



HEAT TREATMENT AND HYDRATION OF CALCIUM SULFATE

by

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and

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Requirements for the Degree of  
Bachelor of Science

from the

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M. I. T. Dormitories,  
Cambridge, Massachusetts  
May 26, 1937

Mr. George W. Swett,  
Secretary of the Faculty,  
Mass. Institute of Technology,  
Cambridge, Mass.

Dear Sir:

In partial fulfillment of the requirements  
for the degree of Bachelor of Science, we are  
submitting herewith our thesis entitled "Heat  
Treatment and Hydration of Calcium Sulfate".

Respectfully yours,

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## ACKNOWLEDGEMENT

The authors are grateful to Mr. Geoffrey Broughton, under whose guidance this investigation has been carried out, and whose suggestions and interest have been of great value. Prof. E. R. Gilliland has also contributed to the progress of this thesis by giving some very helpful advice.

The cooperation of the Dewey and Almy Chemical Company, through whom we were able to make some of our tests, is also appreciated.

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## OBJECT

The object of this thesis was to investigate the properties of Plaster of Paris ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) and Anhydrite ( $\text{CaSO}_4$ ), alone and admixed with other materials, in order to determine the feasibility of their use as oil well casing cements.

### SUMMARY

In order to investigate the feasibility of using plaster of Paris ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) for an oil well cement, the investigation was divided into two main parts. One included the admixture of other substances to the plaster and study of the porosity, permeability, tensile strength, and time of set of the resulting mixtures. The second consisted of heating commercial plaster of Paris to various temperatures, and study of the products with regard to time of set, density, particle size, tensile strength, and porosity.

From the results obtained, it was concluded that plaster of Paris would not be suitable as an oil well cement.

## INTRODUCTION

It was proposed to investigate the possibility of using plaster of Paris as a substitute for cement in oil well casings. It is common practice in the oil industry to pump cement into the annular space between the walls of the well and the casing at certain stages during the drilling, when water sands are encountered. This operation is necessary because water from the upper strata runs down along the outside of the casing thus causing emulsions with the oil. Water in the oil increases the cost of pumping besides making it necessary to separate the oil from the water when it is brought to the surface. In order to get the cement into its final position the well casing-shoe is raised a few feet from the bottom of the well and the cement pumped down through the tubing placed inside the casing. Water or mud is pumped down on top of the cement, thus forcing it into the annular space outside of the casing. Before the cements set the casing is driven down into its final position. After setting, the cement inside of the pipe is drilled out.

## PROBLEM

Ordinary cement, while satisfactory for oil wells of medium depth, is unsatisfactory for cementing in casings of very deep wells owing to the high temperatures encountered. These decrease the time of initial set of the cement, making it difficult to get into position in time. Firms specializing in the cementing of oil wells have overcome this difficulty to a certain extent by careful control of the particle size of the cement used. However, since this method requires exacting control, and there is a probability that still deeper wells will be drilled, it is desirable to obtain some new product with which to fill the annular space between the walls of the well and the casing, or alternatively to alter the present product so as to facilitate its use.

Broughton (1), in his report on the cementing of deep oil wells, states that the desirable qualities of a deep well cement should be as follows:

- (1) Long initial setting time, even at high temperature.
- (2) Low permeability.
- (3) Good bonding power with earth and casing.
- (4) High tensile and compressive strength.
- (5) Low viscosity of slurry.



Plaster of Paris has been suggested as a material for the cementing of oil wells. Ordinary plaster of Paris has neither of the first two desirable properties mentioned above. It was the purpose of this thesis to attempt to improve these conditions. The work done consisted mainly of the following investigations.

(1) Heat treatment of plaster of Paris at high temperatures in an effort to alter the time of set and permeability.

(2) Study of the various forms of  $\text{CaSO}_4$  which are claimed to exist.

(3) Addition of various substances such as bentonite, TDA, calcium stearate, sodium silicate, and mica to plaster of Paris, making a study of the set, porosity, tensile strength and permeability of the resulting mixtures.

(4) Study of the possibility of using anhydrous  $\text{CaSO}_4$ , which has been made by heating  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  to high temperatures, as an oil well cement.

## PREVIOUS INVESTIGATIONS

### Discussion of the Properties of $\text{CaSO}_4$ and its Hydrates

The literature indicates that there are several forms of  $\text{CaSO}_4$  with varying quantities of water of crystallization. Gypsum, which contains two molecules of water, occurs naturally as monoclinic crystals called selenite. A rhombic form also exists, but this is less stable at ordinary temperatures. A fibrous form with this same constitution is known as satin-spar, while still another crystalline form is called alabaster.

The anhydrous salt is thought to exist in three forms. The first, which is known as natural anhydrite or insoluble anhydrite, occurs free in nature and does not set with water. A second form called soluble anhydrite does not occur in nature. As the name implies, it is soluble and sets very quickly with water, even faster than the hemi-hydrate, or plaster of Paris.

There seems to be some question as to the two forms of anhydrite. Some claim that their difference in behavior with regard to water is due to particle size only.

The hemi-hydrate can be made by heating gypsum at  $60 - 90^\circ \text{C}$  in a vacuum over phosphoric acid. The conversion will also take place under atmospheric pressure in the absence of moisture at approximately  $110^\circ \text{C}$ . At this temperature the conversion is supposed to be reversible.

That is, if a humid atmosphere exists over the soluble anhydrite at  $110^{\circ}$  C it will form the hemi-hydrate.

Conversely, if the atmosphere is dry, the hemi-hydrate will lose water to form the soluble anhydrite at this temperature.

A form of  $\text{CaSO}_4$  which is known as dead burnt gypsum, and which is thought by some to be identical with the natural anhydrite, is formed by heating the soluble anhydrite around  $500^{\circ}$  C. It takes up water slowly, but if allowed to stand in moist air for a long time, will regain up to 6 - 7 percent water. This is about the composition of the hemi-hydrate. It is claimed that if this dead burnt gypsum which has taken up 6 - 7 percent water by long standing is mixed with water it will set to practically normal hardness, but only after a very long time. Many contradictory statements exist in the literature concerning a third form of anhydrous calcium sulfate known as Estrichgyps. The temperature at which this is formed is not definitely known. Some authors claim that Estrichgyps is made by heating gypsum above the temperature for the formation of the hemi-hydrate but below that for forming dead burnt plaster. Rohland (2), for example, claims that Estrichgyps is formed at a lower temperature than dead burnt, or at a temperature between  $525 - 600^{\circ}$  C. Rohland's figures are, however, worthless, for he shows no evidence of an equilibrium between the two. His ideas also

contradict the methods used in practice, Estrichgyps being prepared at temperatures over  $900^{\circ}$  C. Glacenapp (3) claims that Estrichgyps is not formed below  $800^{\circ}$  C. He also states that at a red heat, a certain amount of decomposition of the calcium sulfate takes place with the formation of a basic sulfate which may play some part in the hardening. Equilibrium data show that at  $1000^{\circ}$  C, 0.21 percent CaO is formed. At  $1300^{\circ}$  C, 3 percent is formed and at  $1375^{\circ}$  C, 98.67 percent CaO is formed. The minute quantity formed at a temperature of  $1000^{\circ}$  C indicates that CaO, if present in Estrichgyps, is there in small amounts. Some claim that its presence is responsible for the setting of Estrichgyps, while other investigators think that Estrichgyps might be a mixture of the soluble and insoluble anhydrites.

Another explanation advanced for the difference between dead burnt gypsum and Estrichgyps is that there may be a difference in surface area. The smaller particle would tend to set faster than a larger one. Desch (4) holds to this latter opinion, maintaining that there is but one form of anhydrite, the supposed modifications being due largely to differences in fineness of the particles.

A typical analysis of commercial plaster of Paris is given below (5).

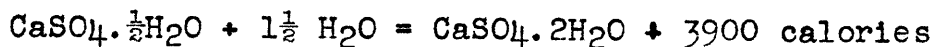
Moisture (loss at 105° C)	3.59
Combined water	5.34
Silica	.14
Ferric oxide and alumina	Traces
Sulfuric anhydride	52.69
Lime	37.94
Magnesia	<u>Trace</u>
	99.70

#### The Setting of Plaster of Paris

The setting of plaster of Paris is a definite chemical transformation from the hemi-hydrate to the dihydrate of  $\text{CaSO}_4$ . Le Chatelier (6) assumed that the hemi-hydrate first forms a saturated solution in water which is supersaturated with respect to gypsum. From this supersaturated solution the dihydrate is deposited as a compact mass of interlocking needles which offer considerable resistance to disruption. Baykoff (7) supports the claim that there is an intermediate gel forming stage in the setting of plaster of Paris, reaching this conclusion as a result of a procedure which he claimed would give a gypsum jelly. However, the arguments for gel formation have been questioned by Weiser and Moreland (7). They show by microscopic examination that Baykoff's "gel" has a network of relatively long crystal needles of gypsum.

This work by Weiser and Moreland seems to prove that Baykoff's gel is a false one.

The rate of set of plaster of Paris can be controlled by the addition of "accelerators" or "retarders". Experiments run by Weiser and Moreland (7) to determine the time of set of various mixtures utilized a calorimeter which measured the temperature use as the mix reacted with the water. Heat is evolved according to the equation:



A plaster which shows a long period of inhibition, before there is any marked rise in temperature, is known as a slow setting plaster, while one with a short period of inhibition is referred to as a rapid setting plaster. Ordinary plaster of Paris sets within 5 - 15 minutes after mixing, but the rate also depends on the time and temperature of calcination of the gypsum. However, the rate of setting can be changed greatly by addition of foreign substances to the plaster. The presence of gypsum nuclei in plaster of Paris increases the rate of set. These gypsum nuclei are thought to provide seed crystals upon which the precipitation of the dihydrate can take place.

Other effects which hasten the rate of setting are prolonged mixing, and addition of electrolytes.

Generally inorganic electrolytes at high concentrations retard the set, while moderate concentrations tend to increase the rate. The ratio of the solubility of plaster of Paris to that of gypsum in water at 25° C is 4.5. If the addition of a foreign electrolyte cuts down the period of inhibition, the initial percentage supersaturation of the solution with respect to gypsum was found to be increased. Conversely, if the addition of a foreign electrolyte to water lengthened the inhibition period, the initial percentage supersaturation of the solution with respect to gypsum is decreased. In general, for a foreign electrolyte to change the initial rate of nuclei formation, and hence the rate of set, it is necessary, other things being equal, for the ratio of the solubility of hemi-hydrate to the solubility of gypsum to be greater or less than 4.5, the ratio of the solubilities in pure water (7).

### Strength

The maximum strength of a plaster cast is reached when the cast becomes completely dry. This was shown by Johnson (8) who tested plaster casts at different times while they were being dried. Further investigation by Johnson showed that continued heating of gypsum at 100 - 104° C decreased the strength of the plaster. This decrease in strength is thought to be due to the reversion of the dihydrate to the hemi-hydrate. Experiments by Weiser and

Moreland (7) indicated that in most cases an electrolyte lowered the tensile strength of the casts.

### Permeability

In discussing permeability, two terms should be defined. The first, porosity, is the quality of containing interstices between the particles of a body. The second, permeability, refers to the property of allowing fluids to pass through the pores or interstices of a body.

Ordinary gypsum plaster due to its rapid set entraps small quantities of water which eventually evaporate but which leave the set mass definitely porous and permeable to liquids. Plaster of Paris in itself is unsatisfactory for oil well work since it would allow water to percolate into the oil beds. It was the purpose of this thesis to attempt to reduce this permeability and to alter the time of set of the plaster in order to make it satisfactory for use in oil wells.



## PROCEDURE

Experimental work was divided into two main parts. One part consisted of adding substances to plaster of Paris in an effort to reduce its permeability, while the other consisted of heating the plaster to various temperatures and determining the time of set, porosity, tensile strength, and density of the resulting products. Commercial plaster of Paris with the designation FFF was taken as a basis for all experiments. This plaster was purchased from the Howe and French Company, of Boston. Admixtures of the plaster with bentonite, calcium stearate, TDA, sodium silicate, and powdered mica were made. Experiments on these mixtures consisted of determining the time of set, the porosity, tensile strength, and the permeability. Permeability was not measured on all mixtures because of difficulties, which are explained in the discussion of the results. The time of set was measured on a modified Vicat apparatus, while the tensile strength was found on a Rhieie standard testing machine. Porosity was measured by immersing the samples in water for a given time interval and then weighing to find how much water was absorbed. Permeability was determined by measuring the amount of water which came through a sample in a given time. In all measurements several samples were taken, the average being used as a final result.

## RESULTS

The following results were obtained from the investigations carried out.

### A. Results obtained from the baking of plaster at high temperatures.

(1) Material heated at  $1040^{\circ}$  C for 48 and 96 hours shows the same initial temperature rise, while that heated for 5 hours does not check the other two.

(2) There appear to be two distinct breaks in the density curve of the heated material with temperature (See Fig. 1).

(3) For temperatures of dehydration between  $200^{\circ}$  and  $420^{\circ}$  C, the time for maximum temperature is directly proportional to the temperature of dehydration (See Fig. II). The setting curves for these materials are given in Fig. XIX of Appendix C.

(4) The anhydrite formed between  $200$  and  $420^{\circ}$  C sets faster than the hemi-hydrate.

(5) For temperatures of dehydration above about  $480^{\circ}$  C the material obtained shows no signs of set until after it has been ground very fine in some form of mill.

(6) Plaster of Paris dehydrated at temperatures up to  $1040^{\circ}$  C and milled will set with water. Temperatures above  $1040^{\circ}$  C were not investigated.

(7) The tensile strength of the resulting set materials, after standing for seven days, vary over the range of temperatures as shown in Fig. III.

(8) The amount of chemically combined water in the set material which had been allowed to stand for seven days varies over the whole range of temperatures. These results are shown in Fig. VI.

(9) After milling for 24 hours in a pebble mill, the samples dehydrated at different temperatures, it was found that the fineness of the resulting products varied. Comparative results are shown in Fig. IV. It should be noted that all samples heated at or below  $365^{\circ}$  C were not milled.

(10) After milling it was found that the time of set as determined by the modified Vicat apparatus varied greatly with the temperature of ignition of the sample. The time was nearly constant for the material heated up to a temperature of  $365^{\circ}$  C. Above that the time of set increased very rapidly (See Fig. V).

(11) The porosity of the set material after standing seven days is a maximum when the temperature of dehydration is about  $500^{\circ}$  C (See Fig. VII).

(12) The initial temperature rise of the different samples varies greatly. This variation is given in Fig. VIII.

(13) The rate of set of commercial plaster of Paris is increased by adding small amounts of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . The larger the quantity of dihydrate added, the greater the rate of set (See Fig. IX).

(14) The rate of set of the anhydrite prepared at  $310^\circ\text{C}$  is also increased by adding small amounts of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . As in the case of the ordinary plaster of Paris, the rate is a direct function of the amount of the dihydrate added. (See Fig. X)

(15) Mixtures of commercial plaster of Paris and plaster dehydrated at  $310^\circ\text{C}$  have setting properties dependent upon their ratio in the mixture. The setting curves are shown in Fig. XI.

(16) A mixture of commercial plaster of Paris and anhydrite obtained by dehydrating at  $660^\circ\text{C}$ . has setting properties intermediate between those of the two constituents (See Fig. XII).

(17) A mixture of commercial plaster of Paris and the anhydrite obtained by dehydrating at  $1005^\circ\text{C}$  has setting properties intermediate between those of the two constituents (See Fig. XIII).

(18) Free lime is found in all samples dehydrated at or above  $480^\circ\text{C}$ . The exact amount for each temperature is shown in Fig. XIV.

(19) Replacement of pure water by saturated lime water decreases the time of set of the ignited material by 50 to 80 percent (See Table II in Appendix C).

(20) Materials heated at or above 420° C and milled in a pebble mill showed no sign of expansion on setting.

(21) The materials heated at or below 365° C and not milled expanded on setting.

(22) Consistent results for the initial temperature rise were not obtainable on milled samples.

B. Results obtained from addition of foreign substances to plaster of Paris.

(1) The set of plaster of Paris can be controlled by the addition of other substances.

(2) Sodium silicate decreases the time of set greatly. The larger the acid concentration in the sodium silicate the shorter the time of set. Ground mica also decreases the time of set.

(3) TDA increases the time of set. The larger the TDA - plaster ratio the longer the time of set. The same is true with calcium stearate. Bentonite suspensions mixed with plaster increase the time of set.

(4) Dry bentonite when mixed with plaster, and water added does not give a good set since the mixture contracts on setting. It also causes the set plaster to crumple easily, and disintegrate when placed in water.

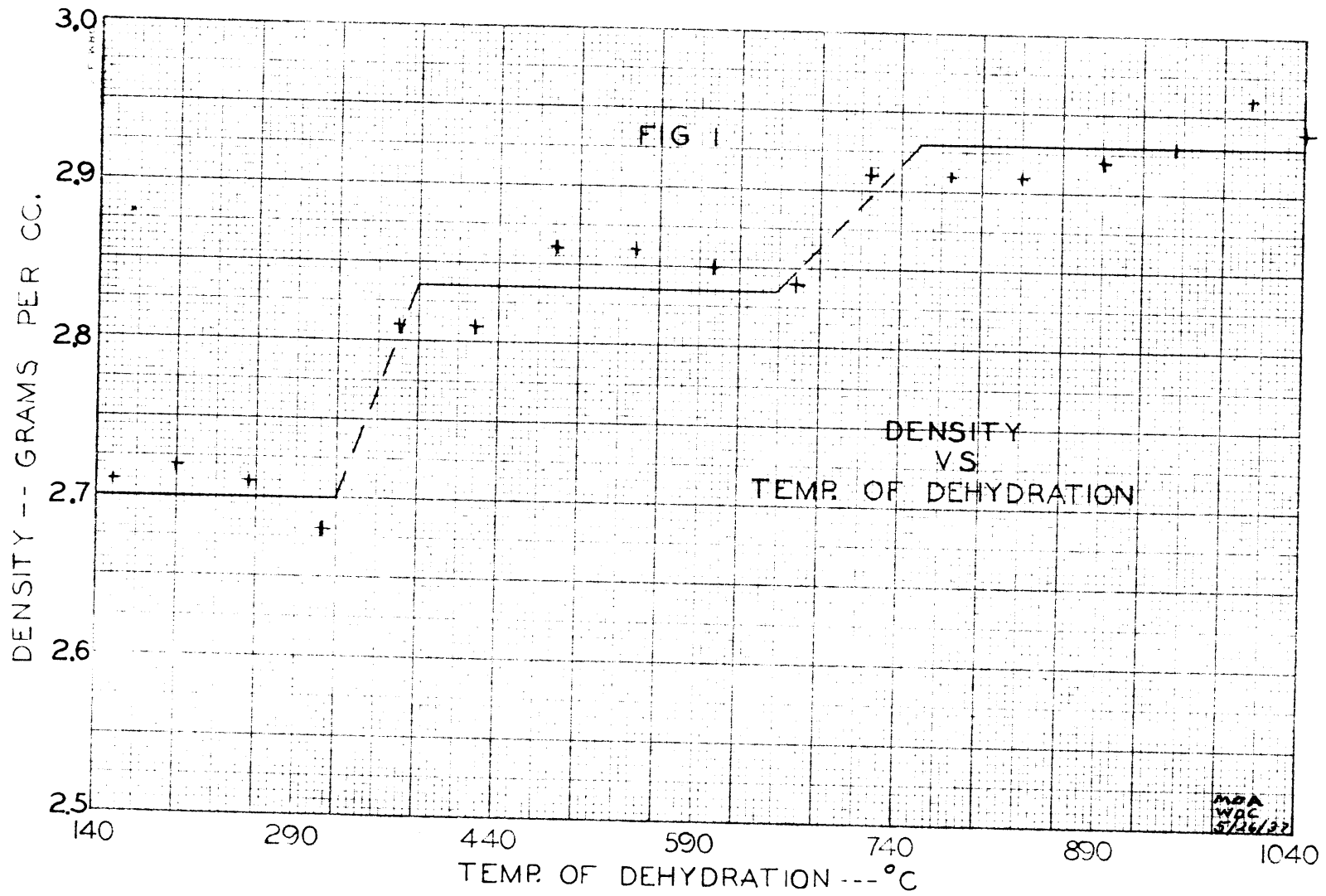
(5) Bentonite, calcium stearate, mica, and sodium silicate increase the porosity of plaster of Paris.

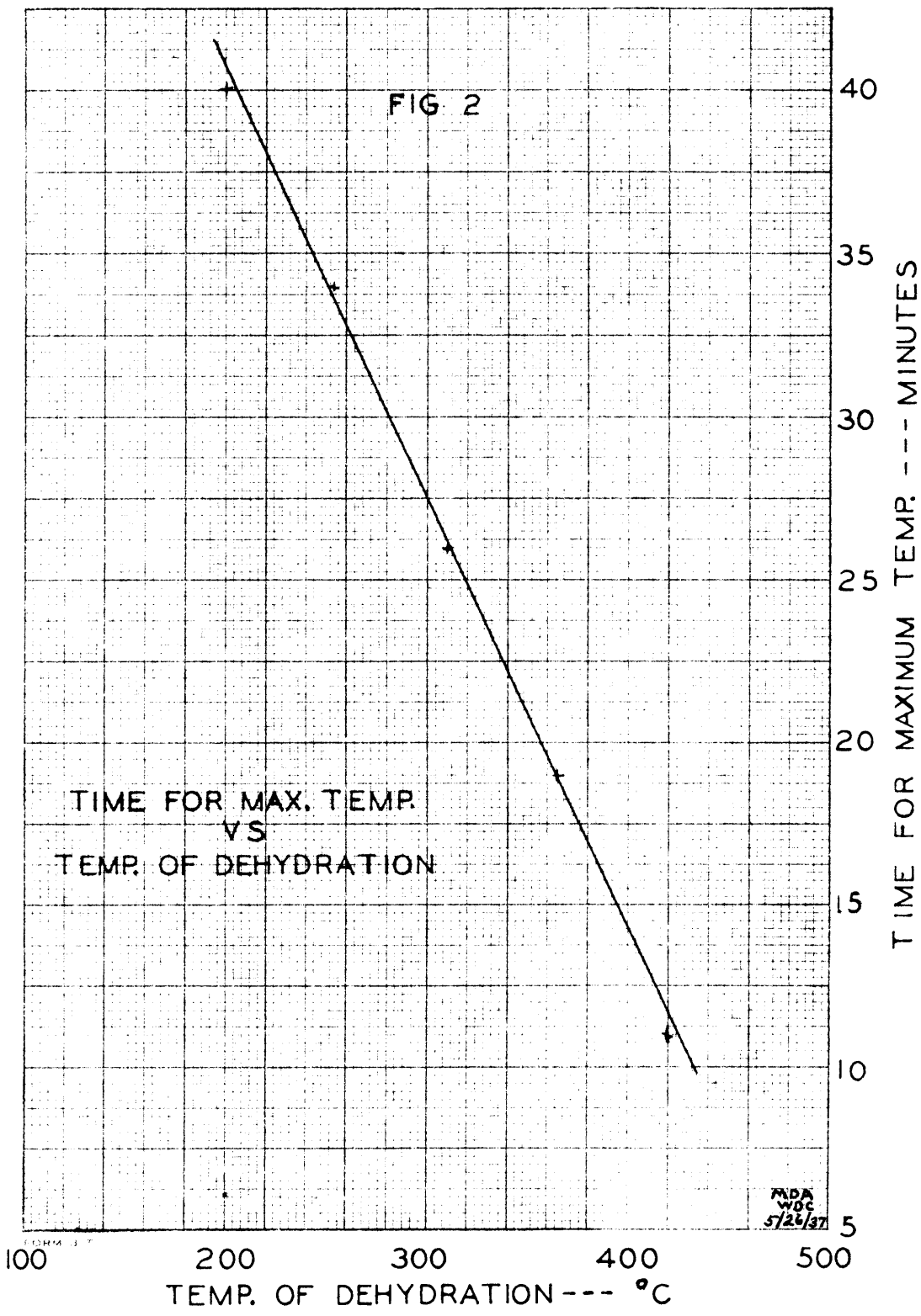
(6) TDA has no marked effect on the porosity.

(7) Calcium stearate, mica, bentonite, and sodium silicate decrease the tensile strength of plaster, the last two most markedly.

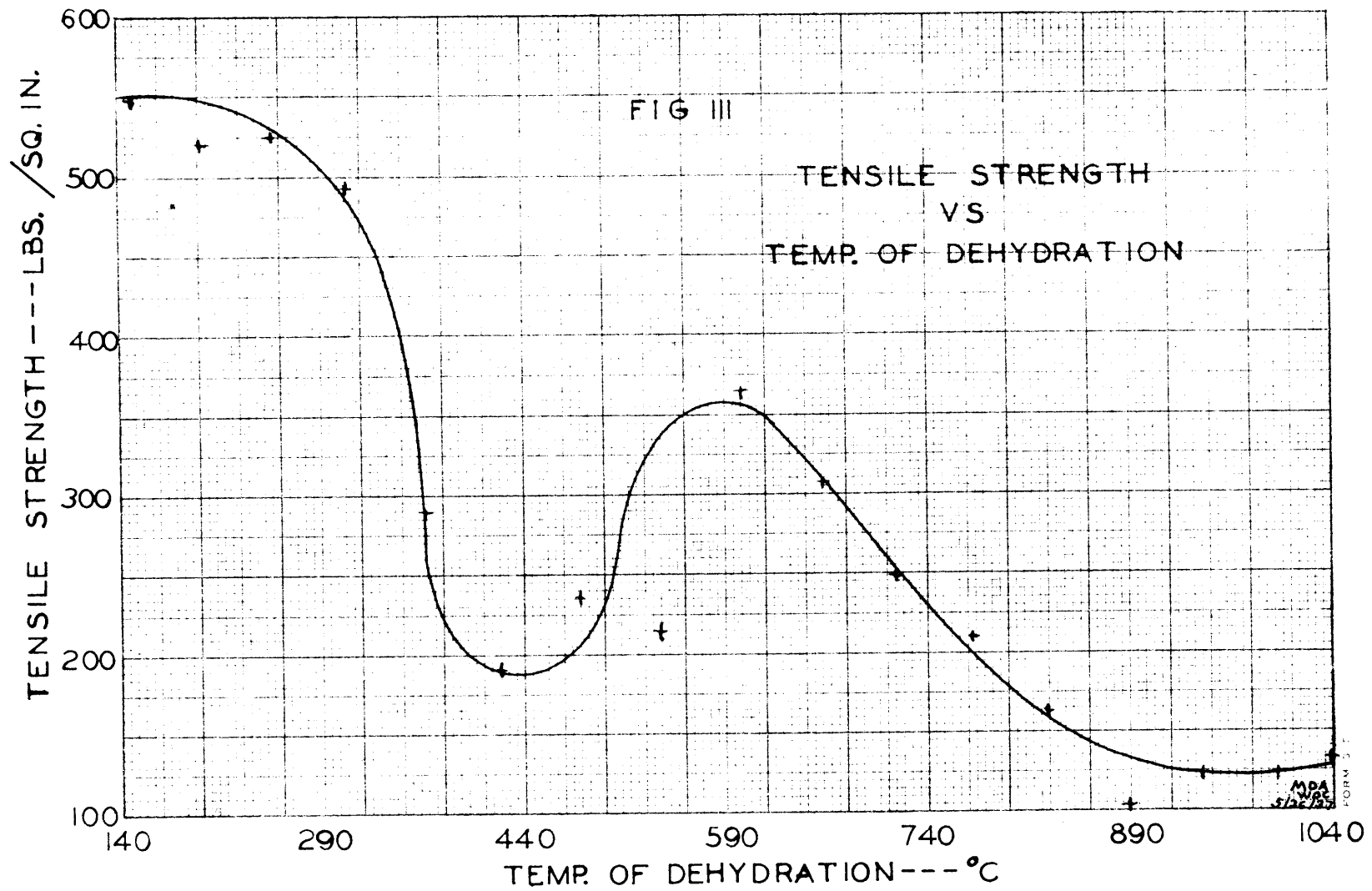
(8) TDA increases the tensile strength of plaster approximately 40 percent.

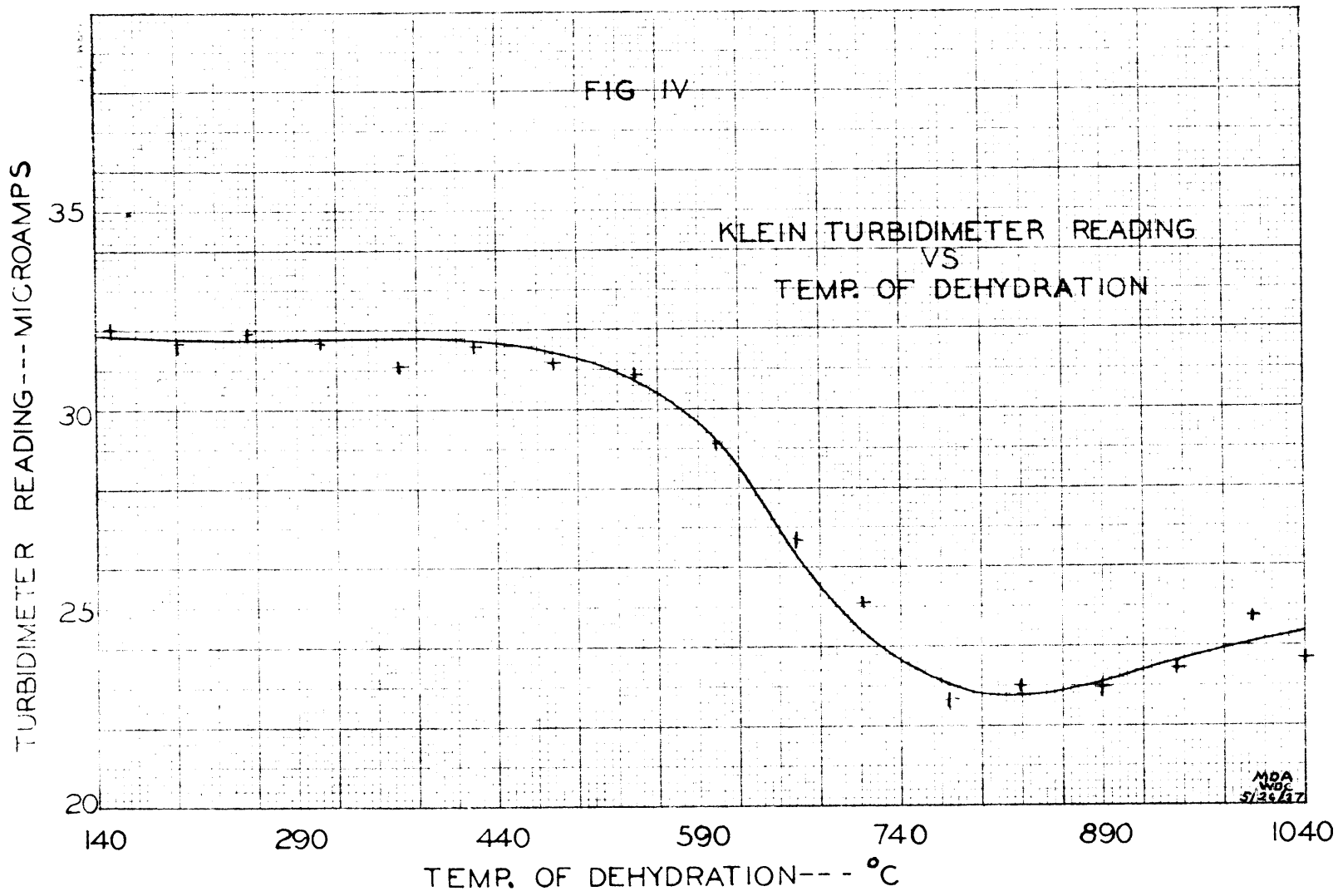
(9) The permeability measurements taken have no significance since the small size of apparatus and sample used were incapable of giving consistent results.

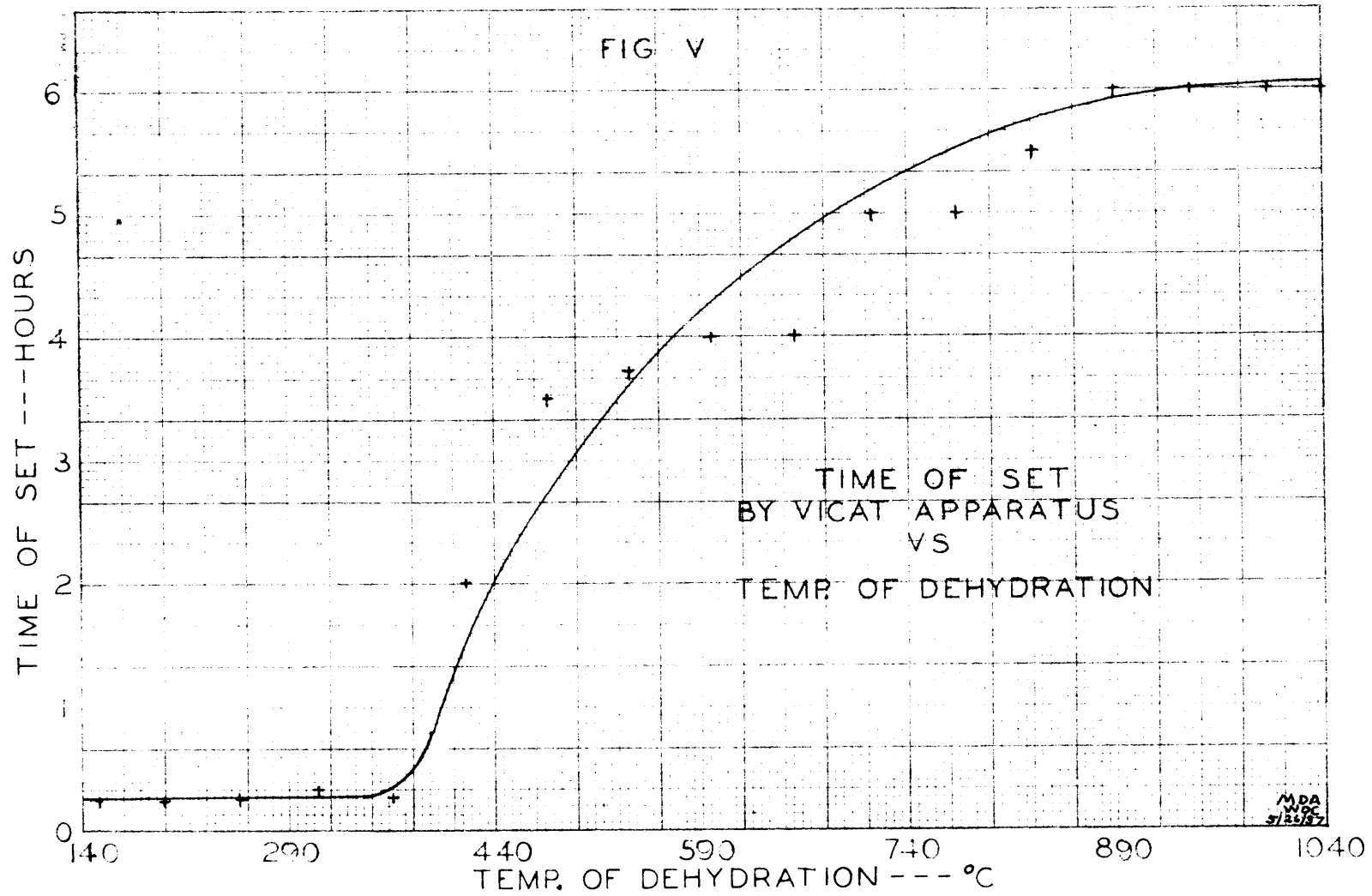


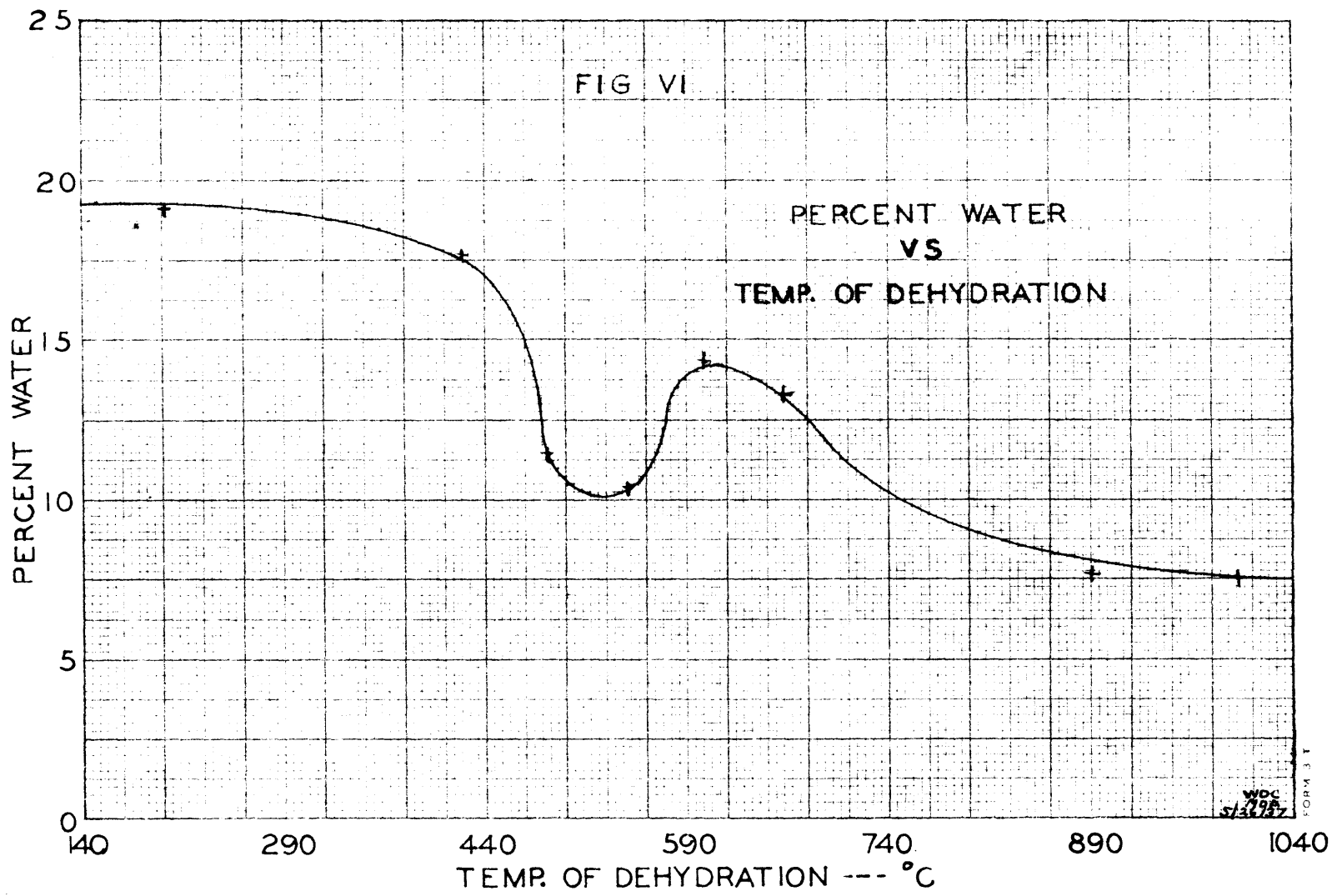


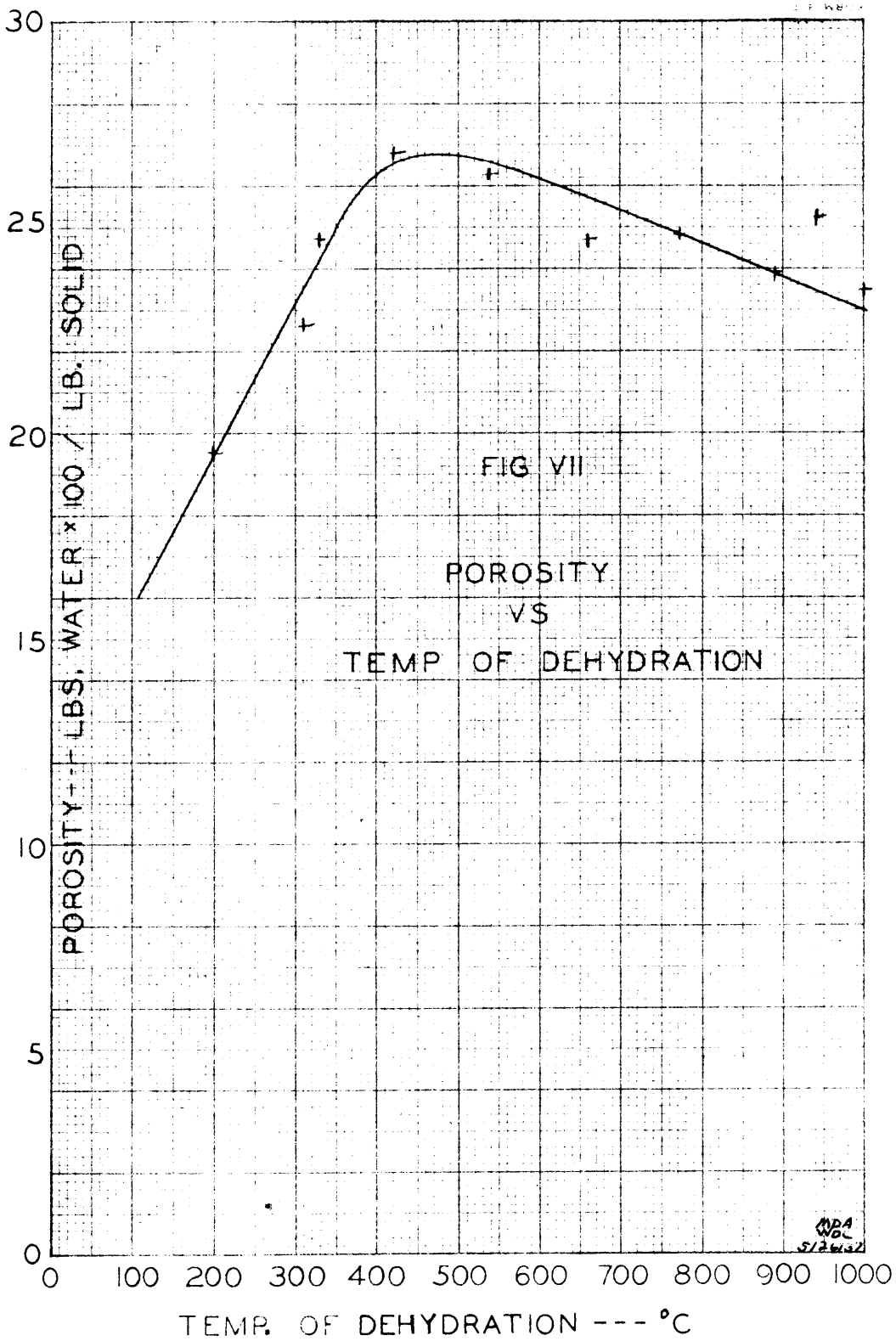


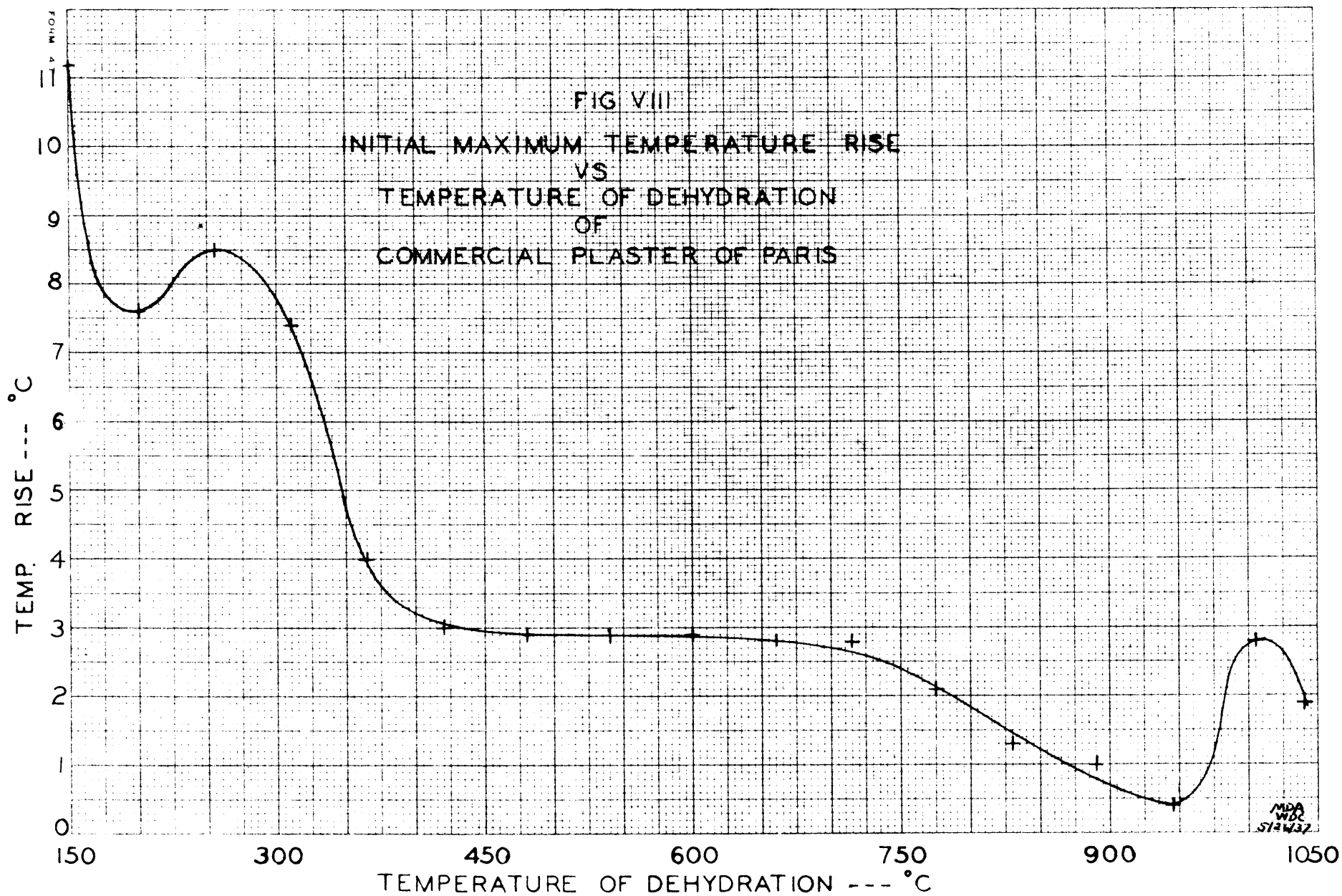


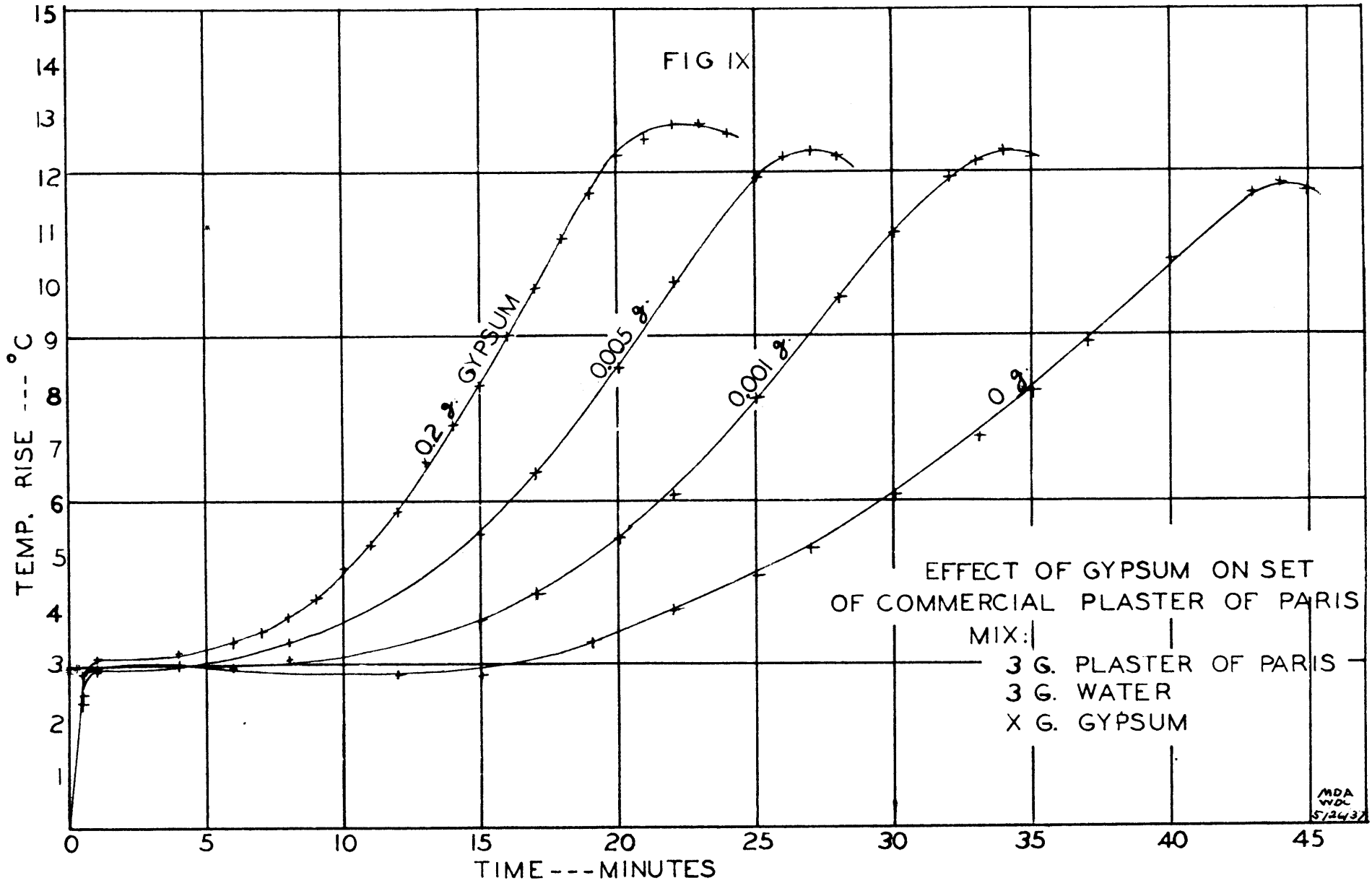


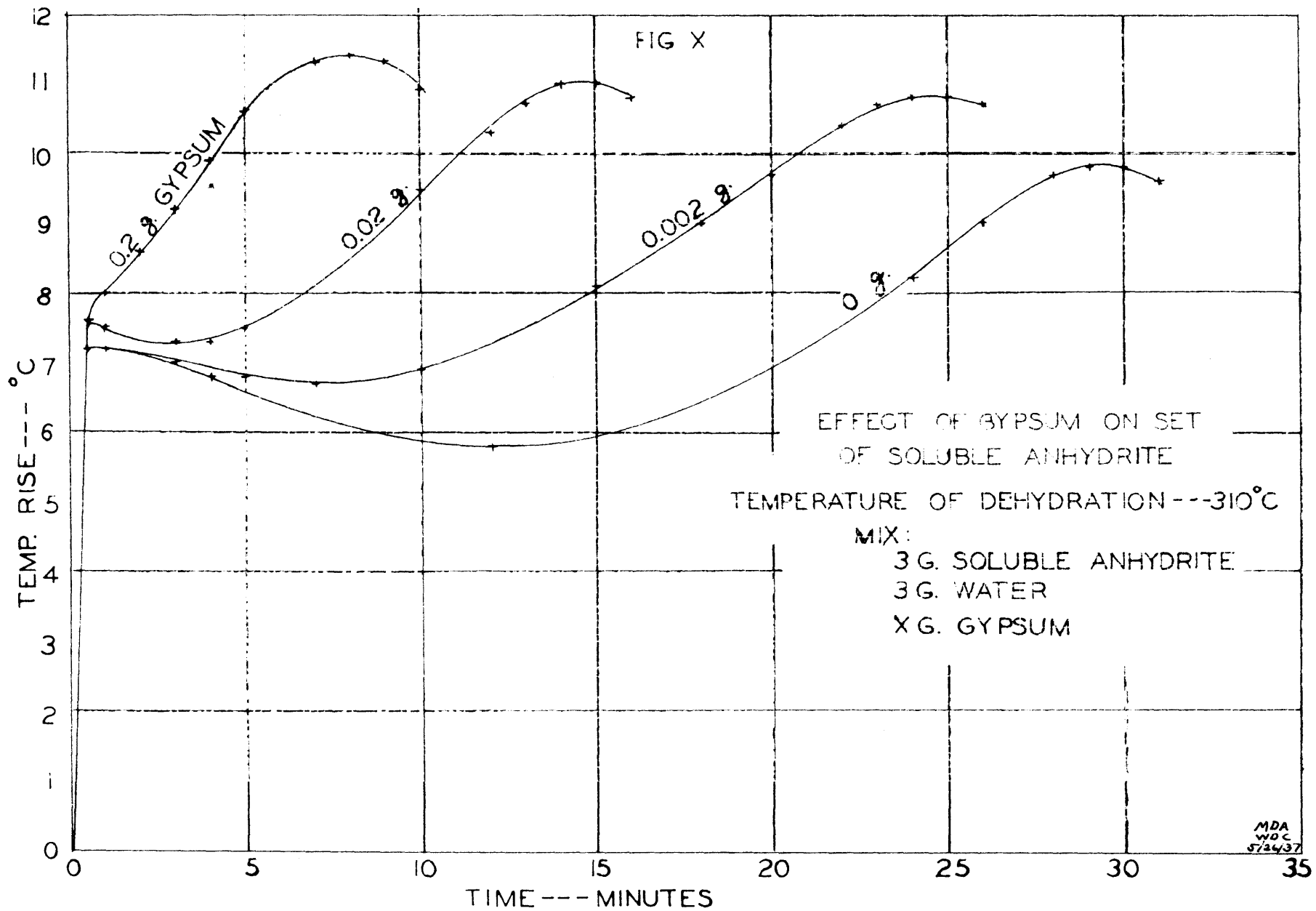














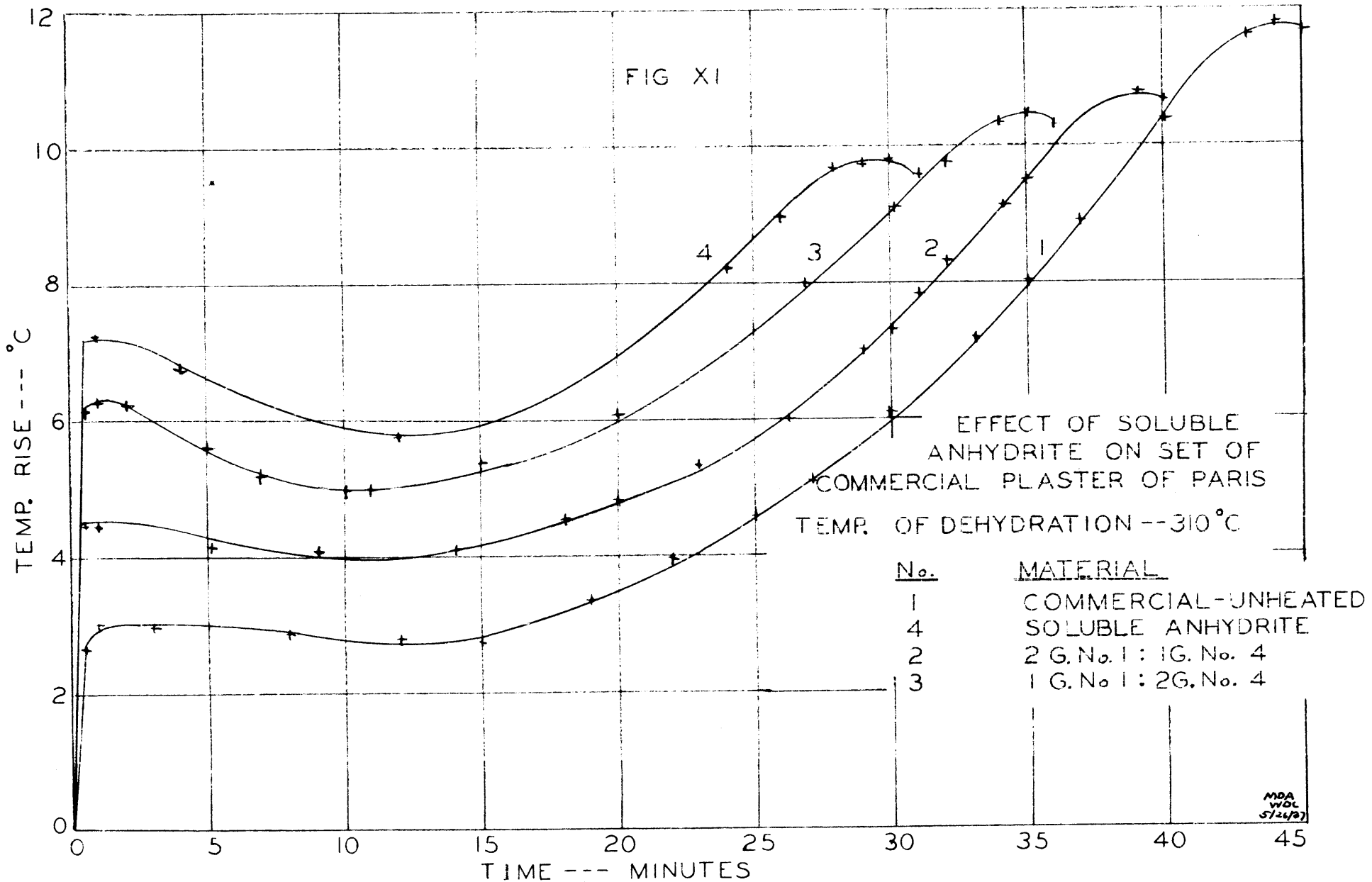
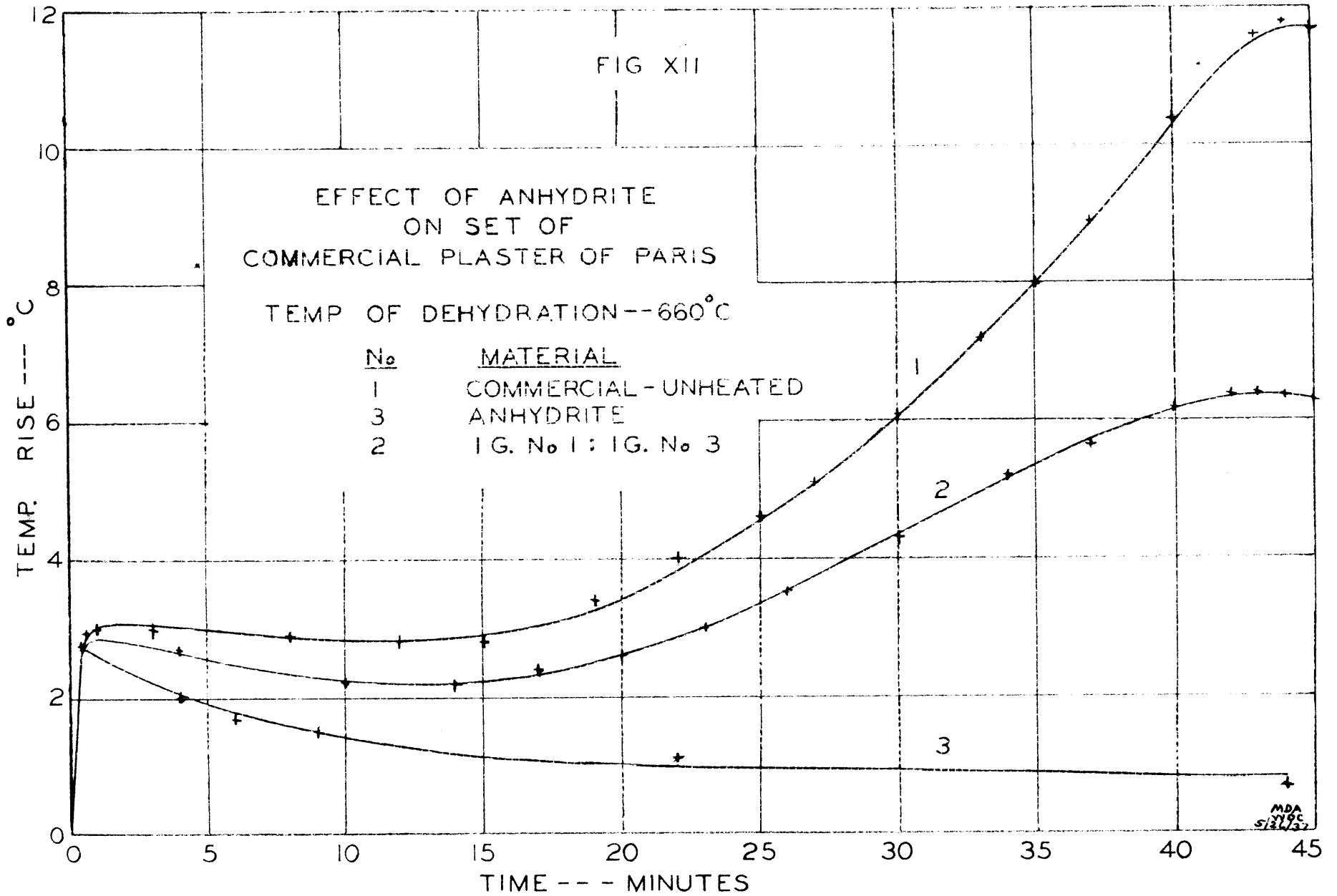


FIG XII

EFFECT OF ANHYDRITE  
ON SET OF  
COMMERCIAL PLASTER OF PARIS

TEMP OF DEHYDRATION -- 660°C

No	MATERIAL
1	COMMERCIAL - UNHEATED
3	ANHYDRITE
2	IG. No 1 : IG. No 3



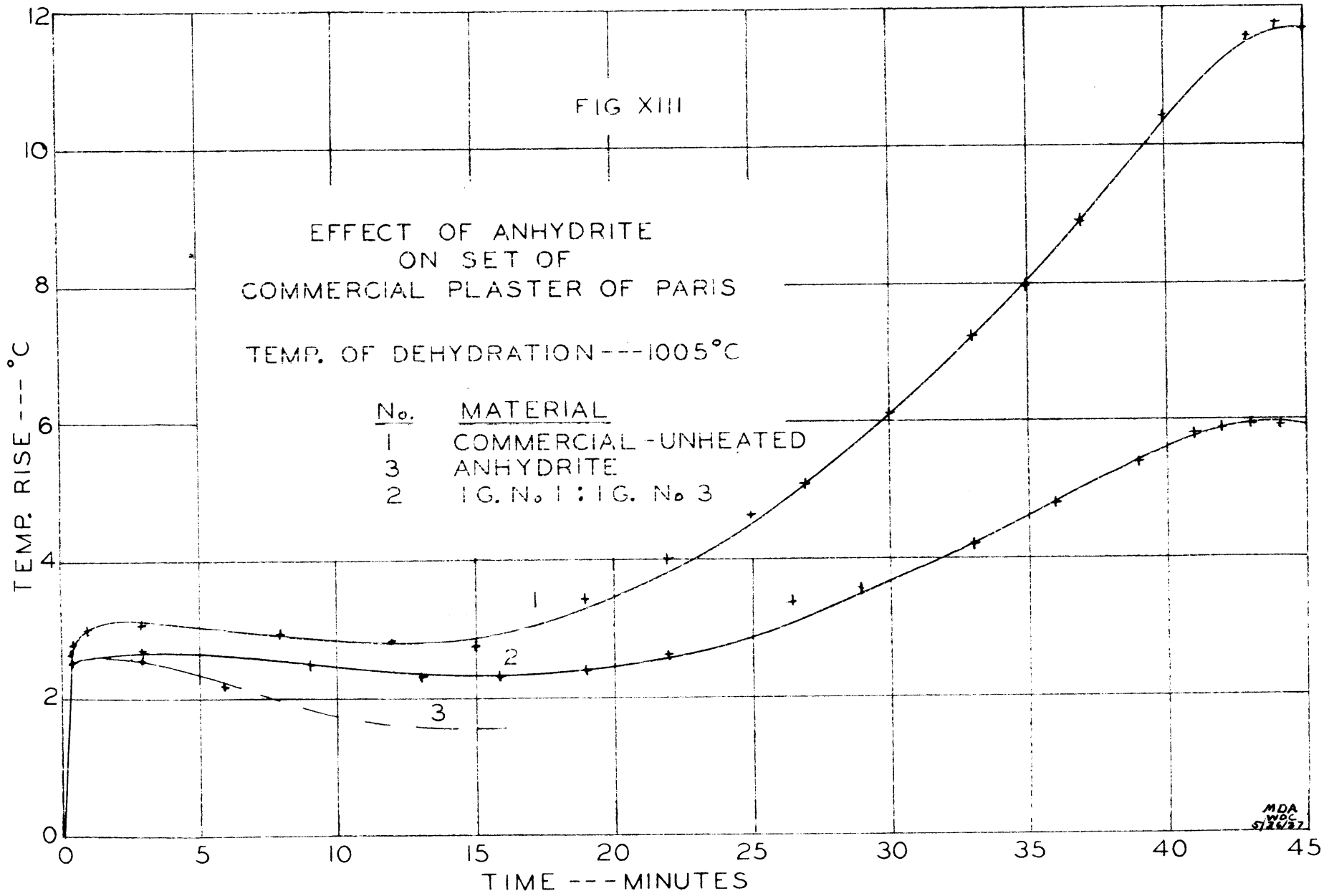
MDA  
5/31/32

FIG XIII

EFFECT OF ANHYDRITE  
ON SET OF  
COMMERCIAL PLASTER OF PARIS

TEMP. OF DEHYDRATION --- 1005°C

No.	MATERIAL
1	COMMERCIAL - UNHEATED
3	ANHYDRITE
2	IG. No. 1 : IG. No. 3



MDA  
WOC  
5/24/27

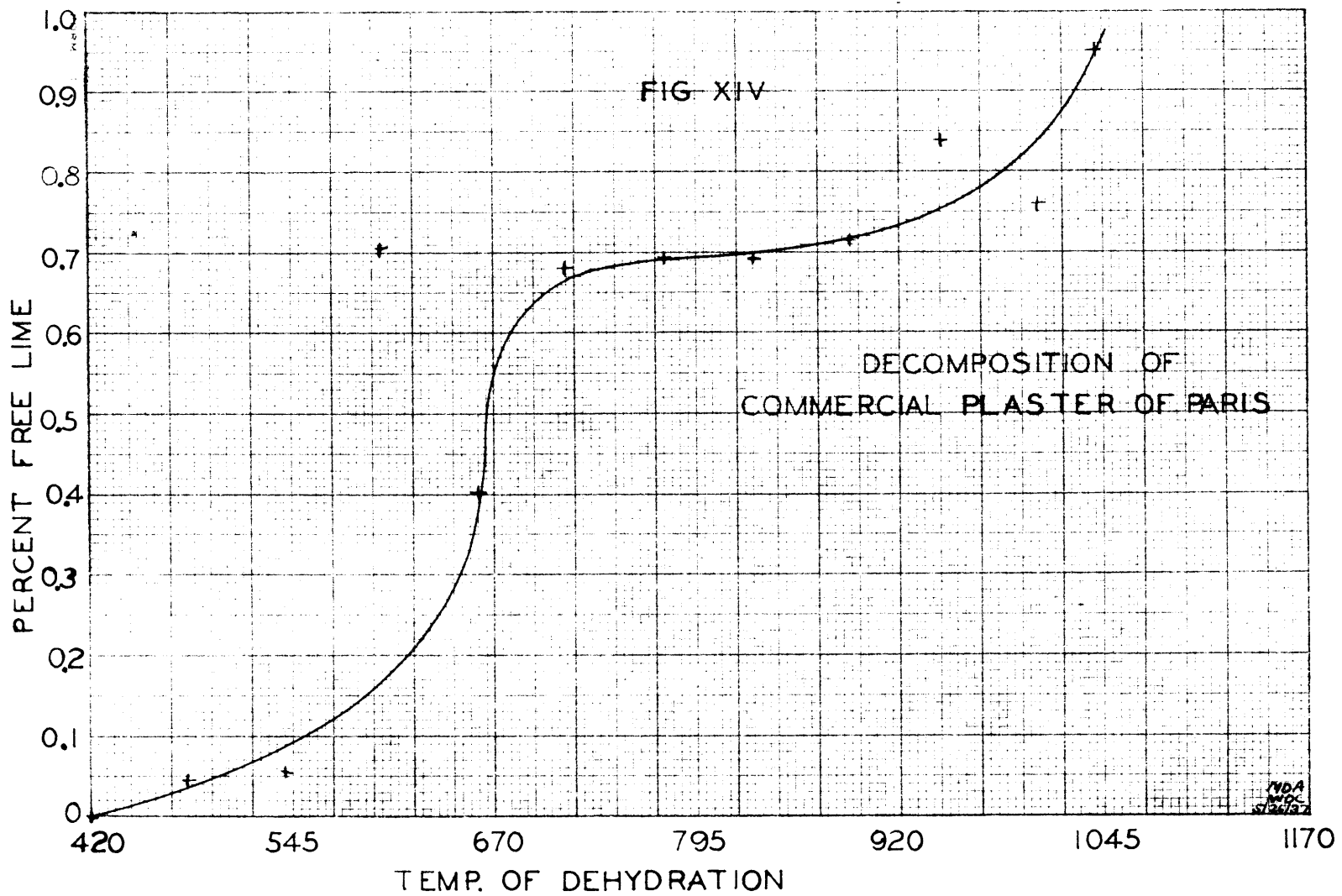
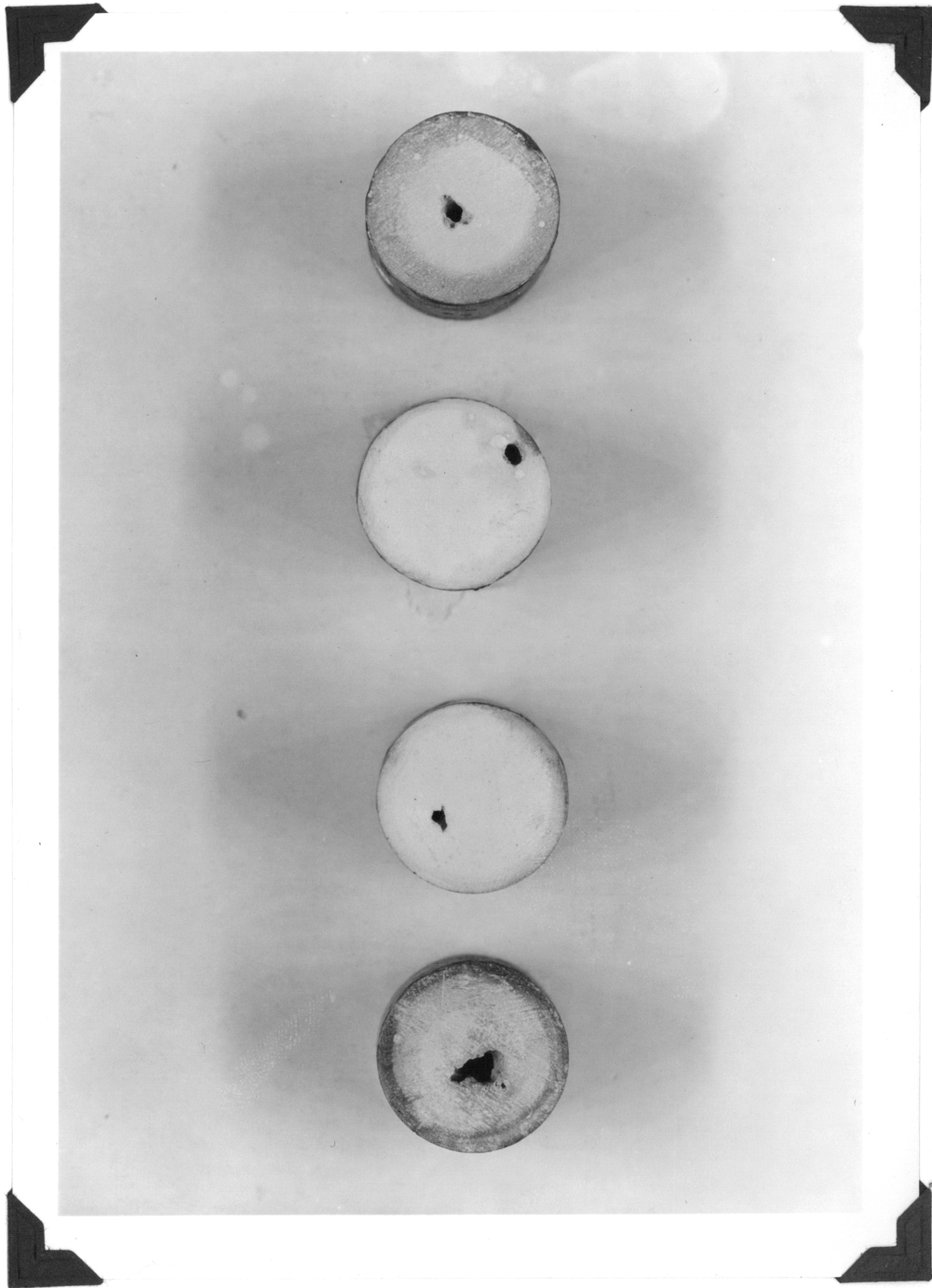


FIG. XV



PERMEABILITY SPECIMENS.

## DISCUSSION OF RESULTS

### A. Results obtained from the baking of plaster at high temperatures.

From the density determinations made (See Fig. I) it would appear that there are three forms of anhydrite formed by mere application of heat to plaster of Paris. The first of these is formed if the temperature of dehydration is kept between the limits of 200°C and 310°C. The second is formed at a temperature between 365°C and 660°C. The last form is encountered for temperatures of dehydration from 715°C to at least 1040°C and possibly higher. The effect of higher temperatures was not studied, because no furnace was available with a temperature range extending above 1040°C.

For convenience the following nomenclature will be adopted throughout the following discussion.

<u>Temperature of Dehydration</u>	<u>Designation</u>
200 - 310° C	I
365 - 660° C	II
715 - 1040° C	III

By referring to Figs. I and VIII it will be noted that the two curves correspond quite well. At the two points at which there appears to be a break in the density curve there are similar breaks in the curve of initial

temperature rise. There are also several other breaks in the curve of initial temperature rise but the authors are unable to give any explanation for these. It is unlikely that experimental error is the reason, for repeated tests show that the values on the initial temperature rise curve are accurate to approximately  $\pm 0.2^{\circ}$  C while the density is accurate to approximately  $\pm 0.02$  g/cc.

Inspection of Figs. III, VI and VII will show that there are no very distinct breaks in the curves of tensile strength, percent water and porosity vs temperature of dehydration; however, they all agree with one another reasonably well. The similarity between the percent water and tensile strength is very distinct. It would appear from these two curves that the material with the designation II either takes up water more slowly than the rest or that it is partially dead burnt, i. e., part of the material has entirely lost its ability to take up water chemically. The porosity curve, while not having the same general shape as the tensile strength and percent water curves, is analogous in that the maximum porosity occurs at the point where the other two curves display a minimum value.

It will be noted by reference to Figs. IV and V that they are almost identical. In connection with these figures it should be remembered that all samples heated at or below

365° C were not milled while those heated above this temperature were milled in a pebble mill for 24 hours. The time of milling was the same for all samples. It should also be noted that a large reading on the Klein turbidimeter indicates a small surface area and consequently a large average particle size. The Klein, of course, is designed primarily for cement testing but it is assumed that comparable results can be obtained on calcium sulfate. Keeping all this in mind and comparing the Klein reading obtained with the time of set as determined by the modified Vicat apparatus, it will be noticed that a surprising result is obtained. The smaller the surface area of the material used, the shorter is the time of set. Obviously this contradicts the well known fact for cement that the greater the surface area the greater the rate of set. This fact is substantiated by the observation that all the samples of calcium sulfate heated above 420° C showed no signs of setting until they had been milled. Of course it may not be justifiable to interpret this observation in this way. It may be that when the plaster is heated above 420° C a thin crust forms over each particle. This crust will not react with water and consequently it is not until the material has been ground and this outer layer broken that the material



will react with water and set. However, this later theory is not upheld by any of the other results obtained. It seems that the only conclusion that can be drawn from the contradiction mentioned above is that, although surface area is a factor in determining whether or not a material will set, other factors probably enter in and thus cause this apparent conflict of data.

Other investigators have thought that maybe the decomposition of the calcium sulfate at high temperatures into lime and sulfur trioxide was a factor which influenced set. In the course of this investigation data were obtained which would tend to substantiate this theory. It was found that by using lime water in place of pure water for mixing with the materials that were formed at or above 420° C, the time of set as indicated by the modified Vicat was greatly reduced. (See Table II, Appendix C) It was also found that somewhere between 420° C and 480° C is the temperature at which the plaster of Paris or some impurity present starts to decompose and give free lime or some other basic constituent. (See Fig. XIV) We may conclude from these two sets of data that since free lime or free alkali is present in the high temperature samples and lime was found to hasten set, this alkali which is present is one of the factors which partially controls the set of these samples and causes them to set faster than they ordinarily would.

The literature indicates that at equilibrium the following percentages of CaO are formed at the temperatures indicated:

* 1000° C	0.21 percent CaO
1300° C	3.0 " "
1375° C	98.67 " "

Comparison with Fig. XIV shows that these values do not check very well with the experimental results obtained. However, it must be remembered that these tests were carried out on a commercial grade of plaster of Paris and that the test merely consisted of titrating the free alkali. Commercial plaster contains certain impurities besides the retarder, which is added in the process of manufacture. Since the exact nature of these impurities and the retarder is not known, it is probable that these decompose and give the alkali, which was found up to a temperature of 890° C and assumed to be free lime. All the impurities are decomposed by the time a temperature of 715° C is reached. This is shown by the horizontal part of the curve from 715° C to 890° C. Above the temperature of 890° C the calcium sulfate itself begins to decompose. By the time 1000° C is reached there is 0.16 percent of CaO contributed by the decomposition of the calcium sulfate itself which is a reasonably good

\*M. S. Burr, Textbook of Inorganic Chemistry, Vol. III, p. 67, Chas. Griffin Co., Philadelphia (1925)

check considering that the points are quite scattered in this range of temperatures.

No definite evidence of a strong setting material was obtained at the higher temperature. Since the tensile strength of the plaster burnt at the higher temperatures was very low, it does not seem that this can be compared with Estrichgyps which is used as a flooring plaster. A possible explanation for this is the following. Since Estrichgyps is made only in Germany it is entirely possible that the native gypsum which is available in that country contains certain impurities which catalyze the set. It is known that such action is possible because in this country a quick setting plaster, Keene's cement, is made by adding  $\text{Al}_2(\text{SO}_4)_3$  to the material and then heating it to a temperature in the neighborhood of  $500^\circ \text{C}$ . No  $\text{Al}_2(\text{SO}_4)_3$  may be present in the native gypsum of Germany, but there may be some other material which has a similar effect.

For the samples heated at temperatures up to about  $420^\circ \text{C}$  it will be noticed that the time for the setting sample to reach a maximum temperature, when put in the thermometric set apparatus, decreased as the temperature of dehydration was increased (See Fig. II and Table I, Appendix C). However, the time of set of these samples as determined by

the modified Vicat was found to increase with increasing temperature of dehydration. (See Table II, Appendix C) Since it was thought by some investigators that the time for maximum temperature to be reached was a measure of the time of set, these results are contradictory. This may be explained by admitting that the original idea was wrong. Instead of the time required for maximum temperature to be reached being a measure of the time of set, it indicates the time when the rate of set of the material is such as to evolve an amount of heat just equal to the amount of heat being dissipated to the surroundings. This is not altogether surprising, since there is no *a priori* reason why the time for maximum temperature rise and setting time should run parallel.

As shown by Figs. XI, XII and XIII, mixtures of samples heated at various temperatures with the ordinary plaster of Paris have setting properties dependent on the amount of each constituent present. There appears to be no effect other than the apparent additive heat effects of each component. That is, the effect observed is that each component sets in the usual way as if the other material were not present and the heats evolved by the two are additive. If, however, gypsum is added to either the commercial plaster of Paris or to one of the heated samples (See Figs. IX and X) the effect is not merely one of

of dilution, but there is a marked increase in the rate of set. A possible explanation is that the gypsum acts as nuclei, or as seed crystals on which the plaster may commence crystallization and then speed up the set. It follows from this that as more of these seed crystals are added the greater will be the rate of set.

B. Results obtained from addition of other substances to plaster of Paris.

The results indicate that none of the substances which were added to the plaster in an effort to reduce the permeability were satisfactory. Some explanation can be offered for this failure.

The first substance added to the plaster was bentonite. Dry bentonite was mixed with the plaster, water being added after the two substances were thoroughly mixed. Dry bentonite increased the time of set to approximately 3 hours, but the casts crumpled very easily after they had set and disintegrated when they were put in water for the porosity test. These bentonite mixes also contracted upon setting. This contraction on setting indicates that dry bentonite mixed with plaster is very unsatisfactory, since a contraction shows that the resulting mix will be weak. Weakness was also observed in the high temperature samples which contracted. Ordinary plaster expands when setting and gives a fairly strong product. The disintegration in water also indicates a poor bond between the bentonite and the plaster. This poor set is probably due to the fact that the dry bentonite, being a colloid, swells when coming in contact with the water, thus preventing the plaster from bonding together in a strong crystalline structure. The fact that the bentonite has a

great affinity for water also accounts for the long time of set, since this also prevents the proper hydration. When the bentonite suspensions were added to the plaster the difficulties met with the dry mixes were alleviated, but the porosity was definitely poor. This may also be explained by the colloidal properties of bentonite. When the casts dried out the swollen bentonite particles, no doubt, contracted leaving comparatively large voids to take up the water and give a large porosity. That bentonite decreased the strength of plaster is probably due to the fact that the gel structure of bentonite interferes with the formation of a crystalline structure in the plaster. Bentonite added to cement does not decrease the strength (9). However, since cement is also thought to possess a gel structure, it would be expected that there would be no great interference as the cement set.

Since TDA is used in cement to increase the strength and to reduce the permeability, it was thought an analogous situation would exist with plaster. This fact was well borne out since the TDA increased the tensile strength of the plaster. As TDA is a wetting and dispersing agent it enables the water to reach the plaster particles thus giving good dispersion and complete hydration. This would account for the increase in strength of the plaster with TDA.

In the sodium silicate mixtures acid was added to the sodium silicate before mixing, since it was reasoned that silica gel might form as the plaster set, thus helping to fill up any voids in the casts, and increase the strength of the set product. However, the same reasoning may be applied to the silicate as with the bentonite. Since the silicate and silica gel have a gel structure, they hinder the formation of gypsum crystals and give a cast which is weak. Upon drying the silicate contracts leaving voids for the water to seep through.

Calcium stearate, and mica were added to the plaster as it was thought that their repelling action to water would keep water from seeping into the voids in the plaster. When the plaster was in the process of being mixed, the stearate repelled the water, but after the plaster had set, the stearate had no effect. No doubt the plaster in the process of setting covered the surface of the stearate particles, making the stearate ineffective. The mica had no observable effects which would indicate a reduction in porosity.

No consistent results were obtained on the permeability apparatus. This was due to the fact that the apparatus and size of sample taken were too small. The small sample prevented getting a consistent cast with any one mixture. That is, if a deep void existed in the cast, then the water was given an opportunity to penetrate very rapidly. A deep



void was practically impossible to avoid even with great care in casting. Another cast of the same mixture might not have any large voids and the water would be held back for a longer time. Thus it can be seen why consistent results were not obtained. If large casts were used there would be more chance of getting more uniform casts with the same mixture and consistent results could be obtained. Lack of time prevented making a larger apparatus.

In spite of their inconsistency, the permeability measurements showed that plaster or any of the mixtures tried would be definitely unsatisfactory for an oil well cement. If the water once works its way through the plaster more plaster is continually dissolved as the water flows through a void. This results in the production of a large fissure which would in time cause all the plaster to dissolve away. Some typical fissures of the casts used are shown in Fig. XV.

## CONCLUSIONS

From the results obtained it is concluded that plaster of Paris or the plaster formed at high temperatures is unsatisfactory for an oil well cement unless some substance can be found which would make it absolutely non-porous to water. However, the set could, no doubt, be made satisfactory for a cement, since it was shown that the time of set can be controlled by the addition of other substances.

The following conclusions are drawn from the results obtained on the plaster burnt at high temperatures.

(1) There are three forms of anhydrite which exist up to a temperature of  $1080^{\circ}$  C.

I.  $200-310^{\circ}$  C (soluble anhydrite)

II.  $365-660^{\circ}$  C

III.  $715-1040^{\circ}$  C

(2) Lime accelerates the set of all forms of II and III.

(3) Particle size is one of the controlling factors concerning the set of II and III.

(4) There are probably other factors which control the set of II and III, but the nature of these was not determined by the authors.

(5) Gypsum nuclei materially hasten the set of commercial plaster of Paris and of soluble anhydrite.

## RECOMMENDATIONS

Further investigation of the effect of heat treatment of calcium sulfate should be made. Among the things to be studied are the following:

(1) Make tests on pure calcium sulfate similar to those made in this investigation to see just what effect the impurities and retarder had on the properties.

(2) Study the effect of age on tensile strength and percent combined water when the specimens are aged in moist air and under water.

(3) A study of the permeability by direct measurement should be made using specimen not smaller than six inches in diameter and six inches long.

APPENDIX

## APPENDIX A

## TABLE OF NOMENCLATURE

TDA	Naphthene Sulfonic Acid
$\text{CaSO}_4$	Anhydrous Calcium Sulfite or Anhydrite
$\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$	Plaster of Paris
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	Gypsum

APPENDIX B  
DETAILS OF APPARATUS AND PROCEDURE

Measurement of Time of Set

The time of set of all samples was measured by an improvised apparatus as shown in Fig. XVI. This apparatus was constructed of two glass tubes each 2 feet long, one being 23 mm. in diameter and the other 20 mm. in diameter. The smaller tube served as a plunger, being inserted in the 23 mm. tube which was clamped to a support. Air rifle shot was put in the plunger tube until it had a total weight of 150 grams. This shot was held in the tube by a stopper in which was inserted a brad 0.1 inch in diameter and 2 inches long. The brad was filed down to a point with a diameter of approximately 0.03 inch. The brad served as a means to indent the plaster moulds thus giving a measure of the set.

In order to determine the time of set of a mix, the plaster of Paris was mixed for  $1\frac{1}{2}$  minutes and then made into moulds of  $\frac{7}{8}$  inch diameter and  $\frac{3}{8}$  inch high. The time of set was measured from the beginning of the mixing, and when the brad made no indentation in the setting plaster, this was taken as the time of set. The plunger was not dropped from any height but was allowed to penetrate the mould starting on its surface from rest.

The standard tests for set, which make use of the Vicat or Gillmore needle, were not used since the size of the moulds required consumed a large amount of plaster and the heavy weight of the plunger would not be satisfactory for the size moulds in tests carried out. Since relative values of time of set were all that were of interest to the authors, the instrument which was constructed served its purpose.

#### Measurement of Porosity

The moulds used in the porosity measurements were of the same size as those used in the determinations of the time of set. Before being tested the plaster casts were allowed to set one week to insure dryness. The dry casts were weighed, then placed in a bell jar and covered with water at room temperature. A vacuum of 10 inches (absolute pressure) of mercury was maintained over the surface of the water throughout the test, which was allowed to run for 1.5 hours. After the casts had remained in the water for the required length of time, the water on the surface of the moulds was gently removed with a dry towel. They were then put in a covered weighing bottle and weighed. The amount of water absorbed served as a measure of the porosity. Any water removed from the pores of the casts by the use of a towel was considered

negligible, since the amount of water absorbed was usually high, the amount removable by the towel would be small in comparison. Therefore this was a justifiable procedure.

#### Permeability Measurements

The casts used for permeability measurements measured 1 inch in thickness and  $1 \frac{1}{16}$  inch in diameter. To measure the permeability the casts were put in a section of standard  $1 \frac{1}{2}$  inch brass pipe, which was  $2 \frac{3}{4}$  inches long (See Fig. XVII). The casts were sealed inside the pipe with 1:1 mixture of hot rosin and paraffin wax in order to prevent water leakage around the casts. Brass caps were screwed over the two ends of pipe section and a constant water pressure of 55 pounds per square inch (gage pressure) was maintained over one end of the casts. Three pipe sections were put in parallel, thus making it possible to test three samples at once. The amount of water which passed through the cast in 2.5 hours was taken as a measure of the permeability. Each cast was allowed to set three days before the permeability was tested.

#### Tensile Strength

The tensile strength of the different mixtures was taken to determine whether admixtures of other substances affected the strength of ordinary commercial plaster of Paris and to assist in studying the properties of samples of plaster dehydrated and burnt at different temperatures.



The tensile briquettes were made up in standard A. S. T. M. moulds and were allowed to set exposed to the air for one week before they were tested in a Rhiele testing machine. Mixing was carried out for 3 minutes before casting the specimens.

#### Effect of Seed Crystals on Set

The thermometric set apparatus shown in Fig. XVIII consisted of a one pint thermos bottle with three 13x100 mm. test tubes inserted through holes in the cork stopper. The thermos bottle merely served to cut down heat losses from the setting mass of plaster of Paris in the test tubes. Thermometer having a range of 0 - 55° C were used to measure the temperature of the mass at any instant.

Three grams of plaster of Paris were thoroughly mixed with the given amount of seed crystals and put in one of the test tubes, three grams of water were added and the thermometer inserted. Using the thermometer as a stirring rod, the mass was mixed vigorously for 30 seconds and the test tube was then put in one of the holes in the cork stopper of the thermos bottle. In general, at least three tests were made on each sample, thus giving a double check on each run. The temperature of the mass was read at frequent intervals and the original water

temperature noted. The difference between these two readings was the temperature rise at any time. It was noted that in general there was a sharp rise in temperature during about the first  $\frac{1}{2}$  minute and that usually the temperature fell off after this. In some cases the temperature again rose and went through another maximum. The first rise, occurring in approximately one-half minute, is referred to as the initial temperature rise and the second maximum is called the final or maximum temperature rise.

#### Grinding of Material

The grinding of samples was accomplished in a one gallon jar type pebble mill. The mill was rotated at the rate of 78 R. P. M. There were 2,150 grams of pebbles in the mill, ranging in size from  $\frac{3}{4}$  inch to 1 inch in diameter. Approximately one pound of material was ground at one time, and each grind lasted 24 hours.

#### Surface Area

The Klein Turbidimeter was used to determine the surface area of the different samples. Only relative values were obtained because it would have been necessary to calibrate the instrument if absolute values were to be obtained. In using the instrument the standard procedure was used. This consists of taking the solid material to be tested and sieving out all particles larger than 200

mesh. From the material passing through the screen, 0.25 grams are weighed out and beaten up with 50 grams of castor oil. The mixing is continued until a good suspension is obtained. Then 25.08 grams of the suspension are weighed out on a standard dish and put in the apparatus. Before the suspension is put in, the voltage on the photo-electric cell is regulated so that 50 microamperes pass through the cell. By inserting this suspension between the light source and the cell, the amount of light falling on the cell is decreased and thus the current through it is decreased. The more light that is cut off, the lower the value of the current through the cell will be. Consequently the larger the surface area of the material used, the smaller will be the reading on the microammeter.

#### Density

A pycnometer with a capillary side arm and a thermometer were used for the density determinations. All weighings and measurements were made at 25° C. A water bath, the temperature of which was controlled by a thermostat was used. The water bath was kept at  $25 \pm .01^{\circ}$  C at all times and approximately 30 minutes were allowed for the material in the pycnometer to come to the equilibrium temperature.

7

The volume of the pyknometer was found by weighing it empty and then weighing it filled with air free distilled water. The pyknometer was then weighed full of dry toluene. From this the density of the toluene was calculated. Then a weighed amount of the solid in question was put in the pyknometer and it was then filled the rest of the way with toluene and weighed. This gives sufficient information for calculating the density of the solid material. A chainomatic balance was used and all weighings made as quickly as possible to minimize the error due to evaporation of toluene.

#### Free Lime

The percent free lime was determined by titrating 0.5 grams of the material in question, in approximately 150 ml of water, with 1/50 normal HCl. Phenolphthalein was used as an indicator. The percent CaO was calculated from the results obtained.

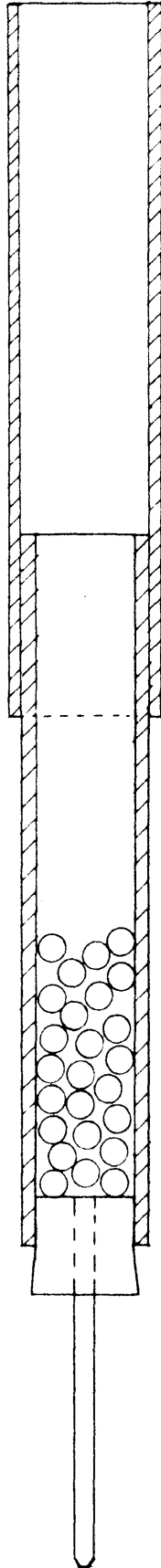
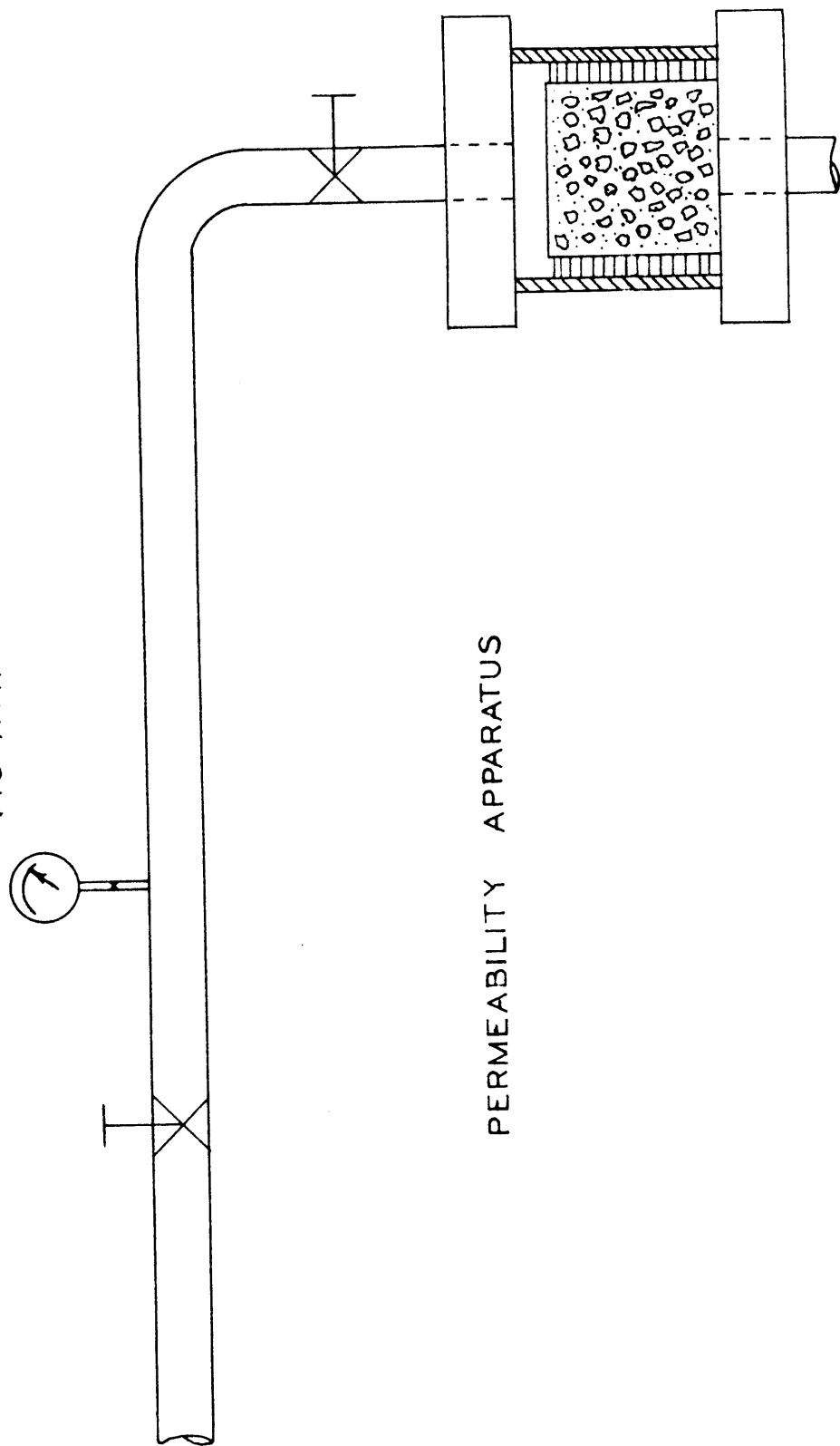


FIG XVI

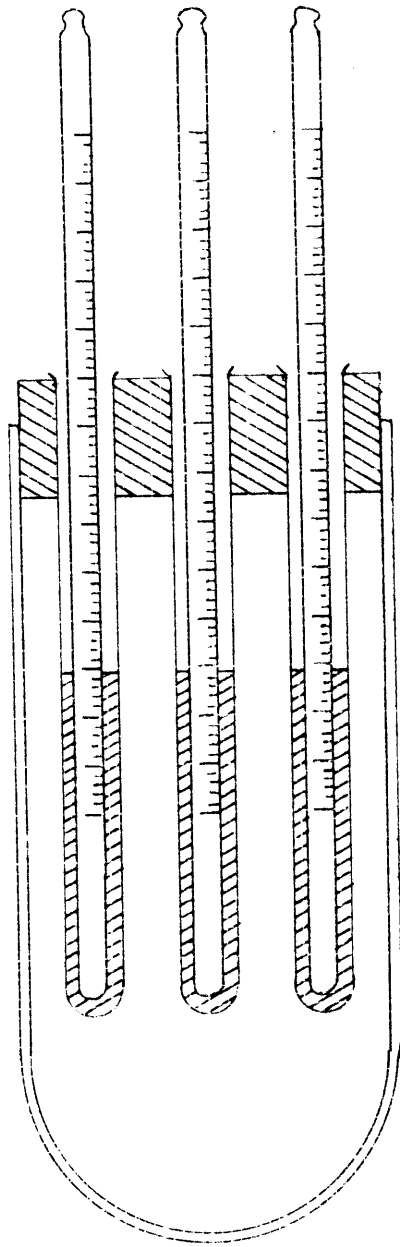
MODIFIED VICAT  
APPARATUS

FIG XVII



PERMEABILITY APPARATUS

FIG XVIII



THERMOMETRIC SET APPARATUS

APPENDIX C

TABULATED DATA

TABLE I

(All Samples Not Milled)

Number	Temperature of Dehydration (°C)	Initial Temperature Rise (°C)	Final Temperature Rise (°C)	Time for Final Temperature Rise (Minutes)	Density Grams per cc.	Percent Free Lime	Expansion on Setting
1	--	3.0	11.9	44	2.72	--	E
2	150	11.2	13.9	60	2.71	--	E
3	200	7.6	10.7	46	2.72	--	E
4	255	8.5	11.4	34	2.71	--	E
5	310	7.4	10.0	26	2.68	--	E
6	365	4.0	5.9	19	2.81	--	E
7	420	3.0	4.0	11	2.81	--	B
8	480	2.9	--	--	2.86	.048	--
9	540	2.9	--	--	2.86	.056	--
10	600	2.9	--	--	2.85	.706	--
11	660	2.8	--	--	2.84	.403	--
12	715	2.8	--	--	2.91	.683	--
13	775	2.1	--	--	2.91	.694	--
14	830	1.3	--	--	2.91	.694	--
15	890	1.0	--	--	2.92	.717	--
16	945	0.4	--	--	2.93	.840	--
17	1005	2.8	--	--	2.96	.762	--
18	1040	1.9	--	--	2.94	.951	--

B - Did not expand on setting.

E - Expanded on setting.



TABLE II

Samples Marked with Asterisk Not Milled

All Others Milled

Number	Temperature of Dehydration (°C)	Time of Set by Vicat Apparatus (Hours)	Tensile Strength Lbs. per sq. in.	Porosity	Expansion on Setting	Klein Turbidimeter Reading (Microamperes)	Percent Combined Water	Time of Set by Vicat Using Saturated Lime Water-Hrs.
1	--	* .13	#536	--	E	35.4	--	--
2	150	* .25	#466	--	--	32.3	--	--
3	200	* .25	#547	*19.5	--	32.0	--	--
4	255	* .28	#520	--	--	31.7	*18.8	*.23
5	310	* .33	#525	--	--	31.9	--	--
6	365	* .29	#493	*22.6	--	31.7	--	--
7	420	2	#290	--	--	31.1	--	--
8	480	3.5	193	26.8	B	31.6	17.2	.33
9	540	3.8	230	--	B	31.2	11.14	--
10	600	4	215	26.3	B	30.9	10.0	.83
11	660	4	360	--	B	29.2	13.95	--
12	715	5	305	24.7	B	26.7	13.2	2.0
13	775	5	248	--	B	25.1	--	--
14	830	5.5	210	24.8	B	22.7	--	--
15	890	6	165	--	B	23.0	--	--
16	945	6	105	23.9	B	23.0	7.4	3.0
17	1005	6	123	25.3	B	23.5	--	--
18	1040	6	125	23.5	B	24.7	7.24	3.0
			133	--	B	23.7	--	--

B - Did not expand on setting.

E - Expanded on setting.

TABLE III

## PROPERTIES OF COMMERCIAL (FFF) PLASTER OF PARIS

Mix	Time of Set	Porosity	Tensile Strength
5 g. Plaster- 2 cc. water	12 min.	16.5%	466 #/in <sup>2</sup> (7 days) 566 #/in <sup>2</sup> (1 mo.)

TABLE IV

## EFFECT OF BENTONITE ON PLASTER OF PARIS

Conc. of Bentonite Suspension (%)	Plaster-Bentonite Suspension Ratio (g-cc.)	Time of Set (Min.)	Porosity (%)	Tensile Strength (#/in <sup>2</sup> )
1	5 - 3	21	23.2	----
2	"	21	26.6	----
2.5	"	16	----	----
3	"	20	30.7	358
4	"	20	29.7	----
5	"	14	27.5	328

TABLE V  
EFFECT OF TDA ON PLASTER OF PARIS

Conc. of TDA Sol. (%)	Plaster-TDA Sol. Ratio (g.-cc.)	Time of Set (Min.)	Porosity (%)	Tensile Strength #/in <sup>2</sup>
.5	5 - 2	13	15.8	--
1	"	18	14.6	670
2.5	"	36	14.0	633
3.5	"	48	16.0	--

TABLE VI  
EFFECT OF SODIUM SILICATE WITH VARYING AMOUNTS OF H<sub>2</sub>SO<sub>4</sub> ON PLASTER OF PARIS

(Analyses of sodium silicate used: 10.1% Na<sub>2</sub>O, 26.7% SiO<sub>2</sub> - Spec. Grav. 1.39)

Sodium Silicate Sol. Ratio of Sodium Silicate-Water-1.75 N H <sub>2</sub> SO <sub>4</sub> (By vol.)	Reaction of Sol to Phenol-phthalein	Plaster-Sol. Ratio (g.-cc.)	Time of Set (Min.)	Porosity (%)	Tensile Strength #/in <sup>2</sup>
5 - 20 - 0	Basic	5 - 3	9	21.4	247
5 - 20 - 2	Basic	"	5	23.0	---
5 - 20 - 4	Basic	"	5	22.2	233
5 - 20 - 7	Acidic	"	3	23.8	---

With 5 cc. of 1.75 N H<sub>2</sub>SO<sub>4</sub> the silica gel precipitates very rapidly.

TABLE VII

EFFECT OF CALCIUM STEARATE ON PLASTER OF PARIS

Plaster-Stearate Ratio (g-g)	Ratio of Plaster Stearate Mixture to amount of Water used (g-cc)	Time of Set	Porosity (%)	Tensile Strength #/in <sup>2</sup>
30 - 1	5 - 2	17	18.6	470
20 - 1	"	21	17.7	---
10 - 1	"	105	19.8	328

TABLE VIII

EFFECT OF GROUND MICA ON PLASTER OF PARIS

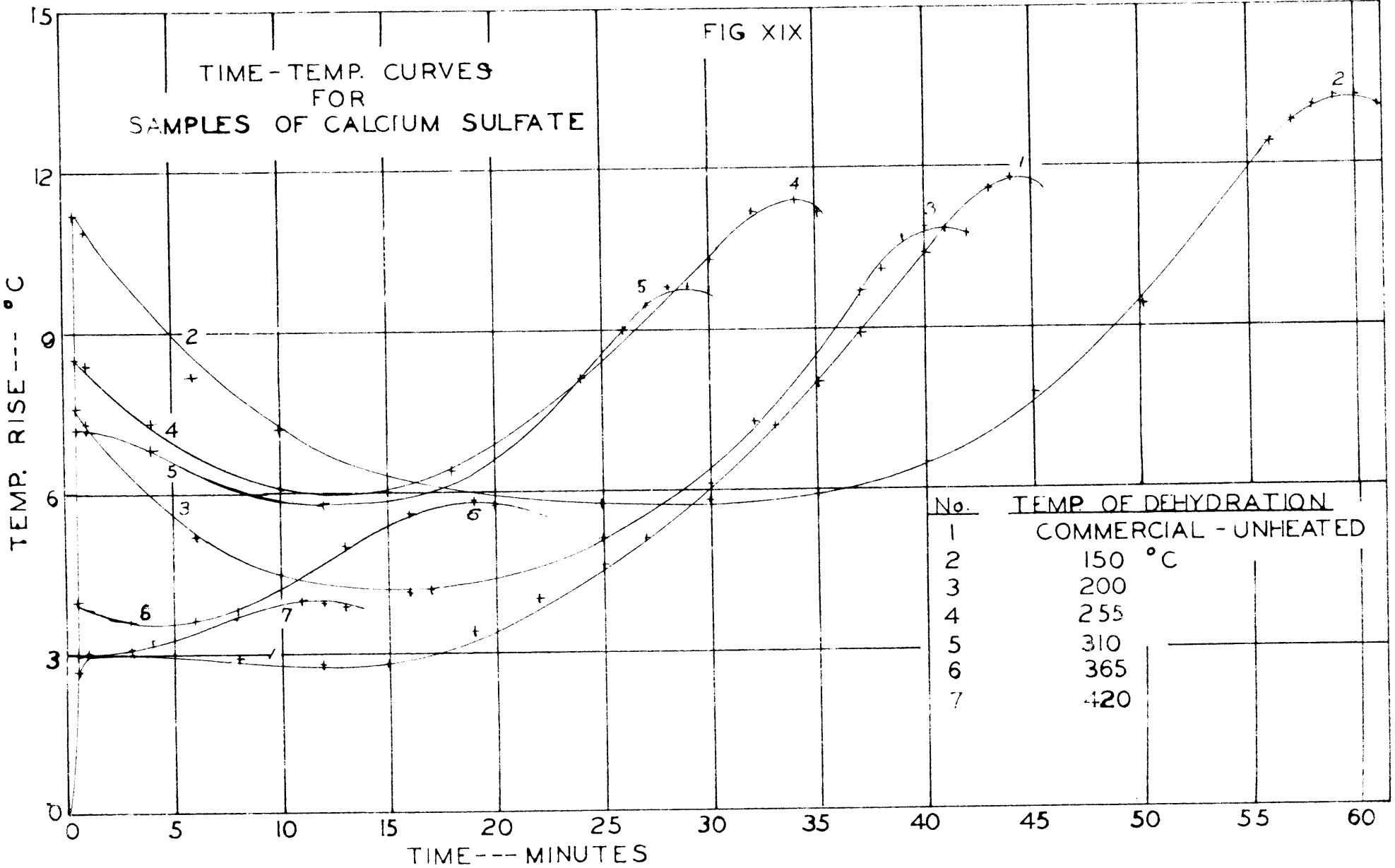
Plaster-Mica Ratio (g-g)	Ratio of Plaster Mica Mixture to Amount of Water Used (g-cc)	Time of Set (Min.)	Porosity (%)	Tensile Strength #/in <sup>2</sup>
5 - 1	5 - 2	5	16.6	240
10 - 1	"	6	17.4	---
20 - 1	"	6	19.1	495

TABLE IX  
PERMEABILITIES OF MIXTURES

	<u>Amount of water Through Mould</u>
(1) Commercial Plaster of Paris 5 g plaster 2 cc water	(a) 1.5 g. in 2 hr. (b) 29 g in 1 hr. (c) 8.2 g. in 2.5 hr. (d) 13.3 g. in 2.5 hr. (e) 1.7 g. in 2.5 hr. (f) Mould broke in 40 min. (g) Mould broke in 1 hr.
(2) Plaster with 5% bentonite solution 5 g plaster 3 cc of solution	(a) Mould broke in 1 hr. (b) Mould broke in 30 min. (c) Mould broke in 45 min.
(3) Plaster with TDA solutions 5 g plaster 2 cc of solution	(.5% TDA) (a) Mould broke in 1.5 hr. (b) 14.1 g. in 2.5 hr. (c) 10.5 g. in 2.5 hr.  (1% TDA) (a) Mould broke in 1 hr. (b) 26.1 g. in 2.5 hr. (c) Mould broke in 1.75 hr.  (2.5% TDA) (a) 0 g. in 2.5 hr. (b) 12 g. in 2.5 hr. (c) 12 g. in 2.5 hr.  (3.5% TDA) (a) 9.5 g. in 2.5 hr. (b) Mould broke in 2 hr. (c) 5 g. in 2.5 hr.

FIG XIX

TIME-TEMP. CURVES  
FOR  
SAMPLES OF CALCIUM SULFATE



## APPENDIX D

### SAMPLE CALCULATIONS

#### Calculation of Porosity

Weight of cast after immersion	5.927
Weight of cast before immersion	<u>5.078</u>
Difference	0.849
$\% \text{ H}_2\text{O absorbed} = \frac{0.849}{5.078} \times 100 = 16.7\%$	

#### Calculation of Percent Free Lime

$$\% = \frac{\text{ml.} \times N \times M \times 100}{W \times 1000 \times 2}$$

Where

ml = milli-liters of acid used  
N = normality of acid used  
M = molecular weight of CaO  
W = weight of sample taken

$$\% = \frac{4.4 \times 0.02 \times 56 \times 100}{0.5 \times 1000 \times 2} = 0.494\% \text{ CaO}$$

#### Calculation of Density

##### Nomenclature

P = weight of pyknometer  
A' = weight of air in pyknometer when full  
W = weight of air free distilled water in pyknometer when full  
V' = volume of pyknometer  
V'' = volume of solid  
B = density of air  
R = density of toluene  
S = density of air free distilled water  
C = weight of solid taken  
A = weight of air over solid in pyknometer  
T = weight of toluene over solid in pyknometer  
T' = weight of toluene in pyknometer when full  
V = volume of toluene over solid  
D = density of solid

From Tables

Density of air at 25° C = 0.001187 g./ml.

Density of water at 25° C = 0.99707 g./ml.

Sample calculation will be made on sample dehydrated at 1040° C.

Data

P + A'	=	33.8051
P + W	=	59.4736
P + T'	=	55.9505
P + C + A	=	34.5032
P + C + T	=	56.4453

As a first approximation we may neglect the weight of the air in the pyknometer (A').

$$W = (P + W) - (P + A')$$

$$\approx 59.4736 - 33.8051 = 25.6685$$

$$\text{and } A' = B \times V' \approx .001187 \times \frac{25.6685}{0.99707} = 0.0306$$

If we now recalculate this part letting A' = 0.0306

$$W = (P + W) - (P + A') + (A')$$

$$\approx 59.4736 - (33.8051 - .0306) = 25.6991$$

$$\text{and } A' = .001187 \times \frac{25.6991}{0.99707} = 0.0306$$

Since this is the same as the original value of A' the assumption was justifiable.

$$P = (P + A') - (A')$$

$$= 33.8051 - .0306 = 33.7745$$

$$W = (P + W) - (P)$$

$$= 59.4736 - 33.7745 = 25.6991$$



$$V' = \frac{W}{S}$$

$$\begin{aligned} \text{or } \log V' &= \log w - \log S \\ &= \log 25.6991 - \log 0.99707 \\ &= (1.40992) - (-0.00127) = 1.41119 \\ V' &= 25.7745 \text{ ml.} \end{aligned}$$

$$\begin{aligned} T' &= (P + T') - (P) \\ &= 55.9505 - 33.7745 = 22.1760 \end{aligned}$$

$$R = \frac{T'}{V'}$$

$$\begin{aligned} \log R &= \log T' - \log V' \\ &= \log 22.1760 - \log 25.7745 \\ &= 1.34588 - 1.41119 = -0.06531 \\ R &= 0.86038 \text{ g/ml.} \end{aligned}$$

Again we will neglect the weight of air (A) in making the first approximation

$$\begin{aligned} T &= (P + C + T) - (P + C + A) \\ &\approx 56.4453 - 34.5032 = 21.9421 \end{aligned}$$

$$\text{and } A = B \times V = .001187 \times \frac{21.9421}{.86038} = 0.0303$$

We will now recalculate this part letting  $A = 0.0303$

$$T = (P + C + T) - (P + C + A) + A$$

$$T \cong (56.4453) - (34.5032 - .0303)$$

$$T = 21.9724$$

$$A = .001187 \times \frac{21.9724}{.86038} = 0.0303$$

Since this is the same as the original value of  $A$ , the approximation was justifiable.

$$T = (P + C + T) - (P + C + A) + (A)$$

$$= 56.4453 - 34.5032 + .0303 = 21.9724$$

$$C = (P + C + A) - (P + A') + (A) - (A') = 0.6984$$

$$C = (34.5032) - (33.8051) - .0303 + .0306 = .6984$$

$$V = \frac{T}{R}$$

$$\log V = \log T - \log R$$

$$= \log 21.9724 - \log 0.86038$$

$$= (1.34188) - (-.06531) = 1.40719$$

$$V = 25.5370$$

$$V'' = V' - V$$

$$V'' = 25.7745 - 25.5370 = 0.2375$$

$$D = \frac{C}{V''} = \frac{0.6984}{0.2375} = 2.94$$

APPENDIX E

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## APPENDIX F

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