples were measured.

The moisture which expressed water contents of grown part of crystals was calculated by equation (1). The weight loss in equation (1) was the difference between weight of crystals dried at 140°C for 90 min and those at 600°C for 120 min.

$$\text{moisture}[\%] = \frac{l_p^3 \cdot M_p - l_s^3 \cdot M_s}{l_p^3 - l_s^3} \quad (1)$$

where $l_p$ is the mean size of product crystals (μm); $l_s$ is the mean size of seed crystals (μm); $M_p$ is the weight loss of product crystals (%); and $M_s$ is the weight loss of seed crystals (%).

The hardness was measured using 50 product crystals classified to about 400 μm. The hardness meter is shown in Fig. 2. The load at which crystal shattered was taken as the hardness of the crystal.

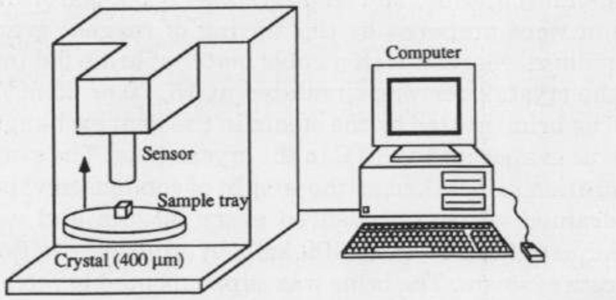

Fig. 2. Hardness meter.

## RESULTS AND DISCUSSION

### Definition of ES (efficiency of adding seed crystals)

If all the seed crystals become the product crystals and secondary nucleation could be ignored because the nucleation rate can be assumed to be very small and that the fine crystals produced by the nucleation disappear by agglomeration, the seeding rate can be taken as equal to the production rate based on the number. As the size distribution in the Rosin-Rammler chart is expressed as equation (2), with the preceding assumptions, the distribution based on mass can be changed to one based on number as in equation (3). The number of seed and product crystals are given by equation (4) by inserting the amounts of seed and product crystals per hour.

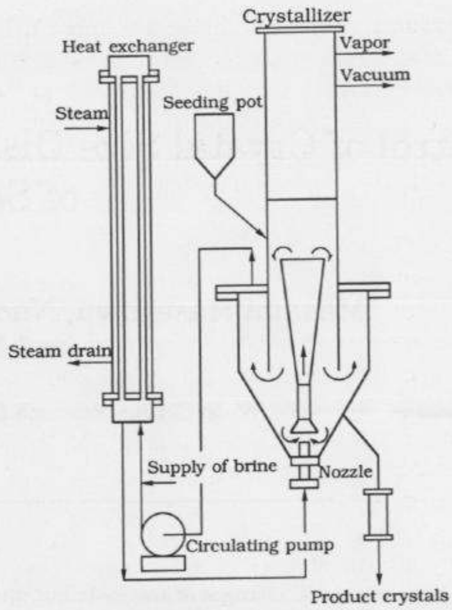

Fig. 1. Jet-mixing crystallizer.

$$\frac{d\gamma}{dl} = n/l_w (l/l_w)^{n-1} \cdot \exp[-l/l_w]^n \quad (2)$$

$$\frac{dN}{dl} = \frac{\{n(l/l_w)^{n-1} \cdot \exp[-l/l_w]^n\} \cdot Wt}{l_w \cdot \varrho_c \cdot l^3} \quad (3)$$

$$N = \int_0^\infty \frac{\{n(l/l_w)^{n-1} \cdot \exp[-l/l_w]^n\} \cdot Wt}{l_w \cdot \varrho_c \cdot l^3} dl \quad (4)$$

$$ES = N_p/N_s \quad (5)$$

where l is the size of crystal; $l_w$ is the absolute size constant on mass; n is the slope of size distribution; Wt is the weight of product crystals or seed crystals; $\varrho_c$ is the density of NaCl; dγ/dl is the size distribution based on mass; dN/d is the size distribution based on number; and $N_p$, $N_s$ are the number of product crystals or seed crystals.

In this case, the production rate is based on a number equivalent to the actual nucleation rate. The efficiency of adding seeds, ES in equation (5), has been introduced as the definition of the ratio between production rate and seeding rate based on number. When the value of ES is smaller than 1, added seed crystals decreased population to become part of agglomerates among the suspended crystals in the crystallizer. On the other hand, when ES is larger than 1, secondary nucleation cannot be ignored.

## Determination of seeding rate

The determination of the seeding rate under various operating conditions was carried out as follows. Toyokura and Aoyama (1987) proposed a relationship among crystal size of products, suspension density, average nucleation rate as shown by equation (6).

As the crystal size varies at one quarter the power to changes of average growth rate, average nucleation rate and suspension density, its change is relatively very small. Therefore, equation (6) can be replaced by equation (7).

From this equation, it is deduced that, if the suspension density is kept constant and also the average growth rate and ES are scarcely changed, the size of product is in inverse proportion to a quarter powers of the seeding rate. So the correlation between two experiments of different seeding rate can be expressed by equation (8).

$$l^{p} = \frac{(1-\varepsilon)\cdot(dl/d\theta)av}{F_{v}'k_{v}\cdot I} \qquad (6)$$

$$l_{p}\propto \frac{(1-\varepsilon)\cdot(dl/d\theta)av}{\text{Seeding rate}} \qquad (7)$$

$$\left(\frac{l_{p1}}{l_{p2}}\right)^{4} = \frac{(\text{Seeding rate})_2}{(\text{Seeding rate})_1} \qquad (8)$$

where $l_p$ is the size of product; $(1-\varepsilon)$ is the suspension density of crystals in the crystallizer; $(dl/d\theta)_{av}$ is the average growth rate; $F_{v'}k_v$ is the average nucleation rate; and I is the constant determined by size distribution of product crystals.

From these theories, the seeding rate for production of a desired size crystal was proposed as follows. At first, preliminary continuous tests was carried out on steady states, A correlation between product size and seeding rate should be obtained. Using this datum and equation (8), seeding rate was easily decided for a desired product. In this study, about 450 μm crystal was obtained by a seeding rate at 20 kg/h as shown in Fig. 3. From these data, a seeding rate of 32 kg/h was estimated for production of 400 μm crystals. For the experiment at this rate, the size distribution product was kept constant at about 400 μm. In almost all the experiments, the seeding rate was found to be determined by equation (8).

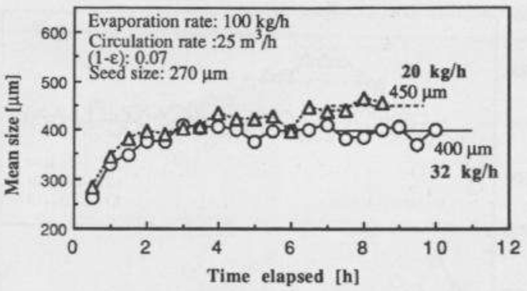


Fig. 3. Example of method for determination of seeding rate.

## Effect on size distribution of product crystals

### *Circulation rate*

The size distributions of product crystals at the steady states obtained at circulation rate of 15, 20 or 25 $m^3$/h are shown in Fig. 4. These distributions were plotted on a Rosin–Rammler chart and the specific values of the distributions could be given for absolute size constant ($l_w$) at accumulations of 36.8% and n as the slope of distribution. In Fig. 4, the absolute size constant increases and the value of n decreases with decreasing circulation rate. The amount of product crystals whose size were between 600 and 700 μm obtained at the operation of circulation rates 15 and 20 $m^3$/h, compared with that at 25 $m^3$/h increases.

Almost all the crystals in this range were found to be agglomerates formed among crystals when viewed under a microscope. The ES mentioned above, increases with increasing circulation rate and these values were less than 1. Consequently, it is considered that agglomeration occurred with decreasing circulation rate. Therefore, the succeeding experiments were carried out at 25 $m^3$/h as the circulation rate.

### *Size of seed crystals*

The mean size of product crystals (at 50%) and values of n obtained from experiments with three sizes of seed crystal against time elapsed are shown

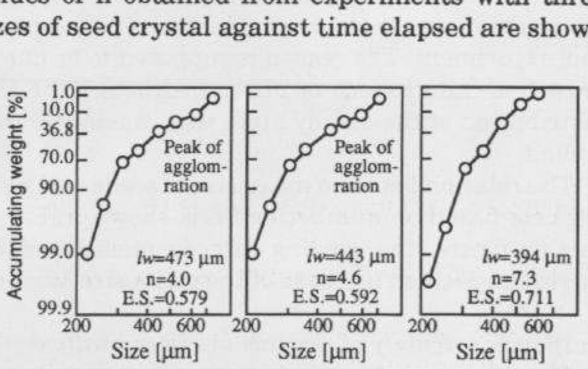


Fig. 4. Effects of circulation rate.

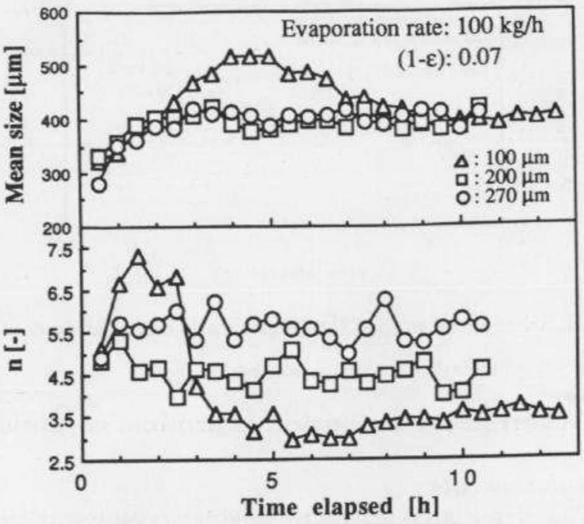


Fig. 5. Changes of size distribution for various seed sizes.

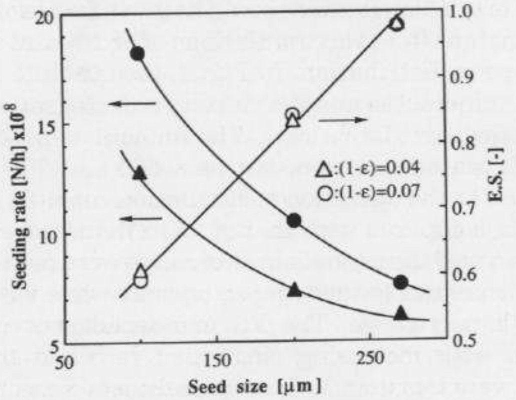


Fig. 6. Seed size vs. seeding rate and ES.

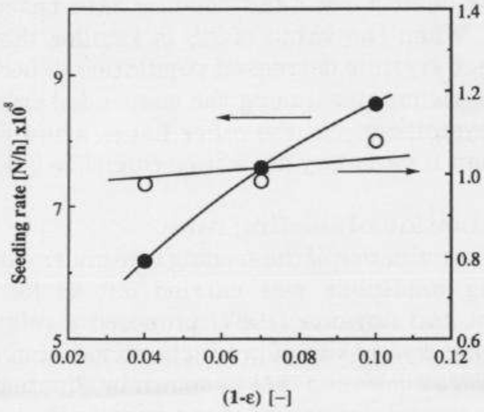


Fig. 7. $(1-\varepsilon)$ vs. seeding rate and ES.

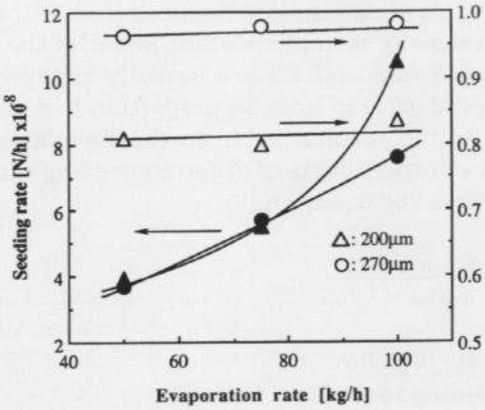


Fig. 8. Evaporation rate vs. seeding rate and ES.

in Fig. 5. In this experiment, the mean size and n were taken as control when using seeds of 200 μm. For 270 μm seeds the size distribution of product crystals varied slightly. In the experiment of 100 μm seeds, the mean size increased in the initial stages of this experiment. The reason is supposed to be due to growth of initial seeds of 270 μm, although the size distribution of the steady state was constantly controlled.

The relation between mean size of seeds and seeding rate based on number or ES is shown in Fig. 6. In this figure, the seeding rate decreased and ES increased with an increase of the mean size of seeds.

*Suspension density of crystals in the crystallizer*

The relationship between suspension density and seeding rate or ES is shown in Fig. 7. The seeding rate increased but ES did not vary with increasing suspension density.

*Evaporation rate*

When the evaporation rate was increased, the seeding rate increased but ES remained almost constant as shown in Fig. 8.

*ES in various operating conditions*

The relationship between the values of ES and seed size in this study is shown in Fig. 9. These values were correlated directly with the size of seeds independent of suspension density and evaporation rate. ES, efficiency of adding seeds, decreased with decrease of seed size. Consequently, agglomeration occurred in the case of small seeds.

## Evaluation of quality of product crystals

An attempt to evaluate the quality of the product crystals was carried out using measurements of the hardness and moisture and observations of the crystals themselves. The hardness of product crystals of

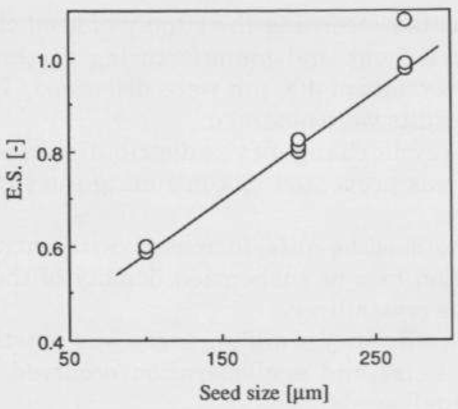


Fig. 9. Relation between seed size and ES.

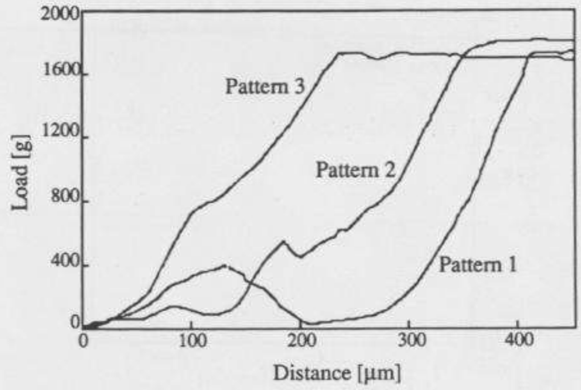


Fig. 10. Three patterns obtained on measurement for hardness.

TABLE 1

Hardness of crystals produced by various seed size

| Seed size (μm) | Mean of hardness (g) | Standard deviation of hardness (g) |
|---|---|---|
| 100 | 347 | 268 |
| 200 | 346 | 286 |
| 270 | 325 | 160 |

400 μm grown from three sizes is shown in Table 1. In this table, it can be seen that there were no significant differences among the average hardness of the samples, but the standard deviation of hardness of crystals produced by seeds of 270 μm was smaller than the others.

In measurement of hardness of crystals, three patterns were observed as shown in Fig. 10. In the case of 270 μm, Pattern 1 was observed for almost all crystals. Patterns 2 and 3 were often observed for the other samples. It was thought that such crystals formed agglomerates, so were shattered as soon as they contacted the sensor of the hardness meter.

The product crystals obtained from 100 μm seed size are shown in Fig. 11. Most of these crystals are agglomerates made of fine crystals.

The relationship between the moisture and size of seed crystals is shown in Fig. 12. The moisture increased with the size of seed. Moisture was not found to be independent of evaporation rate and suspension density. It is thought that agglomeration occurred when using small seed crystals. However, the increase of moisture with increasing seed size cannot

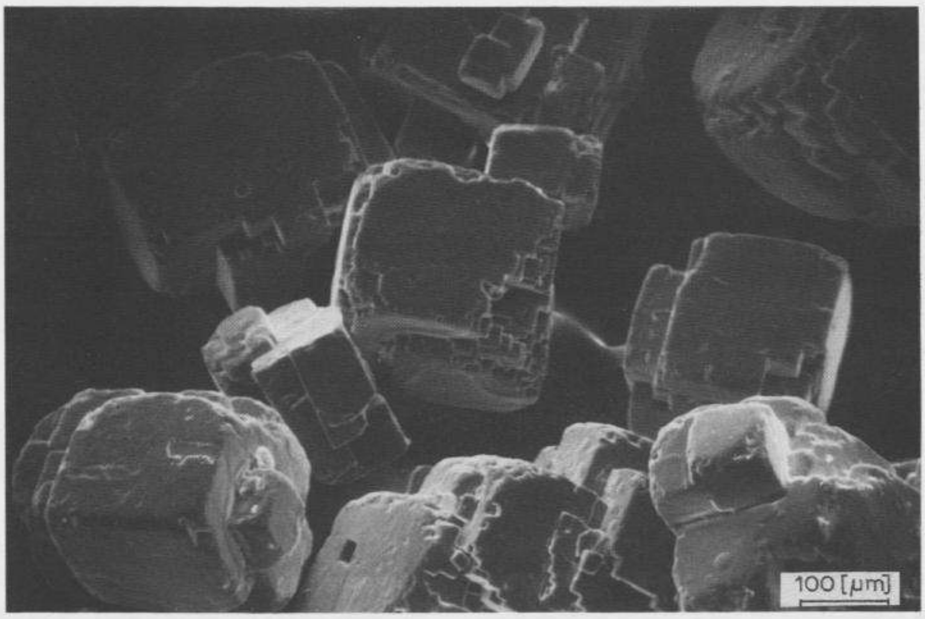


Fig. 11. Product crystals obtained from 100 μm seed size.

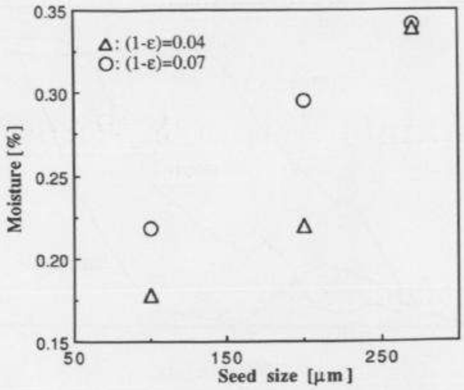


Fig. 12. Relation between seed size and moisture.

be understood at present, so it must be left for future discussion. The measurement of hardness was taken as an effective evaluation of the quality of product crystals.

## CONCLUSIONS

To try to prevent cyclic changes of size distribution of product crystals in industrial crystallizer, experiments concerning the supply of seed crystals were carried out and manufacturing methods for product crystals of 400 μm were discussed. The following results were obtained:

(1) The cyclic change of size distribution of product crystals was prevented by controlling the supply of seeds.

(2) The seeding rate increased with increasing evaporation rate or suspension density of the crystals in the crystallizer.

(3) The efficiency of adding seeds was constant for each seed size and agglomeration occurred in the case of small seeds.

(4) From the results of measurements of the hardness of the product crystals, three patterns were found and these were ascribed to agglomeration.

## REFERENCES

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