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AND

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BY

M. GLASENAPP

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TRANSLATED BY DR. W. MICHAELIS, JR.

PRICE, 50 CENTS

Published by
CEMENT & ENGINEERING NEWS
CHICAGO, ILL.

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The chemical and physical properties of gypsum and of the various commercial products obtained from it by heating and by calcining have so far been studied very little, so that the most erroneous opinions on this subject are daily expressed by men producing and handling these cements.

Every one interested in the manufacture of gypsum and in its wide application, therefore, will welcome the news that Professor M. Glasenapp has made an exhaustive research of the properties of the various products obtainable by heating of raw gypsum at different temperatures. Professor Glasenapp is in charge of the technical laboratory at the University of Riga, Russia, and is considered an authority on building materials. A thorough study of his experiments will greatly benefit every person engaged in the gypsum industry, will serve to spread knowledge among producers and consumers and to make clear a great number of points, about which obscurity prevailed.

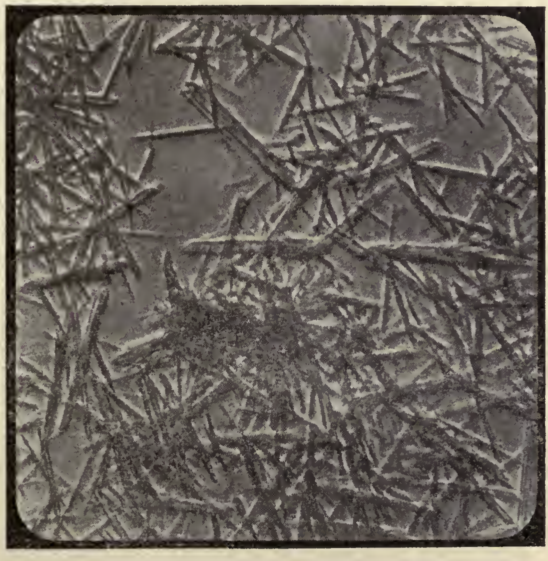
The accurate work done by this scientist will save others, in search of information, a great deal of experimenting and will be a guide to them in the practical operation of their plants as well as in the marketing of their products and in the testing of the manufactured articles. Moreover, the conclusions which the experimenter draws from his work contain a number of valuable suggestions how to improve the commercial products, especially hydraulic gypsum and Keene's cement, in order to make them more valuable, and to substitute them for other white cements commanding a high price. The large number of illustrations accompanying the paper can not fail to make the subject lucid and interesting to the reader:

I. PLASTER OF PARIS OR STUCCO GYPSUM:

If ordinary plaster of Paris, representing mainly the half-hydrate $CaSO_4 + \frac{1}{2} H_2O$, is mixed with water and examined under the microscope, a lively process of crystallization can be observed to set in after 5 or 6 minutes. In the beginning very thin needle-crystals form on the cover glass and shortly afterwards also in the liquid and on the particles of gypsum. After 15 or 20 minutes single needle-crystals and groups of them can be seen in great number, and especially the larger fragments of the half-hydrate are covered with needle-crystals radiating from them; also the characteristic twin crystals appear abundantly. As fast as the crystals form, the original particles of the half-hydrate disappear; after an hour, they are completely used up and transformed into crystals, whereby the larger fragments of them become the centers of accumulations of crystals, while the smaller have been converted into isolated star-shaped groups. Cuts No. 1 and No. 2, illustrate the transformation of the half-hydrate into the crystallized di-hydrate. It may be added that this process goes on in the same way, no matter whether the raw gypsum used in the manufacture of plaster was crystallized gypsum or gypsum of a fibrous nature or granular gypsum.

After the same gypsum was heated for several hours to a temperature of 170 centigrade (whereby the amount of water still remained 6.2%, corresponding with the half-hydrate), crystallization began after 3 to 4 minutes and was practically completed after half an hour; only the largest particles required almost an hour to dissolve and to re-crystallize.

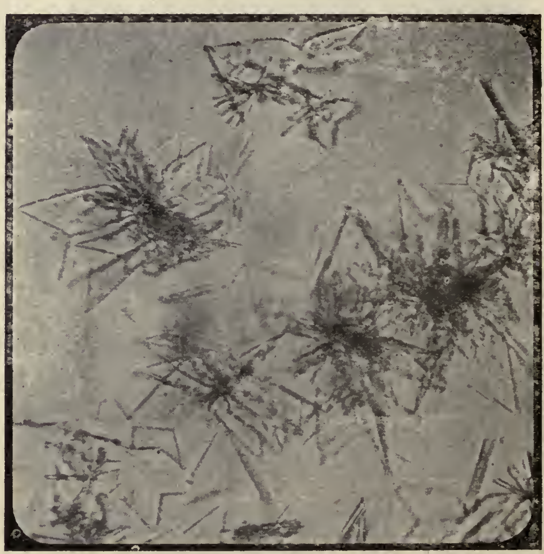
The present state of our knowledge of the hardening of gypsum is that, after having been mixed with water, the half-hydrate, plaster of Paris, and the first anhydrous modification of gypsum, which is supposed to be formed between 130 and 200 centigrade, form over-saturated solutions, from which the di-hydrate precipitates in the shape of small crystals, a process which is finished only after all half-hydrate or anhydrite is dissolved and transformed into crystals of di-hydrate. Apparently the half-hydrate goes into solution more rapidly and crystallizes in a shorter time than the first modification of anhydrite; at least I conclude this from the fact that this first anhydrite, which is considered to be "easily soluble," dissolves



No. 1. Needle-shaped crystals of di-hyrate , formed by mixing of plaster of Paris with water. The plaster was produced by heating native gypsum to a temperature of 130 centigrade. Magnified 360 times.

the more slowly at the higher a temperature it was produced.

The same process of solution and crystallization, disclosed by microscopical examination of plaster mixed with water, takes place also during the setting and hardening of plaster castings, whereby the ratio of plaster to water may vary within wide limits without materially influencing the time of setting. If the plaster consists only of the half-hydrate, the setting of the casting, according to my observations, coincides with the beginning of the formation of crystals of di-hydrate, and the final hardening corresponds with the complete transformation of the half-hydrate into crystallized di-hydrate. However, if the commercial product contains large amounts of the first modification of anhydrite—hereafter referred to as I. anhydrite—, a reaction sets in which accelerates



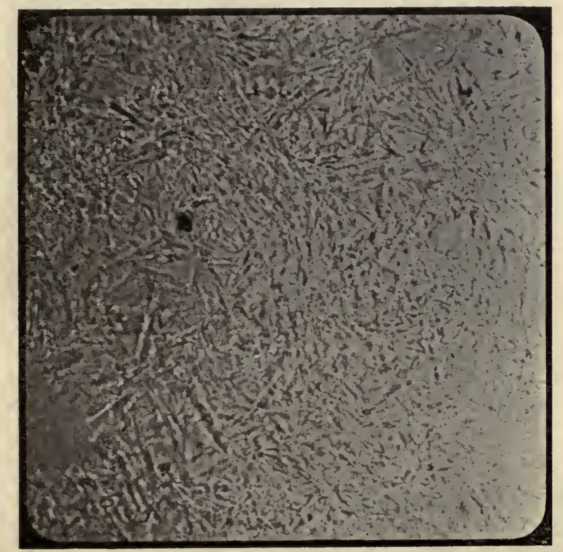
No. 2. Twin-crystals and needle-shaped crystals of di-hydrate formed by the going into solution and subsequent crystallization of the particles of half-hydrate composing plaster of Paris. Magnified 360 times.

the hardening; this I shall describe later when dealing with the so-called "overburnt gypsum."

Microscopic sections of plaster castings readily show the transformation which the powdered burnt gypsum undergoes upon hardening with water, for, as cuts No. 3 and No 4 illustrate, the casting consists of a dense network of interlacing needle-crystals of dihydrate. Also crystal-groups can be distinguished made up of accumulations of twin-crystals and needle-crystals resembling cut No. 2.

A burnt piece of raw gypsum that is to say plaster of Paris in unground form, on the other hand, exhibits an entirely different structure under the microscope. It shows parallel lamination in accordance with the growth of the crystal (see cut No. 5).

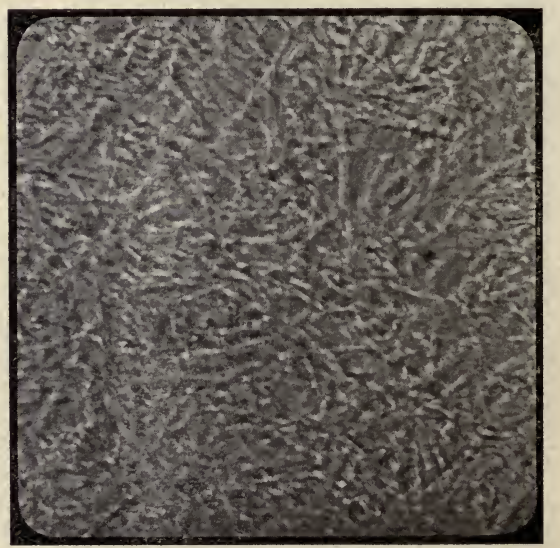
The fact that a process of crystallization is the cause of the hardening of plaster explains the phenomenon that water in the form of steam does not harden it. Plaster is able to set only in contact with



No. 3. Microscopic section made from a piece of a hardened casting of plaster of Paris. The plaster used was very quick-setting. The crystals are very small. Magnified 750 times.

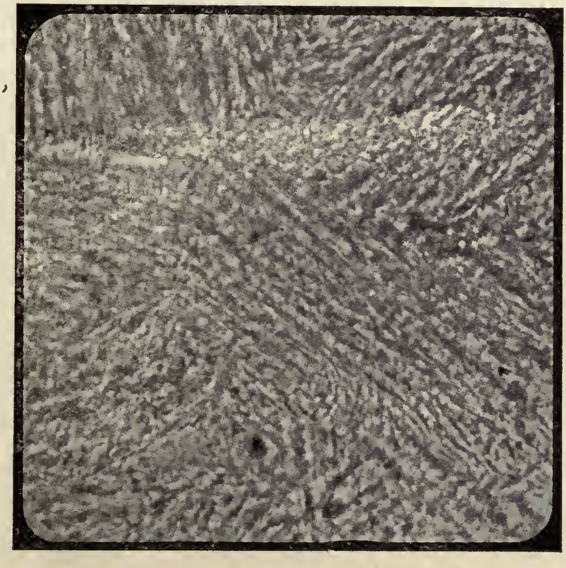
liquid water, in which it can go into solution and crystallize.

To judge from even the most recent statements to be found in books on chemical technology, only few chemists seem to be aware of the fact, that a complete transformation of every particle of plaster is an essential point in its hardening. Owing to the greater solubility in water of burnt gypsum over crystallized gypsum, the hardening of plaster of Paris has been attributed to a process of crystallization for some time; yet, this crystallizing has mostly been regarded as of secondary importance. The prevailing explanation was that the partly or completely dehydrated gypsum hydrated, combined with water and hardened, without changing its form or place, that is to say without previous going into solution. The process, therefore, was considered to be similar



No. 4. Section from a casting of plaster of Paris. The plaster used was less quick-setting than the former. The crystals are larger than in cut No. 3. Magnified 750 times.

to the hydration of calcined magnesia and, in many persons' opinion, seemed to resemble the hardening of Portland cement and of hydraulic limes. This erroneous conception likewise led to the belief, that the strength of the casting depended upon the hardness of the native gypsum from which the plaster



No. 5. Microscopic section of a piece of burnt native gypsum not hardened with water. Magnified 750 times.

was burnt. In fact, the difference in hardness between two kinds of raw gypsum is a matter of no consequence. The strength of the hardened gypsum depends solely upon the shape of the crystals, upon their size and upon their more or less close contact. The more slowly the plaster hardens, the larger and stronger the crystals of di-hydrate grow, and the less water is mixed with the plaster the denser and less porous the casting becomes. Moulds which absorb water readily, therefore, require a plaster containing as little anhydrite as possible; furthermore, such moulds call for a liberal amount of water. Admixtures to the plaster, which retard the setting, so-called negative catalysers, create large crystals and consequently are the cause of more resisting and stronger castings.

The literature on gypsum contains contradictory statements about the suitability of hardened plaster for the manufacture of plaster by re-burning it. Most authors say that hardened plaster is unfit for this purpose, but admit they are unable to give a proper explanation. The answer to this is that a piece of hardened plaster consists of a very porous mixture of small crystals of di-hydrate, which, upon burning and subsequent mixing with water, behaves exactly in the same way as when mixed with water for the first time or as any plaster burnt from raw gypsum. This means the fine interlocking needle-crystals which, by the re-burning have been transformed back into the half-hydrate, but which are still of the same porous structure, go into solution and crystallize again as di-hydrate, a process which may be repeated with the same material as often as desired. The only difference in the use of broken pieces of hardened plaster instead of dense raw gypsum is that, in the former case, the raw material for manufacturing plaster is an exceedingly porous and light mass. The consequence of this is, that this re-burnt plaster, as experiments will readily show, requires more water than the denser plaster burnt form native gypsum. Re-burnt plaster, therefore, yields castings which are too light and, for many purposes, not sufficiently resisting.

II. OVERBURNT OR DEAD-BURNT GYPSUM, SLOW-SETTING PLASTER, DEHYDRATED GYPSUM:

The term "overburnt or dead-burnt gypsum" designates, in most people's opinion, a product too slow-setting for practical purposes or not hardening at all. The literature does so far not contain any definite information about the limits of temperature within which this kind of gypsum is obtained. Rohland places the limits between the temperatures of 130 and 525 centigrade. Below 130 centigrade this so-called first anhydrite (I. anhydrite) of the calcium sulphate is supposed to convert into the half-hydrate and above 525 centigrade into hydraulic gypsum. The temperature of 130 centigrade has been adopted by the Association of German Plaster Manufacturers as that beyond which the formation of this anhydrite begins. Whether or not the half-hydrate breaks up at once into anhydrite and steam, as van't Hoff believes, or whether a gradual process of dehydration sets in under formation of various intermediary products, is so far an open question inconsequental for practical purposes.

It is a well-known fact that the anhydrite burnt at low temperatures, say up to 240 centigrade, which, by the way, still contains 0.2 to 0.5% of water, hardens rapidly and develops fair strength, and, as in the gypsum-kettles customary in practice surpassing of the temperature of 130 centigrade can not be avoided, the commercial plaster of Paris must necessarily be composed of a mixture of half-hydrate and anhydrite, or more or less dehydrated half-hydrate. Gypsum overburnt from a practical standpoint is produced only at higher temperatures, at 300 centigrade and above; but, even at this point, temperature limits can not be defined accurately, as, in addition to the temperature, the time of heating is an important factor. According to Rohland, the anhydrite, obtained by prolonged heating of gypsum at temperatures between 200 and 300 centigrade, is able to hydrate, but loses its capacity to harden. Such widely differing observations naturally surprise and call for an explanation.

The microscopical examination of samples of powdered gysum, burnt at temperatures higher than 200 centigrade, teaches nothing essentially different from the behavior of the half-hydrate or plaster of Paris towards water. Only the ability of this I. anhydrite to form over-saturated solutions is impaired; it is limited the more the higher the burning temperature has been and the longer the material was heated. Transformation into crystals of di-hydrate takes place in the same manner, but more slowly. The following table gives the various temperatures to which the gypsum was exposed, as well as the time of heating in many instances, and the beginning and termination of the process of crystallization corresponding with them:

Temperature.	Burning Time.	Beginning of Crystallisation	Crystallisation. Completed After
107 Celsius		6-7 minutes	1-2 hours
130 Celsius		6-7 minutes	½ to 1 hour
170 Celsius		3-4 minutes	½ hour
200 Celsius	7 hours	30-35 minutes	1-2 days
200-250 Celsius	14 hours	60 minutes	7 days
250-300 Celsius	7 hours	40 minutes	3 days
400 Celsius	½ hour	1¾ hour	17 days
450 Celsius	½ hour	10 days	30 days

As the hardening of the castings of plaster is caused mainly by the transformation into di-hydrate, and as this process of crystallization is the same also for "overburnt" gypsum, the lack of hardening in the case of the latter must doubtlessly be ascribed, wherever it has been observed, to the drying out of the uncovered castings; the process of crystallization, therefore, was interrupted and the casting could not obtain its full strength, which it otherwise would have done. This must happen especially in cases in which the process of crystallization takes a number of days. With gypsum burnt at 200 centigrade the transformation into crystallized di-hydrate is almost completed within 24 hours; only the larger particles take more time, and as, specially in the case of large castings, still a sufficient amount of water remains for crystallization after 24 or even after 48 hours, this explains the fact that gypsum, burnt at 200 centigrade and even above this temperature, unless heated for too long a time, or mixtures of this with standard plaster of Paris, show normal hardening and high strength. Rohland who assumes that only a small portion of the gypsum, its active part, takes a share in the hardening, is therefore mistaken; the entire mass is active, if it be given time and opportunity to exhibit its activity which is greatly diminished indeed. Complete hydration and transformation into di-hydrate without hardening, as Rohland describes it, is consequently out of the question. The term "overburnt or dead-burnt gypsum" is therefore misleading; the proper name for gypsum burnt at temperatures between 200 and 300 centigrade would be "slow-setting."

The process of hardening of such slow-setting plaster shows two distinct phases: In the first place, the plastic dough assumes a dull surface and becomes stiff owing to the transformation of the anhydrite into the half-hydrate. This point is reached after 1 or 2 minutes in the case of gypsum heated to 200 centigrade and after 30 minutes or more with gypsum burnt at temperatures between 250 and 300 centigrade. If further absorption of water is interrupted at this point by a rapid drying process, the stiff plaster is found to contain from 6 to 6.5% of water of combination corresponding about with the half-hydrate. During the second phase, which requires more time, the half-hydrate previously formed goes into solution and crystallizes as di-hydrate. Setting and hardening are, therefore, two well-pronounced processes in this case. Castings that have only time to set yield insufficient strength; they must be given time to harden.

The more the burning temperature exceeds 200 centigrade and the longer the gypsum is heated, the more the anhydrite loses its ability to go back into the state of the half-hydrate and this latter in turn becomes less capable to form over-saturated solutions and to crystallize as di-hydrate, until finally a product is obtained upon which water reacts so slowly that, for practical purposes, it must be considered to be overburnt and worthless. But even this kind of gypsum has by no means lost its capacity to harden, as Michaelis demonstrated long ago by a series of experiments in which gypsum was heated from the lowest temperatures up to intense white heat; all of these products hardened well. However, I must say right here that, at temperatures beyond dark red heat, a product of entirely different properties is obtained, namely hydraulic gypsum which so far was considered to be obtainable at much lower temperatures.

The practice of distinguishing various kinds of anhydrite according to their solubility as "easily soluble" and "insoluble" or "difficult to dissolve" may be permissible for practical purposes, but is not justified from a scientific standpoint, as the solubility decreases very gradually with rising temperatures and as an absolutely insoluble anhydrite has not been obtained as yet. All that can be said about the behavior of the I. anhydrite towards water is that its properties depend upon the burning temperature and upon the time of heating. First anhydrite (I. anhydrite) I call all kinds of anhydrous gypsum burnt below 750 centigrade for reasons to be explained more fully later.

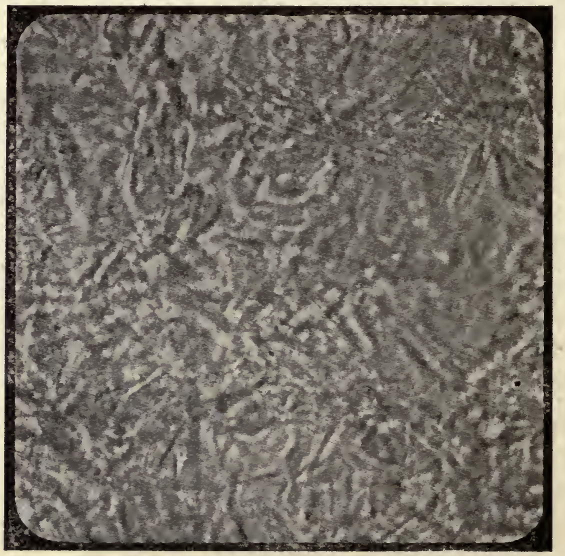
The question, whether or not the various grades of slow-setting plaster, obtainable by the burning of gypsum between 200 and 300 centigrade, can be used in practice, must not be denied, as frequently done, not even, if their hardening takes several days, a time to which we willingly accustom ourselves in making use of Portland cement. Such slow-setting plasters have certainly this advantage over ordinary plaster of Paris that the crystals of di-hydrate grow the larger the more slowly they form, a circumstance beneficial to the grain and the hardness of the casting. The reason, why castings made from ordinary quick-setting plaster are low in strength and possess little resistance towards atmospheric influences, is evidently to be found in the minute size of the interlacing needle-crystals of di-hydrate which, owing to the rapid process of crystallization, have not time to develop and to grow larger. The following table illustrates this point by giving the dimensions of the crystals in millimeters and the corresponding temperatures at which the various kinds of quick-setting and slow-setting plasters have been burnt:

Burning Temperature	Largest Dimensions of Crystals	
	Diameter	Length
107-130 Celsius	0.0025 mm.	0.04 mm.
140 Celsius	0.012 mm	0.14 mm.
250-300 Celsius	0.075 mm.	0.50 mm.
400 Celsius	0.050 mm.	0.35 mm.
450 Celsius	0.035 mm.	0.60 mm.

The plaster burnt at 400 centigrade was heated only for half an hour; that burnt at 250-300 centigrade, however, for several hours. This explains the difference in the dimensions of the crystals. The first two of the plasters given in the preceding table are quick-setting, the last three slow-setting.

The diameters of the needle-crystals of the plaster burnt at 107-130 centigrade are 30 times smaller than those originating from the plaster burnt at 250-300 centigrade; their sectional areas are, consequently, 900 times smaller. It is, therefore, evident that, other things being equal, a casting made from slow-setting plaster must show greater strength. Hence, whenever time has not to be considered and increased strength of the casting is desired, as for instance in the case of statues for art-galleries and so forth, experiments with slow-setting plaster seem to be very advisable, preferably with gypsum burnt at a temperature between 250 and 300 centigrade. The moulds may be removed, if necessary, at an early period, but the casting must not be allowed to dry out before the hardening process is completed. The length of time required for the hardening can best be ascertained by microscopic examination. Samples taken from castings made with slow-setting plaster showed that the hardening process of the casting corresponded in time exactly with the development of crystals of di-hydrate in the microscopic preparation. Cut No. 6, represents a section taken from a similar casting, magnified 750 times. A comparison of it with cuts No. 3 and No. 4, giving sections of quick-setting plasters plainly shows the larger size of the crystals of di-hydrate. It may be mentioned, furthermore, that the slow process of crystallization almost exclusively gives birth to long prismatic crystals, while short plate crystals are exceptions.

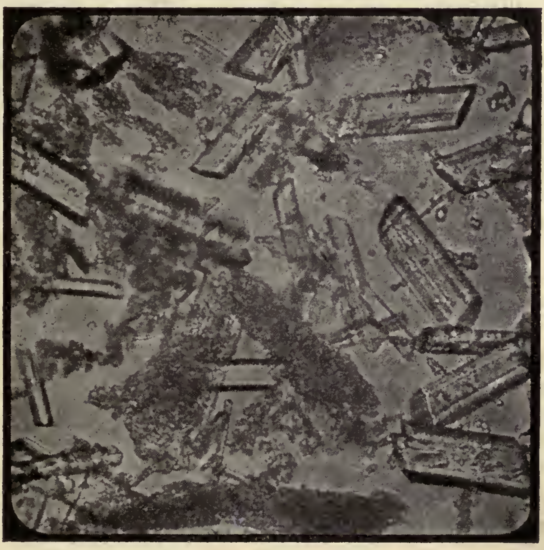
The tensile strength of an "overburnt" gypsum, (slow-setting plaster) produced at a temperature of 250-300 centigrade, was found to be, after the completion of the hardening process, 270 lbs. per sq. in., a very fair strength for plaster indeed. The surface of castings made from it has not the chalk-like appearance of the common plaster of Paris, but possesses a glaze resembling satin or marble; moreover it is harder; yet, it does not obtain the strength of the same plaster mixed with solutions of alum and is likewise far inferior to hydraulic gypsum.



No. 6. Section from a casting made of gypsum burnt at 250-300 centigrade after having hardened for 5 weeks. Compare the size of the crystals with those in cuts No. 3 and No. 4. Magnified 750 times.

Gypsum which may be called "overburnt" from a practical standpoint, that is to say too slow-setting a plaster, is obtained between the temperatures of 400 and 750 centigrade, yet even at lower temperatures, if the heating is prolonged for several hours. The lower temperature limit can, therefore, not be stated at all, while 750 centigrade may be regarded as the upper limit, because beyond this temperature hydraulic gypsum is formed.

Although worthless by itself, the plaster burnt at this interval of temperatures can be made to act very energetically, namely by mixing it, instead of with pure water, with solutions of certain salts which accelerate the hardening process of the common plaster (positive catalysers). Thereby the "overburnt" gypsum regains its capacity to form over-saturated solutions from which the di-hydrate crystallizes. Gypsum burnt between 600 and 700 centigrade, which, according to Rohland's statements, is unable to act even in the presence of positive catalysers, begins to form crystals of di-hydrate after about 45 minutes, if mixed with a solution of potassium-alum and observed under the microscope. After from 30 to 48 hours it is completely transformed into crystals of di-



No. 7. **Transformation of gypsum, "overburnt"** at a temperature of 600-700 centigrade, into crystals of di-hydrate by means of alum solution. To be compared with No. 1. Magnified 360 times.

hydrate. Cold saturated solutions of this salt yield plate-crystals and short prisms (cut No. 7 shows this transformation), while half-saturated and one-quarter saturated solutions chiefly give birth to long prisms. The time required for complete transformation into the crystallized di-hydrate amounts to about 30 hours in the case of saturated solutions and to approximately 48 hours for one-quarter concentration. After 2 days the hardening process is completed in every instance. A gypsum of this kind possesses almost the strength of hydraulic gypsum and of Portland cement; it is so hard that the thumb-nail will not indent it. The tensile strength was found to be as high as 525 lbs. per sq. in.

To this group likewise belongs Keene's cement manufactured by mixing of plaster of Paris with alum solution and subsequent heating to red heat of the formerly hardened mass. The powdered calcined product is afterwards mixed once more with a solution of potassium-aluminum sulphate. The same result, however, is obtained by omitting the first hardening with alum, that is to say by "overburning" the raw gypsum in the first place and then gauging the powdered anhydrite with alum solution.

Another method of making "overburnt" gypsum active and of accelerating the hardening process consists in admixing small amounts of quick-setting common plaster. A gypsum, which was burnt at 550 centigrade and mixed with water, was still soft after 7 days and showed no sign of hardening. Chemical analysis proved it to contain only 2.90% of water of combination. The same gypsum, mixed with only 10% of its weight of a plaster burnt at 107 centigrade, contained 14.88% of water of combination after the same period; it began to set after several hours and developed fair strength. This behavior must be considered a proof of Ostwald's germ theory which attributes the lack of hardening of "overburnt" gypsum to the circumstance that it does not contain undecomposed fragments of crystallized gypsum which could act as germs or nuclei and thus assist in the process of crystallization.

III. HYDRAULIC GYPSUM:

During the last years several papers dealing with hydraulic gypsum have been published. The most noteworthy of them are those by van't Hoff and by Rohland. Nevertheless, its nature, which van't Hoff declares to be "quite mysterious," has not been explained by these contributions. Scientific investigation and practical experience led to a number of contradictory points, so that this subject had still to be regarded as an unsolved problem.

According to the statements found in the most recent literature on hydraulic gypsum (floor-gypsum, flooring-plaster), this modification of calcined gypsum may be briefly summed up to be an anhydrite of gypsum, calcium sulphate, which "under the microscope in nitric acid shows the needle-crystals of the half-hydrate," which "has the same composition as the soluble anhydrite and therefore must be regarded as an isomorphous modification of it," which, furthermore, "forms between the temperatures of 400 and 600 centigrade" and "possesses the remarkable ability not to assume the temperature of its surroundings, if the latter surpasses 600 centigrade" and which ultimately "dissolves in the water with which it is mixed in the same manner as plaster of Paris, though more slowly, and crystallizes as di-hydrate."

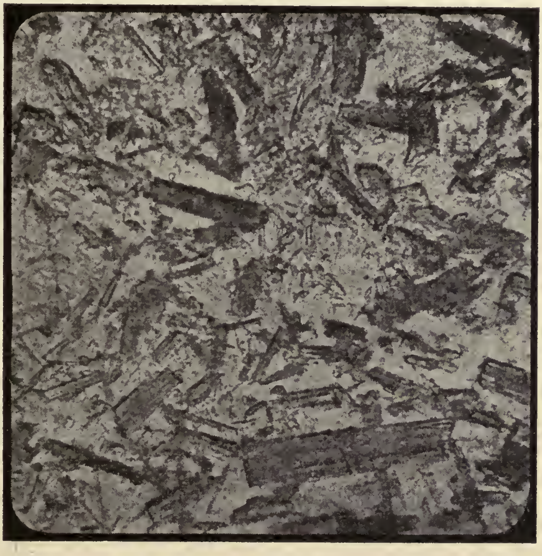
The following description of carefully conducted investigations will show how far the real properties of hydraulic gypsum differ from the above summary from modern literature:

Hydraulic Gypsum Under the Microscope:

Van't Hoff's and G. Just's publication "The Hydraulic Gypsum or So-Called Floor-Gypsum" contains a micro-photograph of a sample of gypsum which the authors believed to represent hydraulic gypsum. However, my microscopical examinations of a number of samples of undoubtedly genuine hydraulic gypsum entitle me to make the statement that the product, which formed the basis for the research-work of these experimenters, was by no means hydraulic gypsum. The micro-photograph published by them (see cut No. 8), as well as the properties of the gypsum which they describe convince me that the manufacturer supplied them not with hydraulic gypsum, but with a sample of "overburnt" gypsum, slow-setting plaster, so-called I. anhydrite, which hardened fairly well, though slowly. It must have been gypsum burnt at a temperature between 250 and 300 centigrade as described in the preceding chapter. The structure of the fragments of their sample (Cut No. 8) indicates that a fibrous raw gypsum was used for its manufacture, which, after having been ground, yields needle-shaped and prismatic crystal fragments.

That their sample was merely slow-setting plaster can, furthermore, be inferred from the remark by the authors that its capacity to harden was found to be decreased and the time of setting retarded after it had been heated at a temperature of 400 centigrade for 10 hours. From this they rightly concluded that their sample was burnt at a temperature below 400 centigrade. A similar behavior, however, can only be discovered in the case of the above described slow-setting gypsum, but is not characteristic of hydraulic gypsum, which is obtained only at temperatures far above 400 centigrade, as will be shown later, and upon which heating at 400 centigrade has no influence whatever.

This confounding of hydraulic gypsum and slow-setting plaster is easily explained by the fact that in commerce these two kinds of gypsum are frequently not properly distinguished one from the other and that the hardening process of both of them shows this resemblance that it is completed only after weeks and months, which plainly distinguishes them from common plaster, Unfortunately, however, van't Hoff's publication, describing a gypsum with entirely different properties, has been widely quoted and thus has spread a wrong conception of the method of production and of the properties of hydraulic gypsum. Also Rohland has been influenced by it; as a consequence, the latter's publication does not contribute anything towards explaining the actual properties of hydraulic gypsum; on the contrary it makes the confusion even greater.



No. 8. Slow-setting plaster. Micro-photograph taken from van't Hoff's and Just's publication. By them believed to be hydraulic gypsum or floor-gypsum.

Remarks by the Translator:

The American reader can best obtain an idea of the confusion existing in the classification of gypsum products and of the unreliableness of statements to be found in modern literature by referring to the fourth chapter of Edwin C, Eckel's book on "Cements, Limes and Plasters," which contains a translation of the above mentioned publication by van't Hoff and Just.

Also Eckel quotes van't Hoff with the greatest reverence. He divides the gypsum products obtainable at higher temperatures than customary for the burning of plaster of Paris into two groups, "Flooring-Plasters" and "Hard-Finish Plasters," and gives the first name to all grades of gypsum "prepared by simple burning at high temperatures" and the second to those "produced by a double-burning with the additional use of chemicals."

He continues: "Neither, product is made to any extent in the United States, though a considerable quantity of hard-finish plasters are imported every year. The data obtainable as to processes of manufacture are scanty, and the descriptions published are often contradictory, so that it has been difficult to prepare a satisfactory account of these products.. It is believed, however, that the descriptions given below contain no errors of importance."

"The flooring-plasters ("Estrichgips" of German reports) include those plasters made by calcination of a relatively pure gypsum at temperatures of 400 Fahrenheit (equal to 200 centigrade) or higher."

"In the literature of gypsum and plaster it is often stated that gypsum, burned at temperatures exceeding 400 Fahrenheit, yields a completely dehydrated product—an artificial anhydrite—which is entirely valueless as a structural material, because it has completely lost its property of recombining with water. This statement is, however, erroneous, for plasters burned at such temperatures are regularly made and used. They set with extreme slowness, however, and require very fine grinding."

"Until very recently no satisfactory discussion of this phenomenon had been attempted, and the few published accounts of the manufacturing processes employed were contradictory as to temperature reached, composition of product, etc. Fortunately, however, a detailed account of the chemical changes involved was published during 1903 by van't Hoff in the Transactions of the Berlin Academy of Sciences. As this paper is practically inaccessible to the American engineer or manufacturer, a translation is here appended:"

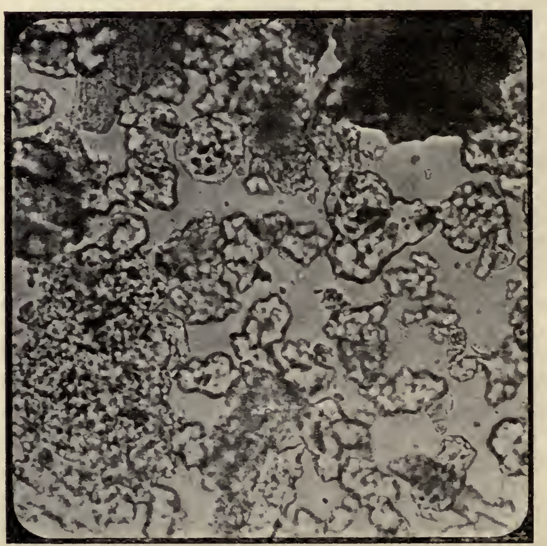
Then follows van't Hoff's and Just's publication on "The Hydraulic Gypsum or So-Called Floor-Gypsum," which, as demonstrated by Glasenapp, refers to a gypsum burnt below 400 centigrade, to a slow-setting plaster, whereas hydraulic gypsum, or the floor-gypsum of commerce, is obtained only at temperatures above 750 centigrade. Van't Hoff concludes his paper as follows:

"The essential result of the investigation, therefore is, that in the heating of gypsum after total dehydration, which occurs at about 190 centigrade, the capacity to bind water is at first retained, and is only gradually lost, either by more intense or by longer heating. The retention of the crystalline form, which is probably due to burning without previous division into small bits, checks this so-called dead-burning, and is therefore of technical importance. **We found no evidence to support the statement that, after dead burning, a new binding capacity appears at a high temperature, in which case even the natural anhydrite would be suitable for burning floor-gypsum."**

In the face of this meagre information available and involuntary misrepresentation on the part of van't Hoff, the reader of Glasenapp's present publication must necessarily admire the thoroughness of his research-work and be thankful to the experimenter for the large amount of data and information supplied. This paper, in my opinion, will elucidate the confusion that existed heretofore and will give rise to a number of additional essays until finally manufacturer, consumer and inspecting chemist will be equally educated on the subject and will all be convinced of the merits of the higher grades of gypsum, namely slow-setting plaster and hydraulic gypsum.

We now return to Professor Glasenapp's paper:

The literature on hydraulic gypsum contains frequent references to "crystals of the half-hydrate." To this I must remark that the half-hydrate constituting plaster of Paris does not possess a crystal shape of its own; what we see under the microscope are the crystal fragments of the partly dehydrated raw gypsum. These fragments, contained in plaster as well as those found in "overburnt" gypsum up to a burning temperature of 800 centigrade, have the shape of splinters and spikes or resemble small rods and pins, if the raw gypsum had a fibrous structure. On the other hand, genuine hydraulic gypsum shows, even if magnified only 300 or 500 times, a peculiar granular structure. After washing out of the fine particles, the coarse feels as hard as sand grains and is difficult to grind. These sintered particles possess polygonal shape and have sharp or rounded corners; they are double-refracting. The laminated structure of the crystal fragments of raw gypsum, however, which becomes visible only upon driving off of the water of crystallization at low temperatures, and which, therefore, characterizes plaster of Paris and slow-setting plaster, is not to be found in the case of hydraulic gypsum. Cut No. 9, shows the coarser particles of genuine hydraulic gypsum, commercial product; cut No. 10, is the same preparation as No. 9, but in this case the coarse particles have been broken up by grinding them between cover glass and



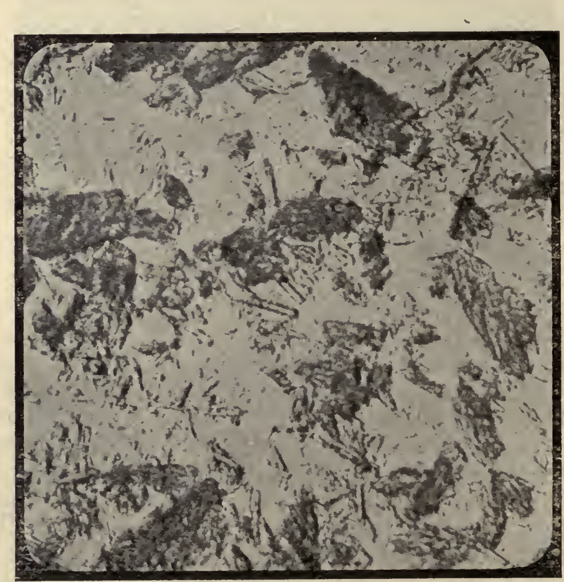
No. 9. Powdered hydraulic gypsum (commercial product) after washing out of the finest particles. The coarse consists of a multitude of grains fused together. They can be separated by pressure on the cover glass and then present the view given by cut No. 10. Magnified 200 times.

slide. Cut No. 11, represents powdered plaster of Paris, commercial product, for comparison. This last cut is likewise an illustration for slow-setting plaster, "overburnt" gypsum.

No. 10. Grains composing hydraulic gypsum. Same preparation as No. 9. Magnified 360 times.

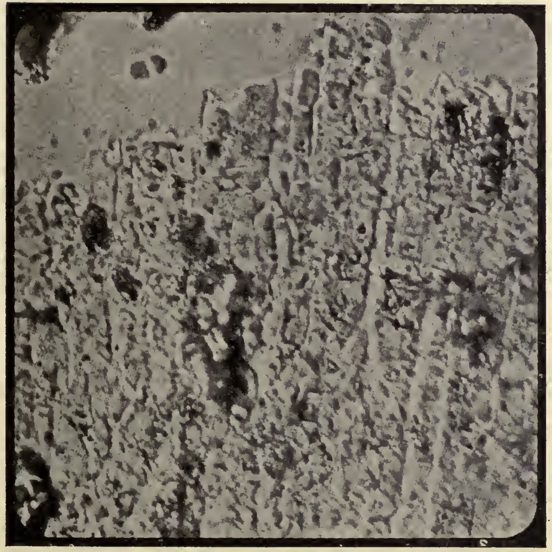
The shape and optic properties of hydraulic gypsum are so characteristic, that it is impossible to mistake it for plaster of Paris. Even a small admixture of one kind to the other can easily be detected by the microscope. A further method of distinguishing them furnishes the examination under crossed Nichols, whereby hydraulic gypsum shows brilliant colors. The grains and other elements of which the hydraulic gypsum may be composed are crystalline, double-refracting and apparently belong to the rhombic system. If placed in water, they do not change their form, not even after several months, and are not inclined to re-crystallize as di-hydrate.

What Temperature is Required for Burning Hydraulic Gypsum? In looking for an answer to this important question in the available literature, one finds nothing but uncertainties and conjectures. While the temperature interval of 525 to 600 centigrade was formerly declared to be the proper burning temperature, modern investigators place it as low as 400 and even between 200 and 400 centigrade. But that in all the numerous observations on record "overburnt" gypsum, slow-setting plaster, was used instead of hydraulic gypsum is evident from the description of the properties of the materials under examination and from the accompanying micro-photographs. All these various grades of gypsum had nothing in common with the commercial genuine hydraulic gypsum which, as every manufacturer of this product knows, can only be obtained at a bright red heat corresponding with a temperature of from 900 to 1000 centigrade.



No. 11. Powdered plaster of Paris (commercial product). All kinds of gypsum obtainable by burning between 107 and 800 centigrade show these same elements. Magnified 360 times.

In order to ascertain the limits of temperature between which the granular modification of the anhydrite is formed, which microscopic investigation proved to be hydraulic gypsum, small samples of various kinds of raw gypsum were burnt in a furnace, heated by electricity, at temperatures of 600 centigrade, 700, 800 and so on, the temperature of each following burning being 100 centigrade higher. The heat was measured by a Le Chatelier pyrometer. The burning time was from 3 to 4 hours which was sufficient for pieces of gypsum of nut size. Microscopic examination of the products obtained had the following result:



No. 12. Hydraulic gypsum burnt at 900 centigrade. Section through an unbroken piece showing parallel stripes originating from the fibers of the raw gypsum. The dark spots are adulterations of clay. Magnified 750 times.

The structure of the samples burnt at 600 and 700 centigrade could not be distinguished from that of plaster of Paris. These temperatures, therefore, yield exclusively "overburnt" gypsum. The product burnt at 800 centigrade, however, if slightly magnified, showed still the same laminated structure characteristic of dehydrated gypsum for all temperatures up to 700 centigrade and as shown by cut No. 5. Upon more powerful magnification, the laminae could be discerned to consist of minute grains, of the shape of those to be found in hydraulic gypsum, especially at the thin edge of the specimen under observation.

No. 13. Hydraulic gypsum burnt at 900 centigrade. Section through an unbroken piece showing the granular elements composing it in their original place. Magnified 750 times.

Mixed with water, this sample hardened well and acted like hydraulic gypsum. The granular modification of anhydrite, however, attains its full development only at a temperature of 900 centigrade, when microscopic sections present the structure given by cuts No. 12 and No. 13.

Cut No. 12 shows the less frequent occurrence of grains arranged in parallel lines by breaking up, on account of sintering, of the fibers composing the raw gypsum; cut No. 13 shows the grains in irregular position and distinctly separated one from another. The samples burnt at 1000 and 1100 centigrade differ from those obtained at 900 centigrade only by the larger dimensions of the grains.

Chemical Composition of Hydraulic Gypsum: The erroneous assumption that hydraulic gypsum was formed at temperatures between 400 and 600 centigrade, within which interval no chemical change in the composition of the gypsum could be discovered to take place, outside of giving off its water of crystallization, induced chemists to declare, that hydraulic gypsum was "a second anhydrous modification of gypsum" and that it had the same composition as the slow-setting I. anhydrite obtainable between 200 and 300 centigrade. Yet, in making this statement it was overlooked that the hydraulic gypsum, as supplied by the manufacturer, invariably contains more calcium oxide than corresponds with the amount of sulphuric acid present. This surplus of calcium oxide may originate from two causes: It may derive from the decomposition of calcium carbonate, if the native gypsum employed in the manufacture contains some of this, or it may be due to a partial evaporation of the sulphuric acid of the gypsum. Now, a similar partial decomposition of gypsum takes place, according to my experiments, at a temperature of 800 centigrade, that is to say at the minimum temperature necessary for the formation of the granular modification of the anhydrite, and must be considered inseparable from the burning of hydraulic gypsum. The surplus of calcium oxide grows with the increase of the burning temperature as the following table illustrates:

Chemical Composition of Burnt Product in Per Cent.

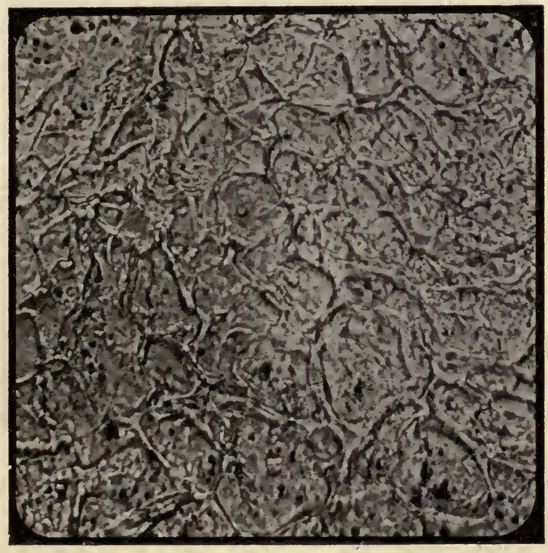
Temperature In Centigrade	Calcium Oxide	Sulphuric Acid	equal to	$CaSO_4$	+ CaO
800	42.64	57.02		96.93	2.73
1100	43.06	56.40		95.88	3.58
1400	47.72	51.88		88.20	11.40

This "free" calcium oxide, originating from a partial decomposition of gypsum, behaves, during the hardening of hydraulic gypsum, in an entirely different way from free calcium oxide derived from calcium carbonate, as my experiments prove. Also micro-photographs show a marked difference. A mixture of 2 parts of gypsum and 1 part of finely pulverized chalk, burnt at a temperature of 1070 centigrade, presented under the microscope the minute grains of calcium oxide between the much larger grains of hydraulic gypsum, which latter also enclosed grains of calcium oxide. No action whatever of one constituent upon the other was revealed by any change of form which might possibly have taken place. In accordance with this observation, the pulverized calcined product developed considerable heat upon being mixed with water and resulted, after having hardened, in a chalk-like mass of low strength, that, by the way, did not show signs of blowing, because the calcium oxide hydrated immediately upon mixing of the powder with water.

On the other hand, the calcined products of pure raw gypsum did not show any signs whatever of free calcium oxide, not even the sample burnt at 1400 centigrade, and all of them showed normal hardening. The hydraulic gypsum burnt at 1400 centigrade developed even a remarkably high strength. Also a sample, placed in a furnace in which china was burnt at 1370 centigrade and which, on account of too long exposure to the fire, contained only 17% of calcium sulphate and 83% of "free" calcium oxide, hardened well and exhibited no signs of blowing.

The next question occuring to one's mind is: **In What Form is the Calcium Oxide Contained in Hydraulic Gypsum?** To this a satisfactory and at the same time surprising answer was obtained from a study of the microscopic sections of the samples burnt at higher temperatures, for instance at 1300 centigrade. As a result it must be stated that hydraulic gypsum is by no means a homogeneous body, as was the general belief so far; it consists of two components, in the first place of the above mentioned grains or polygons and in the second place of a glassy substance surrounding the former. The granular constituent is, as formerly described, undoubtedly crystalline and double-refracting, the latter substance, in distinction thereof, amorphous and from an optical standpoint inactive. On microscopic sections (see cut No. 14) the glass substance appears as network enclosing in its meshes the grains or polygonal bodies.

There is no doubt that the "free" calcium oxide of hydraulic gypsum is contained in the glassy substance, while the grains represent a special granular modification of the anhydrite of calcium sulphate. This follows from the quantitative proportions of the



No. 14. Hydraulic gypsum burnt from alabaster gypsum at 1300 centigrade. The grains of anhydrite lie in a network of a fused glassy "basic calcium sulphate." In comparing the photograph of this preparation with Nos. 12 and 13 it must be remembered that it has been enlarged only half as much as the latter. The grains are much larger in this sample of hydraulic gypsum on account of the higher burning temperature. Magnified 375 times.

"free" calcium oxide to calcium sulphate in the burnt products and from those of the glass substance to the granular part in the corresponding micro-photographs. The commercial hydraulic gypsum, which is burnt at a temperature between 900 and 1000 centigrade, contains on an average 3% of "free" calcium oxide, unless the raw gypsum contained calcium carbonate. The glass substance, therefore, becomes hardly visible and can be distinguished as network only upon powerful magnification. My attention was called to it for the first time by sections secured from samples burnt at higher temperatures which contained larger amounts of "free" calcium oxide. In these the glass substance became plainly noticeable even if magnified moderately.

No. 15. Microscopic section of hydraulic gypsum burnt at 1400 centigrade, showing characteristic plates of sintered anhydrite. The dark parts represent glassy "basic calcium sulphate." Magnified 100 times.

The "free" calcium oxide is evidently an important part of hydraulic gypsum; it belongs to its chemical constitution and must not be regarded as adulteration or occasional admixture as done heretofore. However, it is not contained in it in a free, uncombined state in the usual sense of the word, as it can not be detected by the microscope. The glassy substance, therefore, (which has merely been termed thus on account of its transparency and not because it was supposed to resemble glass from a chemical standpoint) must either be a basic calcium sulphate or must represent a solution of calcium oxide in neutral calcium sulphate,

Theory of the Formation of Hydraulic Gypsum: The results obtained from the foregoing observations explain the chemical processes going on during the burning of hydraulic gypsum. With increasing temperature the raw gypsum passes through the stages of the half-hydrate, of the quick-setting and slow-setting I. anhydrite and as continuation of the latter that of the overburnt gypsum. The point, when the calcium sulphate begins to decompose, under partial evaporation of the sulphuric acid, is at the same time the beginning of the glassy formation of "basic calcium sulphate" and of the granular modification of anhydrite. This takes place at a temperature of about 800 centigrade. The grains are still exceedingly small at this temperature. Upon increasing the temperature to 900 centigrade and upon further evaporation of small amounts of sulphuric acid, which means also further formation of the glassy component, the grains obtain the normal size of the commercial hydraulic gypsum. If the burning temperature is further increased, the glassy "basic calcium sulphate" assumes even larger proportions and the grains of anhydrite become still larger until, at about 1400 centigrade, near the fusing point of the mass, a coarse crystalline product is obtained composed of large amounts of plates and tablets of anhydrite in addition to the customary round or polygonal grains. These plates obtain a length and width of 1 millimeter and more and are divided in smaller areas by shrinking cracks crossing at right angles. Cut No. 15 shows a similar plate; the glassy "basic calcium sulphate" partly fills out the cracks, partly it covers the plate at a number of places. Where it predominates, it often encloses grains of anhydrite on the point of decomposition.

The genuine commercial product of hydraulic gypsum contains all sizes and forms of anhydrite, from the minute grain formed at 800 centigrade up to the large plates coresponding with temperatures of 1300 and 1400 centigrade. The most frequent, however, are the round or polygonal grains of medium size which are principally formed between 900 and 1000 centigrade. This shows that the temperature differs widely in the same furnace, which can not be avoided, of course, if the charge of the kiln consists of alternate layers of raw gypsum and coal. Fortunately the quality of the calcined product is not impaired by it, as all grades of hydraulic gypsum burnt between 800 and 1400 centigrade harden well. A matter of great importance, however, is that the burning is done with an oxidizing flame. A reducing atmosphere causes formation of calcium sulphide and decreases the value of the burnt product.

Setting and Hardening of Hydraulic Gypsum: The statements to be found in the literature on gypsum to the effect that the hardening of hydraulic gypsum was due to the going into solution of the anhydrite and re-crystallizing as di-hydrate from the over-saturated solution, were, as pointed out in the foregoing, based upon observations made on slow-setting plaster and not on hydraulic gypsum. The explanation given was not so incredible, as the hardening process of plaster of Paris could readily be believed to be applicable also to hydraulic gypsum. The slower hardening of the latter was simply attributed to its decreased solubility in water and to its reduced ability to form oversaturated solutions.

However, the observations to be made during the practical application of hydraulic gypsum strongly discredit these views. A hardening process, as that of plaster of Paris, caused by interlacing and growing together of crystals of di-hydrate, appears infeasible in the case of hydraulic gypsum, which requires pounding with wooden mallets and smoothing with trowels after the gypsum has set for a day or two, in order to give it its maximum density and strength. If the hardening were caused by the formation of crystals, a similar treatment would be of no avail, on the contrary it would be highly injurious, because the crystals would be crushed one by another and the cohesion be destroyed. Moreover, it would be inexplainable why hydraulic gypsum possesses far greater hardness and superior strength to plaster of Paris and slowsetting plaster, if the physical and chemical properties of the hardened products were identical, namely the same crystallized dihydrate.

No. 16. Section through a hardened piece of hydraulic gypsum showing the unchanged position of its component parts due to the customary coarse grinding. Magnified 750 times.

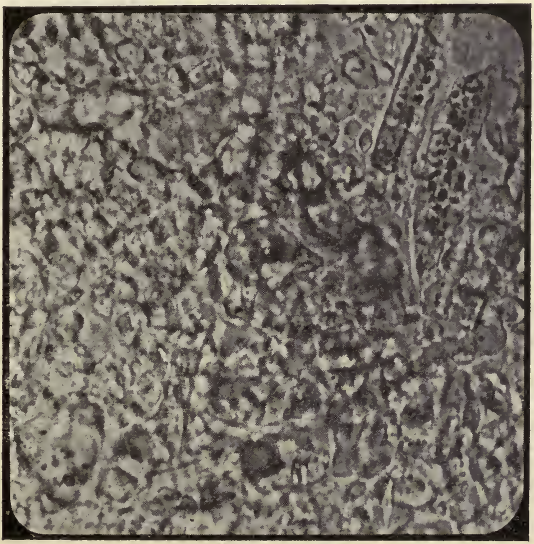
It was mentioned in the foregoing that, according to my observations, powdered hydraulic gypsum placed in water remained, in contrast to plaster of Paris, entirely unchanged for many months and did not show the slightest inclination to form crystals.

This observation alone would have been sufficient to suggest a quite different process of hardening; and, in fact, microscopic sections of thoroughly hardened hydraulic gypsum show hardly a trace of crystallization. The component parts of the original calcined product are found unaltered in the hardened gypsum as cuts No. 16 and 17 prove.

Only now and then hollow spaces can be detected partly filled out by crystals of di-hydrate (see cut No. 18). Crystallization, therefore, is of secondary importance in the case of hydraulic gypsum. Hardened pulverized hydraulic gypsum can be distinguished from the unhydrated calcined product only by the more regular alignment of the grains of the latter. But, owing to the fact, that this gypsum is mostly sold as a coarse powder, the hardened gypsum represents in most cases a conglomerate of pieces showing the granular elements in an unchanged position.

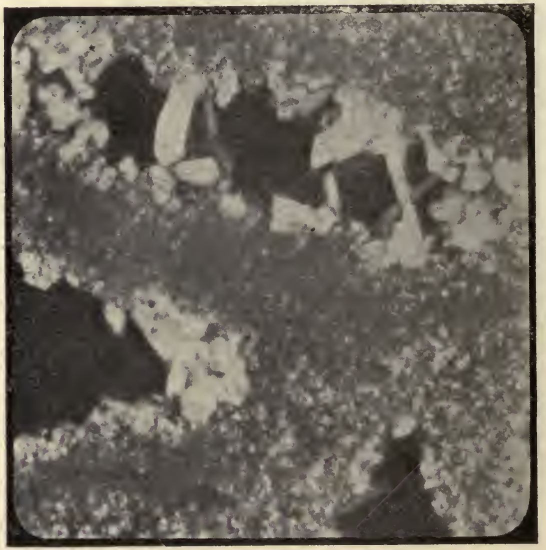
Hence, hydraulic gypsum hydrates principally without changing its form, without crystallizing, because it is unable to form over-saturated solutions. This explains the necessity of densifying the mortar during the early stage of its hardening by tamping it; the particles are thus forced together more closely: hereby the surfaces of contact increase and the grains are cemented more completely. The tamping of the mortar, however, one or two days after hardening has begun, seems to be unavoidable, as the freshly gauged gypsum is too soft to withstand tamping. It would be better, of course, if such a disturbance of the setting process could be avoided; yet, it is of little consequence in as much as, at the time of tamping, the process of hydration is still in its incipiency and as only a small amount of water has gone into combination. A determination of the water of combination of a piece of hardening hydraulic gypsum showed 2.18% after 2 days, 5.60% after 14 days and 12.0% after 11 wecks, while about 21% were required for complete transformation into the hydrated state. This proves the importance of keeping hardening hydraulic gypsum wet for several months, if it is expected to attain its maximum strength. It closely resembles Portland cement in this respect.

While the granular constituent of hydraulic gypsum, the anhydrite, is converted, upon hardening, into di-hydrate without change of form, that is to say without crystallizing, the glassy component may take a share in the hardening in a two-fold manner. In the first place, it is not at all impossible, that its "free" calcium oxide, contained in it in "solid solution," upon coming in contact with water, crystallizes as calcium hydrate. But, this observation I made only in the case of the product calcined in a furnace together with china, which, with its 17% of calcium sulphate and 83% of calcium oxide, represented a very basic glass-like substance. Its powder was acted upon very strongly by water; however, there was no slaking or disintegrating noticeable; the process consisted in a lively formation of small and large plate-



No. 17. Section through hardened hydraulic gypsum. In this case the calcined product was ground more finely. The grains, therefore, do not appear in rows, but are isolated and mixed. Magnified 750 times.

crystals of calcium hydrate belonging apparently to the hexagonal system. In the case of commercial hydraulic gypsum, with approximately 3% of "free" calcium oxide, I never observed similar formation of crystals of calcium hydrate upon adding water, nor did I detect them in hardened pieces of hydraulic gypsum.



No. 18. Hollow spaces in a piece of hardened hydraulic gypsum containing a few crystals of dihydrate. These crystals are due to the evaporation of the water of the saturated (not over-saturated) solution of calcium sulphate that formerly filled out these cavities.

The second possibility of contributing to the hardening for the "basic calcium sulphate," and which is more likely to be the true explanation, immediately suggests itself by the going into solution of calcium hydrate upon pouring hydraulic gypsum into a large amount of water. The water becomes strongly alkaline after a short time and the surface of it soon appears covered with a thin film consisting of minute calcspar-crystals. This process of going into solution of calcium hydrate and precipitating by the carbonic acid of the atmosphere undoubtedly takes place also during the hardening of hydraulic gypsum as long as "basic calcium sulphate" is available. The process is the same as that causing the hardening of ordinary lime mortar, but of minor importance in the case of hydraulic gypsum. The minute calcspar-crystals can be detected in hardened hydraulic gypsum only by the development of carbonic acid, if a drop of hydrochloric acid is allowed to act on a microscopic section. After the "free" calcium oxide has been extracted from the "basic calcium sulphate," the remaining neutral calcium sulphate hydrates in the same way as the granular anhydrite, that is to say without forming crystals, as all sections of hardened hydraulic gypsum prove.

The third factor coming in question in the hardening of hydraulic gypsum, and likewise a point of little consequence, is its solubility in water, which lies between that of the half-hydrate and of the dihydrate and which certainly surpasses that of native gypsum. The small amount of calcium sulphate going into solution may be sufficient to partly or entirely fill out with small crystals of di-hydrate some of the hollow spaces created by the gradual drying out of the hardened gypsum. This feature presents cut No. 18.

A point of greater importance for its technical application is a property characteristic for the grains of hydraulic gypsum, namely that they retain the hardness, which they obtained in the calcining process, also after they have combined with water. This forms the main cause of the strength of hardened hydraulic gypsum. Such strength would be out of the question if the hardening, as assumed so far, would be due to transformation into crystals of di-hydrate.

Influence of Catalysers Upon Hydraulic Gypsum: P. Rohland states that the hardening process of hydraulic gypsum can be accelerated by an admixture of positive catalysers; thus he found the hardening time reduced from 600 to 60 hours by an addition of potassium sulphate. If this were true, it would seem to be of some benefit in the practical application of hydraulic gypsum.

With the aim to throw light on this point I made a series of experiments, especially with potassium aluminum sulphate. These tests prove that hydraulic gypsum, gauged with saturated solutions of alum, precipitates needle-crystals of di-hydrate as early as 15 or 20 minutes after being mixed with the solution. After 2 hours the small grains are completely converted into crystals. After 12 hours about half of it and after 24 or 30 hours almost the whole original mass is crystallized. The process is identically the same as if "overburnt" gypsum is used, which was burnt at temperatures between 300 and 700 centigrade.

The application of accelerating admixtures, therefore, undoubtedly shortens the hardening of hydraulic gypsum, but the hardened product obtained is no longer hydraulic gypsum; it corresponds in every respect with a gypsum burnt at 500 centigrade and subsequently treated with alum solution; owing to the formation of larger crystals, the edges of the hardened mortar are translucid and the whole casting is considerably stronger than hardened plaster of Paris; yet, microscopic examination reveals at a glance, that this is an entirely different hardened product from hydraulic gypsum hardened with pure water.

IV. SUMMARY OF THE RESULTS AND CONCLUSIONS DRAWN FROM THEM WITH REGARD TO PRACTICAL APPLICATION.

By the foregoing observations has been proven that almost all former statements about and conceptions of the origin, constitution and properties of hydraulic gypsum to be found in modern literature are erroneous and that this chapter of technology has to be revised completely in order to make it agree with my observations and with the practical experience of the manufacturer. The general opinion that hydraulic gypsum is obtained at temperatures between 400 and 600 centigrade and even still lower has to be positively abandoned. Furthermore, hydraulic gypsum is by no means identical with the soluble anhydrite; it does not show the needle-crystals of di-hydrate as plaster of Paris and the lower grades of "overburnt" gypsum, slow-setting plaster, do. In opposition hereto, the results obtained from my research-work characterize hydraulic gypsum as follows:

Hydraulic gypsum consists of a mixture of a granular, densely vitrified, hard, strongly light-refracting, crystalline modification of the anhydrite, obtained at red heat, with small amounts of a fused, amorphous, glassy, basic anhydrite, containing calcium oxide in "solid solution." This product requires for its formation and for the complete development of its constituents a temperature of about 900 centigrade. At higher temperatures, at 1300 centigrade and above, the amount of the basic constituent increases and the grains grow in size and hardness. It combines with water without change of shape, that is to say without forming crystals, with the exception of very small amounts of crystallized di-hydrate and calcium hydrate, and retains its optic properties and hardness. Positive catalysers, however, transform it into soluble anhydrite and crystals of dihydrate.

For the practical gypsum burner the most important and noteworthy point is this, that it is almost out of the question to spoil a charge by overburning. The heat may be increased to 1300 centigrade and even higher, but not for too long a time, without impairing the hardening properties, providing the fire is conducted in such a way that the gypsum is not reduced to calcium sulphide. On the other hand, the temperature may go down as low as 800 centigrade; however, it will always be advisable to regard 900 centigrade as the lowest limit, because only then the characteristic hard-sintered grain is formed. The wide interval of from 400 to 500 degrees, within which the heat in the kiln may vary, makes the burning process very convenient and safe. Heating above 1000 centigrade is not economical, of course; yet, I wish to repeat at this place, that at very high temperatures, between 1300 and 1400 centigrade—at least in laboratory experiments—a still coarser and apparently even harder, because more strongly sintered, grain is obtained, which may possibly be of value for some purposes. But as not only the height of the temperature, but also its duration, governs the physical properties of the grain, the same effect is likely to be obtained also at lower temperatures in practical operation.

By my research has been demonstrated, from a scientific standpoint, that hydraulic gypsum represents a product differing in every respect from plaster of Paris and slow-setting plaster, which the manufacturer claimed to be the case for some time. It is a more precious substance, the superior qualities of which are certainly not sufficiently appreciated as yet by the building trade. For many years, for instance, vain efforts have been made to produce a white cement, until at last a number of factories succeeded in turning out a fairly satisfactory but expensive product. Hydraulic gypsum is a white cement of the highest order. On account of its excellent hydraulic properties, being fully equal to those of Portland cement, and because of its dense structure, which minimizes the danger of soiling of the surface, this cement is surely superior to white Portland cement and should be used more extensively.

Among other uses, it would be advisable, for instance, to try hydraulic gypsum for castings of plastic works of art and of architectural decorations. To this suggestion the objection may be made that hydraulic gypsum is mostly too coarsely ground for this purpose and that it is heavier than plaster; moreover, that it does not set as rapidly. There is nothing in the way of grinding it more finely; on the contrary, this would be an easy matter, as the calcined gypsum shows a natural inclination of breaking up into the minute grains composing it. The tamping of such castings, a day or two after having been poured into the moulds, would have to be avoided most likely. Therefore, another method would have to be employed in order to provide greatest possible density. This could be achieved by mixing two kinds of hydraulic gypsum burnt at different temperatures and ground to different fineness, for instance, coarsely ground hydraulic gypsum burnt between 1200 and 1300 centigrade, with its large granular elements, and finely ground hydraulic gypsum calcined at about 800 centigrade. The minute grains of the latter would fill out all voids between the grains of the former. Such a process of mixing would be based upon the experience, that the size of the granular constituents of hydraulic gypsum grows with increased heat and would soon lead to a mixture possessing the greatest possible weight for a given volume. Experiments made in this direction showed a weight of 149 grams per 100 ccm. of hydraulic gypsum passing a 100-mesh sieve and of 190 grams for the same volume of hydraulic gypsum passing the 200-mesh sieve. Of the various mixtures made from these two screenings that showed the highest weight per given volume (100 ccm.), namely 203 grams, which contained 40% of the coarse and 60% of the fine product. For this test only one kind of hydraulic gypsum was used possessing granular elements of almost even size. If two products of widely differing burning temperature would have been used, a still higher weight by volume would have been obtained undoubtedly.

The slow progress made in the hardening of such castings would be a drawback, of course; yet, their strength after a few days is sufficient to allow taking them out of the moulds. Afterwards they have merely to be kept in a chamber saturated with moisture and to be sprinkled with water now and then in order not to interrupt the hardening process by drying out of the castings. If the moulds have to be used again very soon, the hardening of hydraulic gypsum may be accelerated by small admixtures (about 10% of its weight) of slow-setting plaster, burnt between 200 and 220 centigrade. A similar plaster hardens more slowly than ordinary plaster of Paris, but sets sufficiently fast and has this advantage over the latter, that it forms larger crystals of di-hydrate. On the other hand, the strength and durability of plaster of Paris could be improved by an admixture of hydraulic gypsum.

Microscopic Determination of the Commercial Products of Gypsum: On account of the present uncertainty, or even confusion, prevailing in the definition of hydraulic gypsum and on account of its frequent being mistaken for the slow-setting "soluble" or first anhydrite (burnt between 200 and 350 centigrade) and even for plaster of Paris, a simple, reliable and brief determination of the various products manufactured from native gypsum would certainly be desirable and of great value. The microscopical examination enables the investigator to attain this end speedily and safely. Genuine hydraulic gypsum, that is to say gypsum calcined at a temperature of at least 900 centigrade, can be easily distinguished through it from all other kinds of burnt gypsum and also from powdered raw gypsum, so that this method should be employed in all doubtful cases. A similar investigation requires but a few minutes. A trace of the powder to be examined is stirred with a drop of water on a miscroscopic slide and a cover glass is placed upon it. Then the cover glass is subjected to a slight pressure in order to disintegrate the coarser grains and to make the conglomerations of the granular constituents of hydraulic gypsum separate into their elements, grains or plates or whatever the case may be. The preparation should be magnified 300 or 400 times; but even 200-fold magnification suffices in most instances.

In analyzing the fragments to be observed under the microscope the following must be borne in mind: All particles of fibrous and translucid appearance and those of a yellowish-brown color are burnt below 800 centigrade and have nothing in common with hydraulic gypsum. They have the shape of prongs, spikes or splinters and contain numerous needle-shaped fragments deriving from the crystallized fibers of the original raw gypsum. Cut No. 11 and No. 8 illustrate these fragments. In opposition hereto, the microscopic elements of hydraulic gypsum show not the least sign of a fibrous structure (with the exception of that burnt at 800 centigrade, the temperature at which the formation of hydraulic gypsum begins). They are entirely clear and transparent in almost every instance and, owing to their strong light-refraction, appear lighter than the surrounding water. The grains and rows of granular elements possess forms so characteristic (as cut No. 10 and No. 12-17 show), that a particle of hydraulic gypsum, which happens to be in plaster of Paris, is detected at a glance. Needle-crystals or fragments of them do not occur in hydraulic gypsum burnt at 900 centigrade and above, so that the absence of them is a sure sign of genuine hydraulic gypsum. Another characteristic for hydraulic gypsum are the minute holes often found in the granular elements. In polarized light the particles of hydraulic gypsum can be readily distinguished from all kinds of gypsum burnt below 800 centigrade by their remarkably strong iridescence.

The microscope, however, furnishes still further information about hydraulic gypsum. It permits to determine approximately its burning temperature on account of the growing size of its constituents with rising temperatures. Large grains indicate a high burning temperature, while rectangular plates (see cut No. 15) or fragments of them prove that the product was calcined at a temperature slightly below its fusing point. In connection with these views, presented by the microscope, it must be remembered that the hardness of the grain and consequently the strength of the resulting mortar grow with the size of the granular component of hydraulic gypsum.

Plaster of Paris can be distinguished from the slow-setting I. anhydrite by the time when crystallisation of di-hydrate begins. The exterior shape of their particles offers no marks of distinction.

In conclusion the various calcined products obtainable from raw gypsum may be classified in accordance with the results derived from the foregoing research. The limits of temperatures stated must only be considered as approximate figures, of course, as the change from one kind to the other takes place very gradually and because, as repeatedly stated, not only the height of the temperature, but also its duration, determine the properties of the calcined product:

A.	Native Gypsum		—Di-hydrate, containing 2 molecules of water.
B.	107	Celsius	—Half-hydrate, containing ½ mol. of water.
C.	107-170	"	—Consists mainly of half-hydrate.
D.	170-200	"	—More or less dehydrated half-hydrate. Combines with water readily until half-hydrate is obtained. **C. & D. represent the commercial plaster of Paris.**
E.	200-250	"	—Contains a very small amount of water. Sets more slowly than the former.
F.	250-400	"	—Contains only a trace of water. Slow-setting. **B., C., D., E, & F. form crystals of di-hydrate, if mixed with water. Hardening due to crystallization.**
G.	400-750	"	—Completely dehydrated, anhydrite, over-burnt from a practical point of view.
H.	750-800	"	—Gradual transformation into the granular modification of

anhydrite; beginning of the formation of hydraulic gypsum.

G. & H. Show, in contact with water, no hardening or only very imperfect hardening.

I. 800 " —Hydraulic gypsum, containing minute grains of anhydrite.

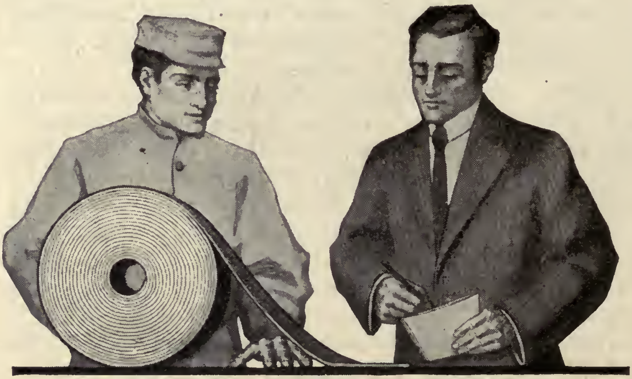
K. 900-1000 " —Genuine hydraulic gypsum; grains fully developed.

L. 1000-1400 " —Hydraulic gypsum, showing grains increasing in size and hardness with rising temperature. The percentage of "basic calcium sulphate" likewise increases in the same ratio.

I., K. & L., harden slowly with water without crystallizing.

G., H., I., K., & L. crystallize with alum solution.

A temperature of from 1300 to 1400 centigrade, in my opinion, can be employed in the manufacture of hydraulic gypsum only in cases, in which the gypsum does not come in immediate contact with the fuel, as, for instance, in laboratory experiments, in which the burning is done with gas. Where coal is used, the ashes of it as well as the reducing carbon are bound to contaminate and spoil the calcined product. Moreover, temperatures as high as these are almost out of the question in practical operation.

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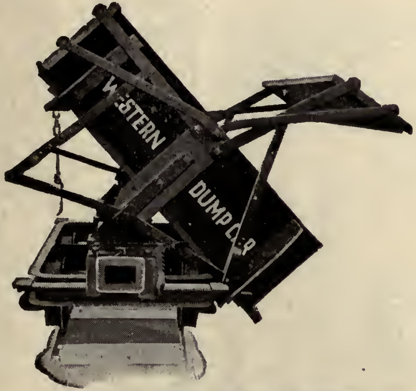
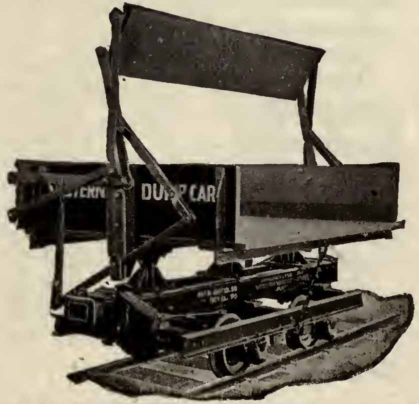


1¼-yd. Car in Dumped Position



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