Studies on the Water-Settable Cement

Part 11. Preparatory Experiments on Water-settable Phosphate Cement and Properties of Water-settable Primary Calcium Phosphate

by

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Introduction

In Part 1 to 5[1–5], prior to the exploitation of a new type water-settable cement, the authors closely examined the setting mechanism of zinc phosphate cement on the market, and as the result arrived at a very epochal and important conclusion as follows: the setting of this cement is, due not to the formation of secondary or tertiary zinc phosphate crystals through reaction of zinc oxide and phosphate acid, which has hitherto been widely believed to be the cause[6–15], but to the fact that through reaction of the above-mentioned two components, tertiary zinc phosphate $[\text{Zn}_3(\text{PO}_4)_2]$ is first of all formed. Then its solution occurs with water formed at the same time or already existing in the reaction system as dispersion medium, and after supersaturated, gelation is induced and finally it is cured. The setting product gradually crystallizes with water existing among gells, and turning into the stable tertiary zinc phosphate crystals $(\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O})$, becomes harder. Morimoto[16], from this theory of setting, foreboded the existence of water-settable tertiary zinc phosphate (water-settable normal zinc phosphate), and with much effort, succeeding in discovering it, substantiated the theory.

In Part 6 to 9[17–21] in order to get to the above-mentioned conclusion the authors closely examined the conditions of formation of primary zinc phosphate, secondary zinc phosphate and tertiary zinc phosphate, and pointed out, “Tertiary zinc phosphate is formed in all the reaction ranges of the water solutions of zinc and its compounds, phosphoric acid and its compounds and phosphoric acid and its salts, and in these cases pH values are always on the acid side”. Then, to the tertiary zinc phosphates formed under various conditions, such methods as microscopy, thermal analysis and x-ray diffraction were repeatedly applied, and finally succeeded in discovering the expected water-settable tertiary zinc phosphate. It was made clear that

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the tertiary zinc phosphate, formed by the following chemical equilibrium, had water-settability.

(chemical equilibrium in the primary zinc phosphate water solution)

Again it was made clear that there were differences in physical properties between the water-settable tertiary zinc phosphate and non-water-settable normal tertiary zinc phosphate as follows:

1) The existence of twin crystals, which is very rare in orthorhombic system was confirmed in the case of the water-settable tertiary zinc phosphate.

2) According to the differential thermal analysis the crystals of the water-settable tertiary zinc phosphate are much dehydrated at the range of temperature, higher than 200°C, while in the case of non-water-settable zinc phosphate, the dehydration is remarkably done at the lower range of temperature.

3) According to x-ray diffraction, in the case of water-settable tertiary zinc phosphate, the crystal lattice planes ($2\theta = 11.1^\circ$), newly formed by dehydration at around 210°C, are stable, while in the case of non-water-settable one, changes are observable on crystal planes. Furthermore, in dehydration at 380°C, there exists two kinds of crystal planes, $2\theta = 11.1^\circ$ and $2\theta = 12^\circ$, in the former case, while in the latter case, there exists $2\theta = 12^\circ$ crystal planes only.

4) In both cases crystals after cured are of tetrahydration of the tertiary zinc phosphate, but the crystals of the former are well developed as compared with those of the latter.

In Part 10[21] with water-settable tertiary phosphate as base material, a trial product of water-settable cement was prepared as the first step, whose properties were made clear as follows:

1) The base material, water-settable tertiary zinc phosphate, whose pH value indicates that it is nearly neutral, has no injurious effect (merit).

2) As it is insoluble in water, the strength of the cured material is not lowered in water (merit).

3) No heat is generated when it is cured. Therefore, there is no fear of injurious effect of the heat, and it has very small dimensional change when cured (merit).

4) Because it is water-settable, its manipulation is simple and safe (merit).

5) The water-settable tertiary zinc phosphate is stable in the air. Therefore, no transmutation occurs during storage (merit).

6) Its producing conditions are comparatively complicated, and a considerably highly skilled technique is required for its production (demerit).

7) The strength changes to a great degree with the change of molding pressure. This is not always disadvantageous to industrial use, but inadequate for dental use (demerit).

8) It has weaknesses both in the degree of film and viscosity (demerit).

Among the above-mentioned 8 items 1) to 5) can be considered to be excellent characteristics which the old zinc phosphate cement has never had, but the trial

product is not considered adequate for dental use until the demerits, items 6) to 8), especially, item 8), are solved.

As mentioned above the water settable zinc phosphate cement with water-settable tertiary zinc phosphate as base material shows many remarkable characteristics as compared with the old zinc phosphate cement which is used, kneaded together with phosphoric acid water solution. But still there remain the serious demerits. However further improvement on this trial product of water-settable zinc phosphate cement will make it possible to produce a water-settable cement suitable for clinical application. From this viewpoint, the following studies are attempted.

Preparatory Experiments

As stated above, water-settable tertiary zinc phosphate is formed by chemical equilibrium in the primary zinc phosphate water solution. The following preparatory experiments are attempted for the purpose of preparing new water-settable cement with this primary zinc phosphate regarded as starting point.

1) Primary zinc phosphate solution, prepared by adding 3 moles of phosphoric acid to 1 mole of tertiary zinc phosphate, was condensed and crystalized at room temperature under reduced pressure. Then the crystals of primary zinc phosphate were dried in a 80°C thermostat for one hour, and phosphoric acid sticking to the crystals was removed by acetone washing. With this primary phosphate, the calculated amount of powdered clinker of zinc oxide was mixed and then the mixture was kneaded together with water, added at the water-powder ratio of 12/100. A strong setting product of cement was then obtained after 10 minutes through approximately the same process as seen when the old zinc phosphate cement was kneaded.

2) In order to examine whether the chemical equilibrium in the primary phosphate water solution can be obtained by use of other metallic salts than zinc salt, the same experiment was carried out by use of primary calcium phosphate $[\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}]$ [22] on the market instead of primary phosphate used in 1). As the result it was cleared that though the setting time became longer, approximately the same setting product as produced in 1) was obtained after 30 minutes.

3) Primary calcium phosphate, dehydrated for 30 minutes at 250°C (at around this temperature the salt is translated into acid calcium pyrophosphate) was kneaded together with other components at the same mixing ratio used in 1) and 2). After 5 minutes it was hardened into set product of superior quality after showing approximately the same viscosity as of the old zinc phosphate cement.

From the results of preparatory experiments it was made clear that by using primary phosphate, especially, primary calcium phosphate on the market, as base material, a water-settable phosphate cement could be easily produced.

Accordingly, primary calcium phosphate, dehydrated by heating, was used as the base material of a water-settable phosphate cement, and the effects of heating conditions on the compressive strength was examined.

Materials and Methods

I. Materials

1) Primary calcium phosphate

Primary calcium phosphate of the best quality on the market was adopted.

2) Zinc oxide clinker

88% zinc oxide, 8% magnesium oxide, 3% calcium fluoride and 1% bracic acid were well mixed in a mortar. Then the mixture, after being compressed and molded by a compressor, was sintered in electric furnace at 1,320°C. The sinter was pulverized at first roughly, then finely with a porcelain ball mill, 10 cm in diameter, for 30 hours, and it was used as clinker.

II. Apparatus

For measurement of the compressive strength, Tokyo Kooki Co., lever-type material tester (maximum load, 1 ton) was used. Test material was fixed at 6 mm ϕ x 12 mm in dimension, in accordance with JIS.

III. Experimental methods

Effects of dehydration temperature and time on the compressive strength of primary calcium phosphate.

The change of the compressive strength, corresponding to the dehydration temperature ranging from 170°C to 250°C was measured, and the effect of dehydration time on the compressive strength was examined in each case of 30 minutes and 60 minutes.

Experimental Results

Of primary calcium phosphate, Fig. 1 was prepared with the heating dehydration temperature (°C) as the x coordinate axis and the compressive strength (kg/cm²) 24 hours after mixing as the y coordinate. The solid line graph shows the change of compressive strength when dehydrated for 30 minutes at every dehydration temperature, and the dotted line graph shows the change of strength when dehydrated for 60

Fig. 1 Effect of dehydration temperature and time on the compressive strength

Fig. 2 D.T.A. of primary calcium phosphate

minutes at every temperature. For the measurement of temperature a mercury thermometer was used, directly inserted into the test material. As cleared in Fig. 1, the most suitable temperature for heat dehydration is presumed about 230°C from the fact the viewpoint of compressive strength. Judging from the fact that the 60 minutes dehydration shows higher values of the compressive strength than 30 minutes dehydration, it is considered desirable to spend enough time in dehydration. The dehydration temperatures shown above were the temperature of the test material directly measured, and the atmosphere temperature in the furnace, when the temperature of the test material read 230°C, was 250°C.

Discussion and Summary

From the results of the experiments it was made clear that the heat dehydration temperature at which the compressive strength became highest was around 230°C in the inner part of the test material, that is, the temperature at which primary calcium phosphate was about to be translated into acid calcium pyrophosphate ($\text{CaH}_2\text{P}_2\text{O}_7$), as presumed from the fact that the atmosphere temperature in the furnace at this very time was 250°C.

From reaffirmation of this point, the differential thermal analysis of primary calcium phosphate was performed. The results are given in Fig. 2. Graph A shows the heating temperature curve (°C), graph B, the endothermic curve (μV) and graph C, the heating loss curve (mg). From these results it can be presumed that the above assumption was right. Again, when the temperature rises more than 230°C, the compressive strength remarkably decreases, and at the same time the setting velocity also lowers remarkably. These phenomena are presumably due to the translation of acid pyrophosphate into pyrophosphate.

As stated above, the compressive strength of the water-settable cement is much effected by the conditions of heat dehydration, and the compressive strength of this trial product, at its maximum, can be favorably compared with that of the dental zinc phosphate cement which has hitherto been widely used. Therefore, the authors will further report on the properties of this kind of cement.

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