STUDY OF THE SETTING OF PLASTER

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INTRODUCTION

THIS is a report on the investigation of the volumetric and crystallographic behavior of $CaSO_4 \cdot \frac{1}{2} H_2O$ (i.e., plaster of Paris) when reacted with water or aqueous solutions of various salts. This study could lead to a better understanding of the hydration of this hemihydrate into gypsum, $CaSO_4 \cdot 2H_2O$.

It has long been known that the apparent setting expansion of $CaSO_4 \cdot \frac{1}{2} H_2O$ may be changed by the addition of certain chemicals to the slurry of plaster and water. Sodeau and Gibson[1] demonstrated that K_2SO_4 and several other potassium salts, when added in the proper proportion, will reduce the setting expansion to about 25 per cent of its normal value. No basic explanation of these observations has been given to date.

The final product in the setting of plaster consists of an interlocking mass of gypsum crystals.[2] The setting expansion depends upon the specific volume of the newly formed dihydrate crystals, the size and shape of these crystals, and the nature of the water solution remaining in the crystal mass after the plaster is set.

Van't Hoff and his co-workers[3] have pointed out that the hydration of plaster into gypsum is followed by a contraction of the equivalent volume of the crystals formed. Because of this contradiction, the sum of the volumes of the crystals of hemihydrate and the reacted water is greater than the volume of the resultant dihydrate (gypsum) crystals. Thus, the hydration of plaster of Paris at 33° C. results in a 10.9 per cent contraction in total volume, since, when 1.0 gram of $CaSO_4 \cdot \frac{1}{2} H_2O$ reacts with water, a contraction of 62.49 mm.[3] takes place.

This paper is designed to investigate the factors affecting normal and reduced setting expansion. The dilatometer experiments involve the specific volume of the crystals and the nature of the solution phase. The crystallographic studies are concerned with the effect of morphology on setting expansion.

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MATERIAL AND METHODS

The dilatometer parts *A* and *B* (Fig. 1) were kept in a water bath at a temperature of 30 ± 0.1° C. Before the several parts of the dilatometer were assembled, a weighed amount of $CaSO_4 \cdot \frac{1}{2} H_2O$ was put into flask *A* together with a plastic-covered magnet for stirring. After assembly, the dilatometer was evacuated for 15 minutes, bringing the air pressure down to 10^{-4} mm. Hg. Reservoir *D* was filled with (a) distilled water which had been boiled previously

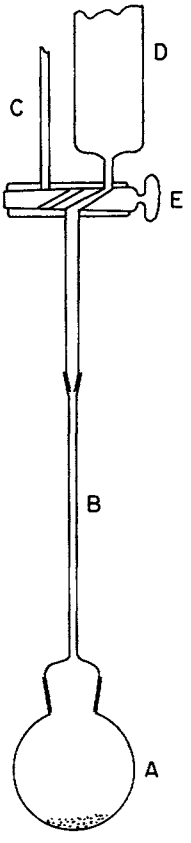

Fig. 1.—Diagram of the dilatometer used in the experiments. Flask *A* has a volume of approximately 50 ml.

to drive off air and equilibrated at 30° C. in the water bath or, (b) salt solution* made from this distilled water. The time when the stopcock *E* was opened was registered as the start of the experiment (time zero). Usually the water was allowed to run in rapidly, thus plaster and water were thoroughly mixed immediately. In some experiments the water was added slowly, so that only a minor part of the plaster was mixed with water at time zero.* After the water had filled *A* and *B*, the upper part of the instrument was removed

*The exact experimental conditions of the dilatometer experiments are given in the legends for Figs. 2, 3, and 4.

from *B*. The water level in *B* was adjusted with a hypodermic syringe and the first reading was taken. Readings of the water level in the capillary *B* were taken at suitable intervals to permit plotting of a smooth curve. The experiments usually were continued until equilibrium was reached (a minimum of 24 hours).

RESULTS AND DISCUSSION OF DILATOMETER EXPERIMENTS

The accuracy of the dilatometer was determined by a series of readings on the volume of pure water. The volume at 30° ± 0.1° C. varied less than 0.3 mm.^{3} during 75 minutes. Thus, any subsequent volume measurements reported have this accuracy limitation. Each curve plotted in Figs. 2, 3, and 4 represents a single series of readings taken periodically under the specific conditions mentioned in the figure legends.

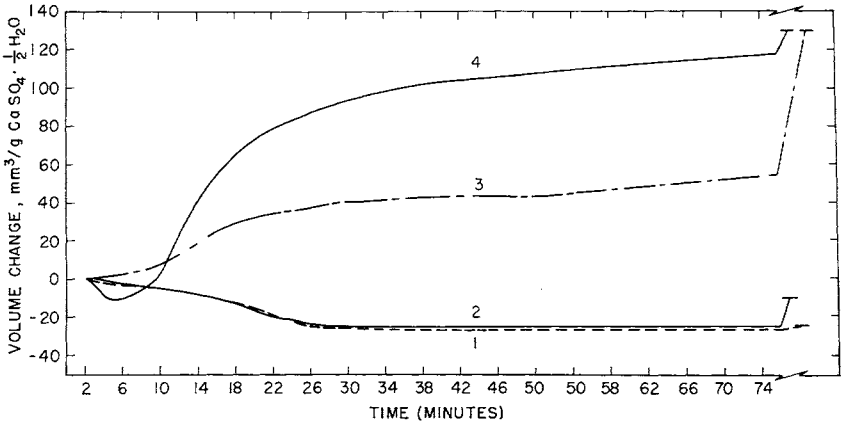

Fig. 2.—Dilatometric curves for mixtures of $CaSO_4 \cdot \frac{1}{2}H_2O$ and distilled water.
Curve 1: 5.0 grams plaster, water added slowly, no mechanical stirring after time zero.
Curve 2: 2.5 grams plaster, water added slowly, no mechanical stirring after time zero.
Curve 3: 0.5 gram plaster, water added quickly, no mechanical stirring after time zero.
Curve 4: 0.5 gram plaster, water added quickly, mechanical stirring during entire reaction.

A. *Hemihydrate and Water.*—

Fig. 2 shows the results of four dilatometric experiments in which $CaSO_4 \cdot \frac{1}{2} H_2O$ and distilled water were reacted. The volumetric changes are plotted on the ordinate in cubic millimeters per gram of $CaSO_4 \cdot \frac{1}{2} H_2O$, while the time in minutes is plotted on the abscissa. The final volume level, indicated on the right by a line, gives the volumetric change after equilibrium was attained. It is characteristic of all these experiments that the expected contraction of 62.5 mm.^{3} per gram of plaster did not occur. In experiments 1 and 2, a slight contraction did take place, although much smaller than expected, and, in experiments 3 and 4, the final results showed rather pronounced expansions.

The probable explanation of these results follows. When plaster and water are mixed at the beginning of an experiment, a solution is formed which tends to be concentrated with respect to $CaSO_4 \cdot \frac{1}{2} H_2O$. Hemihydrate dissolves very rapidly in water and this initial solution probably has already taken

place when the first reading is taken. At the end of an experiment, when equilibrium has been attained, the water still contains dissolved calcium sulfate, but at this point the concentration is dependent upon the solubility of gypsum.

When calcium sulfate is dissolved in water, there is a volume contraction of the solution. By means of density measurements in a pycnometer it was found that a 0.237 per cent solution of dihydrate in water (below saturation), at 30° C., resulted in a contraction of 0.58 $mm.^3$ per cubic centimeter. The dihydrate is less soluble than the hemihydrate, resulting in a diminished effect upon the volume contraction due to the partial molar volume of the dissolved calcium sulfate. This solubility difference is large enough so that one observes an expansion in solution volume when hemihydrate is converted to dihydrate.

There is another factor involved in the total dilatometer volume change which is dependent upon the solubility difference between hemihydrate and gypsum. Since the former is more soluble than the gypsum, the volume occupied by the undissolved crystals of the final solid (gypsum) will be greater than the volume occupied by the original crystals of hemihydrate at time zero. This works against the volume contraction resulting from the reduced specific volume of the gypsum crystals as compared to the hemihydrate crystals. Both of these factors can be grouped together as the volume change due to the crystal volume differences. The sum of these two effects can be positive or negative, depending upon the factor predominating.

In summary, the total volume change, ΔV_{total}, in the above dilatometer experiments is the sum of (a) ΔV_c, the volume change due to crystal volume differences of the final product when compared with the original solid, and (b) ΔV_s, the volume change due to the differential in partial molar volume of the dissolved sulfate at the end of the experiment. Thus:

$$\Delta V_{total} = \Delta V_c + \Delta V_s.$$

In experiments 1 and 2 (Fig. 2), water was added slowly enough to avoid a thorough mixing of plaster and water and this probably resulted in the formation of a less concentrated solution of calcium sulfate at the start of the experiment than in experiments 3 and 4. The volume increase due to the solubility differential between plaster and gypsum, ΔV_s, would be expected to be smaller than in experiments 3 and 4, where the water at the beginning of the experiment was probably saturated with plaster. The results of experiments 1 and 2 are in agreement with this assumption. The fact that the curve rises to a slightly higher value in experiment 2 than in 1 is probably due to a higher concentration of calcium sulfate at the beginning of the readings in experiment 2.

In experiment 4 (Fig. 2), an initial contraction was observed which did not occur in experiment 3. Both experiments had stirring at "time zero" but 4 had continuous stirring during the reaction, while 3 did not. The initial stirring, as stated above, results in the saturation of the dilatometer liquid with respect to the hemihydrate. If stirring continues, the production of the dihydrate is accelerated and curve 4 can be seen to approach equilibrium at a

faster rate than curve *3*. Note that both achieve the same equilibrium volume at the end of the reaction. This stresses the importance of the initial saturation of the water with hemihydrate in the production of the final volume expansion due to ΔV_s.

The continuous stirring (curve *4*, Fig. 2) resulted in a faster initial precipitation of gypsum with no appreciable change in the concentration of calcium sulfate in the liquid, since the hemihydrate still dominates the solubility at this time. Thus, ΔV_s is minimal within the first 10 minutes of the experiment, while during the same period ΔV_c is appreciable and there is an initial contraction, since ΔV_{total} is negative. Shortly thereafter, ΔV_s becomes more effective than ΔV_c and there is an expansion. In experiment 3, a slight effect of this nature is evident in the slope inflection in the first 15 minutes of the experiment. However, without constant stirring after the initial mixing, the ΔV_s always dominates ΔV_c and the ΔV_{total} is continuously positive.

From the practical view, increased agitation will decrease the setting time of a plaster ($CaSO_4 \cdot \frac{1}{2} H_2O$) slurry. The explanation for this well-known "rule of thumb" is clearly seen in the foregoing experiments, where the production of gypsum is accelerated by stirring. It is not possible to calculate the exact value of ΔV_s (per gram of gypsum produced) as was done with the value for ΔV_c (per gram of hemihydrate converted to gypsum). This value cannot be calculated without an exact knowledge of (a) the solubility of hemihydrate in water, and (b) the change in partial molar volume of calcium sulfate due to changing concentration of solution. If (b) is found experimentally, the value for (a) can be calculated if an experiment can be devised where the exact volume of the dilatometer liquid can be measured at time zero. All the volume values given in this report refer to changes in volume with the first reading taken arbitrarily as the zero volume reading.

B. *Reaction of Hemihydrate in Solutions of K_2SO_4.*—

a. *Dilatometer studies:* The change in volume of a dilatometer liquid as a result of the reaction between $CaSO_4 \cdot \frac{1}{2} H_2O$ and different aqueous K_2SO_4 solutions was recorded. Fig. 3 shows the results for pure water (curve *1*), a 1 per cent K_2SO_4 solution (curve *2*), a 4 per cent K_2SO_4 solution (curve *3*), and a 10 per cent K_2SO_4 solution (curve *4*). All the reactions involving K_2SO_4 are accelerated, as indicated by the rapid rise of the curves in Fig. 3.

Weiser and Moreland[4] claim that the accelerating effect of K_2SO_4 on the setting of plaster is due to an increase in the solubility difference between hemihydrate and dihydrate. This is borne out by the shape of curves *2, 3,* and *4*, where the effect of an increased ΔV_s is seen in the rapid rise of volume in the first 10 minutes of these reactions. All of the accelerated setting reactions (curves *2, 3,* and *4*) are changing in volume so rapidly in the early stages that a more exact knowledge of the volume at time zero is needed if the exact volumes at the end of the experiments are to be known. Therefore, any comparison of the final volumes of curves *2, 3,* and *4* is not significant.

X-ray diffraction studies, pycnometric density measurements, and index of retraction readings (Becke line method) have shown that the equilibrium products of experiments 1, 2, and 3 are pure gypsum ($CaSO_4 \cdot 2H_2O$). The same technics showed the final product of experiment 4 to be a hydrated sulfate of potassium and calcium known as syngenite, $K_2Ca(SO_4)_2 \cdot H_2O$.

When K_2SO_4 is added to a thick $CaSO_4 \cdot \frac{1}{2} H_2O$ slurry (as in a typical casting for dental purposes), a decrease in the normal setting expansion takes place. The equivalent volume of syngenite is 126.8, as compared to 121.7 calculated for the following hypothetical sum: (equiv. vol.) $CaSO_4 \cdot 2H_2O$ – (equiv. vol.) H_2O + (equiv. vol.) K_2SO_4. From these figures one would expect

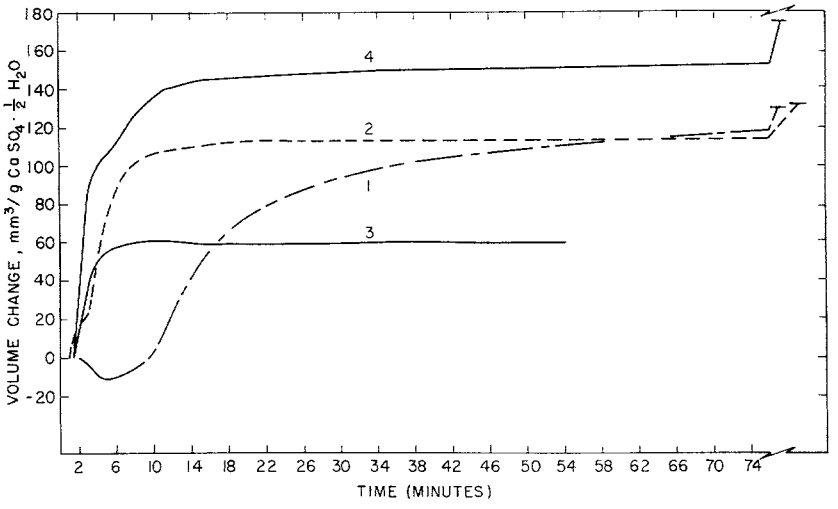

Fig. 3.—Dilatometric curves for mixtures of $CaSO_4 \cdot \frac{1}{2}H_2O$ and different K_2SO_4 aqueous solutions. Dilatometer was filled quickly and mechanical stirring was used throughout all four experiments.

Curve 1: control curve, 0.5 gram plaster and distilled water. (Same as curve *4*, Fig. 2.)
Curve 2: 0.5 gram plaster and 1% K_2SO_4 solution.
Curve 3: 0.5 gram plaster and 4% K_2SO_4 solution.
Curve 4: 0.5 gram plaster and 10% K_2SO_4 solution.

an expansion on setting due to a positive ΔV_c. This is corroborated by the expansion shown in each of curves *2*, *3*, and *4*. In these experiments, the volume expansion is certainly due to the fact that both ΔV_c and ΔV_s are positive. Another explanation must be sought for the decrease in setting expansion of gypsum when K_2SO_4 is added. Another approach to this problem is reported in Section 4 of this paper.

b. *Solid samples of gypsum:* A series of solid discs of gypsum were prepared by mixing 5 grams of plaster with 5 ml. of K_2SO_4 solutions and allowing the slurries to set between two parallel flat glass plates. The following percentages of K_2SO_4 were used: 2, 4, 5, 6, 7, 8, and 10 per cent. In all cases except 2 per cent, the x-ray diffraction pattern of syngenite was detected. In the dilatometer experiments, above, it was necessary to have between 4 and 10 per cent K_2SO_4 solution before syngenite was formed in the setting of plaster.

The obvious explanation is that, in a thick slurry, water is quickly removed from the reaction in the formation of gypsum, thus enriching the remaining liquid in K_2SO_4.

c. *Plaster and retarding solutions:* The effect of two retarders, borax and gelatin, upon the volumetric behavior of the hydration of plaster was studied by means of the dilatometer. The results (Fig. 4) show that the rate of reaction is markedly decreased in both cases. The reaction between hemihydrate and a 0.5 per cent borax solution (curve *2*) gave a smaller expansion than the reaction between hemihydrate and distilled water (curve *1*). This is probably due to a relatively smaller difference in the calcium sulfate concentration in the dilatometer liquid at the start than at the finish of the experiment. The retarder undoubtedly reduces the rate with which hemihydrate goes into solution

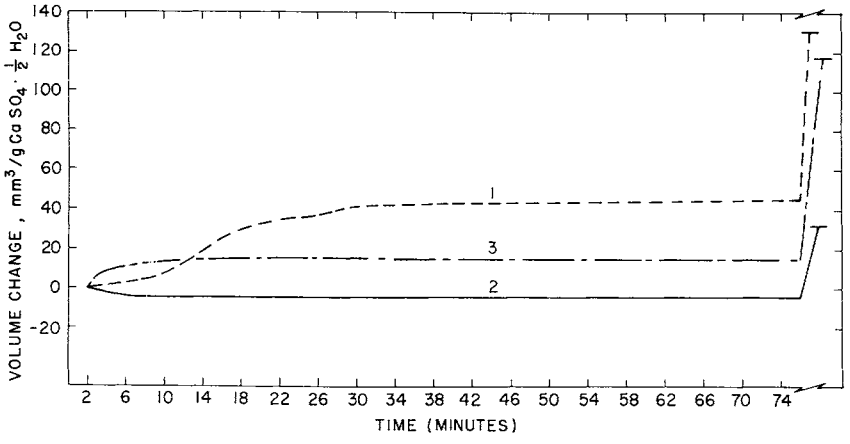

Fig. 4.—Dilatometric curves for mixtures of $CaSO_4 \cdot \frac{1}{2}H_2O$ and retarding solutions. Dilatometer was filled quickly but no mechanical stirring was used in any experiment.
Curve 1: Control curve, 0.5 gram plaster and distilled water. (Same as curve *3*, Fig. 2.)
Curve 2: 0.5 gram plaster and 0.5% borax solution.
Curve 3: 0.5 gram plaster and 0.2% gelatin solution.

just as the lack of stirring did in the experiments with pure water (Fig. 2, curves *1* and *2*). Buchanan and Worner[5] postulated this when they said the retarding effect of borax on plaster setting was due to physically adsorbed borax on hemihydrate crystals resulting in a reduction of solution of the hemihydrate.

The retarding effect of gelatin upon the setting of plaster (Fig. 4, curve *3*) is probably of the same nature as that of borax.[4] The dilatometer curves show the final volume change to be greater for the gelatin than for the borax reaction. Perhaps the borax forms a screening film more quickly and effectively than the gelatin.

CRYSTAL MORPHOLOGY

A series of $CaSO_4 \cdot 2H_2O$ samples was prepared by hydrating 1 gram of plaster of Paris in 100 ml. of different aqueous solutions. Solutions were chosen which had a known effect upon the setting expansion of plaster. Each batch

of $CaSO_4 \cdot \frac{1}{2} H_2O$ and salt solution was stirred magnetically for 24 hours. The resulting gypsum was harvested by filtration and examined in the polarizing microscope for crystal shape.

The setting expansion of plaster is probably due, in great part, to the thrust of the gypsum crystals upon each other during growth. A recent article by Jørgensen[6] presents a summary of this theory. It is reasonable to assume that the tendency for plaster to expand upon setting will change if the crystal morphology changes with a resulting change in the crystal thrust.

The results of this study are shown in Table I. Special attention was given to the changes in the crystal size and shape due to the addition of certain chemicals to the setting water.

TABLE I
CRYSTAL MORPHOLOGY OF GYPSUM FORMED FROM DIFFERENT SETTING LIQUIDS

SOLUTION	EFFECT OF SETTING EXPANSION*	SHAPE OF GYPSUM
Distilled water		Needle-like, very slender
1% K_2SO_4	Pronounced reduction	Needle-like, relatively short and thick
4% K_2SO_4	Pronounced reduction	Needle-like, relatively short and thick
4% KNO_3	Pronounced reduction	Needle-like, relatively short and thick
1% K_2CO_3	Pronounced reduction	Mostly small and spheroid
4% $Al_2(SO_4)_3 \cdot 18H_2O$	None	Needle-like, very slender
4% KCl	Rather pronounced reduction	Needle-like, relatively short and thick
5% Rochelle salt	Pronounced reduction	Very short and massive
4% $Na_2SO_4 \cdot 10H_2O$	Small reduction	Needle-like, relatively short and thick

*According to Sodeau and Gibson,[1] 1927.

The salts which reduce the setting expansion of plaster also change the morphology of the dihydrate crystals in the manner shown above. The only compound which had no effect upon the setting expansion, $Al_2(SO_4)_3 \cdot 18H_2O$, was also found to have no effect upon the crystal shape. This observation on the relationship between the change in crystal habit and the change in setting expansion may be the key to the understanding of the modifying effects of different salts upon the setting expansion of plaster. More work will have to be done in this field to confirm the preliminary results reported herein.

SUMMARY

This study was performed to obtain a better understanding of the setting properties of plaster of Paris, $CaSO_4 \cdot \frac{1}{2} H_2O$. Dilatometer studies have been completed, showing the effect of stirring, accelerators, and retarders on the kinetics of the setting of plaster. Crystal morphology studies show that when plaster is reacted with different salt solutions the crystal habit of the resultant gypsum changes. This change in shape of the final crystals may explain the reduction in setting expansion effected by various additives to the plaster slurry.

The dilatometer experiments exaggerate the contribution of the final water solution to the setting expansion of plaster of Paris. In a set plaster there is

no doubt that the bulk volume will depend principally upon the packing arrangement of the crystals rather than upon the solution effect.

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