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Publisher's version / Version de l'éditeur:

ASTM Bulletin, 237, pp. 55-62, 1959-04

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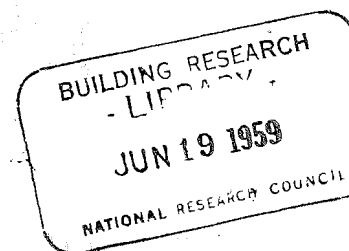
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RESEARCH PAPER NO. 80
OF THE
DIVISION OF BUILDING RESEARCH

NRC 5134

OTTAWA
JUNE 1959

PRICE 10 CENTS

Physical Changes in Setting Gypsum Plaster

By B. M. O'KELLY

The object of the reported work was the study of physical changes in a setting plaster mass including exchanges and equilibria between the solid and liquid phases. Studied were: (a) variations in the suction of the mass to free water; (b) water sorption; (c) variations in apparent volume. Water sorption studies showed the initial presence of water in excess of saturation requirements and that water sorbed closely approximated the amount required to fill emptied pores. As a result of these considerations it is suggested that plaster hardening involves only mechanical interaction of growing gypsum crystals. How the consolidation mechanism results in apparent volume changes and suction development is shown. Development of a logical concept of the sequence of physical changes in the setting mass is attempted.

THE work reported in this paper comprises the results of tests designed to provide information regarding the physical changes taking place in setting plaster and the changes in the characteristics of the mass toward free water. Where possible the tests used were car-

ried out simultaneously on three samples of a single batch of plaster and water. The tests used were: (a) determination of volume changes, (b) measurement of the amount of freely available water sorbed by the plaster; and (c) measurement of the tendency of the plaster to



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April 1959

ASTM BULLETIN

(TP 75) 55

Authorized Reprint from the Copyrighted ASTM BULLETIN No. 237, April, 1959
Published by the American Society for Testing Materials, Philadelphia 3, Pa.

sorb water when no water was, in fact, allowed to be imbibed. For convenience, the test results, in so far as this was feasible, are reported individually and are then considered collectively in a final section. For the tests a pottery plaster was used (a gypsum plaster formulated for use by the ceramic industry in the preparation of absorbent slip-casting molds). A mix ratio of 2 parts plaster to 1 part water, by weight, was used throughout. The mixing procedure consisted of adding the plaster to the water at 0 sec, spreading it over the surface of the water with the mixing beaters from 5 to 10 sec., inserting the beaters at 10 sec and mixing until 40 sec had elapsed. All time periods in this paper are measured from start of mixing.

The following relationships will be referred to in the paper:

	$\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O} + 1\frac{1}{2} \text{H}_2\text{O} = \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$		
Weight, g.....	145.00	27.0	172.00
Absolute specific gravity.....	2.75	1.0	2.32
Absolute molecular volume, cu cm..	52.73	27.0	74.14
	79.73		74.14

Decrease in absolute volume = 5.59
 Per cent increase in solid volume (on $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$) = $\frac{21.41}{52.73} \times 100$ per cent = 40.60 per cent

Decrease (cu cm) in absolute volume per g of gypsum = $\frac{5.59}{172} = 0.033$ cu cm

Previous Work

Only in the field of volume change has work been reported (1,2,3,4,5,6,7).¹ These references are believed to be the more important contributions in this field but do not comprise a complete list.

The techniques reported for volume measurement fall into three classes. The most widely used technique (2, 5,6,7) was that of confining the plaster in a container having one movable wall, the movement of the wall mirroring the volume change and being observed by a suitably sensitive method. Reference (4) is typical of a technique which involves the filling of a rigid container with plaster and embedding in the plaster a flexible container filled with water. The flexible container is connected by a

rigid tube to a graduated tube, and the volume change in the plaster registers as a change in level of the water in the graduated tube. Finally, the technique reported by Murray (3) restrains a plaster mass as little as possible consistent with preventing flow, and measures volume change by observing the movement of reference points floating on the plaster. After study, the most valuable contributions are believed to be in references (2,3,5,6,7) of which (5) is outstanding.

It is worth noting that the movable wall technique works best when the movable wall constitutes the lid of a tall slender flexible container. However, in this arrangement, the results obtained are difficult to interpret. While the plaster is fluid, as it is in the initial stages, the movement of the measuring wall is a function of the volume change of the plaster. When the plaster has achieved a rigid structure the movement of the sensing wall may more nearly represent a linear dimensional change. The measurements obtained in the period between the fluid and the solid states may be difficult to interpret.

Chassevent (5), when invited to comment on this point, replied that he believed his apparatus (a rubber tube capped with a sensing element) measured true volume expansion only when the plaster was covered with water, since in this case the initial contraction was prevented by penetration of water into any pores formed, and stated that "... swelling... is followed and measured during 95 to 98 per cent of the hydration of the plaster."

When the plaster is not covered with water, Chassevent believes that results obtained are comparative only being due to "... two phenomena acting in inverse senses: the decrease in absolute volume and the increase in apparent volume."

Suction Development

The surface of a solid which is wetted by water possesses the property of holding water molecules and thereby lowering their free energy level below that of bulk water. This situation produces a free energy gradient between the solid and any bulk water available to it, and a transfer of water molecules will occur from the bulk water to the surface of the solid. This transfer will continue until the final layers of held water molecules possess virtually the free energy of bulk water molecules.

If the solid is present in the form of small solid particles, some or all of which are close together, the layer of water held on one particle will coalesce with the water layer on an adjacent particle to form concave menisci. The

vapor pressure at the surface of these menisci will be less than that existing at the surface of bulk water under the same pressure. Water will therefore transfer from bulk water to the porous solid mass until the menisci in the mass are all flat.

Thus water will transfer from bulk water to a dry porous solid until the pores are all filled, but the process will be initiated by one property of the system and completed by another. No differentiation is made between these two processes, and the difference of energy level which causes the transfer of water at any time is said to be the "suction" of the porous system for bulk water at that time.

These statements are true irrespective of the mechanism of water transfer.

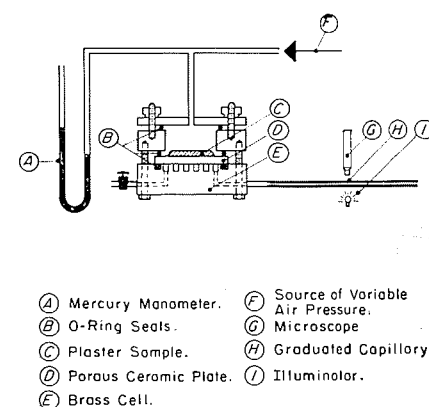


Fig. 1.—Suction apparatus.

Apparatus

The apparatus for determining suction is shown schematically in Fig. 1. It consists of a brass and plastic cell into which is sealed, by means of O-rings, a 3-in. diam porous ceramic plate approximately $\frac{1}{4}$ -in. thick. The ceramic plate was chosen so that the pores did not begin to empty of water below a pressure of 40 psi. The plate so chosen presented a high resistance to the flow of water through it, but this limitation had, of necessity, to be accepted. Beneath the ceramic plate is a small chamber consisting of interconnected annular grooves filled with water and connected to a capillary tube. Above the plate is a chamber connected to an air supply whose static pressure can be varied. The ceramic plate is saturated with water for the test. The plaster sample is placed on the ceramic plate. The meniscus in the capillary is observed through a microscope and movements corresponding to 10^{-4} cu cm are readily detected.

Test Results

After the plaster sample was placed on the ceramic plate, the cell was closed and

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¹ The boldface numbers in parentheses refer to the list of references appended to this paper.

observations started. Water drained out of the plaster sample for some time. (Compare the account of water sorption test.) The relative impermeability of the ceramic plate precluded any rapid drainage even if this tended to occur. Drainage ceased and sorption of water by the plaster began. The pressure in the chamber above the plaster and ceramic plate was increased until the movement of the meniscus in the capillary ceased. With time the pressure necessary to prevent movement of the meniscus increased to a maximum (21.8 in. Hg with a probable error of ± 2.0 in. Hg) and then decreased to a value less than the maximum where it stayed more or less constant.

Figure 2 gives the results of twelve consecutive tests. Up to the point of maximum suction the plots represent the average of the times at which a chosen percentage of the maximum suction was attained. After the point of maximum suction, the plots represent the percentage of maximum suction obtained at chosen time intervals after maximum suction. Thus, up to maximum suction the probable error is one of time while after maximum suction the probable error is one of percentage suction. While all data used to obtain the curve shown were normally distributed, the data from one of the twelve curves deviated sufficiently from the remainder, after the point of maximum suction, for the data to be rejected after that point, and at 30 min after maximum suction time two of the remaining eleven curves gave data deviating widely enough to be rejected. The explanation for these anomalies is not known.

The method of least squares showed that suction began at 17.3 min and reached a maximum at 44.2 min.

Discussion of Results

In the earliest stage of the changing system being considered here, consisting of solid particles in contact with water, and in some cases with each other, by far the greater proportion of the solid surface available is so disposed as to represent the confining walls of pores, however ill-defined these pores may be. Withdrawal of water from this system results in a consolidating force acting on the particles of plaster. If consolidation cannot take place and the porous mass contains precisely that quantity of water needed to saturate it, then the menisci in the open mouths of the pores will depress and the free energy of the water in the mass will be lowered. Free water placed in contact with the porous mass will then be sucked into it.

If the particles provide little or no resistance to consolidation and do in fact consolidate, then the volume of the pore system is reduced, which tends to

maintain the initial curvature of the menisci and the initial energy level.

Since the pore system formed by the mixture of particles and water is non-rigid and capable of consolidation under gravity forces, it may be concluded that, as this consolidation takes place, an excess of free water can result. It is believed that this is what occurs in a 2:1 plaster-water mix. Water can therefore drain from the plaster, though slowly because of the relative impermeability of the ceramic plate. From the experimental data, suction is seen to begin at 17.3 min. However, before this time the excess mixing water, at least in part, is available to satisfy any demand for water by the plaster. Thus, almost certainly, a tendency to imbibe water (a state of "suction") is actually developed in the plaster before 17.3 min. When suction begins, and causes increased concavity of the meniscus in the observed reference capillary, pressure is applied to counteract it. The action of the pressure is to depress the menisci in the plaster and in the ceramic plate to provide water to satisfy the plaster's demand. The force necessary to do this is the same as the force with which water would tend to be imbibed by the plaster, under no-flow conditions, if the latter were placed in contact with free water. A curve of suction against

time is thus built up by observing the suction pressure at various times. It should be noted carefully that the test described measures the force necessary to depress menisci so as to supply water to satisfy a demand, but does not provide information concerning the reason for the existence of the demand, or its magnitude.

As previously stated, manifestation of suction by a tendency to imbibe water indicates that the plaster is resisting consolidation.

The decay of suction from a maximum value is interesting. It might be explained either by a decrease in the total pore volume or by an increase in the average pore diameter.

A consideration of the absolute volumes of hemihydrate, dihydrate, and water shows that the hydration of hemihydrate to dihydrate produces a volume of the latter lower than the combined volumes of the hemihydrate and the water which formed it. However, the absolute volume of the dihydrate is about 40 per cent greater than the absolute volume of the hemihydrate from which it was formed. The density of the wet 2:1 plaster mix being considered here is 1.72 g per cu cm. For such a mix it may be calculated that the absolute solid-volume increase on hydration, expressed as a per cent of the total

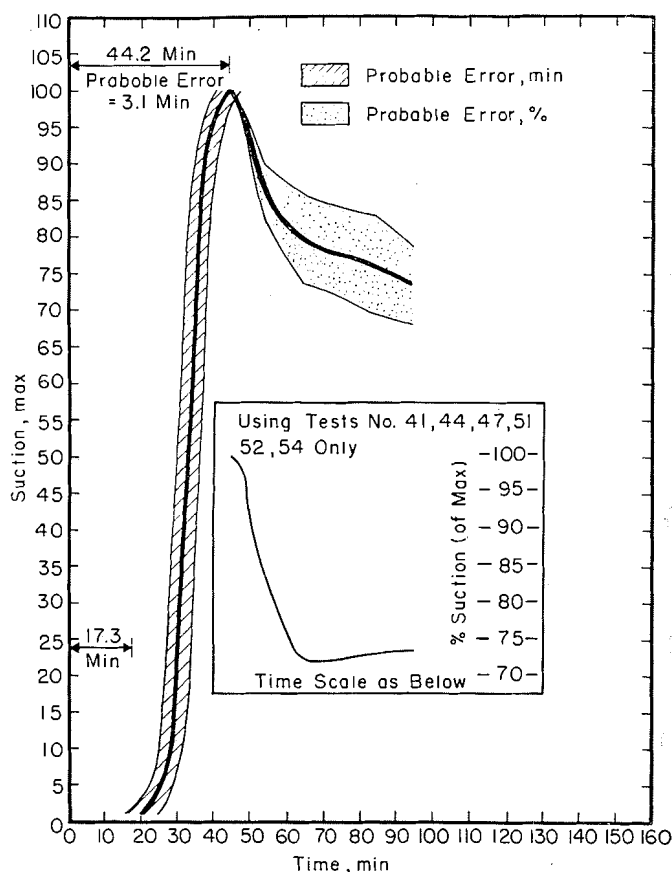


Fig. 2.—Development of suction.

volume of the mass, is 16.9 per cent.

$$100 \text{ cu cm mix} \equiv 172 \text{ g} \equiv 114.67 \text{ g CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$$

$$114.67 \text{ g CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O} = \text{absolute vol. of}$$

$$\frac{114.67 \text{ cu cm}}{2.75} = 41.70 \text{ cu cm}$$

Increase in volume on hydration of 41.70 cu cm of $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$

$$= \frac{40.6 \times 41.70}{100}$$

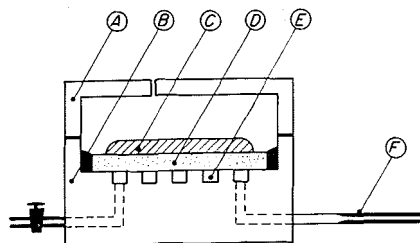
$$= 16.93 \text{ cu cm}$$

If the apparent volume of the hydrating mass remained constant throughout the period of hydration it may readily be seen that the total pore volume of the mass would decrease from the start of hydration to accommodate the increased volume of the solid phase; the volume of water available to fill the pores would also decrease but at a rate somewhat higher than the rate of pore-volume decrease. However, as will be shown, the apparent volume of the mass at first decreases and then increases. The increase in apparent volume is of the order of 1 per cent. It is obvious that the 1 per cent apparent volume increase will have only a small effect in opposing the decrease in pore volume due to the growth of the solid phase. Thus to suppose that the drop in suction from a maximum is due to a decrease in the total pore volume necessitates the assumption that, at the time of the suction decrease, the decrease in pore volume normal to the hydration process is augmented by a mechanical consolidation of the solid material in the mass, as otherwise the relative rates of decrease of pore volume and free water respectively, will be undisturbed and will therefore increase the pore volume. Since the impossibility of such consolidation is believed to underlie the development of suction, this explanation for the suction decrease is not satisfactory.

The decay of suction from a maximum value is most readily explained by assuming an increase in the average pore diameter. This in turn could be explained by assuming the growth of large crystals at the expense of small, after the marked activity, which gives rise to the steep portion of the suction curve, has subsided. This suggestion is in line with the findings of Rebinder, *et al.* (10) and Bogautdinova, *et al.* (12) who found, within 1 hr of mixing, a decrease in strength after an initial maximum was reached. Rebinder, *et al.* (10), also refer to "disappearance of nonequibrated crystal contacts" in connection with the mechanism of hardening of plaster.

Water Sorption

The technique adopted was to seal a disk of porous sintered bronze into a plastic dish, the bottom of which consisted of annular grooves. A sintered



- (A) Removable Lid for B.
- (B) Plastic Cell.
- (C) Plaster Sample.
- (D) Porous Bronze Plate Waxed into B.
- (E) Annular Grooves.
- (F) Graduated Capillary.

Fig. 3.—Water sorption cell.

bronze disk was used in place of a ceramic disk, because the sintered bronze was highly permeable and afforded the least possible resistance to flow of water into and out of the plaster sample. The grooves of the plastic dish were joined and then connected to a capillary tube fitted with a scale and having a capacity of 0.05 cu cm per cm. Two filter papers were placed on top of the bronze plate, the upper one being weighed dry. The plaster sample was placed on the filter papers. The apparatus is shown schematically in Fig. 3. To prevent flooding of the surface of the filter papers, the level of the capillary was placed about $\frac{1}{2}$ in. below the upper surface of the bronze plate and so maintained the plate at a slight suction. This suction was considered negligible compared to

the suctions developed in the setting plaster. The plaster sample was from $\frac{1}{8}$ to $\frac{3}{16}$ in. thick. Mixing technique was the same as described under the section on Volume Change. The cell was vented through a 3-ft long capillary tube to diminish loss of water by evaporation. The timing of the steps necessary to start this test was reproduced from one test to another. Due to the operations necessary in starting the other two tests, observations of water sorption did not begin until 4 min, 25 sec.

Test Results

After the plaster sample was placed in the cell and the lid was closed, observations were started. Water drained rapidly from the sample, a period of inaction followed, and the plaster began to sorb water at about 7 to 8 min. The amount of water lost initially and the amount subsequently sorbed (overnight sorption = 100 per cent) is shown in Fig. 4.

Assuming that the plaster sets completely overnight, it was found that, on setting, the plaster sorbed 0.045 cu cm per g of dry set plaster with a probable error of 0.001 cu cm.

To check the reality of the period of inaction in water sorption mentioned above, three experiments were carried out in which the observations of water sorption were begun 50 sec after start of mixing. From these tests it was found that drainage proceeded as before, ceased at about 3 min and was followed

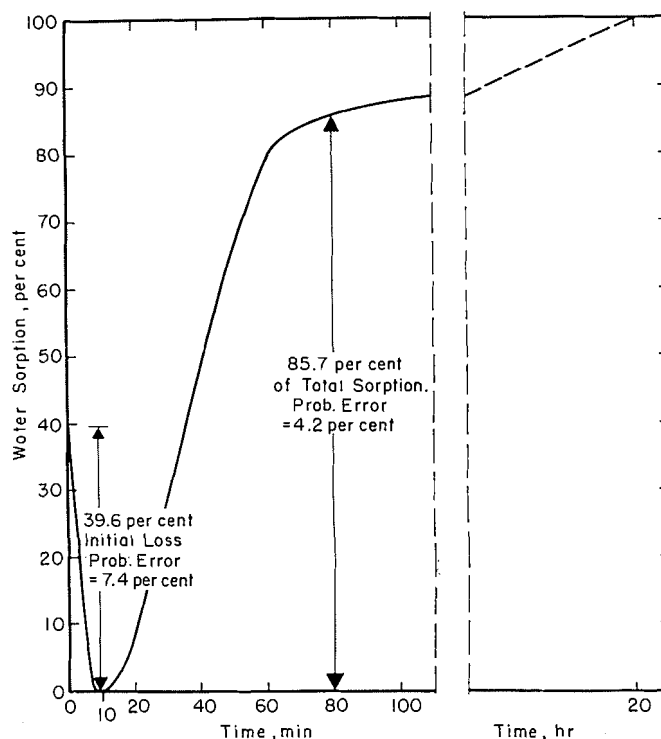


Fig. 4.—Water sorption.

by a period of apparent inaction lasting about 4 min after which sorption of water began. These results show that the period of "inaction" is not due simply to the particular experimental technique being used.

Discussion of Results

The phenomenon of initial drainage is believed to be due to the presence of water in excess of that necessary to saturate the hemihydrate present (see Suction Development). The period of apparent inaction is believed to be due to the compactable nature of the plaster mass at this stage of setting and the consequent possibility of supplying a demand for water by compaction of the mass, with release of free water. The compacting force is, of course, supplied by the surface tension of the water and/or gravity.

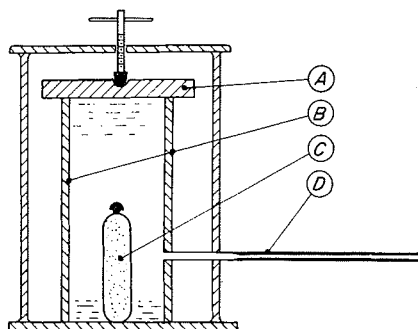
The sorption of water, following the period of apparent inaction, can be explained in large part by the demand for water caused by chemical hydration. The test provides no information as to whether this is the sole agency responsible. The mechanism causing the demand for water is believed to be operative before the water uptake begins and prior to this point to obtain necessary water by compaction of the plaster mass.

It is believed that the long duration of water uptake may be due partly to the impermeability of the set plaster mass to water under only moderate pressure differentials. Empty pores will be left in the plaster mass by chemical binding of water to form dihydrate. In regions of the mass remote from the source of free water, these pores will have to be filled by migration of water through the mass from the free water source. In this case the hydration proper will be largely complete in some time less than the period of water uptake. From the suction test data, 60 to 80 min does not seem unlikely.

Volume Change

The technique adopted for the present work was to fill a thin-walled rubber membrane with plaster, seal it securely, and place it in a brass tank filled with water and connected to a capillary tube (Fig. 5). A lid was then placed on the tank and readings started. The capillary tube was graduated and had a capacity of 0.05 cu cm per cm. Volume changes in the plaster registered as movement of the meniscus in the capillary.

Objections to the method are mainly that the tank and water in it expand under the influence of the heat released by the plaster hydration and consequently give a "thermometer-effect" error in the volume change. Pressure variations in the atmosphere will cause the



- (A) Removable Lid Clamped in Position
- (B) Brass Cylinder Filled with Water
- (C) Plaster in Membrane
- (D) Graduated Capillary

Fig. 5—Volume change apparatus.

apparatus to behave in some measure as a barometer. The latter objection is considered to be negligible and the former is thought to influence only the order of the volume change and not its position in time. In the initial stages of the hydration, indeed, when the temperature rise is very small, the thermometer effect is negligible.

Test Results

Due to the procedure involved in starting the water sorption and suction

tests, the first reading in the volume change test was usually not made before 5 min after the start of mixing. Invariably at this time, a rapid contraction was taking place. This contraction proceeded more or less uniformly for some time and then abruptly changed to an expansion. The expansion proceeded rapidly, gradually slowed to a stop, and was succeeded by a slow contraction. The shape of Fig. 6 is typical of the tests considered.

Consideration of fourteen consecutive tests (the data from which were found to follow closely a normal distribution pattern) showed the following:

- (a) Start of reading was, in all cases, 5 min.
- (b) Contraction proceeded until 25.6 min had elapsed (probable error was 4.4 min).
- (c) Expansion occurred for a subsequent period of 34.8 min (probable error was 2.2 min).
- (d) The percentage contraction was 0.25 per cent (probable error was 0.04 per cent).
- (e) The percentage expansion was 0.92 per cent (probable error was 0.03 per cent).

Since percentage contraction and contraction time showed normal distribution, the ratios of the duration of contraction to the percentage of contraction for the fourteen tests showed normal

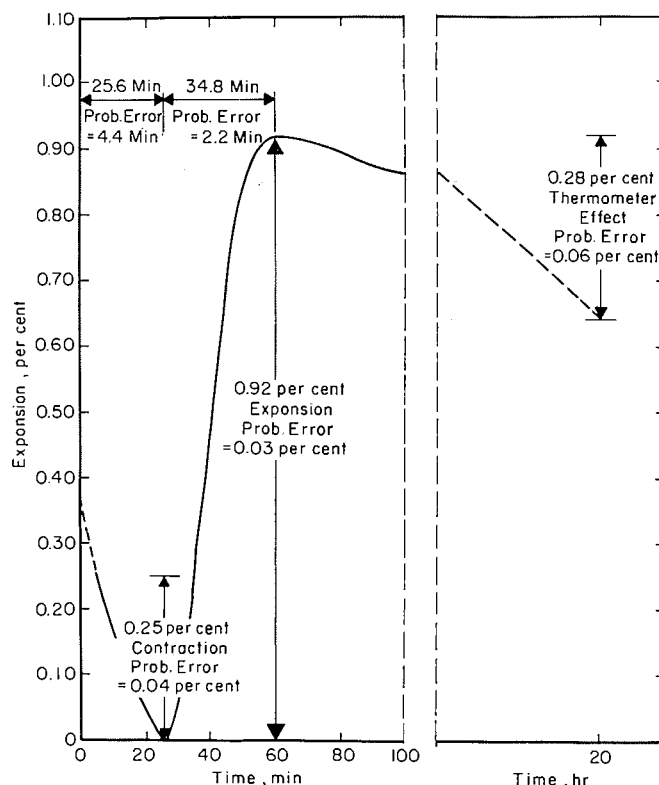


Fig. 6.—Volume change.

distribution. Arithmetic mean of the ratio was 102.4 with a probable error of 8.8. The method of least squares gave the relation:

$$c = 0.0074t + 0.061$$

where:

c = per cent contraction and
 t = duration of contraction.

It is obvious that this relation does not hold to " t_0 " since at $t = 0$, $c = 0$.

The comparative linearity of a typical time per contraction curve is of interest (Fig. 6) but should not be confused with the curve for which the equation has just been given. An attempt was made to determine temperature changes in the setting plaster and in the surrounding water but the reproducibility was poor due to the difficulty of positioning the thermocouples in the plaster mass. Such data as were obtained indicate an initial drop in temperature immediately after mixing, followed by a rise in temperature starting at about 14 min.

Discussion of Results

Ottoman (1) and Chassevent (5) have stated that the initial contraction is a manifestation of the decrease in absolute volume which occurs when hemihydrate and water react together to produce gypsum. This is believed to be the correct explanation. Apropos to Chassevent's comments quoted earlier, the present author is of the opinion that all results obtained in tests on plaster are comparative only and must always be related to the environment of the plaster mass being tested.

Average wet density of the plaster used in these experiments was 1.72 g per cu cm. Plaster to water ratio was 2:1. Average contraction was 0.25 per cent. Consideration of the molecular volumes of hemihydrate, gypsum, and water shows that a contraction of 0.25 per cent represents 5.6 per cent of the contraction to be expected on full hydration.

$$100 \text{ cu cm mix} \equiv 172 \text{ g} \equiv 114.67 \text{ g CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$$

$$145 \text{ g CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} = 5.59 \text{ cu cm contraction in absolute volume on full hydration}$$

$$\therefore 114.67 \text{ g CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} = 4.47 \text{ cu cm contraction} \\ = 4.47 \text{ per cent contraction}$$

$$\therefore 0.25 \text{ per cent contraction} = \frac{0.25 \times 100 \text{ per cent of full contraction}}{4.47}$$

$$= 5.6 \text{ per cent}$$

This indicates not only that hydration and its accompanying contraction in absolute volume is more than adequate to

explain the contraction found experimentally, but also that hydration of the hemihydrate begins at an early stage in the setting process.

Examination of the data available shows that the maximum contraction which could be accounted for by the decrease in temperature referred to above is approximately 0.05 per cent, and is probably considerably lower. The reason for the temperature drop is not clear unless it is due to the negative heat of solution of hemihydrate in water.

The conditions of the suction tests are such that drainage of free water out of the sample is virtually prevented, so that the conditions existing in the suction and volume tests may be compared directly. Since suction began at about 18 min., it follows that all free water in the volume tests was used up at this time or shortly afterwards. Since the first volume reading was taken at 5 min, the per cent contraction was linearly extrapolated to t_0 . The average extrapolated contraction was 0.37 per cent (probable error of 0.05 per cent). Contraction ceased at 25.6 min (probable error of 4.4 min) and a contraction of 0.37 per cent represents 8.3 per cent of full hydration. Reference to the water sorption test (Fig. 4) gave the degree of hydration, at 25.6 min, as 18.9 per cent of total. Therefore $18.9 - 8.3 = 10.6$ per cent of full hydration has occurred in the volume test sample without apparent manifestation as decrease in volume. This 10.6 per cent of hydration must, therefore, be represented by pores emptied of water within the volume sample. An absolute volume decrease of 0.47 per cent (of the absolute volume of the reactants) occurs for 10.6 per cent of the full hydration. Presumably, therefore, when the volume sample starts to expand, the mass contains pores empty of water to the extent of 0.47 per cent of the total volume of the sample.

Following the contraction, an expansion of 0.92 per cent (probable error of 0.03 per cent) occurs. No information regarding the mechanism causing the expansion is provided by the volume test, but see section on General Discussion.

Finally a contraction is observed following the expansion. This contraction is due to cooling of the plaster and apparatus after the exothermic hydration and provides a measure of the volume correction to be applied to the data to take account of the thermometer-like action of the apparatus in responding to the heat output of the setting plaster. The correction found is -0.28 per cent with probable error of 0.06 per cent.

Taking into account the decrease in absolute volume, together with the in-

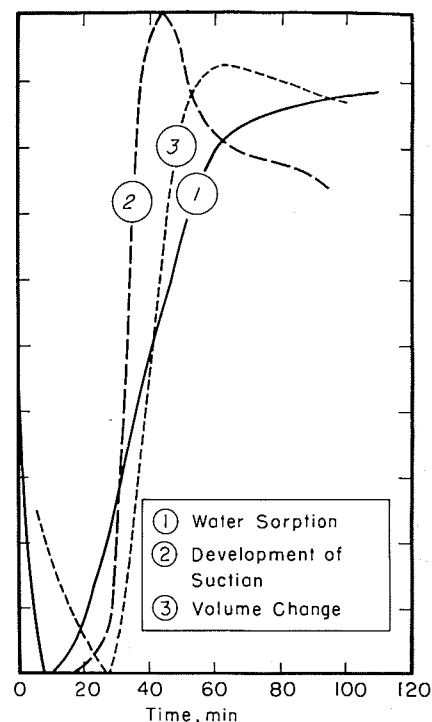


Fig. 7.—Composite curves.

crease in apparent volume corrected for temperature effects, it may be calculated that in a hardened wet 2:1 plaster mix there will be 6.4 cu cm of pores empty of water for each 172 g of gypsum produced.

The order of reproducibility given previously for the various measurements warrants attention. Reproducibility for the duration of contraction and for the percentage contraction is poor; it is somewhat better for the duration of the expansion, and good for the percentage expansion. These data are believed to shed some light on the well-known difficulty of obtaining a reproducible setting time with a neat plaster mix.

The fact that the ratios of duration of contraction to percentage of contraction are normally distributed is tentatively interpreted as showing that contraction occurs as a result of a reaction proceeding at a more or less uniform rate, and which continues until some limiting stage in the process is reached. It is believed that the limiting stage is the point at which compaction of the plaster mass can no longer readily occur and the variable factor is thought to be the amount of mixing water taken up when the sample for the test is removed from the main batch of plaster.

General Discussion

In this section an attempt will be made to correlate the data from the three tests one with another, and to attempt to establish the relation of these data with the relevant published literature. A composite showing the three superimposed curves is given in Fig. 7.

Assuming that plaster is completely set overnight, then, as stated before, the water sorbed is 0.045 cu cm per g of dry set plaster.

Again, expansion of the plaster from start of expansion (corrected for temp. effect) was 0.64 per cent. This may be compared with Chassevent's (5) expansion of a plaster not covered with water. Chassevent found a ratio of 1.37 for the expansion of a plaster covered with water to the expansion when not covered with water. Lehmann and Kreuter (2) found 1.40 for the ratio.

The plaster in the water sorption cell may be compared to Chassevent's plaster covered with water. Thus the expansion of the plaster in the sorption cell may be assumed to be 1.37×0.64 per cent = 0.877 per cent.

Dry set density for plaster is 1.33 g per cu cm. (probable error very small).

∴ Expansion is 0.877 cu cm per 133 g of dry set plaster = 0.0065 cu cm per g of dry set plaster.

It may be shown readily from considerations of molecular volumes that the decrease in absolute volume associated with 1g of dry-set plaster (gypsum) is 0.033 cu cm.

For 1 g the total increase in the volume of pores not filled with water for the plaster on setting is thus $0.033 + 0.0065$ cu cm = 0.040 cu cm.

This is to be compared with the 0.045 cu cm per g found experimentally for water uptake.

It is believed that the assumptions made in assessing the porosity of the set plaster are legitimate, and it is concluded that the amount of water sorbed overnight is the full amount which will be taken up.

Where the initial set was determined with a Vicat needle (and due to a desire to save plaster the usual batch was too small for such a determination), it was found to occur at 20 min. At this time, water uptake was about 12 per cent of the overnight amount. Bogautdinova, *et al* (12), state that, at the initial set, 40 to 50 per cent of the water necessary to convert all the hemihydrate "to a dihydrate gel" was used. The difference in the two results may arise from different criteria for "initial" set and the permeability factor previously discussed.

It is of interest at this point to consider suggestions to account for the volume contraction other than the one discussed above. Williams and Westendick (4) suggest that the contraction is due to dissolving of the hemihydrate in the mixing water, while Neville (9) suggests a process of adsorption onto the hemihydrate as causing the contraction. Fisher (8) postulates that up to about 30 min after mixing only a process of adsorption occurs, a gradual change to

chemisorption taking place after this time. Thus by implication he agrees with Neville. Powell (11) on the other hand has published contrary data.

Simple calculation shows that the volume of hemihydrate dissolved in the mixing water is inadequate to explain the contraction found, and there is little evidence to show any marked decrease in the volume of the water molecule on entering the adsorbed state. The postulations regarding adsorption as a mechanism leading to initial set, Fisher's (8) concept (involving adsorption) of the mode of action of retarders, and the concept of Rebinder, *et al.* (10), of the plaster, up to a time of 5 min after mixing, as a coagulated mass of low shearing strength, may be reconciled with the data which suggest a purely crystallizational hardening, by supposing that adsorption takes place, but only in the first few minutes of the plaster's setting time. Penetration of fine pores by an adsorption process occurs until the water makes contact with gypsum nuclei whose presence is a virtual certainty, and from these centers crystallization spreads throughout the mass. The limiting factors which determine the induction period of the set are the number of gypsum nuclei present and the fineness of the plaster grains. Support for this suggestion is furnished by the findings of Neville (9) that a crystalline hemihydrate, prepared by boiling gypsum shows anomalous setting properties, by the findings of Murray (private communication) that a perfectly pure hemihydrate will not set, and by the findings of Enley and Welch (13) that the finer the plaster the quicker the set.

Conclusion

Hydration of the hemihydrate plaster mix considered here begins virtually at once after mixing with water. Until about 17 min demands for water occasioned by hydration are met by compaction of the plaster mass under the influence of surface tension and/or gravity. At the same time a rigid structure is rapidly developing in the mass due to microcrystallization, interlocking of crystals, and trapping of hemihydrate particles. Increase in volume of pores empty of water has started by now. Compaction becomes more difficult to achieve by surface tension from 17 to 26 min, and by 26 min it has virtually ceased. Increase of the apparent volume now begins.

The reason for the increase in apparent volume is as follows: Needle-like crystals do not pack well. The gypsum formed on hydration is in the form of needles. Consequently the increase in the absolute volume of the solid phase is not manifested by the

growth of gypsum crystals into the pores of the setting plaster, to produce a mass of increasing density; instead, crystals of gypsum grow until they make contact with other growing crystals. Increase in the number of such crystal contacts, together with continual growth of the solid phase, produce a skeletal structure of ever-increasing strength, the individual structural members of which continue to increase in size. Such increase in size of structural members causes the increase in the apparent volume of the setting mass. By 44 min equilibrium is established between the demand for water occasioned by hydration and supply of water by depression of menisci. However, immediately after establishment of this equilibrium, growth of large crystals at the expense of small and disappearance of "non-equilibrated crystal contacts" (10) increases the average pore size and decreases suction. Cessation of the bulk of these crystal changes allows suction once more to reach equilibrium. Further slow hydration causes suction to rise once more to a level higher than the lower equilibrium level.

Acknowledgment:

This paper is a contribution from the Division of Building Research, National Research Council of Canada and is published with the approval of the Director of the Division.

REFERENCES

- (1) J. Otteman, "Über die Volumenvergrößerung des Anhydrits bei Seiner Hydratisierung" (On the Increase in Volume of Anhydrite by its Hydration), *Planen und Bauen*, Vol. 5 (3), pp. 68-69 (1951). Great Britain, Dept. Scientific and Industrial Research, Building Research Library Communication No. 52, Her Majesty's Stationery Office, London (England).
- (2) H. Lehmann and W. Kreuter, "Über die Quellung von Gips" (The Expansion of Gypsum Plasters), *Tonindustrie Zeitung und Keramische Rundschau*, Vol. 77 (17/18), pp. 298-301 (1953). Great Britain, Dept. Scientific and Industrial Research, Building Research, Library Communication No. 449, Her Majesty's Stationery Office, London (England).
- (3) J. A. Murray, "The Expansion of a Calcined Gypsum During Setting," *Rock Products*, Vol. 31, pp. 88-92 (1928).
- (4) F. J. Williams and F. C. Westendick, "Relation Between the Temperature Curve and the Expansion Curve in the Setting of Plaster," *Journal, Am. Ceramic Soc.*, Vol. 12, p. 377. (1929).
- (5) L. Chassevent, "Study of the Variations in Volume of Plasters During and After Setting," *Revue Matériaux Constructions*, Edition C, No. 405, pp. 188-194; No. 406, pp. 219-224;

- No. 407, pp. 267-272; No. 408, pp. 304-308 (1949). National Research Council of Canada, Technical Translation TT-689.
- (6) S. Ito, I. Teraoka, and S. Yoshihama. "Variations in the Volume of Plaster During and After Setting," *Gypsum & Lime (Sekko to Sekkai)*, Vol. 5, pp. 225-229 (1952). National Research Council of Canada Technical Translation TT-643.
- (7) C. S. Gibson and R. N. Johnson. "Investigations of the Setting of Plaster of Paris," *Journal, Soc. Chemical Industry*, Vol. 51, p. 25 (1932).
- (8) H. C. Fisher, "The Setting of Gypsum Plaster," *ASTM BULLETIN*, No. 192, Sept. 1953, p. 43 (TP 133).
- (9) H. A. Neville, "Adsorption and Reaction, I—The Setting of Plaster of Paris," *Journal Physical Chemistry*, Vol. 30, pp. 1037-1042 (1926).
- (10) V. N. Igmailova, E. E. Segalova, and P. A. Rebinder. "A Study of Structure Formation in Water Suspension of Calcium Sulphate," *Doklady Akademii Nauk S.S.S.R.*, Vol. 107 (3), pp. 425-427 (1956). National Research Council of Canada, Technical Translation TT-672.
- (11) D. A. Powell, "Setting of Gypsum Plaster," *Nature*, Vol. 178, pp. 428-29 (1956).
- (12) O. V. Kuntsevich, P. E. Aleksandrov, V. B. Ratnov, T. I. Rozenberg, and G. G. Bogautdinova, "The Theory of the Setting of Gypsum Bonding Materials," *Doklady Akademii Nauk S.S.S.R.*, Vol. 104 (4), pp. 587-588 (1955). National Research Council of Canada, Technical Translation TT-685.
- (13) W. E. Emley and F. C. Welch, "The Relation Between the Fineness and Other Properties of Calcined Gypsum," *Journal, Am. Ceramic Soc.*, Vol. 4, p. 301 (1921).
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