

Incorporation Phenomena of Impurity Ions into Sodium Chloride Crystals

Salt Production

Keywords: Ion-exchange membrane method, Component control, Potassium ion, Bromide ion, Iodide ion

Abstract

With the ultimate goal of controlling the components of table salt, we examined the phenomena resulting from the incorporation of potassium, bromide, and iodide ions into sodium chloride crystals. The results of semi-batch crystal growth tests revealed that the incorporation phenomena is accelerated by limiting the crystal growth rate and the deformation of the crystal lattice as a result of the incorporation of potassium and bromide ions. We concluded that a high crystal growth rate and the use of high-purity seed crystals provide an effective means of preventing the incorporation of potassium and bromide ions in an ion-exchange membrane method like that used for salt production in Japan. On the other hand, we can conclude that the use of a low-purity mother solution, typified by the ion-exchange membrane brine, is effective for accelerating the incorporation of iodide ions.

1. Introduction

In Japan, common salt is produced from concentrated seawater by an electro-dialysis process using ion-exchange membranes (ion-exchange membrane manufacture). This method involves the use of a mother solution which includes impurity ions at a relatively high concentration (in the percent order) as inorganic ions originating from the seawater. In particular, bromide and potassium ions are incorporated at a markedly higher selectivity relative to the other impurity ions. Therefore, the bromide and potassium ions are the major impurities to be found in Japanese sea salt products. The incorporation phenomena are not linked to liquid inclusion, and the selectivity of their incorporation is independent of the incorporation of other ions. The degree of incorporation is known to increase with the concentration of the mother solution. Although the details of these phenomena are uncertain, if we could identify the mechanism and thus reduce the incorporation of potassium and bromide ions, the cost of high-purity salt could be reduced. Moreover, if we were to apply the method of incorporation to the control of incorporation of a target substance (e.g. iodine or fluoride ions), we could maintain the desired component for an extended duration.

We examined a method for controlling potassium, bromide, and iodide ion incorporation. Semi-batch crystal growth tests were performed under a variety of crystallization conditions; production rate, solution temperature, properties (size, purity, suspended density) of the seed crystals, etc., using a small evaporating crystallizer. From the results, the effects of crystal growth rate, seed purity, and mother solution purity on the incorporation rate were determined.

2. Experimental

2.1 Apparatus

Figure 1 shows our apparatus which models a reverse cone crystallizer. The solution volume is 10 L. The mother solution is circulated by a circulation pump (4) from the evaporator (1) to the crystallizer (3) (3 L) through the heating tube (5). The mother solution is boiled in the evaporator, and the resulting vapor is cooled and condensed in the condenser (7). The cooled vapor is then collected in the drain tank (9). In the crystallizer, suspended crystals grow and are classified, such that only fine crystals overflow with the mother solution, while the suspended crystals are left behind. Next, a 20 wt% sodium chloride solution is fed in from the feed tank (11) using the feed pump (12).

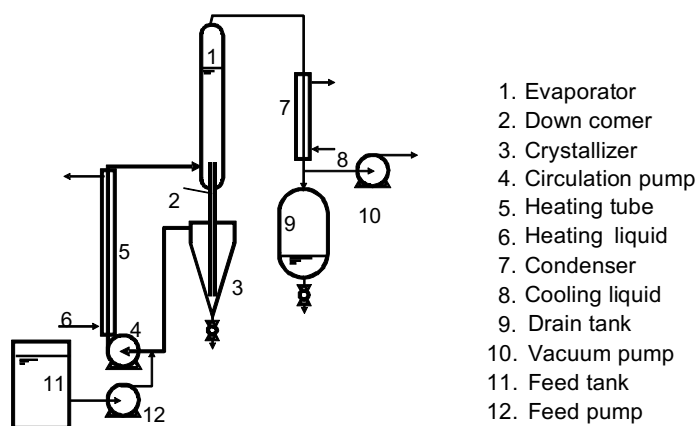


Figure 1: Experimental apparatus

2.2 Method

The apparatus was first filled with mother solution, which was a saturated sodium chloride solution at 70°C. The impurities were varied depending on the experiment. The compositions of the mother solutions are listed in **Table 1**. The circulation pump was run at a flow rate of 3 L/min. Next, the seed crystals, as listed in **Table 2**, were added to the crystallizer. Then, the mother liquids were sent to the heating tube (5), which was set to a temperature that is capable of maintaining a predetermined evaporation rate. The 20 wt% sodium chloride solution was then fed from the feed tank as a feed solution at 25°C. The temperature on the top surface of the mother solution was maintained at 70°C by controlling the pressure in the apparatus with a vacuum pump (10) during the test. The batch crystallization experiment was performed for an hour. After the crystallization experiment, the mother solution and product crystals were sampled from the bottom of the crystallizer. Similarly, batch crystallization tests were performed under the crystallization conditions listed in **Table 3**. The concentration of the sodium, magnesium, calcium, potassium, chloride, and bromide ions in the sampled solution and crystals were measured by the salt analysis method of Japan¹⁾. The concentration of iodide ions was measured by ion chromatography. Here, the crystal samples were washed with a saturated sodium chloride aqueous solution prior to measurements being performed. The particle size distributions of the seed crystals and grown crystals were measured by sieve analysis after washing the sodium chloride with saturated ethanol and then drying at 60°C²⁾.

	Concentration [g/kg]						
	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	Br ⁻	I ⁻
A	94.9	7.9	3.3	2.3	166.8	1.5	-
B	89.5	-	10.5	-	167.9	-	2.4
C	89.5	-	10.5	-	166.0	5.5	2.4
D	77.2	19.0	10.5	6.3	166.4	4.0	2.4

- : No addition

Table 1: Composition of mother solution

	Particle size distribution [μm]		Concentration of impurity [g/kg]	
	Mean particle size	Standard deviation	K	Br
a	416 – 435	32 – 38	0.52	0.39
b	305 -340	32 – 44	0.01	0.03
c	864 – 890	56-58	0.10	0.22
d	815	55	0.19	0.57

Table 2: Seed crystals

Name of test	Evaporation rate [L/h]	Concentration of feed [g/kg]	Circulation of solution [L/min]	Weight of seed [g]	Seed	Solution
Standard	0.2	200	3	530	a	A
Evaporation rate	0.4, 0.8					
Concentration of feed	0.2	250	3.7, 5.5	230, 830	b	
Circulation of solution		200				
Weight of seed			High-purity seed			
Iodide ions		0.2, 0.4		200	3	

Table 3: Experimental conditions

3. Results and discussion

3.1 Relationship between crystal growth rate and incorporation of potassium or bromide ions

After each test, fine particles and agglomerates of seeds were not found in the product crystals. Therefore, we suspected that the differences in the particle size distribution before and after the tests were a result of the crystal growth of seeds, except for the nucleation and agglomeration between the seeds within the range covered by this study. Then, the crystal growth rate was calculated from the difference in the mean particle size of the seed crystals measured before and after the experiment. The relationship between the crystal growth rate and potassium ion incorporation is shown as black and grey plots in Figure 2. Here, we calculated the incorporation rate using Eqs.1 and 2.

$$R_{i-C} = (C_i W - C_{i-0} W_0 - C_{i-L} W_L) / (W - W_0 - W_L) \quad \text{Eq. 1}$$

$$W_L = (C_{Mg} W - C_{Mg-0} W_0) / C_{Mg-L} \quad \text{Eq. 2}$$

R_{i-C} : incorporation rate of i in product crystals [g/kg], C_{i-0} : concentration of i in seed crystals [g/kg], C_i : concentration of i in product crystals [g/kg], C_{i-L} : concentration of i in mother solution [g/kg], C_{Mg-L} : concentration of Mg^{2+} in mother solution [g/kg], W : weight of product crystals [kg], W_0 : weight of seed crystals [kg], W_L : weight of mother solution in product crystals [kg]

As shown in Figure 2, the potassium incorporation rate was distributed over a range of up to 2 g/kg when using the same seed crystals, which decreased as the crystal growth rate increased regardless of production rate: evaporation rate and concentration of the feed. If we assume that potassium is incorporated by the adsorption of potassium ions as alkali metal ions on the adsorption sites for sodium ions on the crystal surface, we can assume that the incorporation is determined by the balance between the crystal growth rate and the adsorption rate of the potassium ions.

The relationship between the crystal growth rate and the incorporation of the bromide ions is indicated by the black and grey plots in Figure 3. The distribution in the incorporation rate of each ion is the same as in the case of potassium, and decreases with an increase in the crystal growth rate. We thought that bromide ion incorporation would be determined by the balance between the crystal growth rate and the adsorption rate of bromide ions at the site for chloride ion adsorption.

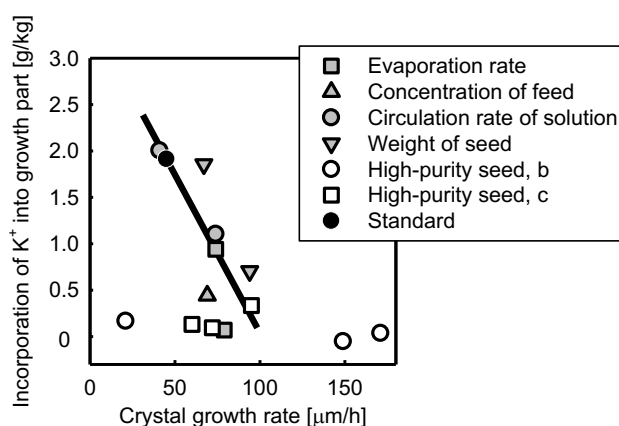


Figure 2: Relationship between crystal growth rate and potassium ion incorporation in solution A

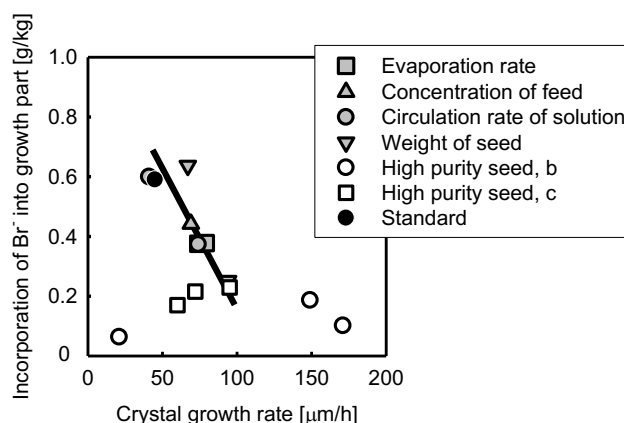


Figure 3: Relationship between crystal growth rate and bromide ion incorporation in solution A

3.2 Effect of purity of seed crystals on incorporation phenomena

The effects of the type of seed crystals on the incorporation of potassium or bromide ions are indicated by the white plots in Figures 2 and 3. The relationships between the crystal growth rate and the incorporation of the potassium and bromide ions differed depending on the seed crystals.

The incorporation of the potassium and bromide ions increased in those tests using high-purity seeds. Therefore, it is thought that the deformation of the crystal lattice by the incorporation of these ions assists with the incorporation of these ions in subsequent crystal growth, regardless of the type of the impurities. Therefore, we can conclude that the use of high-purity seeds is effective for limiting the incorporation of potassium and bromide ions.

3.3 Effect of purity of mother solution on iodide ion phenomena

Figure 4 shows the relationship between the purity of the sodium chloride in the mother solution and the incorporation rate of iodide ions in the case of the iodide ion test in Table 3. The incorporation rate showed a similar trend as in the case of the potassium and bromide ions, decreasing with an increase in the crystal growth rate. On the other hand, the incorporation rate in the high-purity solution B was very low relative to C and D. Then, the incorporation rate in solution D, when modeling an ion-exchange membrane, was higher than C, with more bromide being present in B. Based on these results, we believe that the deformation of the crystal lattice by the incorporation of both potassium and bromide ions assists with the incorporation of iodide ions in the later stages of crystal growth.

We can conclude that low-purity mother solutions, like the concentrated seawater used in the Japanese ion-exchange membrane method, are effective for iodide ion fixation in sodium chloride crystals.

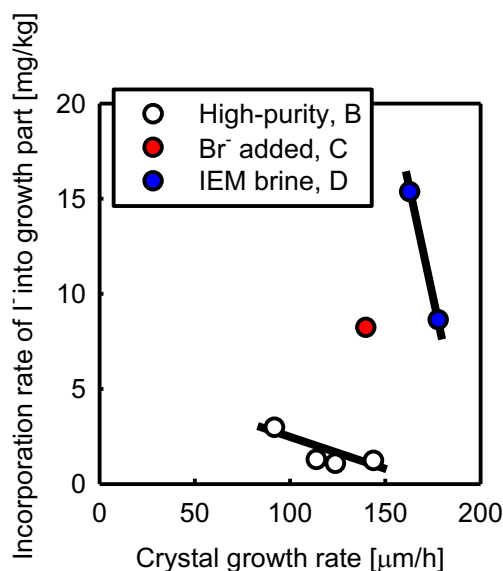


Figure 4: Effect of composition of mother solution on incorporation rate of iodide ions into seed d

4. Conclusion

We examined method used to control the incorporation of potassium, bromide, and iodide ions. From the results of semi-batch crystal-growth tests, we determined that the incorporation phenomena can be accelerated by limiting the crystal growth rate and the deformation of the crystal lattice by incorporating potassium and bromide ions. We concluded that a high crystal growth rate and the use of high-purity seed crystals are effective means of preventing the incorporation of potassium and bromide ions in the ion-exchange membrane method used in Japanese salt making. On the other hand, we can conclude that the use of a low-purity mother

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solution like the ion-exchange membrane brine provides an effective means of accelerating the incorporation of iodide ions.

References

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