STUDIES ON THE SETTING PHENOMENA OF THE PLASTER (PART VII)
COMPLEMENTARY EXPERIMENTS AND CONCLUSION

BY

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INTRODUCTION

In order to assure the understandings which were reached by the discussions of the results of preceding experiments of Part I-IV to Part VI, the authors wish to exercise complementary experiments in this report, namely inspecting the relationship between pH value and ζ-potential, observing the process of setting by microscope or polarizing microscope and others were exercised to reach a conclusion about the setting mechanism of the plaster.

COMPLEMENTARY EXPERIMENTS

1. Measurement of pH value and ζ-potential

As previously mentioned, if the setting of plaster is caused chiefly by founding upon the gelation of aqueous sols of CaSO₄·2H₂O, the setting rate should chiefly be depended on the stability of those sols.

In general, the stability of sols is determined by the electric charge of the surface of those sols, as is well known by us. Namely the more the absolute value of the charge becomes, the larger occurs the stability of those sols.

Concerning with the factor to give effect on the ζ-potential of those sols, numerous elements will be considerable, but among those elements, pH value will certainly have most intimate relation. Then the authors measured the ζ-potential being represented by the fine particles of CaSO₄·2H₂O.

It was exercised by the method of electrophoresis, namely by observing the velocity of electrophoresis by means of microscope, and then ζ-potential was calculated. As test material, fine particles of CaSO₄·2H₂O which was

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Received for Publication, July 3, 1962.
produced by the authors were employed, and as medium, 0.1 N HCl, 0.1 N CH₃COOH, H₂O and 0.1 N NH₄OH were used.

Fig. 1 illustrates the relationship between pH value and ζ-potential. The values of ζ-potential showed a considerable fluctuation, but when the values were compared to the results of the measurement of setting rate in the same temperature [Fig. 39 in Part VI⁶], they showed a satisfactory correspondence with each other.

In case of the measuring of ζ-potential, it is inevitable to put a little quantity of particles into a large amount of liquid, and the time necessitated to measure the electrophorisis is at least longer than 10 minutes, so thus the true conditions will hardly be given by the above method, the authors think.

II. Microscopic observation

In order to observe the process of setting that the deposition of gels state is first taken place and then the gels change to the crystals of CaSO₄·2H₂O, the microscopic observations were exercised as followings, by means of a microscope or a polarizing microscope.

In this case of experiment, the authors employed the material which was made by the heating in moisture and contains comparatively large scaled particles of almost the like sizes.

Fig. 2 illustrates the results obtained by means of an ordinary microscope.

It is understood by the figure that according to the lapse of time after mixing, the particles of plaster gradually change to amorphous state from their surfaces, and after about 30 minutes, the producing of acicular crystals is clearly seen among those particles.

It is thinkable that the portion which already changed to crystals will become bright in comparison with the portion of showing yet amorphous state if the cross-Nicol of a polarizing microscope would be employed.

Fig. 3 illustrates the results of experiment when the crossed-Nicol of polarizing microscope was employed.

According to those photographs, bright portion is gradually made up from the dark surface of the particles corresponding to the progression of reaction, and then bright portion of CaSO₄·2H₂O is gradually made larger from the outside of the above dark portion and also the portion in which CaSO₄·½H₂O crystals were hardly observed in the beginning.

Fig. 4 also illustrates the results of experiment when the crossed-Nicol of polarizing microscope was employed against the material of CaSO₄·½H₂O which was produced by the authors.

In this case, too, dark amorphous portion was observed in the photographs after 17 and 25 minutes from the mixing operation, and the like
dark portions were also observed by the photographs of after 30 and 40 minutes from the mixing operation.

The above experiments were exercised by employing small W/P ratios and mixing sufficiently with water in a rubber bowl. When W/P ratio was too larger or mixing operation was not sufficient, the dark portion did not be observed, but the producing of acicular crystals was observed on the surface of the particles as well as the spaces among those particles.

III. Observation by X-ray diffraction

In order to observe the processes of crystallizing of plaster, the authors practiced the observation by X-ray diffraction method.

In the above experiment, focussing method was employed, using Cu as target, Ni-foil as filter and CuKα.

The pattern illustrated in Fig. 5 was obtained about the naturally produced CaSO₄·2H₂O which was thought to be sufficiently crystallized.

According to the figure, a distinguished peak was appeared in the spacing of 7.7 Å, 2θ=11.5°.

Fig. 6 illustrates the pattern obtained about the plaster which was produced by steam burning and thought to be better crystallized. According to the figure, there appeared no peak up to 2θ=14.7°.

In the next, the observation of the growth of crystals corresponding to each lapse of time was practiced by reciprocating the test piece of plaster around 2θ=11.5°, i.e., from 9° to 14°.

Fig. 7 illustrates the results of above experiment.

The label of the time on the graph was determined when the test piece just passed through the point of 2θ=11.5°, being measured from the end of mixing operation.

According to the figure, it was understood that in the beginning, CaSO₄·2H₂O showed almost amorphous state, and then grew to crystalline form gradually corresponding to the lapse of time.

The authors calculated approximately the diameter of the particles by the following equation:

\[ L = 0.89 \lambda / \sqrt{B_0^2 - B_\theta^2 \cdot \cos \theta} \]

where \( L \) = diameter of particle

\( \lambda \) = wave length of X-ray

\( B_0 \) = thickness of half-value layer

\( B_\theta \) = thickness of half-value layer of better crystalized crystal (employed in the case of Fig. 5)

\( \theta \) = diffraction angle

The results was that the mean diameter was 46 Å in 3.5 minutes which is thought to be in the scale of colloids, and it became 229 Å in 8 minutes, but the latter result was said to be out of the utilized range of the equation.
CONCLUSION

Numerous reports were published regarding the setting phenomena of plaster, but the true mechanism was yet undetermined. This is perhaps be caused by its complicate changes owing to water powder ratio, surrounding temperature, mixed substances and the others.

Some one endeavoured to explain this by founding upon the standpoint of ionizing, the others planned to solve the same from the stand point of solubility difference, and further the others examined to give answer for this question by founding upon the gelation of aqueous sols in the domain of colloidal chemistry, but the deceive result has not still been obtained.

In order to solve such a difficult question, we must, first of all, find out the outstanding feature that will give us the key to open the unknown door by discussing and analyzing various results of experiment.

The authors reported numerous results of studies in the present series of report from Part I to Part V, and examined to discuss and analyse those results in also the reports of Part VI, and thus succeeded to find out that outstanding feature which may be expected to become the key.

It was the peculiar boundary which revealed in the surrounding temperature of about 27°C.

In the above boundary, a distinguished change was observed in pH value. Namely, owing to the observation of pH value during setting when 0.1 N NH₄OH was employed as mixing solution, it showed from about 9 to 10 in the alkaline zone in the higher temperature range of the above boundary, even though it represented a rapid descending from alkaline to acidic of about 5 within the lower temperature of the same boundary, overgoing the neutral pH zone deeply.

This peculiar boundary was, too, caught by the measuring of hardness. Namely, owing to each observation when water, 0.1 N HCl and 0.1 N CH₃COOH were employed as mixing solutions, hardening of plaster showed an unusual delaying effect just in the above boundary, so thus the graph which represented hardness-temperature curve in each time lapse showed a deep V-type valley.

Higashi, one of the present authors, had already found out the similar effect in his researches for the mechanism of setting of alginate impression materials, and he appointed that the setting of those materials was caused in the higher temperature range of the above boundary by founding on a phenomenon of gelation of aqueous sols as shown by the following equation of P.P. von Weimann,

\[ V = K - \frac{Q}{S} \]
where $V =$ gelation rate
$Q =$ total concentration
$S =$ solubility
$K =$ constant

and also appointed that in the above equation when $Q$ becomes far larger than $S$ ($Q \gg S$), the gelation rate $V$ should only be determined by concentration $Q$, and thus consequently $V$ becomes hardly affected by temperature and other conditions.

Higashi advocated that the above boundary was first found by him, and this has truly been unknown in the world, and this would perhaps be caused by founding on the problem of vapor pressure.

The authors have found the like effect in this time of the setting phenomena of plaster very clearly both in the changes of pH value as well as hardness, and thus succeeded to find out that in the higher temperature range of about 27°C, the setting of plaster should chiefly be caused by founding on the gelation of aqueous sols.

Namely, when the plaster was mixed with water, $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2 \text{O}$ becomes aqueous sols of $\text{CaSO}_4 \cdot 2\text{H}_2 \text{O}$ in the first step by absorbing $\frac{1}{2} \text{H}_2 \text{O}$ and at the same time liberating considerable heat due to reaction, and after reaching an over saturated state of those sols, it coagulates to gels which are usually enclosing unchanged $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2 \text{O}$ particles and, in this state, hardness curve reaches its first bending point $I_1$. In the state of $I_1$, the unchanged $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2 \text{O}$ particles are thought to be still largely remained and located among gels, but they begin to absorb necessary amount of water to become aqueous sols and then to coagulate to gels to form special net-like skeleton, then the second bending point $II_1$ is accomplished. In the state of $II_1$, the hardness reaches almost its peak, but after then the remained sols and the ions of calcium ($\text{Ca}^{++}$) and sulfate ($\text{SO}_4^{--}$) gradually change to precipitation of $\text{CaSO}_4 \cdot 2\text{H}_2 \text{O}$ and coat the skeleton of gels to occur a kind of recrystallization until the maximum hardness is reached ($III_1$).

Otherwise, within the boundary of about 27°C, as well be comprehended by the results of experiment in which 0.1 N $\text{NH}_4 \text{OH}$ mixing solution was employed, a rapid descending of pH value was observed. This descending of pH value is thought to be caused by founding upon the dissociation of calcium sulfate which produces stable sols in the alkaline environment into $\text{Ca}^{++}$ and $\text{SO}_4^{--}$, so thus the chemical reaction as shown in the following equation is taken place considerably in the lower temperature range,

$$\text{CaSO}_4 + \text{NH}_4 \text{OH} \rightarrow \text{Ca(OH)}_2 + (\text{NH}_4)_2 \text{SO}_4$$

and then consequently pH value occurs lowering until it is put in the acidic zone which makes the aqueous sols unstable, so thus the similar
gelation of the over saturated sols is caused as previously mentioned. Because the Ca (OH)$_2$ is apt to be very readily absorbed by CaSO$_4$·2H$_2$O gels in the lower temperature range, the above chemical reaction of producing (NH$_4$)$_2$SO$_4$ is furthermore activated, so consequently pH value shows the less than the case of mixing only with water.

The descending curve revealed in the beginning portion of temperature-time diagram is assumed to be caused by the heat absorption due to the dissociation of calcium sulfate into Ca$^{++}$ and SO$_4^{--}$.

As was already mentioned, because the setting of plaster is not only caused by founding on the gelation of aqueous sols, but also is depended upon the solubility differences which give the effects on the stability of sols and gels, as well as it is concerned with the problems of dissociation of calcium sulfate into Ca$^{++}$ and SO$_4^{--}$ or production of precipitation, it is thought to be very complicate. Notwithstanding the processes of setting of plaster are classified into two main streams, namely in the higher temperature zone of about 27°C, it is chiefly be founded upon the gelation of aqueous sols in an over saturated state, otherwise within the above temperature, the first step is the dissociation of calcium sulfate into Ca$^{++}$ and SO$_4^{--}$, the second step is the producing of CaSO$_4$·2H$_2$O, the third step is the producing of CaSO$_4$·2H$_2$O sols and the final step is the gelation of the above sols.

However, the above streams would not always occur as being so definitely separated one by one, but they are always mixed up with each other, so thus in this meaning, the works established by numerous predecessors would surely be all valuable and be recognized.

ACKNOWLEDGEMENT

The authors are very much obliged to the kind directions given by Prof. Kouemon Funaki, Prof. Raisaku Kiyoura, Prof. Kiichiro Kubo, Prof. Noboru Nagasako, Prof. Kiichiro Sugino in The Tokyo Institute of Technology and Prof. Yasuo Kanzawa in The Tokyo Medical and Dental University.

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Fig. 1. ζ—Potential—pH Diagram. Temperature: 27°C

Fig. 5. X-Ray Diffraction Pattern of CaSO₄·½H₂O.
X-Ray: CuKα
Scanning Speed: 2°/min

Fig. 6. X-Ray Diffraction Pattern of CaSO₄·½H₂O.
X-Ray: CuKα
Scanning Speed: 2°/min

Fig. 7. X-Ray Diffraction Peaks of CaSO₄·½H₂O Slurry.
X-Ray: CuKα
Scanning Speed: 4°/min
Fig. 2. Microscopic Studies on the Hydration of $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$.
Temperature: 30°C
$\times 300$
Fig. 3. Polarizing-Microscopic Studies on the Hydration of CaSO$_4$·1/2H$_2$O.
By Crossed Nicols
Temperature: 30°C
×240
Fig. 4. Polarizing-Microscopic Studies on the Hydration of CaSO₄·½H₂O.

By Crossed Nicols

Temperature: 30°C

×240