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Primary Glass Manufacturers Council
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KIRK-OTHMER

GYPSUM

GYPSUM
MANUFACTURING
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Table 1. Composition Requirements for Calcium Ch

Attribute	Specification Type 1	Specification Type 2
$CaCl_2$, min %	77.0	94.0
total alkali metal chloride, as NaCl, max %	2.0	5.0
total magnesium, as $MgCl_2$, max %	0.5	0.5
other impurities, excluding water, max %	1.0	1.0

screen test data:

sieve	3/8 in.	#4 ($\nless 4760\mu$)	#20 ($\nless 840\mu$)
% passing	100	80	10

(*1*) brine making in refrigeration plants; (*2*) control of snow and ice on highways, streets, and sidewalks; (*3*) dust control on secondary roads, unpaved streets, and highway shoulders; (*4*) freezeproofing of coal and ores, both in shipping and stockpiling; (*5*) brine for filling inflated tires to increase traction and draw-bar pull on tractors and earthmoving equipment; and (*6*) use in concrete mixes to give quicker initial set, higher early strength, and greater ultimate strength (see Cement). (Construction work on concrete placed during the winter may be accelerated by adding calcium chloride to the concrete.)

The increase in sales in recent years is largely attributed to the expanding highway building program.

"Calcium Chloride" treated in *ECT* 1st ed., under "Calcium Compounds," Vol. 2, pp. 759–761, by G. H. Kimber, Calcium Chloride Association.

E. M. Allen
Pittsburgh Plate Glass Company

CALCIUM CYANAMIDE, $CaCN_2$. See Cyanamides.

CALCIUM CYANIDE, $Ca(CN)_2$. See Cyanides and cyanogen compounds.

CALCIUM FLUORIDE, CaF_2. See Fluorine compounds, inorganic.

CALCIUM HYDRIDE, CaH_2. See Hydrides.

CALCIUM HYDROXIDE, $Ca(OH)_2$. See Lime and limestone.

CALCIUM HYPOCHLORITE, $Ca(ClO)_2$. See Chlorine oxides and oxyacids.

CALCIUM OXIDE, CaO. See Lime and limestone.

CALCIUM PEROXIDE, CaO_2. See Peroxides and peroxy compounds, inorganic.

CALCIUM PHOSPHATES. See Fertilizers; Phosphoric acids and phosphates.

CALCIUM SILICATES. See Silica and inorganic silicates.

GYPSUM

CALCIUM SULFATE. Calcium sulfate, $CaSO_4$, is of interest and importance because of the interrelationship of the anhydrous salt with its two hydrates, the dihydrate, $CaSO_4.2H_2O$, and the hemihydrate, $CaSO_4.0.5H_2O$. The principal commercial forms are *gypsum*, the naturally occurring dihydrate; *plaster of Paris*, the hemihydrate, formed by calcining gypsum; and *anhydrite*, $CaSO_4$, occurring as a mineral and prepared in both insoluble and soluble forms by dehydration of gypsum. Although calcium sulfate is usually considered to be a simple compound, this is far from being the case. This substance is probably the subject of more confused and discordant statements, misinterpretation, and persistent lack of exact information than any other compound in the category of inorganic materials. The multiplicity of known and postulated forms, besides those just mentioned, and the range of their usefulness have engaged the interests and intensive study of many of the best scientists and technologists for nearly two-hundred years, and yet the most recent writers recognize that uncertainties still exist.

Because of the confusion in the literature only a brief historical review is given here, and a complete bibliography is not attempted. The references cited are the more significant ones in covering the various phases of the subject and those that include the more extended bibliographies.

Historical Review. In two important papers presented to the Royal Academy of Science on February 27, 1765, and March 19, 1766, Lavoisier determined the saline nature of the mineral gypsum and described the setting of plaster of Paris as due to the interlocking of crystals of the dihydrate formed by the reaction of the calcined (dehydrated) salt with water. In the period from 1883 to 1887, Le Châtelier published his important researches on hydraulic mortars, which established the existence of two hydrates and explained the dehydration of the dihydrate and the identity of plaster of Paris as the hemihydrate, as these facts are understood at present. Van't Hoff and co-workers published several papers (1900–1903) on vapor-pressure equilibria and transition temperatures, introducing discrepancies that were pointed out by Davis in 1907 in the first important paper on the subject in the English language. Davis published valuable data on dehydration and rehydration, vapor pressures, solubilities, setting times, crystal forms, etc. Glasenapp in 1908 published the results of extensive microscopical research intended to "end the confusion in the classification of gypsum products," a goal worthy of the very excellent paper. In 1917 Wilder (1) published a comprehensive survey of all the earlier work on the geology, chemistry, and technology of gypsum and included an exhaustive bibliography.

Important publications by various Government departments include those of Cameron and Bell, Stone and others (2), and Newman (3). An important discussion of crystal forms is that by Ramsdell and Partridge (4), who agree with Linck and Jung (5) in concluding that soluble anhydrite is identical in crystal structure with the hemihydrate, and that the latter loses and gains water of hydration without change in crystal structure, in the manner of a zeolite.

Calcium sulfate is said by Kelley, Southard, and Anderson (6) to be capable of existence in at least nine different forms—two forms of the dihydrate, $CaSO_4.2H_2O$; three forms of the hemihydrate, $CaSO_4.0.5H_2O$; and four forms of the anhydrous salt, $CaSO_4$.

It is in regard to the thermodynamic and crystallographic properties observed in studies of the three well-established forms—the two hydrates and the anhydrous salt—that most of the confusion and uncertainties exist. However, the several known varieties and the varying and elusive behavior of the three basic forms offer sufficient challenge to the practical worker and the industrial technologist. Accordingly, in the remainder of this discussion, emphasis will be placed on the more important forms of this compound, the processes involved in their production, and their uses in a wide range of application in agriculture, art, science, and industry.

Forms, Occurrence, and Properties

Gypsum. This material, properly defined, is the natural mineral form of calcium sulfate dihydrate, $CaSO_4.2H_2O$—sp gr, 2.31–2.33; Mohs hardness, 1.5–2. It is widely and abundantly distributed in nature and occurs in an interesting variety of forms, conditions, associations, and colors. In pure form, gypsum is snow-white and occurs in stratified layers, doubtless of marine origin. Either because of varying conditions at the time of precipitation or through recrystallization, the mineral occurs in various conditions from hard, solid rock to fragmentary and granular forms. In some deposits the rock occurs in easily friable masses of coarsely crystalline beds, which are *appropriately* called "sugar rock." Many deposits yield the massive mineral through the body of which occur crystals of selenite (see below), these deposits being described as selenitic gypsum. Most deposits of gypsum occur closely associated with either strata or random occurrences of the mineral anhydrite, suggesting a question of the geological origin and the possible transformation of one form into the other after deposition.

Gypsum is widely distributed over the earth and is commercially available in quantity in most industrial nations. More than one-third of the states in the U.S. have abundant resources, as reported in the *Minerals Yearbook* (7).

Gypsum dissolves in water to the maximum solubility of approximately 2.1 g/liter at about 40°C and has the lower solubility of approximately 1.8 at 0°C and 1.9 in the range of 70–90°C. The concentration varies erratically with traces of electrolytes and variations in pH and, preferably, should be determined experimentally for all systems other than pure water solutions.

Alabaster. This is a massive, densely crystalline, softly textured form of practically pure gypsum. It is usually translucent and frequently tinted with beautifully variegated colors due, probably, in some cases, to optical effects in the crystalline mass and, in other cases, to traces of foreign materials. Several deposits in Colorado supply practically all of the alabaster used in the U.S. These deposits furnish the mineral in white and a variety of attractive color tints and blends. The mineral is taken from the mines with care in moderate to large lumps.

Alabaster, being relatively soft yet dense and fine-textured, is easily worked by the carving knife and the saw, and may be readily shaped by abrasive papers and polished to a fine smooth finish. Much of the shaping and finishing of alabaster is done while the stone is kept wet. Alabaster has been known and used for many centuries for the carving of cruses, urns, and other small vessels, and for the making of images, statuary, and other art objects. Many ancient structures have been embellished by columns, porticoes, and other decorative finishes of alabaster.

Selenite. It is a pure form of gypsum crystallized in the monoclinic system in the form of sheets or plates that show a perfect and easy cleavage parallel to the plane of crystallization. Sheets or slabs of selenite occur in sizes up to several feet in width and length, and these sheets, with characteristic oblique corners, break down in parallelograms of similar proportions. Selenite crystals up to several inches in thickness are completely transparent. Thin sheets of selenite polarize light and are used in laboratory equipment for this purpose. Selenite does not have the elastic return of mica and, when once distorted, remains so.

Satin Spar. This is another form of pure crystalline gypsum and is known as gypsum var. satin spar (not to be confused with calcite var. satin spar, $CaCO_3$). The crystals are monoclinic and in the form of parallel threads. A mass of satin spar, therefore, resembles somewhat the common forms of asbestos and, in many cases, the threads can be picked or raveled out of the mass. In the more densely formed growths, satin spar is translucent and lends itself readily to fabrication and polishing into trinkets and small art objects. Satin spar is formed in seams, sutures, and faults in or near gypsum deposits by the precipitation from, or the evaporation of, ground water carrying the mineral in solution. It is, accordingly, sometimes called secondary gypsum. Formations of satin spar are frequently observed in abandoned mines and in the joints of masonry through which gypsiferous water reaches the open air.

Anhydrite. The natural mineral form of anhydrous calcium sulfate is known as anhydrite; it has a sp gr of approximately 2.8–2.9, and a Mohs hardness of 3–3.5. It is usually densely massive and frequently shows light tints of color as blue, pink, etc. Anhydrite has the same solubility in water as gypsum but does not react rapidly to form hydrates. It is, accordingly, less valuable as a raw material when this property is desired. It can be used as a sulfate source for ammonium sulfate (see Vol. 2, pp. 329–330).

Gypsite. This is an earthy deposit at or near the surface of the ground and consists of finely crystalline gypsum mixed with loams, clays, sands, and humus; it ranges from 60 to more than 90% gypsum. These deposits are formed by the movement of ground water carrying gypsum in solution and the deposit of the mineral by evaporation at the surface, or as windblown "loess" from disintegrating rock deposits. Surface beds or quarries of gypsite, chiefly in the southwestern states, have been worked in the production of plaster, structural tiles, etc, in the building industry but, in general, are at present of little commercial importance.

Gypsum Sands. Enormous deposits of practically pure gypsum in the form of fine, white sands occur at various points in Arizona, New Mexico, and Texas. These sands, covering many thousands of acres in some deposits, appear as drifts and dunes and are doubtless the result of evaporation of gypsum-bearing water rising to the surface of the earth through seepage springs or by uniform movement over wide areas of land. This is a natural result of the normal arid condition of the atmosphere in these regions. Practically without exception these deposits are contaminated with sodium sulfate to such an extent that they are valueless for structural or hydraulic purposes.

CHEMICAL CHARACTERISTICS

Calcium sulfate in any known form dissolves in water more or less readily. The calcium and sulfate ions behave as would be expected with respect to the ions of other compounds. Beyond the normal behavior of these ions, calcium sulfate is relatively inert toward other materials. It is practically insoluble in most organic liquids and solvents and does not cause or stimulate organic reactions. However, the active anhydrous form extracts water instantaneously from organic compounds or systems and may in this way affect reactions that are influenced by the removal of water.

When calcium sulfate is heated at temperatures in the range of 900–1200°C, decomposition takes place with the formation of calcium oxide (lime), CaO, and the loss of sulfur trioxide, SO_3 (6).

Commercial Forms

Practically all the commercial forms of calcium sulfate are obtained from the earth in the form of gypsum.

In the chemical industries certain processes yield calcium sulfate as a by-product or waste, as in the treatment of the calcium phosphates with sulfuric acid (see Phosphoric acids). This by-product, sometimes called "by-product gypsum," is normally in the form of a sludge or suspension of the dihydrate; there have been only minor operations in the utilization of this material. The free acid must be neutralized, and the soluble efflorescent salts must be removed before use.

In the ceramic industries large amounts of plaster of Paris molds are used for forming the ware. When worn, broken, or otherwise obsolete, these molds are discarded as an industrial waste. However, the composition is practically pure dihydrate and, in certain localities in Ohio, Pennsylvania, and West Virginia, these molds have been used in considerable tonnage as an ingredient in the manufacture of portland cement.

GYPSUM

The mineral occurs normally in horizontal strata or veins varying from a few inches to many feet in thickness. Open-pit or strip mining is employed for deposits near the surface; both slope and shaft mines are common for deeper deposits. The importance of the mineral gypsum as a source of almost all commercial forms of calcium sulfate is shown by the fact that in 1962 there were approximately 68 gypsum plants in the U.S., distributed through 22 states and operating 16 underground mines, 54 open quarries, and a number of mine–quarry combinations. The industry established a record of production in the year 1959 due to large demands from the building industry. The industry produced and imported 15,390,000 short tons of gypsum in 1962 (7). Mining in the U.S. amounted to 9,969,000 tons as compared with the record set in 1959 of 10,900,000 tons. The principal producing states are Arizona, California, Colorado, Iowa, Michigan, Nevada, New Mexico, New York, Ohio, Oklahoma, Texas, and Virginia. Importation, almost entirely from Canada, in 1962 amounted to 5,421,000 tons. Crude gypsum mined in 1962 was valued at $3.65/ton at the mine as compared with $1.83 in 1945. Of the total 9,969,000 tons mined in the U.S., about 85% was processed by the producing companies; thus it did not enter the open market. Table 1 shows production and values of crude gypsum and the major

Table 1. Gypsum Statistics, U.S.

Production–value[a]	1960	1961	1962
active establishments[b]	96	98	102
crude			
mined, ton	9,825	9,500	9,969
value, $	35,690	34,996	36,343
imports for consumption, ton	5,301	4,967	5,421
calcined			
produced, ton	8,591	8,246	8,819
value, $	120,984	118,145	127,436
products sold, $	361,190	358,811	392,300
gypsum and gypsum products:			
imports for consumption, $	10,426	10,306	11,912
exports, $	1,293	1,299	1,302

[a] All figures in thousands; short tons or dollars.

[b] Each mine, calcining plant, or combination mine and plant is counted as one establishment.

Table 2. World Production of Gypsum[a]

Continent	1960	1961	1962
North America	16,445	16,135	16,753
South America	452	542	584
Europe	24,130	26,135	26,720
Asia	3,946	3,843	4,291
Africa	933	982	934
Australia and New Caledonia	651	681	683
Total world production, estd	46,560	48,320	49,965

[a] Production figures in thousands of short tons.

products produced from this mineral (7); the world production figures are given in Table 2(7).

Uses. Gypsum, as such, has only a few major uses but these are important. In the manufacture of portland cement gypsum is a necessary ingredient and is used to lengthen the time of setting of various cements and mortars to allow for depositing and placing in forms. The "raw" gypsum is moved to the cement plants, usually in open cars, in the form of rock crushed to about 1.5 in. and finer. Automatic machines charge the crushed gypsum into the flow of cooled clinker in the amount of 3–5% as the mixture goes to the grinding mills (see Cement).

In some foreign countries (as Germany), gypsum has been used as a source of lime, CaO, in the manufacture of portland cement. This involves the complete decomposition of the gypsum at the temperature of the cement kiln and then recovery of sulfur trioxide, SO_3, as a by-product.

An important large-scale use of gypsum is in the treatment of soils, particularly those used for leguminous crops and in the culture of peanuts. For this use the gypsum (or occasionally anhydrite) is finely ground and is known as "land plaster." Benjamin Franklin is credited with the introduction into the U.S. of this application as the result of his observations in France. Finely ground gypsum, when mixed with manures, acts to stabilize the volatile and dissolved nitrogenous compounds, thus preventing their loss by volatilization and leaching. A major use in arid climates is neutralization of "black alkali" soil by reaction with the alkali carbonates that cause this condition.

As a stable, nontoxic, tasteless, odorless, nonabrasive, practically chemically inert powder, known as *terra alba*, gypsum is used in paints, pharmaceuticals, paper filling, insecticide dusts, yeast manufacture, water treatment, and many other industries. In brewing, it may be added to the water to lower the pH of the mash.

Some Recent Developments in the Use of Gypsum. Low-grade nickel ore is subjected to sulfide smelting by the addition of coal and gypsum in a continuous reverberatory furnace operated at 1300°C. The ore is crushed to 10 mm size (8).

Calcium sulfate and coke are heated in an electric furnace to give calcium carbide, carbon dioxide, carbon monoxide, and sulfur. The proportion of anhydrite to coke is 1.4:0.6 (9).

Sulfuric acid is prepared by heating gypsum at 1200°C to produce sulfur trioxide. The required temperature can be lowered to 1000°C by the addition of quartz and the velocity increased by the addition of sodium chloride and moist air. A yield of 99% SO_3 is reported (10).

Ammonium sulfate is produced from calcium sulfate by reacting it with ammonia, carbon dioxide, and water. Calcium carbonate is produced as a by-product (11).

Gypsum is added to opal or transparent soda–lime or soda–potash–lime glasses as a coloring agent. The combined sulfur is reduced by elemental silicon or aluminum to produce colors varying from ivory to amber (12).

Porous polytetrafluoroethylene (Teflon) is made by mixing an aqueous dispersion of the polymer with plaster of Paris, pouring the mixture into a mold, and heating it until the polymer fuses. The plaster of Paris is then dissolved out, leaving a porous molded product (13).

PLASTER OF PARIS

In American industrial practice the dehydration of gypsum is carried out by two processes: (*1*) The powdered mineral is heated in kettles; or (*2*) gypsum, crushed to walnut–pea size, is heated in rotary kilns.

Kettles. These are vertical cylinders having heavy steel bottoms that are convex upward with, usually, four horizontal flues to allow the combustion gases to pass through the body of the charge; the kettles are fired with either coal, fuel oil, or gas. A vertical shaft carries strong agitating arms; those at the bottom drag heavy chains that sweep the heated bottom of the kettle. The capacity of the kettles varies from 10 to 25 tons.

The powdered gypsum is fed to the kettle by a screw conveyor; dehydration begins as soon as the material strikes the hot bottom of the kettle. The complete kettle charge is added within ten to fifteen minutes, and the mass is gradually heated, while being agitated, to the range 120–130°C. Heating is continued, and the temperature remains constant; the charge "boils" vigorously until approximately 1.5 moles of water are expelled. The heat consumed during this period is used to bring about the dehydration of the gypsum to the form of the hemihydrate. As this phase nears completion the charge in the kettle, which has been literally floating on an atmosphere of steam, settles, the turbulent boiling ceases, and the temperature rises rapidly. In practice, the charge is "dumped" at a temperature of about 160°C, and the product, known as calcined gypsum or plaster of Paris, is passed through a cooling pit and conveyed to storage bins by elevators and conveyors in which a necessary cooling takes place. In the trade this product is frequently called "first-settle" stucco.

If, instead of dumping the charge after the first-settle, heating is continued, the temperature rises higher to about 190°C, at which temperature a second boiling begins and continues at constant temperature until the last 0.5 mole of water is expelled. During this shorter boiling period the charge is again lifted in the kettle by the escaping steam and, at the end of the phase, shows a second sinking in the kettle. Heating is continued and the temperature rises rapidly to about 220°C, at which point the charge, known as "second-settle" stucco, is dumped and handled as in the case of plaster of Paris.

By 1961 there were fully automatic gypsum calcining kettles in operation controlled entirely by electronic computers (14).

Owing to local overheating in the kettle, a portion of the charge undergoes complete dehydration so that calcined gypsum always contains more or less soluble anhydrite, whereas the so-called second-settle stucco (which is no longer produced in any considerable tonnage) consists primarily of soluble anhydrite. The soluble anhydrite present in calcined gypsum gradually absorbs moisture from the air to form the stable hemihydrate. As mentioned, little second-settle stucco is now produced as the absorption of moisture, which took place in the many commercial products during storage, caused undesirable lengthening in the time of setting and thus caused considerable annoyance and loss in the industry. Castings and structural products formed from freshly prepared second-settle or soluble anhydrite showed greater density and structural strength but, after ageing and the accompanying absorption of water, it became practically identical in composition and behavior to the hemihydrate and thus led to misunderstandings while offering no advantages over the latter product. This condition led to the practical abandonment of production of the second-settle product during the period 1920–1930.

Rotary Kilns. These are similar to those used in the production of portland cement. In these kilns the control of temperature is more difficult than in kettles, and the product contains variable proportions of soluble anhydrite. An important part of this process is the cooling of the product by exposure to atmospheric air; this serves both to lower the temperature of the material and to allow the soluble anhydrite to absorb water, bringing the product to the condition of the stable hemihydrate.

Some calcined gypsum products are "aridized" (chemically preaged) by a treatment designed to yield a uniform-setting product of high structural value for the building industry. Chemical preageing is done by adding a small amount (0.01–0.05%) of a deliquescent salt, such as calcium chloride, during or after calcination.

The phase changes taking place in the dehydration of gypsum in the kettle process are shown in Figures 1 and 2. Figure 1 shows the data obtained by Le Châtelier on the laboratory scale. Figure 2 shows a portion of an actual kettle thermometer chart, which records the temperature changes during the production of two kettle charges, A and B, producing second-settle or soluble anhydrite, and two charges, C and D, of ordinary calcined gypsum or plaster of Paris.

During 1962 the value of calcined gypsum at the mill averaged $14.43/short ton, an increase of $8.44 over the value in 1945.

Uses. The innumerable uses of plaster of Paris all depend upon the setting and hardening of the mass when calcium sulfate hemihydrate is mixed and agitated with sufficient water to form a plastic mix of suitable consistency. The mix is poured, pressed, or troweled into molds or other forming devices to give the shapes and forms desired.

An enormous tonnage of plaster of the highest quality is used in the ceramic industry for the forming of dishes, sanitary ware, terra cotta, etc. In one application the plaster molds, of the split type, are formed around original patterns; the ceramic mixture in the form of a thin "slip" is poured into the hollow mold into the space formed by the pattern. The plaster mold then acts as a blotter to suck the excess water from the ceramic mix. When the mold is opened the ceramic body may be removed and handled under its own strength. Various other types of molds or dies are used, the mold serving to give shape, surface detail, and dimension to the finished ceramic article.

In the field of architectural decoration, "molding plaster" is used in the formation of decorative friezes, cornices, columns, and other decorative features in interior finishes. Quantities of molding plaster are also used in certain smaller articles as furniture, clock frames, and the like.

In the dental trade, plasters are used in the making of impressions for dentures, inlays, and for the casting of metal fillings, bridges, etc. This work requires high

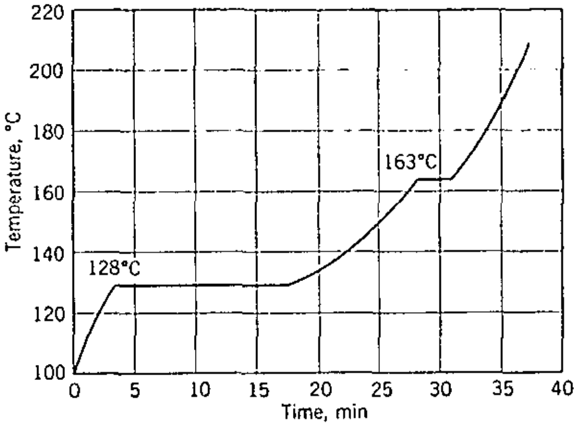

Fig. 1. Time-temperature relation for dehydration of gypsum on a laboratory scale.

precision, and the dental plaster specialties are prepared so as to give this trade the highest possible degree of accuracy in dimensions, expansion on setting, setting times, etc. The two major forms in this field are known as "stone," for models and forming dies, and "investments," for casting precious metal dentures (see Dental materials). "Investment" plasters are admixtures of calcined gypsum and refractories, made to resist baking temperatures up to 1300°F. Another type, orthopedic plaster, is used in the medical and surgical fields for the setting of broken bones and holding parts of the body in place for periods of time.

Art molding includes the making of a great variety of art objects and novelties formed by the casting of gold, silver, and other nonferrous metals in plaster of Paris

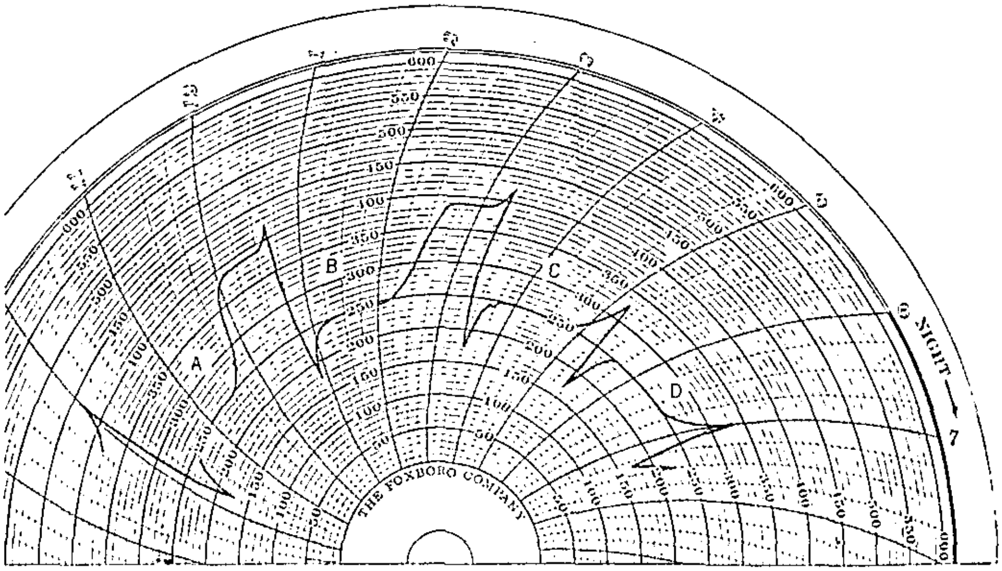

Fig. 2. Recording-thermometer chart on gypsum calcining kettle. A and B, production of second-settle stucco or commercial soluble anhydrite; C and D, production of first-settle stucco or commercial plaster of Paris.

investment molds. Extremely small objects, such as a model of a small beetle, may be reproduced with fidelity to the finest striations by the "lost wax" methods using plaster of Paris investment molds.

As an outgrowth from and development of dental and art molding, a very considerable industry consists in the forming of nonferrous metal objects and mechanical parts by use of plaster of Paris investment molds. Many small objects of aluminum and other low-melting metals and alloys are cast in this way.

The largest single use of plaster of Paris is in the making of various wall plasters, wallboard, lath, structural tile, and block for the building industry. Wall plasters consist of various mixtures of sand, wood fiber, animal hair, and retarder for controlling the set. Sand and, in general, any foreign material greatly accelerates the setting of plaster of Paris, so that a retarder consisting of a gluelike colloidal material is used to delay the setting to allow time for application.

Partition tile, floor tile, and roof tile consist chiefly of plaster and a suitable fibrous material, as shredded excelsior, that serves as a binder. These blocks and tiles are non-load-bearing structural units and are valuable because of their light weight and their high fireproofing property. Gypsum wallboards are made by forming a mixture of plaster with wood dust, foamed plastic, or other light filler between two sheets of structural paper. While wet the board is ironed to uniform thickness, allowed to set as it moves on a long conveyor, and then cut to desired lengths, and dried. Gypsum wallboard has gained wide application in residential and other smaller constructions. A form of gypsum wallboard is cut to suitable dimensions and used as lath where wall plasters are applied. The "dry wall" or taped-joint system uses a similar gypsum wallboard with an improved surface. In this construction the wallboards are nailed to studs, and the joints are taped. The taped joints and nail heads are surfaced with a topping or bedding compound that produces a smooth wall ready to paint, thereby eliminating the plaster coat entirely.

OTHER FORMS OF THE HEMIHYDRATE

Early investigators established that the dihydrate is converted into the hemihydrate in contact with water and certain aqueous solutions at various temperatures and vapor pressures. Thus, gypsum heated in water and under pressure at the temperature of 107°C was found to be converted into well-formed crystals of the hemihydrate. The same transformation takes place at temperatures above 77°C in a saturated solution of common salt; at 40–50°C in nitric acid of specific gravity of 1.4; and in other strong salt solutions at various temperatures and pressures. These transformations require 12–24 hr for completion. This has led to an industrial application of this principle for the production of a form of the hemihydrate known as "alpha gypsum" as described by Offutt and Lambe (15). In this process, lumps and fragments of gypsum rock of 1–2 in. in size are heated in an autoclave in an atmosphere of steam at about 120°C (16). The gypsum is dehydrated and converted uniformly to the form of rather large, dense, and nonporous crystals of the hemihydrate. These solid or nonporous crystals, when ground to powder and mixed with water to form a paste or plaster of normal consistency, pass through the stages of supersaturation and recrystallization to form the interlocking crystal mass that is characteristic of the setting of plaster of Paris to the form of dihydrate. The nonporous particles of this alpha gypsum do not require water to fill a porous structure as in the case of the usual particles of plaster of Paris and thus a normal consistency is obtained by the addition of considerably smaller proportions of water. Thus in the production of castings and other structural forms, a finished casting is obtained of greater density and, therefore, of greater structural strength and durability. Castings made from this form of the hemihydrate are of fine texture and excellent finish. Preparations of this product, under the trade name of Hydrocal, are characterized by the strong and dense property of the structural forms. This product is widely used in the fields of casting where strength, hardness, exactness of dimensions, etc, are required. Dry crushing strengths up to 12,000 psi are readily obtained on the set material. The many possible modifications of this product have brought its application to fields where ordinary plasters were formerly used, and it has replaced wood and other types of pattern and die raw materials because of its extreme strength and ready utility.

INSOLUBLE ANHYDRITE

This form is also known as dead-burned gypsum. Pure gypsum, when fully dehydrated at temperatures above 1200°F, has the same crystal structure as the mineral anhydrite. When finely milled, it forms the base of the so-called Keene's cement. It is also one of the brightest low-cost paper fillers available, and is widely used in this field. . Also, like finely ground raw gypsum, or terra alba, it has widespread use wherever low-cost, nonabrasive, inert, white, nontoxic filling or loading properties are indicated.

SOLUBLE ANHYDRITE

When any of the forms of the dihydrate, $CaSO_4.2H_2O$, are heated, the water of crystallization is released in two stages to form first the hemihydrate, $CaSO_4.0.5H_2O$, and finally the anhydrous salt, $CaSO_4$. Contrary to many statements in the older literature, it was shown by Hammond and Withrow (17) that even large granules or lumps of the mineral retain their original form and shape and much of their physical strength after complete dehydration. This appears to mean that the crystal lattice itself is maintained, and that the water of crystallization may be driven off and recombined in whole, in part, in portions, or stages at a time without affecting the crystalline structure. The work of these writers also shows that any of the forms of gypsum described above, when completely dehydrated at temperatures below, say, 300°C, not only retain their original forms and shapes, but also show the extremely low vapor pressure of 0.005 mm and a corresponding high avidity for the absorption of water. The anhydrous form, obtained from whatever source, corresponds to what van't Hoff appropriately called "soluble anhydrite." The affinity for water makes this form of the anhydrous salt, whether granular or powdered, serve as an efficient drying agent, indicating the ability to absorb moisture rapidly and progressively from the surrounding atmosphere. When placed in a humid atmosphere the anhydrous salt rapidly absorbs water vapor to the amount of 8, 10, 12, or even 14% of its weight, depending on the temperature and relative humidity. However, a sample that has been allowed to absorb, say, 10% by weight of water vapor, when placed in a closed vessel containing an excess of the anhydrous form, quickly loses water vapor down to the percentage of approximately 6.6%, which corresponds to the formation of the hemihydrate and, thereafter, remains stable indefinitely. When a sample of this active or soluble anhydrite, either granular or powdered, is exposed to ordinary air of any absolute humidity, it rapidly absorbs water vapor. If the sample is removed from the humid atmosphere at any stage before absorbing 6.6% by weight and placed in a container or desiccator with an excess of the anhydrous form, the water content of the sample will remain constant indefinitely. That is, the active or soluble anhydrite will absorb water vapor to any percentage value up to 6.6% by weight to form stable molecules of the hemihydrate to the limit of the amount of water available. This means merely that the crystal lattice is open for the absorption of water as it becomes available and that the hemihydrate and the anhydrous form may remain stable in the presence of each other.

Kelley, Southard, and Anderson state (6). "Thus there is both x-ray and analytical evidence that the hemihydrate crystal lattice will accommodate greater or smaller amounts of water than required by the formula without serious alteration. This form will be called alpha—$CaSO_4.0.5H_2O$, in the subsequent discussion." This appears to mean only that the crystal structure of the hemihydrate and the active anhydrite are identical and that in a given sample some of the molecules of the anhydrous form may absorb water vapor to form molecules of the hemihydrate. If the available water vapor is limited the remaining molecules of the anhydrite will remain as such and continue to show the strong tendency to absorb water if, or as it becomes available. Powell and others have done additional work on this subject (18). There appears, therefore, to be no conclusive ground for the postulation of an alpha-hemihydrate, or of a beta-hemihydrate that happens to hold exactly the theoretical percentage of water in a sample. The complete dehydration of the dihydrate yields a body containing approximately 38% pore space by volume; therefore, starting with a sample of the active anhydrite in granular or powdered form, the amount of water vapor absorbed above the percentage of 6.6% represents merely physically adsorbed or hygroscopic moisture taken into the body of the porous granule or particle.

Thus, there are clearly recognized, therefore, only the hemihydrate and an active and readily soluble form of the anhydrous salt obtained at low temperatures. On further heating at higher temperature and for various lengths of time, the active anhydrite is gradually transformed into an inactive and much less readily soluble form and this inactive artificial form of the anhydrite corresponds in crystal structure and behavior to the mineral anhydrite. Neither the length of time nor the temperature required for the complete conversion can be stated. Yet, notwithstanding the work of Glasenapp on this point, numerous efforts and proposals have been made to assign a definite transition temperature. Also, various proposals have been made of α-, β-, γ-, etc, anhydrites, but it is highly probable that all of these are merely stages representing partial transformation or mixtures.

Uses. Soluble anhydrite is used as a desiccant of high efficiency and unusual versatility (19–21) (see *Drying agents*). Under the trade name of Drierite it is widely used in the laboratory and industry in the drying of solids, organic liquids, and gases. When gypsum, in either powdered or granular form, is heated uniformly in an oven-type heater at temperatures up to about 200°C, complete dehydration takes place. The granular solid retains its form and shape and much of its physical strength. The reaction involved in the absorption of water vapor as a drying agent is as follows,

$$CaSO_4 + \tfrac{1}{2}\,H_2O \rightleftharpoons CaSO_4.\tfrac{1}{2}\,H_2O + 2700\ \text{cal}$$

and represents the absorption of 6.6% by weight of the anhydrous salt. Since the reaction is reversible indefinitely, the drying agent may be used and regenerated through many cycles of operation. The drying efficiency, determined by the vapor pressure of the system $CaSO_4$–$CaSO_4.0.5H_2O$, is approximately 0.005 mm at 25–

30.5°C and corresponds to a residual moisture content of 0.005 mg of water vapor/liter or 0.31 lb of water/1,000,000 ft^3 or a dew point of approximately −80°C. Since calcium sulfate is practically insoluble in, and inert toward, all ordinary organic liquids and solvents, the drying agent serves for the complete and rapid drying in either the liquid or vapor phase of organic liquids and compounds.

Drierite is manufactured in the form of fine and coarse powders and in granular sizes of 4-mesh, 6-mesh, 8-mesh, 10-20 mesh, and 20–40 mesh to meet particular needs and specifications. Several hundred tons are used per year. As a laboratory desiccant this form of calcium sulfate is used in desiccators, drying tubes, and columns for the drying of air, all the common gases, and all the organic liquids and solvents.

The refrigerants used in household and commercial refrigeration, such as methyl chloride, sulfur dioxide, the Freon compounds, etc, must be extremely dry to prevent ice formation at the expansion valve; Drierite is widely used in this industry both in the construction of new units and in the servicing or repairing of old units. Many millions of refrigeration units have been treated in this way.

In the splicing of telephone cables, which requires an extremely dry condition, Drierite was the original solid desiccant used and remains the most efficient desiccant known for this purpose. It has been used in millions of units by the telephone companies of the U.S., Canada, South American countries, Italy, and other foreign countries. The U.S. Signal Corps has used it in cable splices since the original application, about 1935.

An important application of soluble anhydrite as a desiccant is in the protection of delicate optical and electrical instruments. Thus the modern electron microscope, the most delicate and accurate potentiometers, and scores of other delicate instruments, such as periscopes, gun sights, radio proximity fuses, radar, measuring instruments, and the like are protected from moisture by soluble anhydrite.

Preparations of serums and other biological products for use in medicine are dried by evaporation of water under a vacuum in the presence of a drying agent. Drierite has been widely used for this purpose since about 1935 and this process makes possible the preservation and storage of the most sensitive serums and similar pharmaceutical products.

Granular soluble anhydrite is used in breathers on tanks to protect oils and other liquids, which are damaged by contact with moist air. Placed in a suitable holder within fire extinguishers containing carbon tetrachloride, it keeps the liquid dry and thus prevents corrosion. The large-scale drying of air and industrial gases, as an important phase of manufacturing and processing in many industries, can be effected by large, two-tower, regenerative drying units using soluble anhydrite.

By the use of cobalt chloride as a color-changing ingredient, a product known as Indicating Drierite has gained wide acceptance for use in transparent drying tubes and columns. On absorption of moisture the column of desiccant changes in color from blue to a rose red, giving a clear visual indication of the progress of the drying action along the column and the ultimate exhaustion of the unit.

By impregnating granular soluble anhydrite with a small percentage of calcium chloride and then completely dehydrating the product, the water-absorbing capacity is materially increased. The calcium chloride, by its tendency to develop an aqueous solution, supplies liquid water to the calcium sulfate and thus promotes the hydration from the stage of the hemihydrate to the dihydrate. This form of the drying agent used in towers or columns for the drying of all the gases except ammonia has a capacity of 20–25% by wt per regenerative cycle.

All of the forms of this drying agent may be regenerated by heating uniformly in the range 375–425°F or to complete dehydration. By regeneration, a given charge may be used many hundreds of times or until fouled or contaminated by foreign materials.

In addition to its high drying efficiency soluble anhydrite is neutral, stable, constant in volume, inert (except toward water), insoluble in organic liquids, nondisintegrating, nonwetting, nonpoisonous, noncorrosive, repeatedly regenerative, and low in cost. Because of these favorable physical and chemical properties, this agent may be used for a wider range of drying application than any other drying agent known.

Bibliography

"Calcium Sulfate" treated in *ECT* 1st ed. under "Calcium Compounds," Vol. 2, pp. 767–779, by W. A. Hammond, W. A. Hammond Drierite Company.

1. F. A. Wilder, *Iowa Geol. Survey Ann. Rept.* **28**, 275 (1917–1918).
2. R. W. Stone et al., *U.S. Geol. Survey Bull.* **697**, 15–27 (1920).
3. E. S. Newman, *J. Res. Natl. Bur. Std.* **27**, 194 (1941).
4. L. S. Ramsdell and E. P. Partridge, *Am. Mineralogist* **14**, 59 (1929).
5. G. Linck and H. Jung, *Z. Anorg. Allgem. Chem.* **137**, 407 (1924).
6. K. K. Kelley, J. C. Southard, and C. T. Anderson, *U.S. Bur. Mines Tech. Papers* **625**, 3 (1941).
7. W. V. Kuster and J. B. Mallory, "Gypsum," *Minerals Yearbook U.S. Bur. Mines* **1** (1962).
8. J. Barthel, *Bergakademie* **3**, 17–26 (1952).
9. Fr. Pat. 981,499 (1954), Société des Produits Azotes.
10. J. A. Hedvall and S. Nordengren, *Acta Polytech. Chem. Met. Ser.* **4** (7), 17 (1955).
11. Brit. Pat. 815,941 (July 1, 1959) (to N. V. de Bataafsche Petroleum Maatschappij).
12. U.S. Pat. 3,003,887 (1962), L. Pither (to Kimble Glass Co.).
13. U.S. Pat. 2,997,448 (1962), J. Hockberg (to E. I. du Pont de Nemours & Co., Inc.).
14. J. H. Bergstrom, *Rock Prods.* **64** (11), 82–85 (1961).
15. J. S. Offutt and C. M. Lambe, *Am. Ceram. Soc. Bull.* **26**, 29–36 (1947).
16. U.S. Pat. 1,901,051 (March 14, 1933), W. S. Randel and M. C. Dailey (to U.S. Gypsum Co.).
17. W. A. Hammond and J. R. Withrow, *Ind. Eng. Chem.* **25**, 653, 1112 (1933).
18. D. A. Powell, *Nature* **182**, 792 (1958).
19. U.S. Pat. 1,887,349 (Nov. 8, 1932), W. A. Hammond.
20. U.S. Pat. 2,008,955 (July 23, 1935), W. A. Hammond.
21. U.S. Pat. 2,203,144 (June 4, 1940), W. A. Hammond.

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