

STUDIES ON THE SETTING PHENOMENA OF THE  
PLASTER (PART I)  
INTRODUCTION, PREPARATION OF MATERIAL  
AND METHOD OF EXPERIMENT

BY

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INTRODUCTION

It was an old history that the plaster was recommended to the world as an industrial material.

In old times the general acknowledgement for the real merits of the plaster was low, and the usage of the plaster can be said only limited to make artistic products.

In accordance with the progress of the culture, the utilization of the plaster has been highly developed, increasing its amount of consumption rapidly.

Now a days, large amount of the plaster is used for the setting rate regulating agent of the industrial cement. Furthermore as the plaster of Paris, it has also been used in many directions such as; for making original mould of China wares, adhesive use of many kinds of material, for the manufacture of artistic products, medical use in dentistry and surgery, as painting plaster, architectural materials. Especially, the plaster is greatly used for making the pattern of the parts of oral cavity, namely for taking the impressions, otherwise it has a large amount of utility for the binding material of moulding sand for the precision casting of alloys for dental use. In the process of dental precision casting, casting contraction of the metals and alloys is used to be compensated by the thermal expansion of the sand as well as the hygroscopic expansion of the plaster.

Particularly up to the date, the preciseness in casting has eagerly been demanded in dentistry, so thus it becomes very important to know correctly the characteristics of the sand being used in moulding pattern as well as the binding plaster.

As is shown in the following equation (1), the setting of the plaster is thought to be caused when the hemihydrated gypsum becomes the di-

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hydrated gypsum which is brought out by hydration, liberating a considerable amount of reaction heat, and consequently the apparent volume of the plaster itself causes an expansion.



On the way of the above reaction, should an excessive water be added, the degree of expansion would further be increased.

On the other hand, the kind of mixing solution will give complicated changes upon the setting, for instance, setting will be accelerated by mixing with a low concentrated NaCl solution, but be retarded with that of higher concentration.

If a little amount of the powder of dihydrated gypsum was added to the plaster before mixing with water, the setting rate would remarkably be accelerated.

Protective colloids such as agar agar, sodium alginate and others retard the setting rate of the plaster.

These characteristics as above mentioned have widely been utilized practically, but till now, opinions to clarify the reasons have not been consented.

The authors think that this confusion is caused probably due to the fact that the setting of the plaster shows so complicated steps and phenomena, thus the mechanism of its setting have not been clarified exactly.

The first person who had given a comparatively clear explanation on the setting phenomena of the plaster was Lechatelier<sup>1)</sup>. According to his explanation, the solubility of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  is the least in comparison with  $\text{CaSO}_4$  and  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ , so thus when  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  particles are over saturated in the water, the precipitation of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  would necessarily be taken part in the crystalline form. This explanation made up the foundation of the theory of solubility difference as well as crystal precipitation.

This theory of solubility difference is now widely supported due to the fact that we can also obtain the crystals of dihydrated gypsum by adding water to the dehydrated gypsum or calcium sulfate<sup>2)</sup>.

Notwithstanding, judging from the fact that adding of the protective colloids invites the retardation of setting, it may be supposed to be clear to have an intimate relation with the phenomena of gelation in the colloidal chemistry.

Cavazzi<sup>3)</sup> advocated the theory which manifested that  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  produced by the reaction of  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  with water showed gels state at first, and from this gels  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in crystalline form would certainly be deposited.

Traube<sup>4)</sup> had found the fact about the function of the accelerator and

the retarder of setting of plaster that solution of the salt of 0.5 N in concentration containing the cation of mono-valency showed the maximum accelerating action and the action of anion of mono-valency was weaker than that of the former, and the ranking of their activities was almost showed a coincidence with Hofmeister series.

Both Cavazzi and Traubes' theories had given the basic doctrines of the colloidal theory of today regarding the setting of the plaster. After then numerous studies were practiced by Ward, Neville, Clotz, Rolland, Ostward, Chassevent, Hansen, Allen and others and thus the ionic theory, the theory of crystal precipitation etc. were established.

Otherwise the plaster has been widely used in both dental and medical clinics, but many problems are still remained undissolved. For an instance, the problem of suffering of the patients is often seen in surgery owing to the heat liberation of the plaster when the fractured bones are fixed by it. And on the other hand, the problems of surface fixing of the alginate impression materials and the compensation of contraction of casting as above mentioned are still there in dentistry.

In view of clarifying many problems that have not been yet dissolved in dentistry and medicine, the authors wish to analyse the phenomena in the setting of plaster referencing those predecessors' reports, and in so doing, the observations of temperature rising, increasing of the hardness and the change of pH value during the process of setting will be exercised corresponding to the different kinds of mixing solution.

#### *Preparation of Material and the Method of Experiment*

##### PREPARATION OF MATERIAL

As the raw material,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  ore of high purity was employed. The raw material was crushed and it was heated in the temperature of  $130^\circ\text{C}$  during 5 hours in order to powder it into very fine particles.

In order to exclude a very little content of  $\text{CaCO}_3$  which is usually contained in the ore of gypsum, the above powders were washed by 0.01 N  $\text{H}_2\text{SO}_4$  throughly to get it back to  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  again. After then, washing was practiced throughly to exclude  $\text{H}_2\text{SO}_4$  until the electric conductivity of water showed a constant value, and then drying was practiced in  $70^\circ\text{C}$ .

The degree of drying was tested by heating a little amount of the material up to  $200^\circ\text{C}$  in order to measure the amount of produced  $\text{CaSO}_4$ .

In order to produce  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  again from the above material, heating was practiced in  $110^\circ\text{C}$  during about 15 hours.

The confirmation of thus-obtained material to test whether it was changed completely to  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  or not was practiced by weighing  $\text{CaSO}_4$

after dehydrating a given amount of  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  by heating in  $200^\circ\text{C}$  just as well in the preceding method. After then, the ripening of the material was continued in an air-tight vessel during about three months.

The normal consistency of thus-obtained material was measured as when  $W/P=90/100$ , and the setting time was observed to be about 15 minutes.

#### METHOD OF EXPERIMENT

In order to keep the surrounding temperature of the experiment in constant, an air thermostat with automatic controlling device was employed.

The experiment was practiced about the test material of 15 g in each case by mixing it during 30 seconds with the given quantity of distilled water or solutions in a rubber bowl after ascertaining the temperature of both material and liquid to be corresponding to that of the thermostat, and by pouring immediately the mixture in the slurry state onto a rubber ring, and then by observing the changes of temperature, hardness and pH value corresponding to the lapse of time.

Following items are the conditions and devices of the experiment;

- (1) The water power ratio ( $W/P$ ) was selected for the following group by referencing with the value of normal consistency.  
 $w/p=80/100$ ,  $w/p=90/100$ ,  $w/p=100/100$
- (2) The temperature of experiment was, in general, given at  $21^\circ\text{C}$ ,  $24^\circ\text{C}$ ,  $27^\circ\text{C}$ ,  $30^\circ\text{C}$  and  $35^\circ\text{C}$ .
- (3) The mixing solutions were as followings.  
(a) distilled water, (b) 0.1 N HCl, (c) 0.1 N  $\text{CH}_3\text{COOH}$ , (d) 0.1 N  $\text{NH}_4\text{OH}$
- (4) Devices of measurement.
  - (a) temperature  
A mercury thermometer was used.
  - (b) hardness  
A Shore's Durometer (Shore A) was used.
  - (c) pH  
A pH metre of glass pole system was employed with caution not to make unstable the measurements by the drying up of water on the glass poles owing to dehydrating action of the plaster.

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