



Title	THE FORMATION OF MAGNESIUM-AMMONIUM-PHOSPHATE CRYSTALS IN CANNED SEA FOODS : The Growth of the Crystals of $MgNH_4PO_4 \cdot 6H_2O$ in Glass Vessel
Author(s)	TANIKAWA, Eiichi; NAGASAWA, Yoshio; SUGIYAMA, Takashi
Citation	北海道大學水産學部研究彙報, 8(1), 69-73
Issue Date	1957-05
Doc URL	<a href="http://hdl.handle.net/2115/22988">http://hdl.handle.net/2115/22988</a>
Type	bulletin (article)
File Information	8(1)_P69-73.pdf



[Instructions for use](#)

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

### V. The Growth of the Crystals of $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ in Glass Vessel

Eiichi TANIKAWA, Yoshio NAGASAWA and Takashi SUGIYAMA  
*Faculty of Fisheries, Hokkaido University*

If the respective chemical constituents of the struvite are existing in amounts over a definite (minimum) quantity in canned sea foods, the constituents will combine with each other in the juice as a result of heating (sterilization), and some nuclear crystal will be formed. The nuclear crystals<sup>1)</sup> will grow to visible size, if surrounding factors, *e. g.*, temperature, the concentration of the solution, pH, etc. are kept in the suitable condition.

As the growth of the struvite in the canned foods will be influenced by various intricate factors, it is difficult to clear up the mechanism of the formation. Therefore, the authors have at first tried to find out the formation of  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  in the true solution in glass vessel.

#### 1. In the case of storing of the mixing solution without heating

##### (1) *Experimental method*

After each solution<sup>2)</sup> of A and B was mixed, the mixture was kept in a thermostat of  $37^\circ \pm 1^\circ\text{C}$ . The size and form of the crystals which formed were observed on every other day. For the observation, 0.05 cc of the solution was taken onto a slide glass by glass tube, and size and shape of the crystals were observed under a microscope three times for each observation to obtain the averaged values.

##### (2) *Experimental result*

Results obtained are shown in Table 1.

As seen in Table 1, it is evident that there is a relation between the change of the form and size of the crystals at the time of the storing of the mixed solution and the rate of mixing the solutions.

The shape of the crystals formed in the slowly (within two minutes) mixed solution did not change even if the crystals were stored for a long time; on the other hand, the shape of the crystals formed in the instantly mixed solution changed during the storing.

The size of the crystals formed in mixtures at both rates increased with aging. Further, as seen in Table 1, the conditions of the aging and the growth of the crystals vary by the concentrations of the solution. The higher the concentration of both solution, the greater is the number of floating crystals on the surface of the solution. The crystals formed from the mixed solution of 0.01 Mol (0.0122 % of Mg) and 0.02 Mol

(0.0224 % of Mg) appeared at the bottom of the Petri-dish after 80 ~ 120 hrs.

The amount of Mg in the mixed solution of 0.01 Mol ~ 0.02 Mol corresponds to the minimum amount of Mg in the pickle of canned crab. The fact that there are many struvites in the bottom of the canned crab which is covered with pickle is perhaps due to the same causes.

Next, it was undertaken to observe the form of the crystals grown during the storing. The arborescent crystals formed at the initial period of the storing collapse gradually and divide into small crystals during long storing time. As time goes on, the divided crystals gradually become shaped ones. This may be considered to occur as follows: the phenomenon of dissolution will occur partially on the surfaces of the divided crystals and the partly dissolved crystals will be recrystallized to form the regular shape.

## 2. The growth of the crystals formed in the mixed solution during the storing after heating

### (1) Experimental method

Each 5 cc of solutions<sup>2)</sup> A and B of concentrations 0.2~ 0.005 Mol were mixed with each other. Each mixed solution was heated at 109.9°C for 2 hrs., like the sterilization of canned crab and cooled gradually at room temperature, then stored for 25 days. The visible crystals which formed were observed.

### (2) Experimental result

Results obtained are shown in Table 2.

Table 2. Change in the crystal during the aging after the heating of the mixture of the component ion

Concentration of the reagents (Mol)		0.2	0.1	0.05	0.033	0.025	0.02	0.01	0.005
The ratio of each components	Mg (%)	0.153	0.075	0.038	0.025	0.018	0.015	0.0075	0.0038
	PO <sub>4</sub> (%)	0.207	0.103	0.052	0.035	0.026	0.021	0.010	0.0052
	NH <sub>3</sub> (%)	0.093	0.047	0.023	0.016	0.012	0.0093	0.0047	0.0023
Visible crystals		+	+	+	+	+	+ -	- +	-
Microcrystals		+	+	+	+	+	+	+	+
Form of the crystals		A E	1000~ 2000 × 3000 D'	3000~ 5000 × 8000 D'	500~ 1000 × 1000 C		126 × 63 D E	60 × 20 D E	20 × 6 C

Note: Signs which are described in this table show the states of the formed crystals as follows.

A=arborescent C=columnar crystal D=columnar crystal separated  
D'=rather large columnar crystal E=amorphous

Table 1. Changes in the crystal of  $MgNH_4PO_4 \cdot 6H_2O$  during growing

Concentration of the solution		0.4 Mol		0.2 Mol		0.1 Mol		0.05 Mol		0.02 Mol		0.01 Mol		0.005 Mol		0.0025 Mol		0.001 Mol		0.0005 Mol		0.0001 Mol	
Leaving time	Adding time State of the crystal	Instant	2 Minutes	Instant	2 Minutes	Instant	2 Minutes	Instant	2 Minutes	Instant	2 Minutes	Instant	2 Minutes	Instant	2 Minutes	Instant	2 Minutes	Instant	2 Minutes	Instant	2 Minutes	Instant	2 Minutes
		0	Size ( $\mu$ )	18×1.3	63×2.5	14×2.5	25×2.5	120×2.5	126×2.5	92×1.5	330×1.3	54×1.3	239×1.3	59×0.9	63×1.0	40×2.2		24×7.6		37×2.7		57×3.8	
Form	A F		A B	A B	A B	B A	B	B C	C B	C	C	C	C	C E		C		C		E		E	
24	Size ( $\mu$ )	18×1.3	50×2.5	57×6.3	25×2.5	63×3.0	55×2.5	76×1.9	170×1.3	69×1.3	190×1.3												
	Form	C	A	A	A	B	B	B	C B	C	C												
72	Size ( $\mu$ )	25×6.3	12×6.3	63×10	31×4.5	63×3.0	38×2.5	76×1.9	200×1.3	88×1.3	190×1.3	142×14.3	180×28.4	30×8.2		40×12		41×16		38×16			
	Form	C	C	C	C	C B	C	B	C B	C	C	C	C	C E		C		C		C			
100	Size ( $\mu$ )	25×6.3	19×6.3	63×10	38×5.0	60×3.0	38×2.5	120×2.0	200×1.3	95×2.3	130×1.3	208×17		56×13		52×13		51×16		14×16			
	Form	C	C	C	C	C B	C	C	C B	C	C	C		C E		C		C		C			
120	Size ( $\mu$ )							126×2.0	200×1.3	76×1.9	130×1.3	200×26	170×34	42×25		52×13							
	Form							C	C B	C	C	C	C	C E		C							

Note: Signs which are described in this table show the states of the formed crystals as follows.

A=arborescent B=broad blanches C=columnar crystal E=amorphous

As seen in Table 2, the minimum amount of Mg, by which the visible crystals can be formed, is above 0.015 % Mg, *i.e.*, 0.02 Mol of each solution. This substantiates positively the results reported in previous paper II<sup>2)</sup>. In the more diluted solutions (0.0038 % of Mg), a few microscopical crystals whose sizes are about  $20 \times 60 \mu$  are formed.

As stated in previous paper II<sup>3)</sup>, if Mg exists to an amount more than 0.0025 % in the mixed solution, the microscopical crystals are observed to begin to appear at about 25°C.

In both cases of the mixed solution heated or unheated, the size and number of the crystals formed differ from the concentration of the mixed solution rather than from heating. The higher the concentration is, the smaller in size and the more in number are the crystals. In the higher concentration of the mixed solution, the crystallization is more rapid, therefore the crystals are many and floating.

In the solution of the concentrations of 0.02 Mol ~ 0.01 Mol, the crystals attached to the side wall of Petri-dish generated after 80 ~ 120 hrs. In those solution, each chemical constituents exist saturatedly according to temperatures. Therefore, the constituents combine with each other and some solid crystallize out by a medium of a part of side wall of the dish as nucleus, and then the nuclear solid will grow gradually.

The comparatively more regular form of the crystals will generate and grow from the concentration of 0.02 ~ 0.01 Mol at about 37°C.

From the agreement of the amount of Mg employed in the above described experiment with the amount of Mg in the pickle of canned crab, and the storing temperature after the processing being 30° ~ 40°C in holds of floating canneries, it may be stated that nuclear crystals attaching to the inside wall of can container or to the surface of the crab meat generate and grow to become struvites. When the conditions of the formation are suitable, the struvites grow much larger. During the aging of the crystals formation, the crystals having coarse surfaces dissolve once, because of the difference of the solubilities at different temperatures and then the regular surface of the crystals will be completed by the mechanisms as above stated.

### 3. The influence of temperature upon the growth of the crystals which have been formed by different cooling velocities and were left at different temperatures

In the previous paper<sup>2)</sup>, the shape and size of the crystal were observed to be different according to the velocity of cooling. Here the changes of the growth of the crystals which have been formed by different velocities of cooling were observed under different storage temperatures.

#### (1) *Experimental method*

In order to experiment on the formation of the crystals under similar conditions

to those pertaining in the canned food juice, 0.05 Mol magnesia mixture solution and 0.05 Mol sodium phosphate solution containing 1% pepton were prepared. Each 5 cc of the two solutions were mixed in 4 separate large test tubes. In each mixture, pepton was added to 0.5 %. The 4 test tubes containing the mixture solutions were heated at 5 lbs (108.4°C) for 90 minutes. Each two test tubes were cooled by rapid or slow cooling as previously defined. After cooling, one of the two test tubes was kept at room temperature (15° ~ 20°C) and the other was kept at 37°C, respectively. At definite intervals the shape and size of the crystals which were formed in the respective 4 test tubes were observed under microscope.

### (2) Experimental result

The results obtained are shown in Table 3.

Table 3. Change in the size of the crystals which were left at various temperatures after the crystallization at various cooling velocities

Cooling Leaving days	Left at room temp. after rapid cooling	Left at room temp. after slow cooling	Left at 37°C after rapid cooling	Left at 37°C after slow cooling
0	32 × 8 ~ 130 × 16	36 × 8 ~ 250 × 80	36 × 8 ~ 110 × 20	49 × 16 ~ 130 × 16
3	49 × 25 ~ 320 × 98	49 × 32 ~ 2200 × 410	25 × 16 ~ 800 × 250	65 × 32 ~ 750 × 410
10	32 × 16 ~ 370 × 98	58 × 80 ~ 1500 × 580	32 × 16 ~ 1000 × 320	32 × 16 ~ 1500 × 510
20	32 × 16 ~ 490 × 250	32 × 25 ~ 2600 × 450	32 × 16 ~ 950 × 290	49 × 49 ~ 880 × 250
30	49 × 32 ~ 490 × 260	49 × 32 ~ 2600 × 560	32 × 16 ~ 960 × 320	98 × 65 ~ 980 × 490
60	49 × 32 ~ 720 × 320	49 × 49 ~ 2500 × 800	32 × 16 ~ 1300 × 490	112 × 65 ~ 1280 × 560
90	32 × 32 ~ 980 × 450	98 × 82 ~ 2600 × 500	49 × 49 ~ 1300 × 490	98 × 65 ~ 1400 × 560

As seen in Table 3, the size of the crystals which were formed by rapid cooling are smaller than that by slow cooling.

When the formed crystals were kept at room temperature or at 37°C, the size of the crystals which were small because of rapid cooling did not become larger than that those resulting from slow cooling, even if the small crystals were kept at higher temperature (37°C). That is to say, if the size of the crystals which are of comparatively larger size at the initial generation continue so, in comparison with those which were small at the initial generation. After all, the initial size of the formed crystals is the most important factor.

### Summary

The changes in the shape and size of the crystals during storage depend on the rate of mixing of the solutions containing the chemical components, the concentration of the

solutions and the storing temperature. When the mixing of the solutions is done rapidly, the changes in the size and form of crystals are great and when the mixing is done slowly (in two minutes), the changes are slight and little.

The higher the concentration of the mixed solution is, the smaller the size and the larger the number of the floating crystals. From the more dilute solution, a less number of larger crystals attaching to the inside wall of the container generate. The same results were obtained from the heated mixed solution.

When the mixture solution of the component ions is heated and then cooled, the size of the crystals formed is different from those formed at different cooling velocities. If the mixture is rapidly cooled, the size of the crystals is small and the number is great. And if the mixture is slowly cooled, the size is larger and the number is a few. When those crystals which have been small are stored, their size does not become larger than the crystals which have been formed originally in larger size.

That is to say, the increase of the size of the crystals is principally influenced by the initial size of the crystals formed.

#### Literature cited

- 1) Kobayashi, K. (1949). *J. Chem. Soc. Japan* 70 (2), 179.
- 2) Tanikawa, E. et al. (1957). *Bull. Fac. Fish., Hokkaido Univ.* 8 (1), 65 - 68.
- 3) Tanikawa, E. et al. (1957). *Ibid.* 7 (4), 330 - 305.