WORLD SALT SYMPOSIUM

June 19-21, 2018 Park City UT, USA

Incorporation Phenomena of Impurity Ions into Sodium Chloride Crystals

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The Salt Industry Center of Japan

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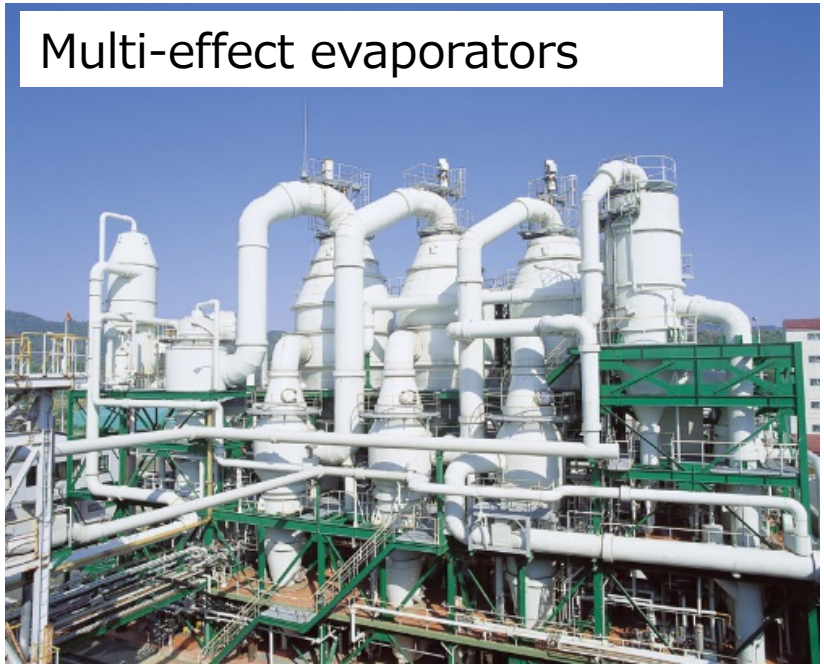
Salt manufacture in Japan

Ion-exchange membrane manufacture
1. Concentration of seawater by electro-dialysis
2. Evaporation by multi-effect evaporators

The mother solution in the evaporator includes impurities in the form of inorganic ions originating from the seawater.
…So the purity of Japanese sea salt is low.

Seawater concentration by electro-dialysis using ion-exchange membranes

Multi-effect evaporators



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HP of Naikai Company

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Impurities in sodium chloride products

Inclusion of mother solution

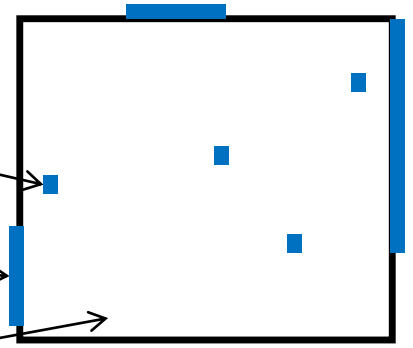
- Minimal

Adhesion of mother solution

- Controlled by centrifuging and washing

Incorporation by lattice defect

- No means of control



Cross-section of a crystal

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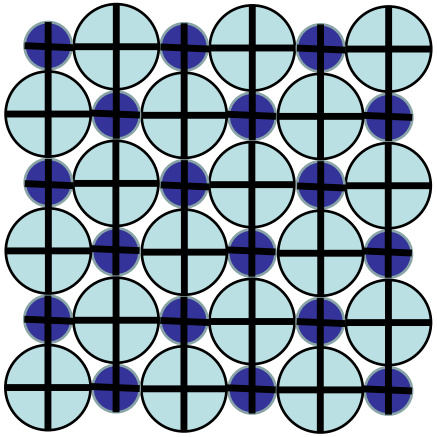
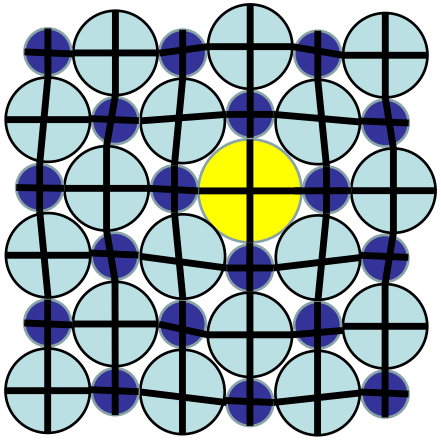
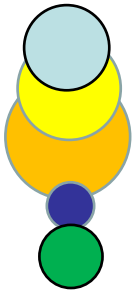
Incorporation of impurities into sodium chloride



Sodium chloride



Sodium chloride incorporating Br^-



Ion radius

Cl^-	1.81 Å
Br^-	1.96 Å
I^-	2.20 Å
Na^+	0.99 Å
K^+	1.37 Å

- K^+ and Br^- are known to be incorporated into sodium chloride crystals
- Incorporation rate increases with concentration of K^+ and Br^- in mother solution
- I^- is a halogen, as are Cl^- and Br^-
- Difference in ion radius is too large to replace Cl^- with I^-

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Our goal

Reduce amount of incorporated potassium and bromide ions

→ Reduce cost of high-purity salt

Promote the incorporation of iodine ions

→ Maintain presence of iodine ions in table salt for long period

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In this presentation

We will describe…

- Means of controlling incorporation of impurities* by crystallization tests under a range of conditions** when using a small evaporator.

  * K^+, Br^-, I^-

  **Production rate, temperature, seed size, seed purity, suspended density, etc..

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Experimental

Mother solution

↓

Seeding

↓

Crystal growth test

↓

Drawing products

↓

Washing with saturated aq.

↓

Composition analysis

Drawing products → Washing with saturated EtOH

↓

Particle size distribution analysis

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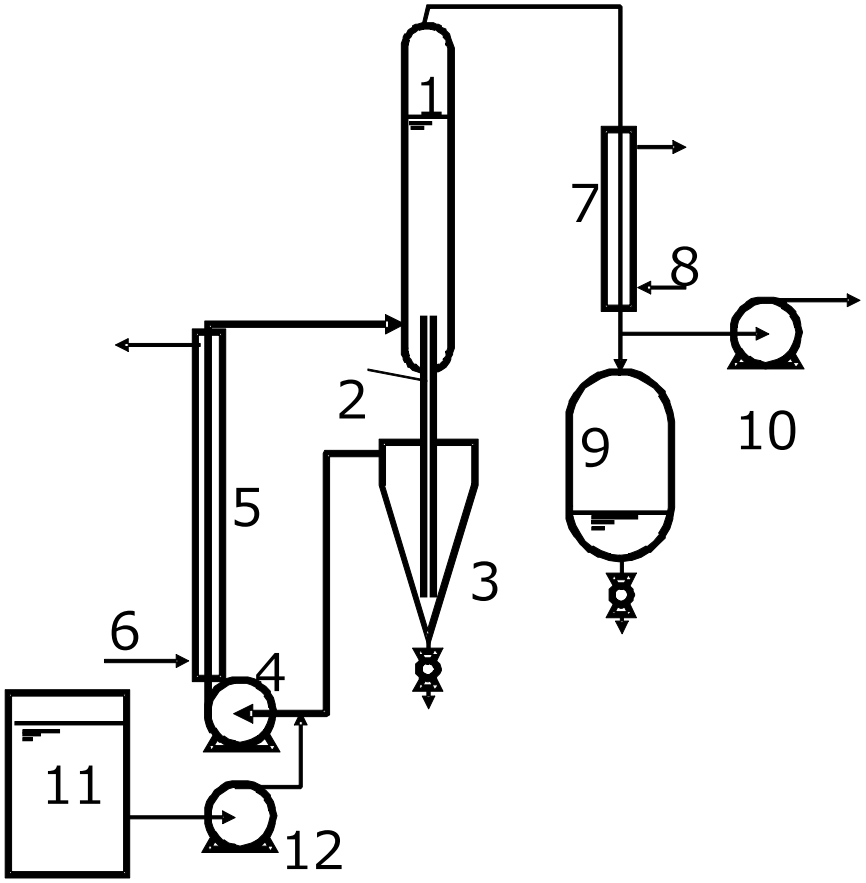
Apparatus



1. Evaporator
2. Down-comer
3. Crystallizer (3L)
4. Circulation pump
5. Heating tube
6. Heating liquid
7. Condenser
8. Cooling liquid
9. Drain tank
10. Vacuum pump
11. Feed tank
12. Feed pump

Crystal-Oslo crystallizer (10L)

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Experimental conditions

<table>
<tr><th>Name of test*</th><th>Evaporation rate [L/h]</th><th>Concentration of feed [g/kg]</th><th>Circulation of solution [L/min]</th><th>Weight of seed [g]</th><th>Seed</th><th>Solution</th></tr>
<tr><td>Standard</td><td>0.2</td><td rowspan="2">200</td><td rowspan="3">3</td><td rowspan="3">530</td><td rowspan="4">a</td><td rowspan="6">A</td></tr>
<tr><td>Evaporation rate</td><td>0.4, 0.8</td></tr>
<tr><td>Concentration of feed</td><td rowspan="5">0.2</td><td>250</td></tr>
<tr><td>Circulation of solution</td><td rowspan="5">200</td><td>3.7, 5.5</td></tr>
<tr><td>Weight of seed</td><td rowspan="3">3</td><td>230, 830</td></tr>
<tr><td>High-purity seed</td><td rowspan="2">230, 530, 830</td><td>b</td></tr>
<tr><td>Iodide ions</td><td>0.2, 0.4</td><td>530</td><td>c</td></tr>
<tr><td></td><td></td><td></td><td></td><td></td><td>b, c, d</td><td>B, C, D</td></tr>
</table>

*Examination about Br, K: Standard ～ High purity
Examination about I : Iodide ions

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Seed crystals

Seed*	Particle size distribution [mm]		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

*Examination about Br, K: a, b, c
Examination about I : b, c, d

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Mother solution

Solution*	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

*Examination about Br, K: A
Examination about I : B, C, D

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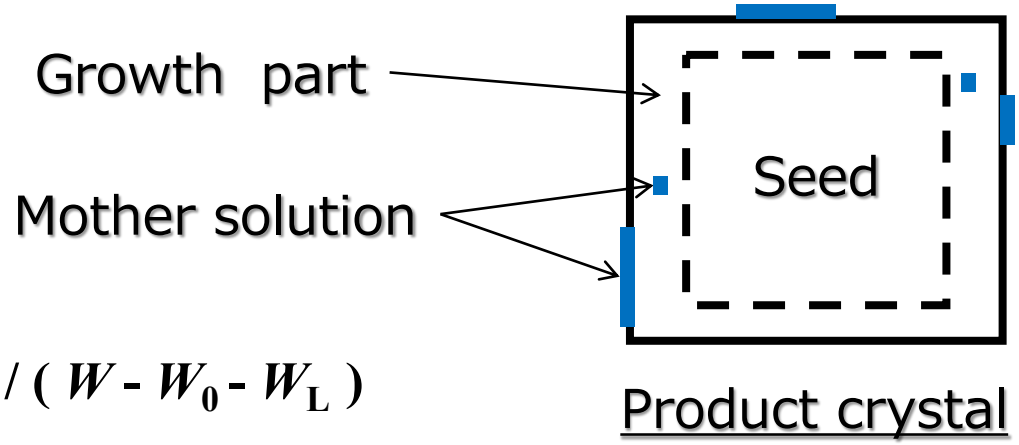
Calculation of incorporation rate



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

$R_{i\text{-C}}$: Incorporation rate of i in crystal-growth process [g/kg]
$C_{i\text{-}0}$: Concentration of i in seed crystals [g/kg]
C_i: Concentration of i in product crystals [g/kg]
$C_{i\text{-L}}$: Concentration of i 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]

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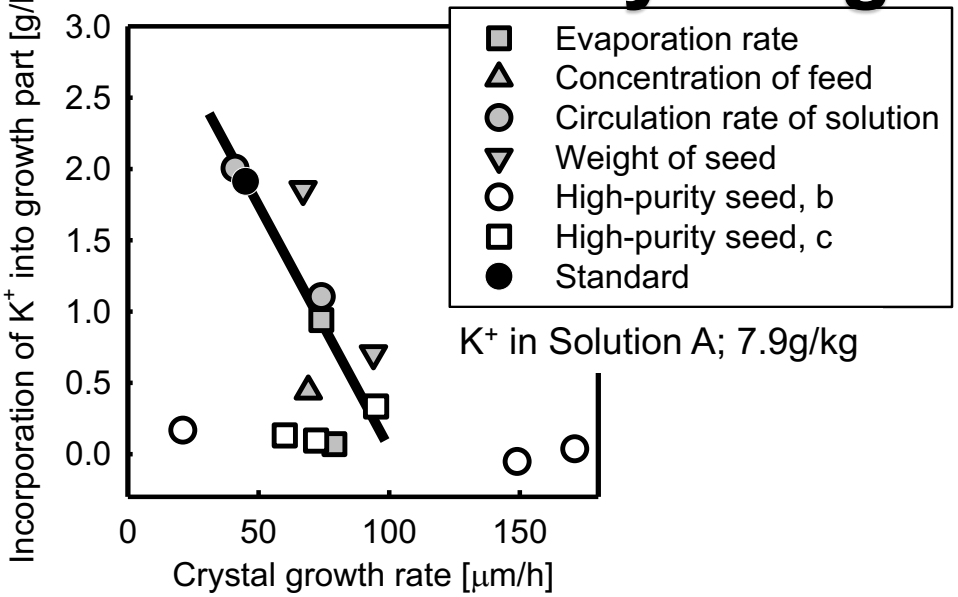
Relationship between incorporation rate and crystal growth rate



- Incorporation rate decreased as the crystal growth rate increased, regardless of the crystallization conditions.
  → Incorporation is determined by balance between crystal growth rate and adsorption rate of K^+ on growth site?
- Incorporation rate decreases when using high-purity seeds.
  → Former incorporation promotes incorporation in subsequent crystal growth?

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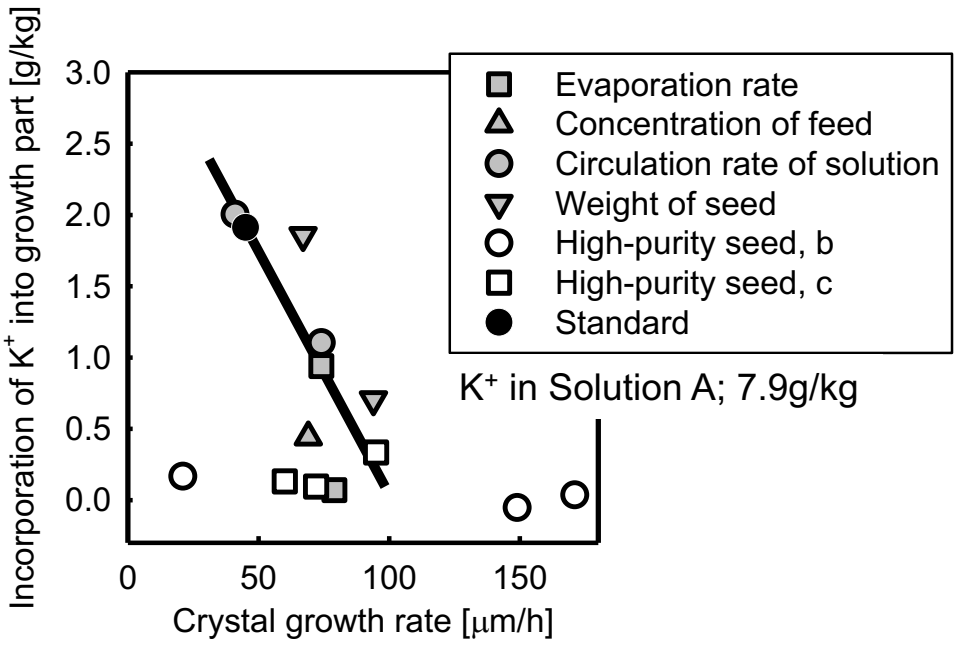
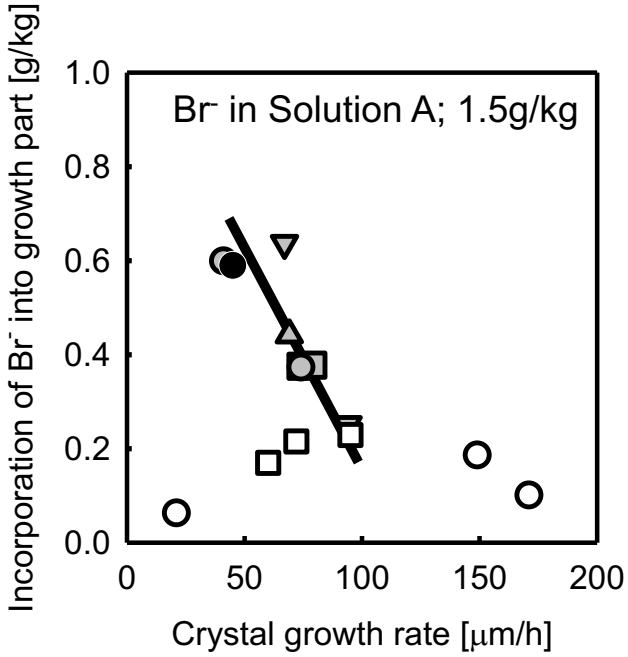
Comparing Br^- incorporation with K^+





- Incorporation of Br^- shows the same tendencies as that of K^+.
  →The K^+ and Br^- incorporation have the same mechanism?

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Proposals for decreasing K^+ and Br^- incorporation

- Increasing crystal growth rate
- Decreasing absorption rate
- Using high-purity seeds

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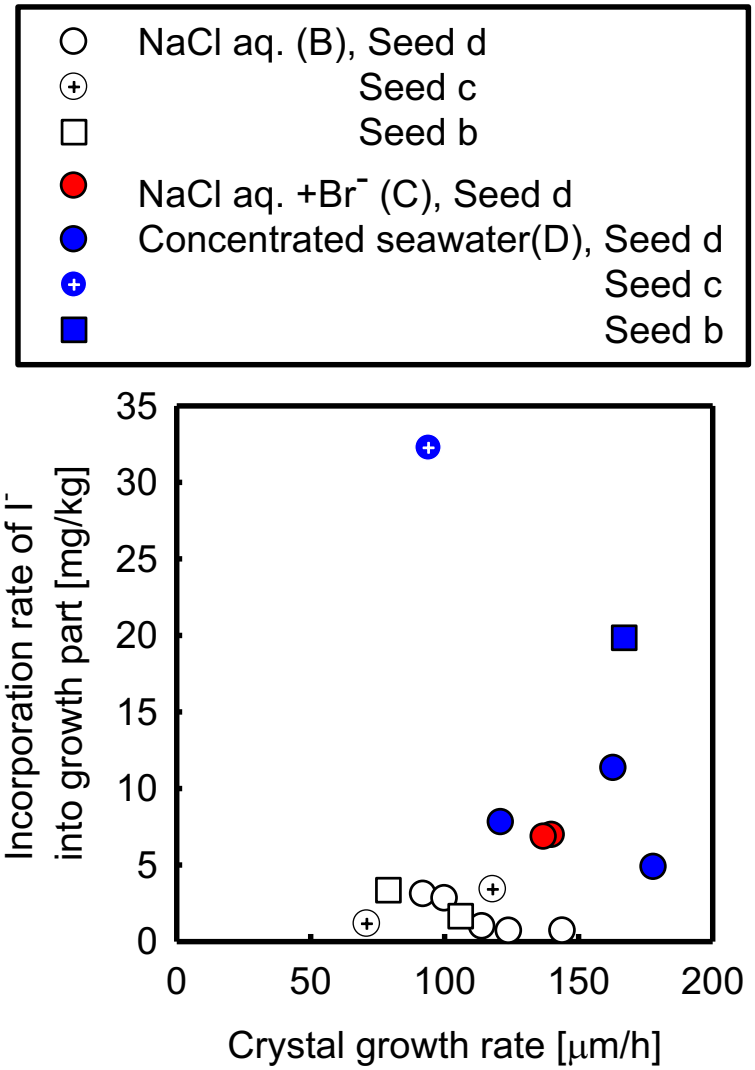
Effect of purity of mother solution on I^- incorporation



- I^- incorporation rate is low relative to that of Br^-.
- I^- incorporation rate in solutions C and D is higher than that in B.

→ Deformation of crystal lattice by Br^- incorporation assists with I^- incorporation in subsequent crystal growth?

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Proposal for accelerating I^- incorporation

- Using low-purity mother solutions including Br^- etc., as typified by concentrated seawater.

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Conclusion

Incorporation rate is accelerated by decreasing the following:

Crystal growth rate
Impurities in suspended crystals
Impurities in mother solution

Proposals for decreasing K^+ and Br^- incorporation

- Increasing crystal growth rate
- Decreasing absorption rate
- Using high-purity seeds

Proposal for accelerating I^- incorporation

- Using low-purity mother solutions including Br^- etc., as typified by concentrated seawater.

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