THE FORMATION OF MAGNESIUM-AMMONIUM-PHOSPHATE CRYSTALS IN CANNED SEA FOODS

III. The Crystallizing State of Chemically Synthesized Crystals at Various Temperatures

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In the previous paper[1], the authors have studied the solubility of chemically synthesized crystals of $MgNH_4PO_4 \cdot 6H_2O$, it was shown that the maximum solubility was at 50°C, and that the solubility became less below or above a boundary of 50°C. From this fact, the crystals are considered to be easily crystallized out at below or above 50°C. However, the crystallizing states at lower or higher temperatures than 50°C are presumed to be different.

In order to ascertain the temperature at which visible crystals generate in commerical products, the authors have observed the size and the shape of the crystals when the component ions are combined at various temperatures and then cooled to various temperatures.

1. In the case when the combining temperature and leaving temperature are the same

The component ions are combined at respective definite temperatures; the conditions of the crystals which generate and are left at the same temperature were observed.

(1) *Experimental material*

One-one hundredth Mol magnesia mixture solution which was prepared according to the method described in the foot note of this page, and 0.01 Mol sodium phosphate were made separatedly and were used for the experiment.

(2) *Experimental apparatus*

The apparatus used in this experiment was the same as the apparatus shown in the previous paper[1].

(3) *Experimental method*

Each 20 cc of 0.01 Mol magnesia mixture solution and 0.01 Mol sodium phosphate

Foot note: Magnesia mixture solution was prepared by mixing 55 g of anhydrous magnesium sulfate with 70 g of ammonium chloride in 400 cc of dist. water, to which 500 cc of 5 % ammonia water was added, and finally was added to make the total volume 1,000 cc.

This solution was diluted with water to make 0.01 Mol on the basis of the quantity of magnesium sulfate in the solution.

solution was combined in large test tubes (160 cc volume) and heated at respective temperatures from 100°C to 0°C for 30 minutes. The shape and size of the crystals generated were observed under a microscope.

(4) *Experimental result*

Photographs of the shapes of the crystals are shown as Fig. 1.

As seen in Fig. 1, the shapes of the crystals are different according to the combining temperatures. As to the boundary of 50°C, the shapes of the crystals generated above 50°C are amorphous, but the shapes below 50°C are beautiful crystals having regular faces. When those crystals are observed under a polarizing microscope, the former did not show polarized light, but the latter did. The difference of the shapes of the crystals generated above or below 50°C is considered to be connected with the maximum solubility of the crystal at 50°C as the boundary.

2. In the case of combining of the component ions at about 100°C and the leaving temperature being allowed to descend to the respective definite temperatures

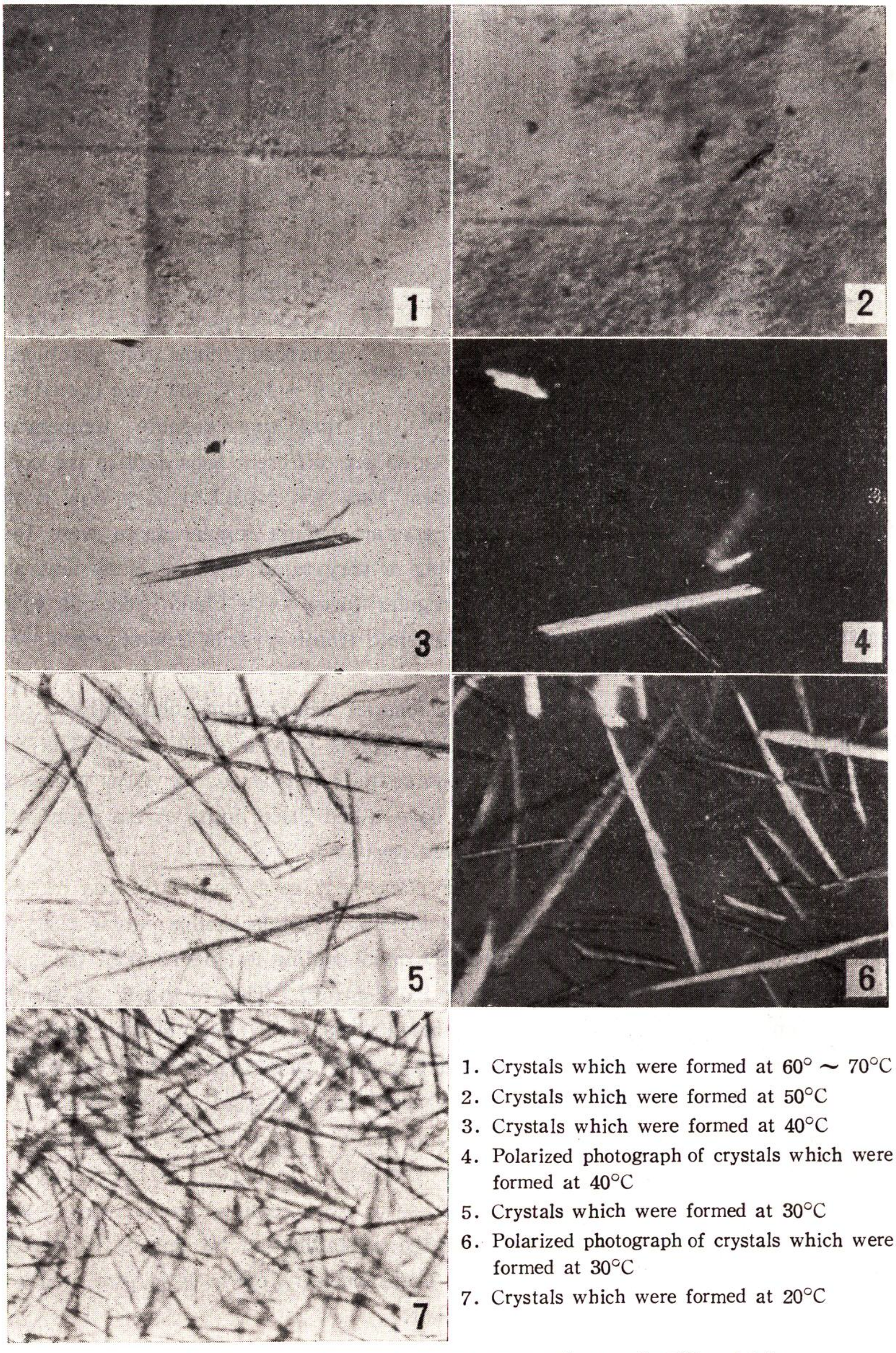
Usually when canned foods are processed above 100°C, the component ions of the struvite in the content will combine and the size and the shape of the crystals generated in the canned foods are considered to change in accordance with the cooling conditions under which the temperature of the center of the canned food is changing.

Let it be supposed in the processing of the canned foods, that magnesia mixture solution and sodium phosphate solution were combined at comparatively higher temperature (at about 100°C) and the mixture was cooled to the respective definite temperature by rapid or slow coolings. The authors have observed the shape and size of the crystals generated.

(1) *Experimental method*

A heating bath shown as Fig. 1 in the previous paper[1] was kept at 98° ~ 100°C. Each 20 cc of 0.01 Mol magnesia mixture solution and 0.01 Mol sodium phosphate were poured into a large test tube which was kept at 98°~100°C. Then cold water was poured into the heating bath in order to change the velocity cooling (rapid cooling or slow cooling). The changes of shape and the size of the crystals are influenced by cooling temperatures and cooling velocities were observed.

"Rapid cooling" means the cooling velocity occurring when the canned foods are cooled in cooling tank water after the processing. "Slow cooling" is the velocity in cooling by electric fun. These cooling velocities are regulated in accordance with the practical cooling of canned foods. Moreover, "very rapid cooling" means to cool the test tube rapidly in running city water after combination of both component ions without



1. Crystals which were formed at 60° ~ 70°C
2. Crystals which were formed at 50°C
3. Crystals which were formed at 40°C
4. Polarized photograph of crystals which were formed at 40°C
5. Crystals which were formed at 30°C
6. Polarized photograph of crystals which were formed at 30°C
7. Crystals which were formed at 20°C

Fig. 1. Shapes and sizes of crystals generated at 100°~0°C and left at the same temperatures

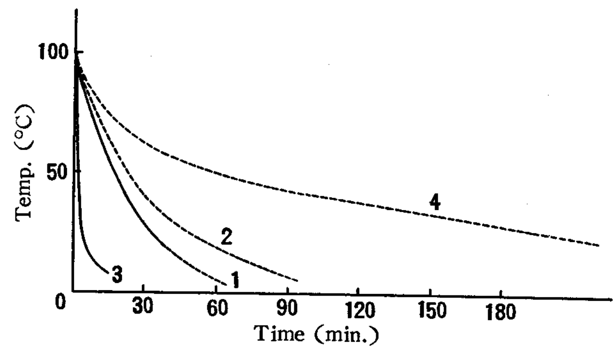


Fig. 2. Cooling velocities of the combined component ions
1: Rapid cooling 2: Slow cooling
3: Very rapid cooling 4: Very slow cooling

accordance with the cooling velocity of processed cans. "Very slow cooling" is to cool the test tube slowly by leaving it in the air.

(2) *Experimental result*

The results obtained are shown in Table 1.

As seen in Table 1, when the component ions were combined at 98° ~ 100°C and were cooled to the respective definite temperatures, the size and the number of the crystals generated are different according to the cooling velocities. When the mixture of the component ions was cooled by very slow cooling, a few amorphous crystals and a few large crystals having regular faces were found. When the mixture was cooled by rapid cooling or very rapid cooling, many amorphous crystals and many small crystals having regular faces were found. That is to say, when the mixture is rapidly cooled, many invisible small crystals having regular faces are found.

It is important that when the component ions are combined at comparatively higher temperatures and are cooled, the size of the crystals formed at 50° ~ 30°C is larger than those at below 20°C; the number of the crystals having regular faces is less than those at other temperatures. The authors have called those limits of the temperature, 50° ~ 30°C, **"Zone of the formation of large crystals".**

In the case of rapid cooling, when the component ions were combined at 98° ~ 100°C and were cooled to below 20°C, small invisible crystals having regular faces were found. The size of the crystals generated by rapid cooling is smaller than the size of those by slow cooling, but the number is the contrary. That is to say, in the slow cooling, when the component ions were combined at 98° ~ 100°C and then were cooled to any temperatures, a few pretty large visible crystals were found. In short, when the crystals generated have rapid temperature changes, the change of supersaturation of the solution becomes large. Therefore, the crystallization become rapid, the growth of the crystals generated becomes small, then it is reasonable to expect to find many small crystals. However, on the contrary, in the case of slow cooling, the change of supersaturation of the solution becomes small; then the crystallization becomes slow, therefore a few crystals generated becomes nuclei. These nuclei grow to large size, and a few large shaped crystals may be expected to result.

Table 1. *The shapes and sizes of crystals which were generated at 98°～100°C and the leaving temperature were allowed to descend to the respective temperatures*

Cooling method	State of the crystals \ Temperature change	100°→70°C Size (μ)	100°→70°C Number (per 0.1 mm³)	100°→50°C Size (μ)	100°→50°C Number (per 0.1 mm³)	100°→40°C Size (μ)	100°→40°C Number (per 0.1 mm³)	100°→30°C Size (μ)	100°→30°C Number (per 0.1 mm³)	100°→20°C Size (μ)	100°→20°C Number (per 0.1 mm³)	100°→10°C Size (μ)	100°→10°C Number (per 0.1 mm³)
Rapid cooling	Amorphous	1 × 1	many	1 × 1	many	1 × 1	many	1 × 1	many	1 × 1	few	1 × 1	few
	Crystals having regular faces	14×7 ～40×14	15	16×8 ～150×25	20	16×8 ～149×30	25	16×8 ～150×33	24	13×7 ～16×57	65	13×3 ～57×8	73
Slow Cooling	Amorphous	1 × 1	many	1 × 1	many	1 × 1	many	1 × 1	many	1 × 1	few	1 × 1	few
	Crystals having regular faces	16×8 ～50×3	13	33×8 ～82×16	15	49×8 ～82×16	15	41×16 ～150×49	13	49×16 ～120×49	20	49×16 ～310×49	22
Very rapid Cooling	Amorphous	1 × 1	many	1 × 1	many	1 × 1	many	1 × 1	many	1 × 1	few	1 × 1	few
	Crystals having regular faces	8×3 ～33×16	7.5	8×3 ～33×16	30	33×16 ～40×16	20	16×3 ～33×8	25	8×3 ～25×8	45	8×3 ～25×8	55
Very slow Cooling	Amorphous	1 × 1	few	1 × 1	few	1 × 1	few	1 × 1	few	1 × 1	few	1 × 1	few
	Crystals having regular faces	8×8 ～82×25	9	49×16 ～110×33	7	8×8 ～49×8	20	98×16 ～180×16	6	49×16 ～180×33	13	49×16 ～450×33	10

Summary

In the crystallization of $MgNH_4PO_4 \cdot 6H_2O$, when the component ions are combined above 50°C and left, amorphous crystals generate. But when the combination is done below 50°C and when the generated crystals are left undisturbed, crystals having regular faces are found. On the contrary, in the case of combination at 98° ~ 100°C, when the leaving temperature is 90°C, amorphous crystals, and when the leaving temperature is 70°C, a few crystals having regular faces as well as many amorphous crystals are found.

Visible crystals having regular faces are found only when the combination is done at 98° ~ 100°C and temperature is allowed to descend to below 50°C. The crystals formed at 50° ~ 30°C are larger than those at other temperatures. The authors have called those limits of the temperature, the **"Zone of the formation of large crystals"**. The size of the crystals generated by rapid cooling is smaller than that by slow cooling; the former are more abundant than the latter. The more rapid the cooling velocity, the smaller are the crystals which generate. This fact suggests a method for making the crystals of struvite in the canned foods invisibly small.

Literature cited

1) Tanikawa, E. *et al.* (1957). *Bull. Fac. Fish., Hokkaido Univ.* 7 (4), 300–305.