

# Impurities Contained Inside the Crystals of Solar and Vacuum Evaporated Salts

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## ABSTRACT

In order to study the amount and the state of impurities contained inside salt-crystals (in crystals), about 200 samples of solar salts produced in various countries and vacuum evaporated salts from salt fields, ion-exchange membrane and refined methods, were washed to remove all the impurities attached on the surfaces of the salt crystals. They were then analyzed chemically and were detected by an orthoscopic observation. The results showed that they contained 0.000 ~ 0.14% insoluble matter, 0.001 ~ 0.12% potassium ions, 0.000 ~ 0.20% magnesium ions, 0.000 ~ 0.13% calcium ions, 0.005 ~ 0.80% sulfate ions and 0.02 ~ 1.7% water according to the crystallizing methods. The most potassium ions were present in place of sodium ions in NaCl lattice. While calcium and sulfate ions were present largely in a form of calcium sulfate (10 ~ 100  $\mu\text{m}$  in length), water, magnesium ions and other ions other than those mentioned were included as mother liquid in 10 ~ 100  $\mu\text{m}$  cube cavities. In solar salts the mother liquid was also included in cave or stria. These cavities formed lines or strata parallel to {100} surfaces of salt crystals and the distance of strata (0.3 ~ 0.7 mm) corresponded to a day growth of salt crystals. The amount of impurities inside salt crystals was related largely to the crystallizing conditions, the chemical composition, the temperature and the amount of suspended matter of the mother liquid where the salt crystals were deposited.

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## INTRODUCTION

Some impurities are contained in common salt (salt crystals, crystals of sodium chloride, NaCl) crystallized from aqueous solution. They are major components ( $\text{K}^+$ ,  $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$  and water ( $\text{H}_2\text{O}$ ) and or clay) and minor components (heavy metals, organic matter). The impurities of these major components are distributed both on the surface of the salt crystal (*on crystals*) and inside the salt crystal (*in crystals*) as illustrated in Figure 1. In addition, there is an intermediate state which has dimples, crevices and caves of solar salts, and clearance enclosed by unit crystals.

In this paper, the author reports the amount and the state of the impurities of major components in crystals. An attempt is also made to discuss the mechanism of inclusion of the impurities of major components in relation to the crystallizing conditions.

## METHOD

**Sample salts used.** About 200 samples of solar and vacuum evaporated salts of various producing methods were used. Solar salts were from Australia, Mexico, China and elsewhere. Vacuum evaporated salts were produced by salt field method (traditional method but abolished in Japan in 1972), by ion-exchange membrane method (now having a capacity in Japan of 1,100,000 tons per year) and by the refined method.

In addition to these salts, 53 sample salts for foodstuffs gathered from abroad in 1972-1974 were used for comparison. They are almost vacuum evaporated, solar and rock salts.

**Removal of the impurities on crystals.** Amount of impurities in crystals was determined by means of chemical analysis of the sample salts, from which the impurities on

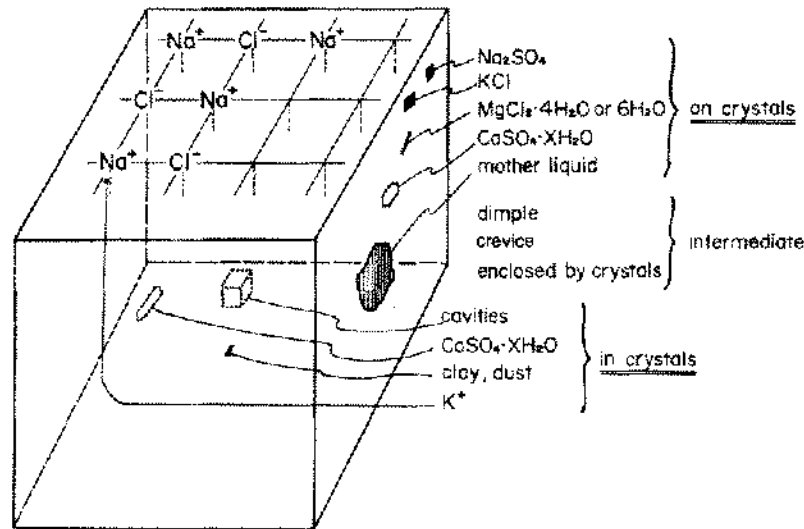


Figure 1. Classification of impurities of common salt crystals.

crystals had been completely washed off previously. The sample salts were washed two times for vacuum evaporated salts (usually the particle sizes were less than 700  $\mu\text{m}$ ) and three times for solar salts with crushing under 2 mm (the particle sizes were 5 ~ 20 mm). The first washing (for two times) was carried out completely in the apparatus shown in Figure 2, which was specially made for this purpose (Yonei and Masuzawa, 1966).

**Analysis of major impurities and cube cavity estimate.** The  $\text{K}^+$ ,  $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{SO}_4^{--}$  and water of the washed samples were chemically analyzed by the revised official method of the Japan Tobacco & Salt Public Corporation (JTC, 1976).

Amount of cube cavities containing mother liquid was determined by means of thermogravimetric analysis. 5g of the washed samples were taken into the especially made tray, then the TGA curve was recorded. The chart of TGA,

shown in Figure 3, indicated that all mother liquid contained in cube cavities began to burst off at 300°C and ended at 600°C. On the basis of the results, the water content (W%) in cube cavities was calculated from the weight loss heated at 600°C for two hours (Ignition Loss, I.L., %) by the following equation (JTC, 1976a).

$$W = \text{I.L.} - 0.4A$$

Here, A is the content of magnesium chloride (%) in the washed sample.

Another estimation of cube cavities was devised on the basis of the assumption that true densities of solar salt decreased with an increase of the water content in crystals. As Figure 4 showed, the following equation experimentally held for solar salts between true density measured by an air comparison pycnometer ( $d$ ,  $\text{g}/\text{cm}^3$ ) and water content in crystals (M,  $\text{g}/100\text{g}$ ) (Masuzawa et al., 1971)

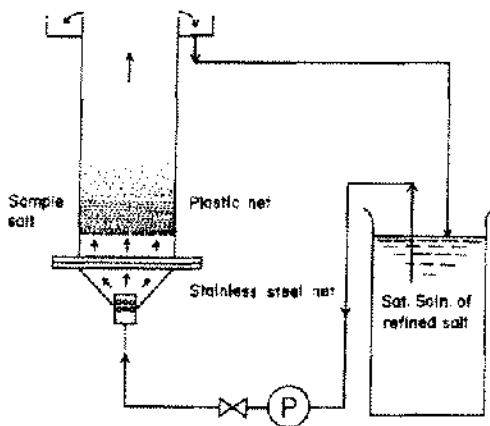


Figure 2. Apparatus for washing impurities on crystals.

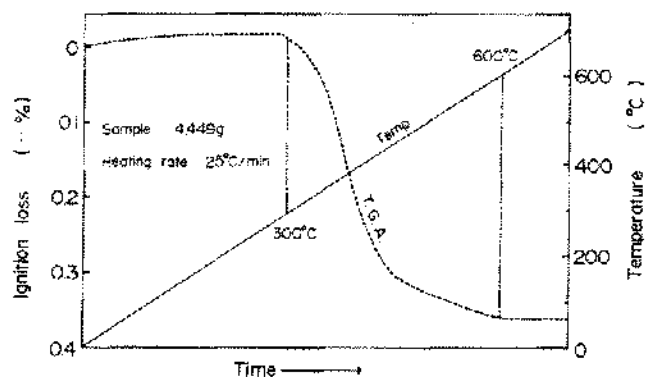


Figure 3. Thermogravimetric analysis of common salts.

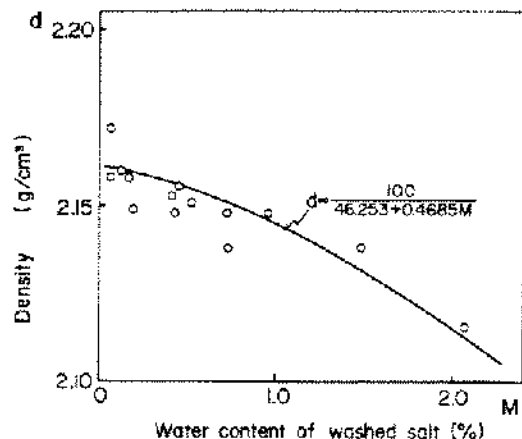


Figure 4. Relationship between water content in crystals and density of the crystals.

$$d = \frac{100}{46.253 + 0.4685M}$$

The salt crystals of sample salt were cleaved with a razor to a slice section as thin as possible. The slice section was observed for cube cavities and calcium sulfate by means of a microscope and orthoscopic method.

### RESULT AND DISCUSSION

Amount of impurities of major components analyzed so far is summarized in Figure 5.

**Water content.** Solar salts contained more than 0.2% water in crystals, the figure of which was much higher than any other salt. Vacuum evaporated salts by salt field and ion-exchange membrane methods contained more than 0.02% water in crystals. This showed that all salts crystallized from aqueous solution inevitably included at least 0.01% water.

**Potassium ions.** Solar and vacuum evaporated salts contained more than 0.01% potassium ions in crystals. Vacuum evaporated salts by ion-exchange membrane method contained about 0.1% potassium ions. The figure was much higher than that of any other salt. This was explained by the fact that ion-exchange membrane has permselectivity of monovalent ions against divalent ions and that hence the brine by ion-exchange membrane method contained much more potassium ions than that by salt field method.

On the other hand, no potassium ion was found in some refined salts in crystals (less than 0.001%), which would have crystallized from the solution containing small amount of potassium ions.

**Calcium ions.** Solar and vacuum evaporated salts contained 0.005 ~ 0.05% calcium ions in crystals. The content of calcium ions of solar salts was always about 0.01% in crystals. Salt by ion-exchange membrane method contained

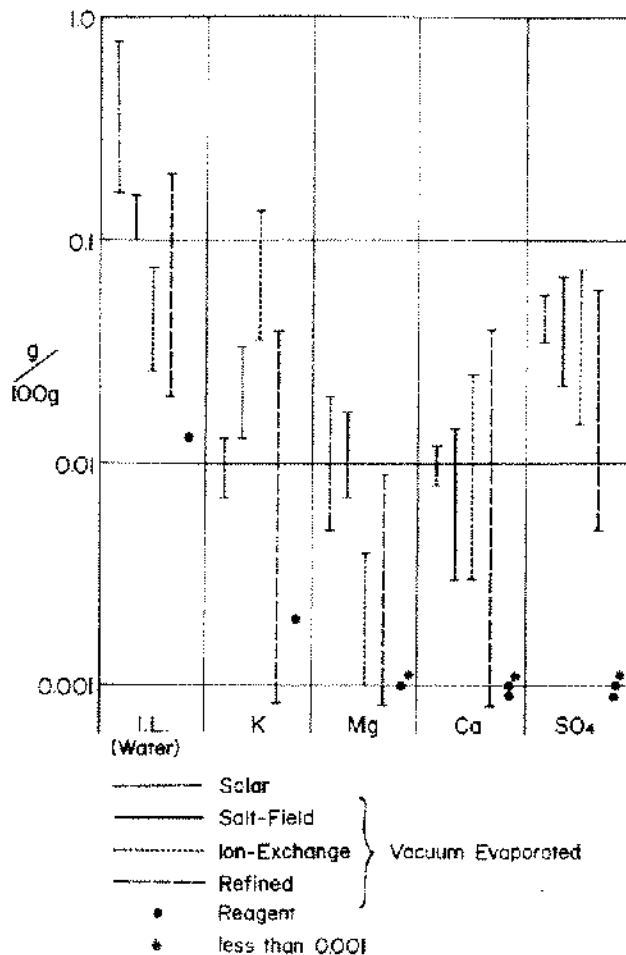


Figure 5. Amount of impurities in crystals of common salts.

more calcium ions than that by salt field method, the cause of which will be discussed later. No calcium ion was found in some refined salt.

**Sulfate ions.** All common salts contained 0.02 ~ 0.08% of sulfate ions usually. Even refined salt had more than 0.001% sulfate ions.

**Total impurities in crystals.** Amount of total impurities of K, Mg, Ca and SO<sub>4</sub> is the limit of quality, to which the purity of salt can be increased by washing the impurities on crystals. These figures were 0.06 ~ 0.19% for solar salt, 0.04 ~ 0.23% for salt by ion-exchange membrane method and 0.008 ~ 0.6% for refined salt.

**Ratio of impurities in crystals to the total (on and in crystals).** Ratio of the impurities in crystals to the total calculated by use of our analytical results, is summarized in Table 1. It shows that whereas in vacuum evaporated and solar salts (Mexico) only less than 10% water of the total was included in crystals. In solar salts, (Australia and China) 20 ~ 40% water of the total was included. In spite of salt manufacturing method, more than 40% of the potassium

TABLE 1  
Ratio of Impurities in Crystals to the Total (%)

	Vacuum Evaporated		Solar		
	Ion-Exchange	Salt-Field	Australia	China	Mexico
K	40~60	20~30	30~90	20~45	67
Mg	5~20	4~6	10~50	10~40	17
Ca	35~50	10~40	20~40	15~25	17
SO <sub>4</sub>	70~90	5~10	30~45	16~30	18
I. M.	—	—	40~90	25~40	19
Water	2~3*	4~6*	35~36	21	6

\*Calculated from the sample without drying.

ions were included in crystals in all salts. On the other hand, little magnesium ions were included in crystals of vacuum evaporated salts. In contrast to magnesium ions, more than 70% of calcium and sulfate ions were included in crystals in the case of the sample salts by ion-exchange membrane method.

Amount of magnesium ions in crystals of various salts was plotted against that of potassium ions as shown in Figure 6. The plots are distributed according to the chemical composition featured with the salt-manufacturing method.

**Chemical composition of impurities in crystals.** Ratio of magnesium, potassium and sulfate or calcium ions in crystals of various salts is shown in Figure 7. In this figure, the ratio of potassium ions of the impurities in crystals is much more than that of the total impurities, although manufacturing methods are different. This was explained by the assumption that sodium ions of NaCl lattice were replaced by potassium ions.

Raw material of solar and vacuum evaporated salts is seawater. Concentration of seawater is supposed to be a sys-

tem of Na-K-Mg-SO<sub>4</sub>-Cl-H<sub>2</sub>O saturated with CaSO<sub>4</sub>. It is conventionally called an oceanic quinary system. In the system, the equivalent of sulfate ions is more than that of calcium ions. Solar salt and vacuum evaporated salts by salt field method are crystallized from this system. Concentration of brine by ion-exchange membrane method is a system of Na-K-Mg-Ca-Cl-H<sub>2</sub>O saturated with CaSO<sub>4</sub>, where equivalent of calcium ions is more than that of sulfate ions. Refined method, where magnesium and calcium ions are usually precipitated with some alkali, is a system of Na-K-Mg-SO<sub>4</sub>-Cl-H<sub>2</sub>O, where magnesium and potassium ions are very small.

### STATE OF THE MAJOR IMPURITIES

The next problem is how major impurities in crystals mentioned above are included. Judging from the results of the author's experiments, they are divided by two groups; the "solid" of the crystals and the "liquid" of aqueous solution.

**Solid.** Both in solar and vacuum evaporated salts calcium sulfate (CaSO<sub>4</sub>, CaSO<sub>4</sub>·½H<sub>2</sub>O and CaSO<sub>4</sub>·2H<sub>2</sub>O) was found and identified by means of microscopy and by X-ray diffractometry. Examples are shown in Figures 18-19.

More potassium ions are present in place of sodium ions in the NaCl lattice, as will be discussed later. Moreover, calcium double salts (sodium penta salt, Glauberite, Syngenite), Na<sub>2</sub>SO<sub>4</sub> anhydrate or 10H<sub>2</sub>O, MgSO<sub>4</sub>·6H<sub>2</sub>O or 7H<sub>2</sub>O, CaCO<sub>3</sub>, Mg(OH)<sub>2</sub> are possibly present in crystals but still not confirmed.

**Liquid.** During crystallization of sodium chloride in crystallizers, mother liquid is included in hollow spaces.

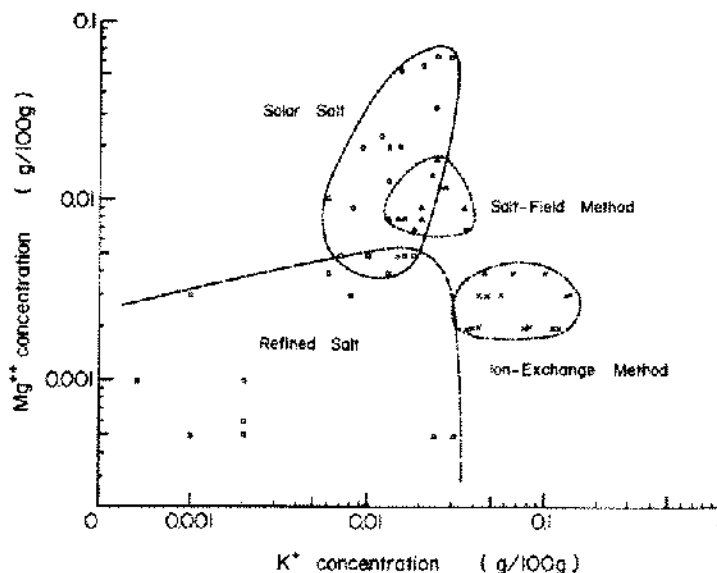


Figure 6. Relationship between K<sup>+</sup> and Mg<sup>++</sup> in crystals of common salts.

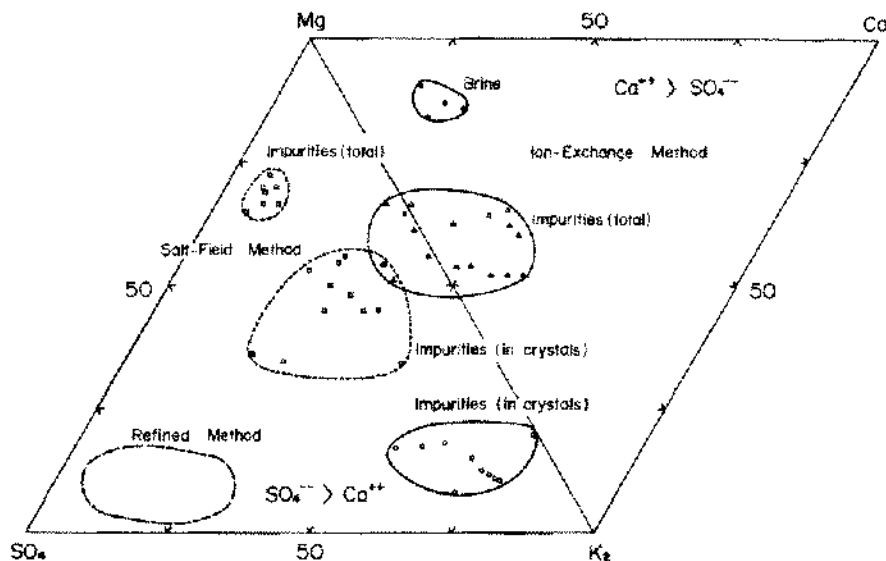


Figure 7. Total impurities and those in crystals of common salts. Note: expressed in mol%.  $K_2$ , Mg, Ca and  $SO_4 = 1$  mol.  $SO_4$  and Ca are expressed by the difference between  $SO_4$  and Ca.

The hollow spaces are 1 ~ 100  $\mu$ m cubes, which are regularly disposed parallel to {100} surfaces. We call them "cube cavities" or "cavities". In terms of formation of cavities, mother liquid is contained.

In vacuum evaporated salts, which were usually cube-like, 50 ~ 700  $\mu$ m in particle-size and contained 0.02% water in crystals, few cavities were observed directly by a microscope. However, when they were ignited above 600°C, traces of minor spots of cube cavities were easily observed. Figure 20 shows cube cavities of vacuum evaporated salt by ion-exchange membrane method, which are several  $\mu$ m in length and disposed along  $\langle 111 \rangle$  axis.

While solar salts (which were various shaped), had 2 ~ 20 mm particle sizes and contained 0.2% water in crystals. Many cube cavities were easily observed. They were distributed in layers or in whole crystals. Cube cavities in solar salts are cube shaped and 1 ~ 100  $\mu$ m in length, and are disposed regularly parallel to {100} surfaces as shown in Figures 8-10 (Hanzawa and Masuzawa, 1962b). Very often cube cavities were observed in lines or layers. They looked like stripes of transparent and opaque layers disposed alternately. It was considered that transparent layers were attributed to the conditions in which salt crystals grew slowly at night, while the opaque layers were attributed also to the reverse conditions, under which it grew faster in the daytime. Thus the distance of the layer of a cavity corresponded to a day growth of salt crystal. An example of the distance of layer of cavity measured on Mexican solar salts is shown in Table 2 (Hanzawa and Masuzawa, 1962c). Mean day growth calculated from the measurement is 0.24 mm.

The cavities of solar salts observed so far in our laboratory are summarized in Table 3. More details are referred to references.

On the basis of our measurements the distance of layer of cavity varied from 0.03 ~ 0.7 mm. Occasionally transparent part changed according to the crystallizing conditions. In some cases, it became very small as shown in Figure 9. When more than 1% water was included in solar salt, cube cavities were distributed in whole crystal as shown in Fig-

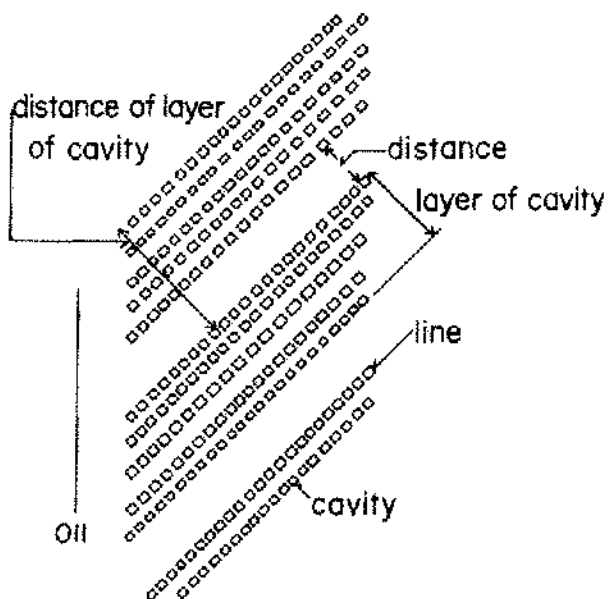


Figure 8. Layers of cube-cavities of solar salt crystals.

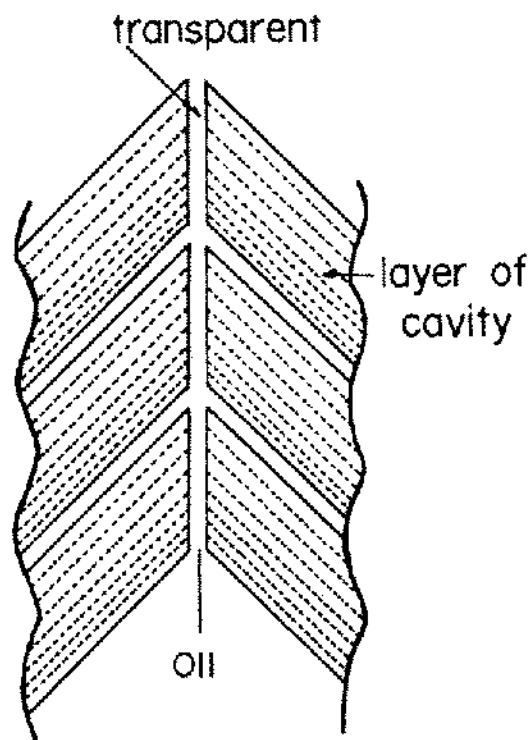


Figure 9. Layers of cube-cavities of solar salt crystals.

Figure 10. Several interesting layers of cavities found in solar salt crystals are illustrated as Figures 11–13.

In addition to cube cavities in crystals in solar salt, mother liquid is present in the clearance enclosed by unit crystals shown in Figure 14, in the cave or crevice shown in Figure 15 and striation shown in Figure 16. These three states are neither on crystals nor in crystals but an intermediate state.

#### Inclusion of impurities and crystallizing conditions.

The amount of impurities in crystals is much related to the crystallizing conditions, the chemical compositions, the temperature and the amount of suspended matters of the mother liquid in crystallizers where the salt crystals grow.

Chemical composition of mother liquid in crystallizer of various salt manufacturing process is summarized as in Table 4.

**Potassium.** When the composition of solution estimated from the amount of impurities in crystals was compared with the composition of the mother liquid from which salt crystals crystallized, the potassium ion concentration of the former was four times larger than that of the latter. Since the mother liquid of the crystallizers of solar and vacuum evaporated process was not saturated with potassium chloride, no potassium salt would crystallize.

On the other hand, potassium and sodium ions are monovalent and have the possibility of replacing each other. Consequently, it could be readily explained by assuming

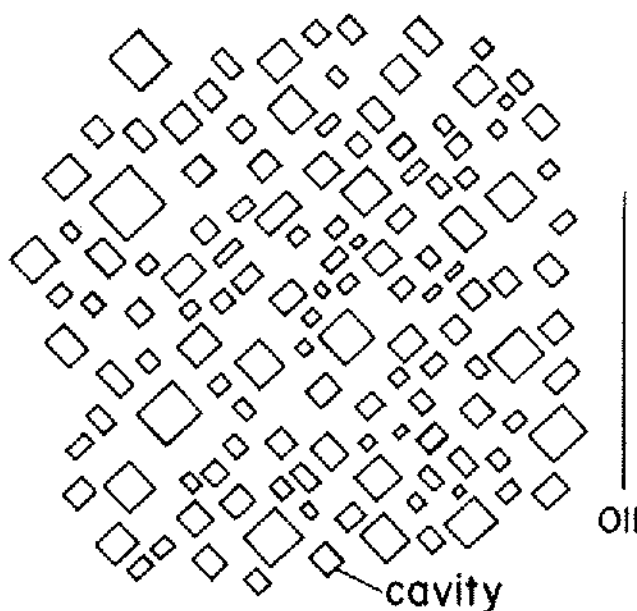


Figure 10. Cube-cavities distributed in whole crystals of solar salt.

TABLE 2

Distance of Layer of Cavity of Mexican Solar Salt

No.	Layer of Cavity mm	Distance mm
1 (Outer side)	0.20	0.02
2	0.24	0.01
3	0.18	0.02
4	0.19	0.02
5	0.15	0.02
6	0.02	0.02
7	0.27	0.02
8	0.20	0.02
9	0.20	0.02
10	0.24	0.07
11	0.12	0.10
12	0.24	0.03
13 (Inner side)	0.32	
Mean	0.21	0.03

Distance of layer of cavity = 0.24 mm

that potassium ions would enter the NaCl lattice in place of sodium ions. In salt-manufacturing process by ion-exchange membrane method, the amount of potassium ions in crystals increased in proportion to the amount of potassium ions in mother liquid as shown in Figure 17.

Potassium ions were also included as solution in cube cavities as magnesium ions. In contrast with the solar and vacuum evaporated salts, no potassium ion was found (less than 0.001%) in some refined salt.

**Magnesium and water.** Salt crystals were usually obtained in normal salt-manufacturing process before the

TABLE 3  
Cavities of Solar Salt Observed by a Microscope

Countries	Date of Import	Cavities (distance of layers mm)	Intermediate	References	
China	1955~1961	2* less than three layers		Masuzawa et al, 1971	
Thailand		1 in whole crystals			
Vietnam		4			
India		2 in whole crystals			
Pakistan		2 in layers	(0.4 ~0.45)		Crevice Striation
Aden		4 few large cavities			Striation
Yemen (rock)		5			
Ethiopia		4			
Egypt		2 in layers			
Tunisia		3	(0.03~0.1)		
Spain		2	(0.50~0.68)		
U.S. A.		4			Crevice
Mexico		2 in layers	(0.2 ~0.4)		
Sudan		4	(0.15)		Crevice
Australia					
Shark Bay	1968~1972	4		Masuzawa and Matsumoto, 1974	
Port Hedland	1968~1972	2 in layers	(0.2 ~0.3)		
Mexico	1969~1974	4 in layers	(0.1 ~0.2)	Masuzawa, 1977a	
China	1976	2 in layers	(0.1 ~0.2)	Masuzawa et al, 1975	
Korea	1971	1 in whole crystals		Masuzawa et al, 1976	

\*The amount of cavities decreases in the order 1, 2, 3, 4 and 5  
5 represents that no cavities are observed by a microscope

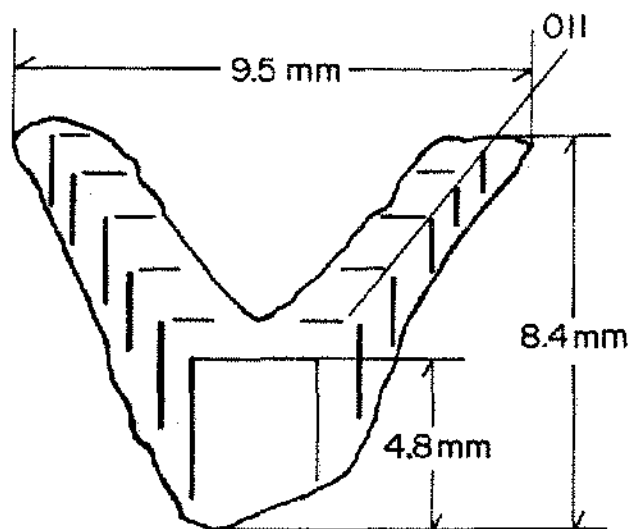


Figure 11. Layers of cavities found in solar salt crystals (1).

mother liquid of the crystallizer was saturated with magnesium salts. The magnesium ion concentration in crystals was in fair agreement with that of mother liquid, from which salt crystals deposited. This indicated that magnesium ions and water in crystals were present not as crystals but only as solution included during crystallization. Thus, in proportion to the amount of water, cube cavities are included. Just in reverse order, magnesium ion concen-

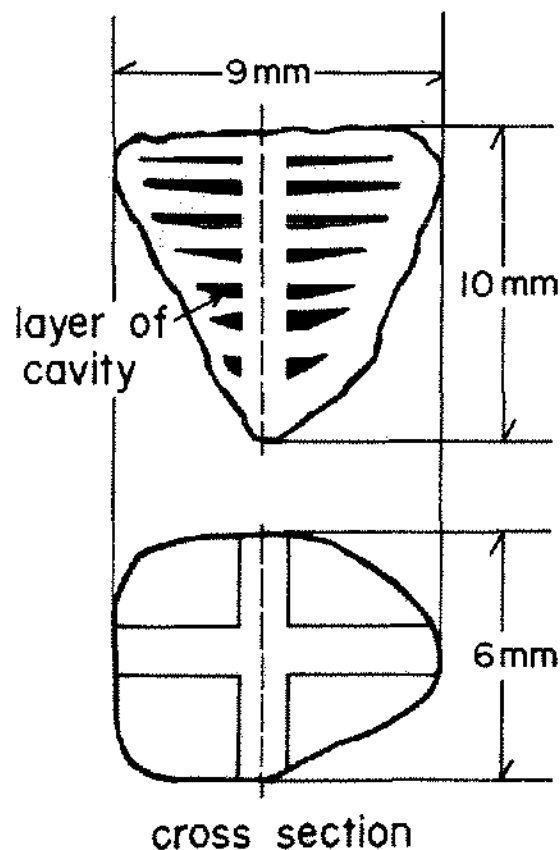


Figure 12. Layers of cavities found in solar salt crystals (2).

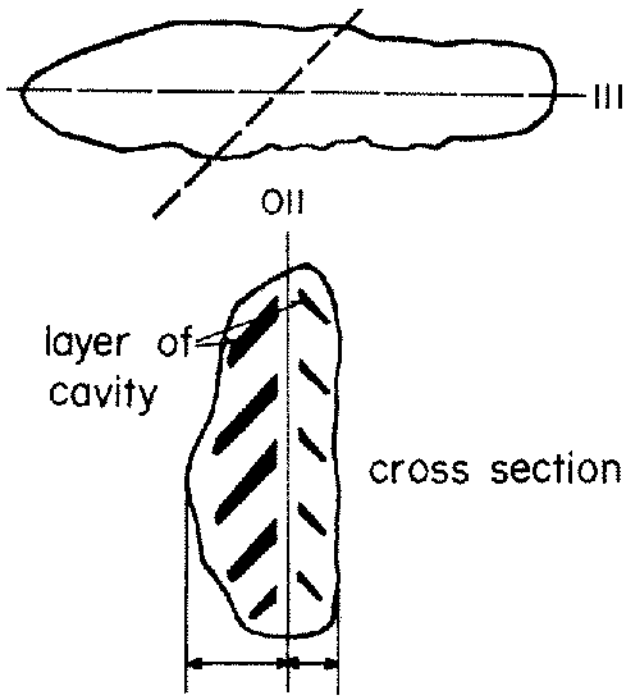


Figure 13. Layers of cavities found in solar salt crystals (3).

clearance of unit-crystals

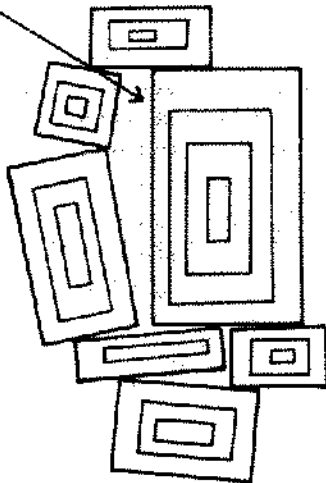


Figure 14. Clearance of solar salt enclosed by unit crystals.

tration of mother liquid could be estimated by means of magnesium ion concentration in crystals.

In addition to this fact, magnesium ions in mother liquid are related to the inclusion of cube cavities. Aqueous saturated sodium chloride containing certain amount of magnesium chloride was heated and stood at room temperature overnight. The observation of the salt crystals deposited is

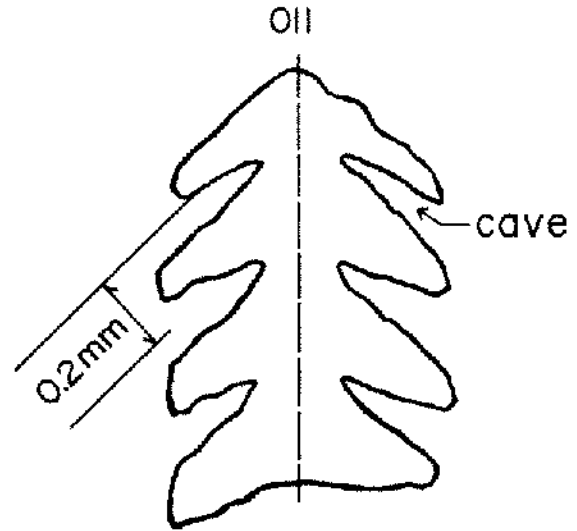


Figure 15. Caves or crevices found in solar salt crystals.

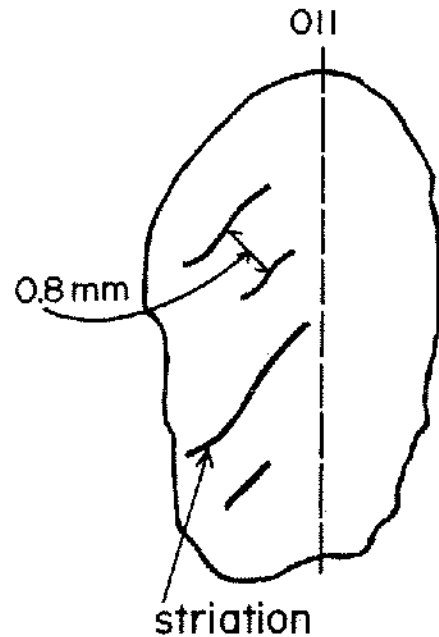


Figure 16. Striations found in solar salt crystals.

TABLE 4

Chemical Composition of Mother Liquid in Crystallizer

Method	Na	K	Mg	(g/100g) Reference
Solar	1~5	0.5~0.6	2.0~2.5	Masuzawa 1976b
Salt-field	3~6	1.2~2.2	3~6	Masuzawa 1965
Ion-exchange		2.4~4.7	1.7~3.4	Masuzawa unpublished data
Refined		0.1~1	0.003~0.01	Masuzawa unpublished data



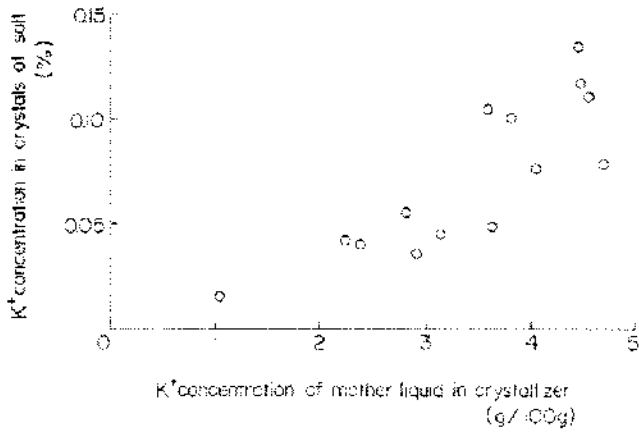


Figure 17. Relationship between K<sup>+</sup> in crystals and K<sup>+</sup> in the mother liquid of the crystallizer.

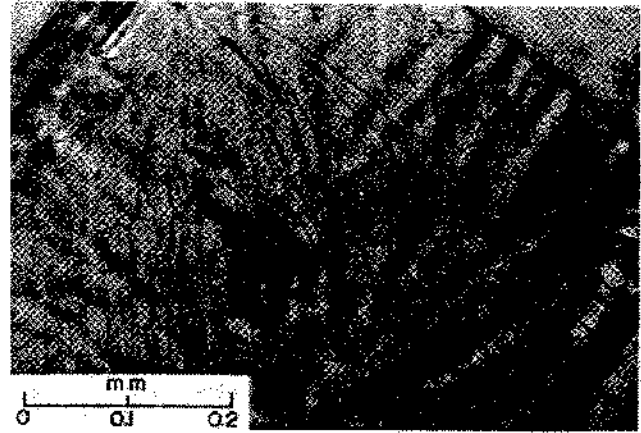


Figure 20. Cavities disposed along  $\langle 111 \rangle$  direction in vacuum evaporated salt.

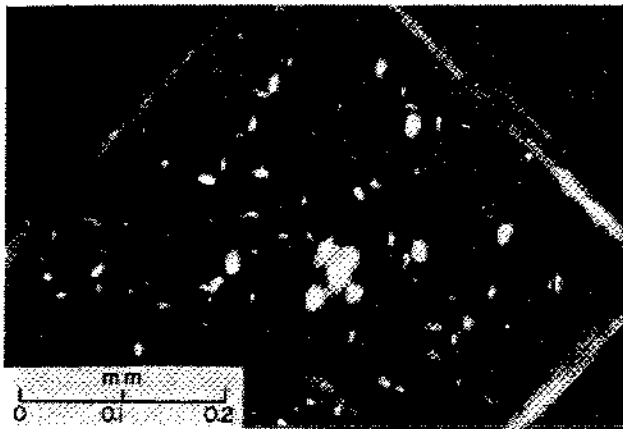


Figure 18. Calcium sulfate included in vacuum evaporated salt by ion-exchange membrane method (by orthoscopic observation).

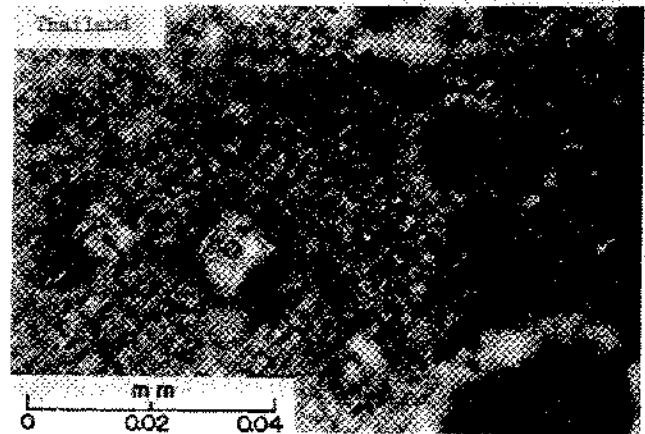


Figure 21. Cube-cavities in whole crystals of solar salt.

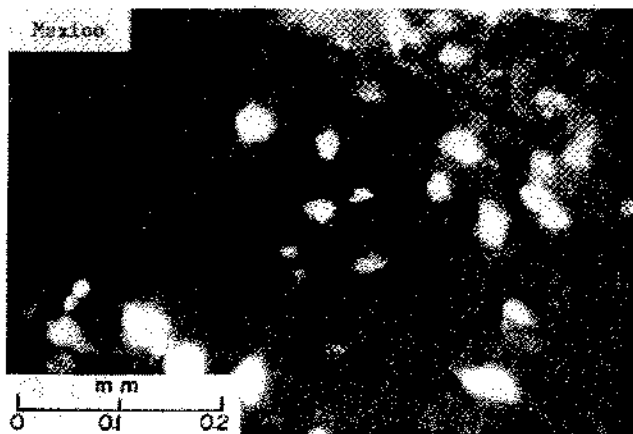


Figure 19. Gypsum included in solar salt (by orthoscopic observation).

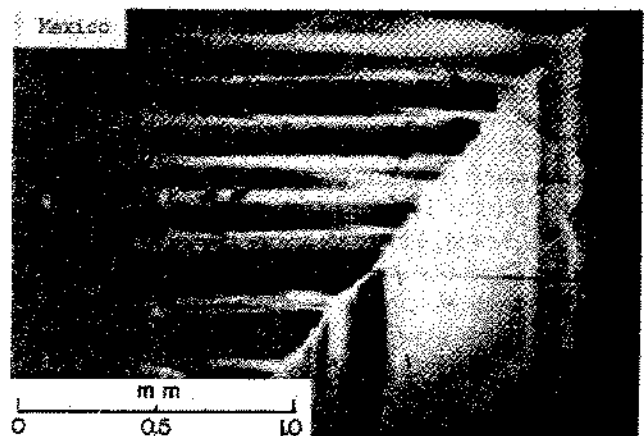


Figure 22. Layers of cube-cavities found in solar salt.

TABLE 5  
Effect of Magnesium-Ion Concentration on the Inclusion of Cavities

MgCl <sub>2</sub> %	Crystallized Salt	Cavities
0	1 mm transparent	4**
7	2~3 mm cube opaque	2 in whole crystal
12	2~3 mm cube opaque	1 in whole crystal
18	2~3 mm cube opaque	1 in whole crystal
Brine* (7)	2~3 mm cube opaque	1 in whole crystal

\*Brine from crystallizing pond of Thailand

\*\*Amount of cavities decreases in the order 1, 2, 3, 4 and 5  
5 represents that no cavity is observed by microscope



Figure 23. Crevice found in solar salt.

shown in Table 5 (Hanzawa and Masuzawa, 1962c). The results showed that the deposited crystals were large and contained more cavities as the magnesium ion concentration of the mother liquid increased. It was estimated that crystallizing pond showed the same tendency as this experiment.

**Calcium sulfate.** As far as the concentration of seawater was concerned, in the solar system, the crystalline form of calcium sulfate is gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and the amount of calcium sulfate crystallized decreases as the concentration-ratio increases. Hence, the amount of calcium sulfate included in crystals decreased. However, in vacuum evaporated system, the crystalline form of calcium sulfate was different depending on the concentration-ratio of mother liquid, circulation system of mother liquid and the temperature of crystallizers. In salt field system, such calcium salts as  $\text{CaSO}_4$ ,  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , Glauberite ( $\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$ ) and Polyhalite ( $\text{K}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) were found in mother liquid (Masuzawa, 1967) but were not yet confirmed in crystals, except single salts. Meanwhile, in the refined system such calcium salts as  $\text{CaSO}_4$ ,  $\frac{1}{2}\text{H}_2\text{O}$ ,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , Glauberite and  $2\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  were found in mother liquid (Masuzawa, 1966), but otherwise in crystals. In ion-exchange membrane system, such calcium salts as  $\text{CaSO}_4$ ,  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ,

TABLE 6  
Calcium Sulfate and Water Content of  
Vacuum Evaporated Salt by Ion-Exchange Membrane Method

Year of Production	CaSO <sub>4</sub>	(g/100g)
		Water Content
1963	0.641	0.298
1965	0.109	0.039
1966	0.329	0.076
1976	0.051	0.040

$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and sodium penta salt ( $\text{Na}_2\text{SO}_4 \cdot 5\text{CaSO}_4 \cdot 3\text{H}_2\text{O}$ ) were found, but only single salts were present in crystals. When the equivalent of calcium ions was more than that of sulfate ions, as in ion-exchange membrane system, calcium sulfate could be easily included in crystals. A typical example of the inclusion of calcium sulfate is shown in Table 6. It indicated that 0.6% calcium sulfate anhydrate was included though under such crystallizing conditions as high magnesium ion concentration and high temperature ( $130^\circ\text{C}$ ) (Yonei and Masuzawa, 1967).

In conclusion, we can safely say that the amount of calcium sulfate included in crystals depends upon the chemical composition of mother liquid, the temperature of crystallizer, suspended calcium sulfate and suspended salt crystals.

## CONCLUSIONS

Inside the salt crystals, 0.000–0.14% insoluble matter, 0.001–0.12% potassium ions, 0.000–0.20% magnesium ions, 0.000–0.13% calcium ions, 0.005–0.80% sulfate ions and 0.02–1.7% water were contained. The amount of impurities in crystals varies according to salt manufacturing method. These contents are the limit, to which the purity of salt can be increased by washing.

As for the state of impurities, potassium ions are present in NaCl lattice in place of sodium ions. While calcium and sulfate ions are included as calcium sulfate crystals, magnesium and water along with other ions are included in cube cavities as solution. In solar salts, cube cavities are included in lines and strata and the distance of strata corresponds to a daytime growth of salt crystals.

The amount and the state of impurities depend upon crystallizing conditions, the chemical composition, the temperature and the amount of suspended matters of the mother liquid, where salt crystals are deposited.

It would be of great interest to extend the study in order to reveal the mechanism of how such crystals as calcium, potassium and magnesium salts are contained and how cube cavities are formed.

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\*All the references are written in Japanese with English summary.