

## THE VOLUMETRIC CONTRACTION OF DENTAL GYPSUM MATERIALS ON SETTING

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OF ALL the materials associated with dental practice and technic, those containing gypsum products are probably used most extensively. In keeping with this fact, a great deal of research has been directed toward problems involving the physical behavior of these materials. It is felt, however, that knowledge is lacking on some of the more fundamental behavior characteristics. The manifestation of this deficiency is the presence of many phenomena which exist when dental gypsums are used. An illustrative example would be the hygroscopic expansion of dental casting investments containing gypsum as a binder. Since there is no established theory on the mechanism of this action, it is just as difficult for the dental manufacturer to compound an adequate material as it is for the dentist to use it properly. The purpose of this paper is to resolve some of these difficulties by studying one very fundamental characteristic of these materials, namely, the volumetric behavior of dental gypsums during the process of setting.

All dental gypsum products which include plaster, stone or hydrocal, the improved stones, and the binder of most gold casting investments are essentially composed of the hemihydrate form of calcium sulfate ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ). When mixed with water, the hemihydrate is converted to the dihydrate form of calcium sulfate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and this process is synonymous with the observed setting action. Specifically associated with this reaction is the paradox which exists with respect to the volumetric behavior of the mixed mass. It is common knowledge that an expansion accompanies the setting process; yet, a contraction should occur based on theoretical considerations as is shown in Table I. Skinner<sup>1</sup> wrote of this anomaly and explained that the expansion is only apparent and is possibly caused by the thrusting of the gypsum crystals in the direction of their growth during setting. It is the specific purpose of this paper to determine whether a volumetric contraction does exist and, if so, how it can be explained in the presence of a measurable expansion.

A thorough search of the dental and chemical literature was of no assistance except for one article by J. H. Van't Hoff<sup>2</sup> in which the author measured a contraction of plaster of Paris during setting. However, the method of measurement as well as the objectives of the experiment precluded any adaptation of the results to the problem at hand. Accordingly, an apparatus was designed and tests were run to measure the true volumetric behavior of dental gypsum materials on setting.

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TABLE I  
 THEORETICAL CONTRACTION BASED ON SPECIFIC GRAVITY VALUES

Chemical reaction	$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	+	$3/2\text{H}_2\text{O}$	→	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Molecular weights	145.148		$1.5 \times 18.016$		172.172
Specific gravities	2.75		.997		2.32
Volume	$\frac{145.148}{2.75}$	+	$\frac{27.024}{.997}$	→	$\frac{172.172}{2.32}$
	52.78	+	27.10	→	74.21
Volumetric contraction =	$\frac{(52.78 + 27.10)}{52.78 + 27.10}$		-	$\frac{74.21}{100}$	× = 7.10%

DESCRIPTION OF THE APPARATUS AND TEST METHOD

Fig. 1 shows the apparatus used, along with a schematic diagram indicating its component parts. The setup operates on a dilatometer principle in which the sample of plaster, stone, or investment is placed in a closed fluid system and the change in volume is determined by the movement of the fluid in a capillary tube.

Immediately after being mixed, the material is poured into an inlay ring having a base on which a wire hook has been soldered. Another long wire hook was used to lift the ring and place it carefully into the flask (D). The glass cap (C) was placed onto the flask (D), a seal being achieved by virtue of a ground glass joint. Another ground glass joint seals the capillary tube into the glass cap (C). The fluid used in this system was water, which was stored in reservoir (A) and allowed to enter the system through valve (B). Thermocouples in series were placed in the fluid system to allow for compensation of exothermic and ambient temperature effects on the fluid system.

With a moderate degree of speed, fiducial measurements could be made 4 to 6 minutes after the start of mix. Volumetric behavior previous to this time was determined by extrapolation.

The capillary tube was calibrated and found to hold .007 c.c. of water per lineal centimeter. Since readings could be taken to within 1 mm., the accuracy of measurement was .0007 c.c. or percentagewise (using 25.7 c.c. as the initial volume) approximately .003 per cent change in volume could be recorded. When the water column in the capillary tube approached the bottom of the scale, valve (B) was opened, the water column rose to the top of the scale, and further readings were taken which were then added to the previous readings, thereby yielding a continuous recording.

The use of water as the ambient fluid in this system might appear to influence the measurements on the basis of the solubility of the hemihydrate in the mixed mass of plaster, stone, or investment; however, tests were run using a saturated solution of the hemihydrate as the ambient fluid and no appreciable differences were recorded.

It is particularly relevant to note that this apparatus measures only true volumetric changes and that apparent volumetric changes are not reflected in the volume change of the fluid system. It is believed that what is commonly

known as setting expansion (due possibly to a thrusting of the gypsum crystals in their growth) is an apparent volumetric change, and although it perceptibly increases the outer dimensions of the sample, the true volume has not been affected. For this particular situation, therefore, no volume change would be registered.

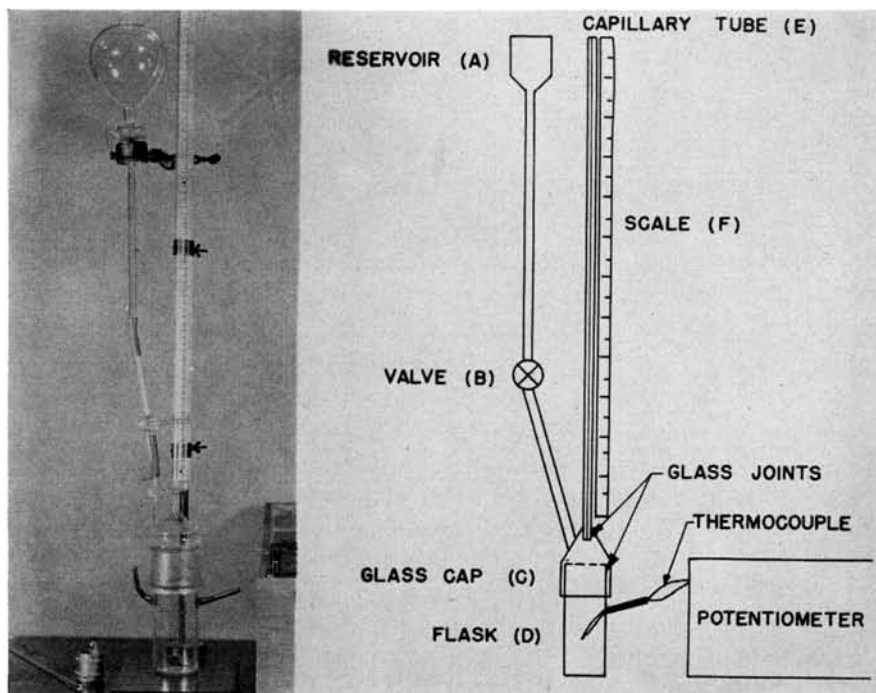


Fig. 1.—Apparatus used to determine the volumetric contraction of gypsum materials.

#### RESULTS AND DISCUSSION

In *Fig. 2* is shown typical curves for the true volumetric behavior of the same initial volume of plaster, stone, improved stone, and a hygroscopic casting investment. As can be seen, a volumetric contraction accompanies the setting process. From these tests, it is apparent that although the outer dimensions of the sample increase slightly, on the basis of setting expansion measurements, the true volume of the mass has decreased. This decrease must be manifest in a porosity formation within the sample, which is about equal in volume to the measured contraction. On the basis of this porosity formation, a driving force must then exist within the setting mass which draws in the ambient atmosphere, whether it be air, water, or any other gaseous or fluid medium.

Several other points of information can be determined by a study of *Fig. 2*: (1) The slope of these curves at any particular point is simply the rate of reaction in the process of conversion of the hemihydrate to the dihydrate form of calcium sulfate. This may prove to be of further research value when the setting process itself is more thoroughly investigated. (2) The completeness

of the reaction at any time after mix can be established. As can be seen from the curves, the major portion of the reaction has been completed at 30 minutes and at 1 hour to 1½ hours, the reaction has been almost entirely completed. This substantiates a point which one of us (D. B. M.)<sup>3</sup> raised previously in which the completion of the reaction on the basis of hardness tests was observed to be approximately 1 hour after mix. In Fig. 3 is shown two curves for a gypsum material which is used as a binder in a hygroscopic casting investment. The setting time of the material has not been controlled, the first run experiencing an initial Gilmore setting time of 9½ minutes and the second,

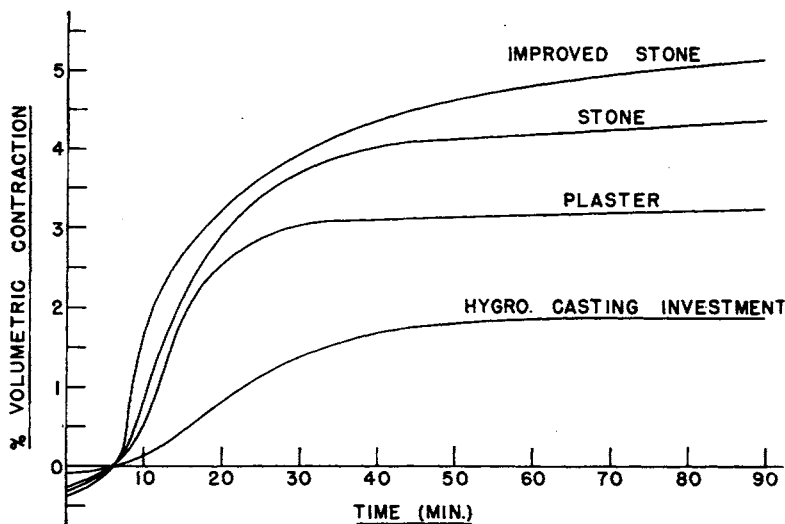


Fig. 2.—Volumetric contraction (c.c.) of the various dental gypsum materials in per cent of the original volume (c.c.) encompassed by the inlay ring.

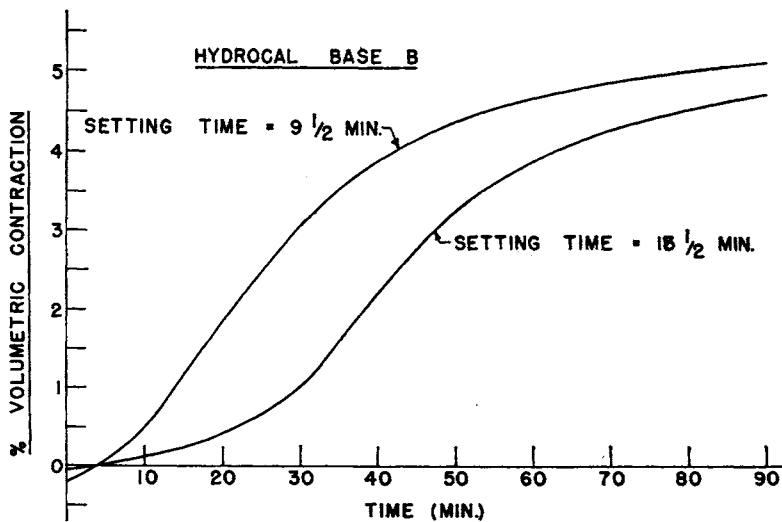


Fig. 3.—Volumetric contraction (c.c.) of the binder used in a hygroscopic casting investment in per cent of the original volume (c.c.) encompassed by the inlay ring.

a setting time of  $18\frac{1}{2}$  minutes. Because of this situation, the significance of these volumetric contraction curves can be illustrated more clearly. The longer setting time run has a relatively slower rate of reaction and completes any specific portion of its reaction at a later time than the shorter setting time run; however, both reactions tend toward completion at about the same time and they observe the same total contraction value after the completion of the reaction, irrespective of the paths they choose to follow. (3) The amount of the ambient atmosphere to be drawn into the sample during the setting process, for the same initial volume of mix, varies with respect to the type of material being used (Fig. 2). The improved stone draws in the most, dental stone next, then plaster, and finally the casting investment. The reason for this is the difference in the amount of hemihydrate present in the volume encompassed by the inlay ring for the different materials. This in turn is due to the different water/powder ratios used and the difference in the amount of hemihydrate present in the original powders. When these conditions are accounted for, the volume contraction of the different materials is about the same, within the accuracy of determination, as will be shown directly.

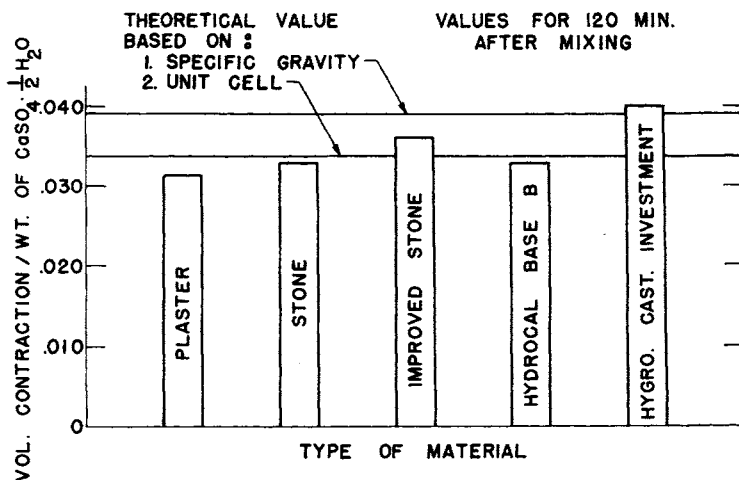


Fig. 4.—Volumetric contraction (c.c.) of the various dental gypsum materials per weight of  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  (Gm.) in the original volume encompassed by the inlay ring.

To analyze these curves more thoroughly and to validate the cause of this phenomenon, a bar graph is presented in Fig. 4 in which the total contraction at 120 minutes after mixing is given for all the materials tested in addition to the contraction which should occur theoretically; however, instead of representing equal initial total volumes encompassed by the inlay ring as is shown in Fig. 2, this graph is the contraction per unit weight of the hemihydrate present in these initial volumes. Theoretically, since the contraction is caused by the conversion of the hemihydrate plus water to the dihydrate, the amount of contraction measured should depend on the amount of hemihydrate present in the inlay ring. The bar graph in Fig. 4 is a result of this postulation. The information and calculations necessary for the values of Fig. 4 are given in

Tables II, III, IV, V, VI, and VII, and are listed as follows: Table II, chemical analysis of the gypsum materials studied; Table III, weight of the powder plus mix water in the original volume and the water/powder ratio of mix; Table IV, calculation of the weight of hemihydrate in the original volume; Table V, unit cell measurements and volumes; Table VI, calculation of theoretical contraction per weight of hemihydrate present; and Table VII, calculation of experimental contraction per weight of hemihydrate present.

TABLE II  
 CHEMICAL ANALYSIS OF GYPSUM MATERIALS STUDIED  
 (BASED ON GALLO-WINTERBOTTOM<sup>4</sup> ANALYTICAL METHODS)

CONSTITUENT	PLASTER	STONE	IMPROVED STONE	HYDROCAL BASE B	HYGROSCOPIC CASTING INVESTMENT
CaSO <sub>4</sub> ·½H <sub>2</sub> O	85.0%	87.0%	85.5%	86.0%	26.0%
Soluble anhydride	2.5	.8	1.7	2.5	3.3
CaSO <sub>4</sub> ·2H <sub>2</sub> O	5.0	3.7	3.3	5.2	5.7
Overburnt anhydride and impurities	7.5	8.5	9.5	6.3	

Effective percentage of CaSO<sub>4</sub>·½H<sub>2</sub>O includes soluble anhydride, since this material is extremely hygroscopic and readily converts to the hemihydrate form.

TABLE III  
 WEIGHT OF GYPSUM MATERIALS STUDIED AFTER MIXING AND FOR THE VOLUME OF THE INLAY RING USED  
 (WATER/POWDER RATIOS OF MIX ARE ALSO GIVEN)

MATERIAL	WEIGHT (GRAMS)	WATER/POWDER RATIO
Plaster	51.0	50/100
Stone	58.5	30/100
Improved stone	62.0	23/100
Hydrocal base B	59.3	26/100
Hygroscopic casting investment	57.5	30/100

Water/powder ratios were determined by a consistency test similar to ADA spec. No. 2 for dental inlay casting investments.

TABLE IV  
 WEIGHT OF CaSO<sub>4</sub>·½H<sub>2</sub>O IN THE GYPSUM MATERIALS STUDIED FOR THE VOLUME OF THE INLAY RING USED

MATERIAL	TOTAL WEIGHT (TABLE III)		WEIGHT OF POWDER PER TOTAL WEIGHT (TABLE III)		WEIGHT OF CaSO <sub>4</sub> ·½H <sub>2</sub> O PER WEIGHT OF POWDER (TABLE II)		WEIGHT OF CaSO <sub>4</sub> ·½H <sub>2</sub> O
Plaster	51.0	×	$\frac{100}{150}$	×	.875	=	29.8 Gm.
Stone	58.5	×	$\frac{100}{130}$	×	.878	=	39.5 Gm.
Improved stone	62.0	×	$\frac{100}{123}$	×	.872	=	44.0 Gm.
Hydrocal base B	59.3	×	$\frac{100}{126}$	×	.885	=	41.7 Gm.
Hygroscopic casting investment	57.5	×	$\frac{100}{130}$	×	.293	=	13.0 Gm.

The over-all conclusion to be drawn from Fig. 4 is that the values of the measured contraction are quantitatively within the range of the theoretically determined contraction, thereby validating the cause of this volumetric behavior.

TABLE V  
UNIT CELL MEASUREMENTS AND VOLUMES\*

MATERIAL	CRYSTAL FORM	A	B	C	$\beta$	Z
$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	Monoclinic	11.94	6.83	12.70	$89^\circ 24'$	12
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Monoclinic	5.67	15.15	6.51	$118^\circ 23'$	4
$V_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}} =$		$\frac{11.94 \times 6.83 \times 12.70 \times \sin 89^\circ 24'}{10^8 \times 10^8 \times 10^8}$			$=$	$1036 \times 10^{-24}$
$V_{\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}} =$		$\frac{5.67 \times 15.15 \times 6.51 \times \sin 118^\circ 23'}{10^8 \times 10^8 \times 10^8}$			$=$	$492 \times 10^{-24}$

\*There is some difference of opinion on the crystal form of the hemihydrate. The values in this table were taken from Gallitelli,<sup>9</sup> who appears to have done the most work on this subject.

TABLE VI  
THEORETICAL VOLUMETRIC CONTRACTION PER WEIGHT OF HEMIHYDRATE ON THE BASIS OF SPECIFIC GRAVITY VALUES AND UNIT CELL VALUES

Specific Gravity (x = weight of hemihydrate)

$$\frac{x}{145.148} \times \frac{145.148}{2.75} + \frac{x}{145.148} \times \frac{1.5 \times 18.016}{.997} \rightarrow \frac{x}{145.148} \times \frac{172.172}{2.32}$$

$$\Delta V = \frac{x}{145.148} (52.78 + 27.10 - 74.21) = .039x$$

$$\frac{\Delta V}{x} = .039 \text{ c.c./Gm.}$$

Unit Cell

$$\frac{x}{145.148} \times \frac{6.06 \times 10^{23} \times 1036 \times 10^{-24}}{12} + \frac{x}{145.148} \times \frac{1.5 \times 18.016}{.997} \rightarrow$$

$$\frac{x}{145.148} \times \frac{6.06 \times 10^{23} \times 492 \times 10^{-24}}{4}$$

$$\Delta V = \frac{x}{145.148} (52.32 + 27.10 - 74.54) = .034x$$

$$\frac{\Delta V}{x} = .034 \text{ c.c./Gm.}$$

TABLE VII  
EXPERIMENTAL VOLUMETRIC CONTRACTION PER WEIGHT OF HEMIHYDRATE PRESENT IN THE INLAY RING VOLUME

Plaster	$\frac{\Delta V}{x} = \frac{.93}{29.8} = .031 \text{ c.c./Gm.}$
Stone	$\frac{\Delta V}{x} = \frac{1.29}{39.5} = .033 \text{ c.c./Gm.}$
Improved stone	$\frac{\Delta V}{x} = \frac{1.58}{44.0} = .036 \text{ c.c./Gm.}$
Hydrocal base B	$\frac{\Delta V}{x} = \frac{1.36}{41.7} = .033 \text{ c.c./Gm.}$
Hygroscopic casting investment	$\frac{\Delta V}{x} = \frac{.52}{13.0} = .040 \text{ c.c./Gm.}$

No attempt will be made at this time to analyze either the difference in values of the various materials or their respective deviations from the theoretical value. This is due to the following observations which may influence the true values of either the experimental or theoretical contraction:

1. The theoretical value of contraction is for a complete reaction which may be difficult to achieve under the conditions of mixing which were used. Also, the experimental values were taken at 120 minutes, at which time some of the contraction curves still indicate a slight positive slope. Therefore, additional conversion of the hemihydrate to the dihydrate can conceivably occur after 120 minutes.

2. It is felt that the theoretical value of contraction based on specific gravity values is not as accurate as that based on unit cell measurements; however, at the present time, there is no unanimity of opinion on the type of crystal structure of the hemihydrate form of calcium sulfate in the chemical literature. Consequently, even the contraction based on unit cell measurements can conceivably be slightly in error.

#### CONCLUSIONS

1. The true volumetric behavior of dental gypsum materials on setting was shown to be a contraction.

2. In view of the observed outer dimensional increase of these materials on setting (commonly known as setting expansion), the physical situation which exists must be a porosity formation within the sample.

3. For a given volume of the mixed mass, the ability of the materials to contract or draw in the ambient atmosphere increases in the following order: hygroscopic casting investment, plaster, stone, hydrocal base B, and improved stone.

4. The measured contraction validates the theoretical change which should occur during the conversion of the hemihydrate form of calcium sulfate plus water to the dihydrate form.

5. The curves obtained by this measurement of contraction indicate the rate of reaction and the completeness of the reaction at any specific time after mixing.

Because of the fundamental nature of this study, it was not deemed necessary to test different manufacturers' products. The results are valid for any material containing the hemihydrate of calcium sulfate. Those materials which have been tested were considered to be representative of the gypsum products used in dentistry.

#### REFERENCES

1. Skinner, E. W.: *The Science of Dental Materials*, ed. 3, Philadelphia, 1947, W. B. Saunders Company, p. 36.
2. Van't Hoff, J. H., Armstrong, E. E., Hiurichsen, W., Weigert, F., and Just, G.: *Ztschr. f. phys. Chemie*, Leipz. & Berlin, p. 272, 1903.
3. Mahler, D. B.: *J. Pros. Dent.* 1: 188, 1951.
4. Gallo, G.: *J. Soc. Chem. Indust.* 694, 1914 (abstract of Italian original).
5. Gallitelli, P., and Büsssem, W.: *Periodic Mineral* 4: 1, 1933.