CALCIUM SULFATE

1. Introduction

Calcium sulfate [7778-18-9], $CaSO_4$, has several forms, ie, calcium sulfate dihydrate (commercially known as gypsum), calcium sulfate anhydrous (anhydrite), calcium sulfate hemihydrate, present in two different structures, α-hemihydrate

Table 1. **Gypsum Forms and Composition**

Common name	CAS Registry Number	Molecular formula	Composition, wt %		
			CaO	SO_3	Combined H_2O
anhydrite	[7778-18-9]	$CaSO_4$	41.2	58.8	
gypsum	[10101-41-4]	$CaSO_4 \cdot 2H_2O$	32.6	46.5	20.9
stucco	[10034-76-1]	$CaSO_4 \cdot {}^1/_2H_2O$	38.6	55.2	6.2

and β-hemihydrate (commercial name of β-form: stucco or plaster of Paris [26499-65-0]). In natural deposits, the main form of calcium sulfate is the dihydrate. Some anhydrite is also present in most areas, although to a lesser extent. Mineral composition can be found in Table 1.

Stucco [10034-76-1] has the greatest commercial significance of these materials. Indeed, stucco is the primary constituent used to produce boards and plasters as the primary wall cladding materials in modern building construction and in formulated plasters used in job- or shop-site applications. Other uses of stucco are in Portland cement (qv) set regulation and agricultural soil conditioning. The hemihydrate is normally produced by heat conversion of the dihydrate from which $\frac{3}{2}$ H_2O is removed as vapor. Methods for control of the set (hydration time) of hemihydrate conversion to dihydrate were developed by the end of the nineteenth century.

About 20–25 million metric tons of calcium sulfate are consumed annually. About 80% is processed into the commercially usable hemihydrate. Gypsum [10101-41-4] and its dehydrated form have been used by builders and artists in ornamental and structural applications for >5000 years, as evidenced by artifacts from the ancient Egyptian and Greek cultures. Processing of gypsum to the hemihydrate in the United States began ~1835. The ore used was imported from the Canadian Maritime Provinces.

2. Properties

Gypsum mineral has several names that are widely used in the mineral trade.

Selenite is the colorless and transparent variety that shows a pearl-like luster and has been described as having a moon-like glow. The word selenite comes from the Greek for moon and means moon rock. Another variety is a compact fibrous aggregate called *satin spar*. This variety has a very satin-like look that gives a play of light up and down the fibrous crystals. A fine grained massive material is called *alabaster* and is an ornamental stone that has been used in fine carvings for centuries. Among other gypsum names, *rock gypsum* and *gypsite* are worth noting. Figures 1–3 show particularly fine gypsum crystals.

Color is usually white, colorless, or gray, but can also be shades of red, brown, and yellow.

Luster is vitreous to pearly, especially on cleavage surfaces; crystals are transparent to translucent.

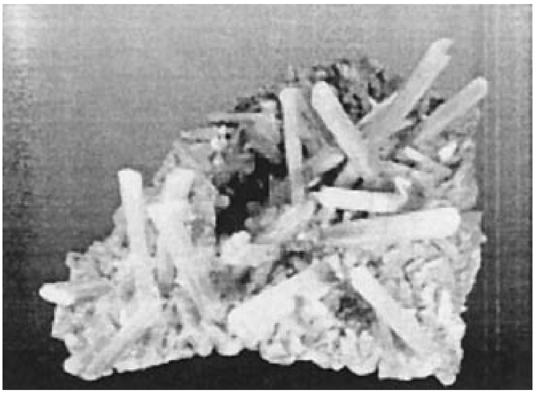

Fig. 1. Five centimeter pencil-sized acicular crystals of gypsum. Specimen from Naica, Chihuahua, S.A., Mexico.

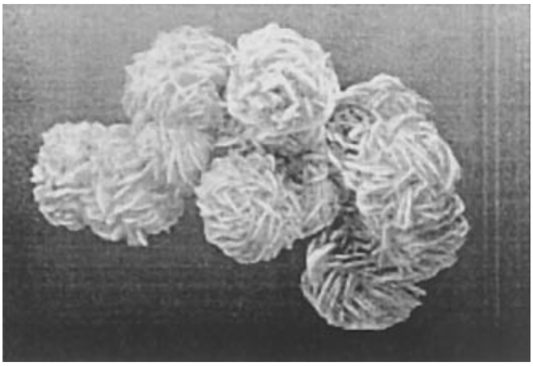

Fig. 2. Six centimeter bladed rosettes of gypsum. Locality unknown.

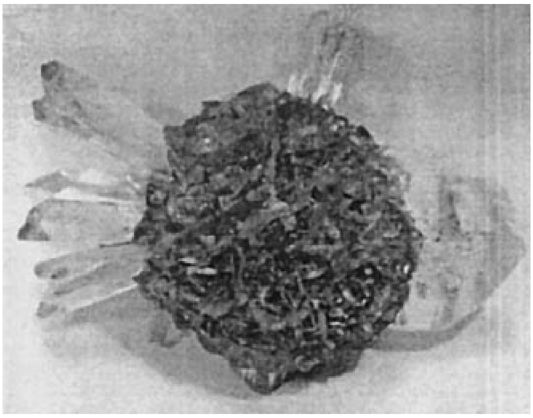

Fig. 3. Gypsum rose Red River Floodway, Winnipeg, 6-cm sphere.

Table 2. **Physical Properties of Calcium Sulfate**

Property	Dihydrate	Hemihydrate	Anhydrite
mol wt	172.17	145.15	136.14
transition point, °C	128[a]	163[b]	
mp[c], °C	1450	1450	1450
specific gravity	2.32		2.96
solubility at 25°C, g/100 g H_2O	0.24	0.30	0.20
hardness, Mohs'	1.5–2.0		3.0–3.5

[a] Hemihydrate is formed.

[b] Anhydrous material is formed.

[c] Compound decomposes.

Crystal system is monoclinic; crystal habits include the tabular, bladed, or blocky crystals with a slanted parallelogram outline; the pinacoid faces dominate with jutting prism faces on the edges of the tabular crystals; long thin crystals show bends and some specimens bend into spirals called Ram's Horn Selenite; two types of twinning are common and one produces a spear head twin or swallowtail twin while the other type produces a fishtail twin.

Cleavage is good in one direction and distinct in two others.

Fracture is uneven but rarely seen. Hardness is 2 and can be scratched by a fingernail.

Specific gravity is ~2.3 (light).

Among other characteristics, thin crystals are flexible but not elastic, meaning that they can be bent but will not bend back on their own. Some samples are also fluorescent. Gypsum has a very low *thermal conductivity* (hence, its use in drywall as an insulating filler), therefore a crystal of gypsum will feel noticeably warmer than a like crystal of quartz (1).

Table 2 lists the physical properties of calcium sulfate in its different forms.

3. Sources

The natural, or mineral, form of calcium sulfate is most widely extracted by mining or quarrying and is commercially used. Natural gypsum is rarely found in pure form. The dihydrate and anhydrous forms are commonly found together. Impurities in gypsum deposits typically include calcium and magnesium carbonates, oxide(s) of silicon, clays, and small amounts of various soluble salts. The last two items generally have the most undesirable effect on commercial processing and production of prefabricated products. In some cases, the crude ore is beneficiated to provide a commercial feedstock in which the percentage of functional dihydrate has been increased. Most commercial gypsum has a purity level of 80% or higher.

The natural ore is quarried or mined in many areas of North America and Europe. Leading regions include Canada, Mexico, and the United States. In

Europe, the countries of France, Spain, Italy, the United Kingdom, and Russia have significant deposits of natural gypsum, as does Germany.

In addition to occurring naturally, calcium sulfate can be obtained by precipitation. In particular, calcium sulfate may crystallize as gypsum, calcium sulfate hemihydrate, and anhydrite.

Gypsum is also obtained as a by-product of various chemical processes. The main sources are from processes involving scrubbing gases evolved in burning fuels that contain sulfur (see Sulfur removal and recovery), such as coal (qv) used in electrical power generating plants, and the chemical synthesis of chemicals, such as sulfuric acid, phosphoric acid, titanium dioxide, citric acid, and organic polymers. The ability to market by-product gypsum, mainly for use in wallboard or cement, depends on the supply-demand situation and the gypsum quality, which in turns depends on the type of process and the operating conditions. In general, the added capital investment and processing costs associated with rendering by-product gypsums suitable as feedstocks for the gypsum board and plaster industry have tended to deter their use where good quality and relatively low cost natural gypsums are readily available. However, high gypsum purity makes by-product sources attractive, especially in regions where natural gypsum is scarce. A notable example of this has been Japan, wherein large tonnages of by-product gypsum from its phosphoric acid industry and flue gas desulfurization plants have been used (see Phosphoric acid and the phosphates). In North America and Europe, the major reason for by-product gypsum production, mainly from flue gas desulfurization (FGD) processes, is to make the disposal of the solid waste less difficult and expensive.

4. Thermodynamic and Kinetics of Gypsum Formation–Decomposition

The thermodynamic properties of gypsum formation by precipitation can be evaluated considering the liquid–solid equilibrium between calcium and sulfate ions in solution and solid $CaSO_4{\cdot}2H_2O$, as described by equation 1.

$$\mathrm{Ca^{2+} + SO_4^{2-} + 2H_2O = CaSO_4 \cdot 2H_2O} \tag{1}$$

The driving force for the formation of calcium sulfate dihydrate is the change in the Gibbs free energy, ΔG, while going from the supersaturated solution to equilibrium. The average energy per ion is given by

$$\Delta G = -\frac{RT}{2}\ln\frac{a_{\mathrm{Ca^{2+}}}a_{SO_4^{2-}}}{K_{\mathrm{ps}}} \tag{2}$$

where a_{I} is the activity expressed as the product of the molality (m_{I}) and the activity coefficient (γ_{I}) of the I species ($\mathrm{I} = \mathrm{Ca^{2+}}$, $\mathrm{SO_4^{2-}}$ and H_2O), R and T are the gas constant and the absolute temperature, respectively, and K_{ps} is the thermodynamic solubility product of gypsum. The supersaturation ratio is defined as

$$\sigma = \frac{a_{\mathrm{Ca^{2+}}}a_{\mathrm{SO_4^{2-}}}a_w^2}{K_{\mathrm{ps}}} \tag{3}$$

The value of K_{ps} can be calculated as a function of temperature by means of the following relationship (2):

$$\ln(K_{ps}) = 390.96 - 152.62 \log T - 12,545.62/T + 0.08T \tag{4}$$

An important parameter in crystal nucleation kinetics is the time that elapses between the onset of supersaturation and the formation of critical nuclei, or embryos [clusters of loosely aggregated molecules that have the same probability of growing (to become crystals) or dissolving (to disappear into the mother solution)]. This time parameter, defined as the true induction period (t^*), primarily depends on solution supersaturation, temperature, and hydrodynamics. However, t^* cannot be experimentally measured, since it is not possible to detect the formation of critical nuclei; rather, in order to perform the measurements, it is necessary to let such nuclei grow until they reach a detectable size. Consequently, it is possible to experimentally evaluate only a time referred to simply as the induction period ($\mathrm{t}_{\mathrm{ind}}$), with $\mathrm{t}_{\mathrm{ind}} \geq t^*$ defined as the time elapsed between the onset of supersaturation and the first changes in the physical properties of the system due to the formation of a solid phase. An analysis of experimentally determined values of t_{ind} gives some important information about the mechanisms of solid-phase formation and the growth process, which leads from critical nuclei to detectable crystals. If the process that takes place is truly homogeneous nucleation, ie, it occurs in a clear solution under the effect of supersaturation alone, t_{ind} is inversely proportional to the nucleation rate, defined as the number of nuclei formed in solution per unit time and volume. Therefore, it is possible to use the experimental knowledge of the induction period to estimate two characteristic thermodynamic quantities: viz, the dependence of t_{ind} on temperature allows us to evaluate the activation energy for nucleation (E_{act}), while its dependence on supersaturation allows us to determine the interfacial tension (γ_{s}) between crystals and the surrounding solution (3,4). Activation energy and interfacial tension values found in the literature for calcium sulfate dihydrate are reported in Table 3. It is well recognized from the data dispersion, and in particular for γ_{s}, that a good agreement among researchers has not been found, especially concerning the dependency of γ_{s} on temperature. The dependence of γ_{s} on T for $CaSO_4 \cdot 2H_2O$ is a controversial matter: According to some researchers,

Table 3. **Values for Gypsum Interfacial Tension and Activation Energy**

T(°C)	E_{act}(kJ/mol)	γ_{s} (mJ/m^2)	Reference
25		41.1	6
25–90	52.6		6
25		39.3	6[a]
70		50.6	6[a]
25–50–70	49.7	37.8	8[a]
25		18.0	9
30		76.0	10
25		95.0	11
30		23.2	12
25–50–70	30.0	37.0	13

[a] With NaCl in solution.

surface tension decreases with increasing temperature (5) while according to others, it increases with increasing temperature either linearly (6) or exponentially (7).

The thermodynamic properties of gypsum decomposition involve two distinct steps,

$$CaSO_4 \cdot 2H_2O = CaSO_4 \cdot \frac{1}{2}\, H_2O + 1\,\frac{1}{2}\, H_2O \tag{5}$$

$$CaSO_4 \cdot \frac{1}{2}\, H_2O = CaSO_4 + \frac{1}{2}\, H_2O \tag{6}$$

which have been the subject of much theoretical and practical study. Two forms of the hemihydrate, α and β, have been identified (14).

The terms α and β are often used to differentiate two generally accepted, yet controversial forms of hemihydrate. The β-hemihydrate has higher energy content and a higher solubility than the α-hemihydrate.

Anhydrite also has three common classifications. Anhydrite I designates the natural rock form. Anhydrite II identifies a relatively insoluble form of $CaSO_4$, which has an orthorhombic lattice. Anhydrite III is a relatively soluble form made by lower temperature decomposition of dihydrate, which has the same crystal lattice as the hemihydrate phase.

5. Manufacture

5.1. Natural Gypsum.

Gypsum rock from the mine or quarry is crushed and sized to meet the requirements of future processing or extracted for direct marketing of the dihydrate as a cement retarder. Once subjected to a secondary crusher, calcining, and drying, the product is fine ground. Fine-ground dihydrate is commonly called land plaster, regardless of its intended use. The degree of fine grinding is dictated by the ultimate use. The majority of fine-ground dihydrate is used as feed to calcination processes for conversion to hemihydrate.

5.2. β-Hemihydrate.

The dehydration of gypsum commonly referred to as calcination in the gypsum industry, is used to prepare hemihydrate, or anhydrite. The β-form is obtained when the dihydrate is partly dehydrated in a vacuum at 100°C or under conditions lacking a nearly saturated steam atmosphere.

Kettle calcination continues to be the most commonly used method of producing β-hemihydrate. The kettle can be operated on either a batch or continuous basis. Its construction is shown in Figure 4. The kettle is a cylindrical steel vessel enclosed in a refractory shell with a plenum in between. The steel vessel is suspended above a fire box from which heated air flows up and into the plenum surrounding the steel vessel and through multiple horizontal flues that completely penetrate the vessel. The plenum and flues provide heat to the kettle contents before the heated air is exhausted. An agitator with horizontal arms penetrates the depth of the kettle and is driven from above. Land plaster, usually ground 85–95% through 100 mesh (149 μm) is fed from the top. In batch operation, using an 18.1 metric ton capacity kettle, filling takes 20–30 min. Another

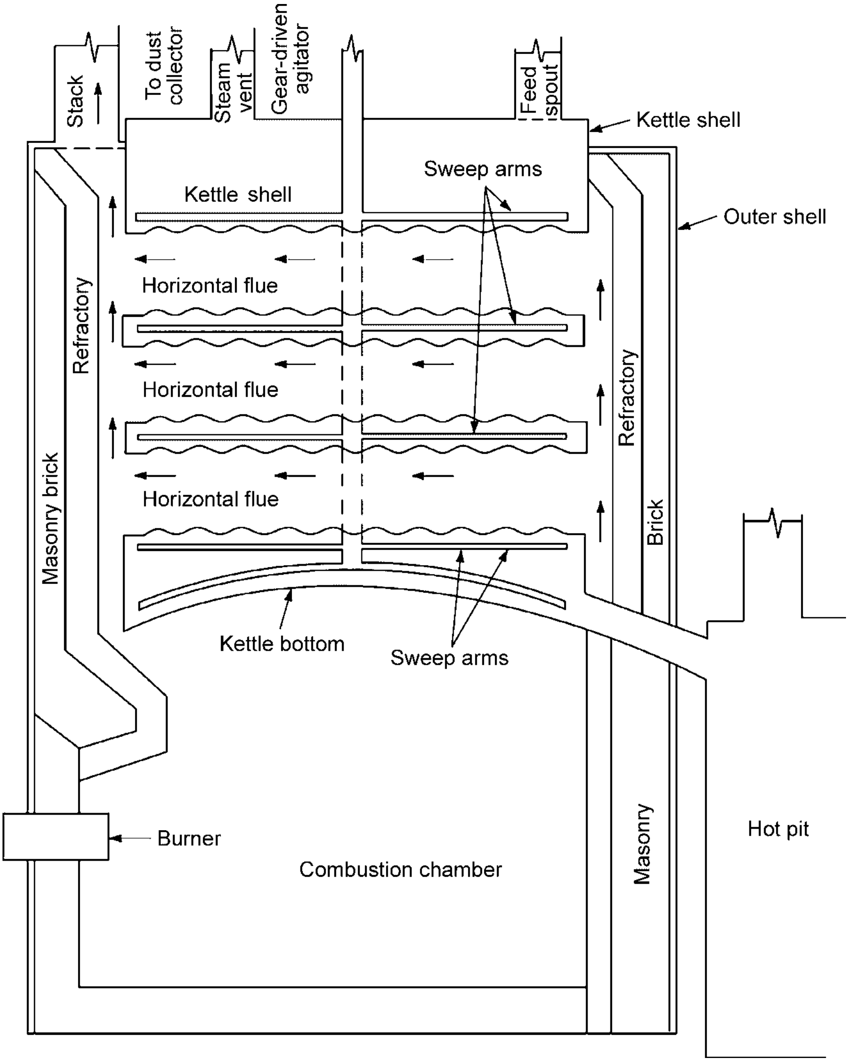

Fig. 4. Generalized vertical cross-section of a calcining kettle.

90–120 min are usually required to convert the dihydrate to hemihydrate. The steam released from the dehydration reaction is vented from the kettle top. When conversion to hemihydrate is complete (usually determined by temperature measurement of the kettle contents), the stucco is discharged by gravity through the quick-opening gate located at the periphery and bottom of the steel vessel. A typical temperature pattern for the kettle contents is shown in Figure 5. Approximately 1 GJ/t of hemihydrate is required in a well-designed kettle.

During the fill portion of a kettle cycle, the firing rate is usually controlled to maintain the kettle contents at a temperature of ~104°C. When the fill is complete, the firing rate is increased to a level dictated by the desired stucco properties. The mass boils at a temperature of 115–120°C. The boil or drag

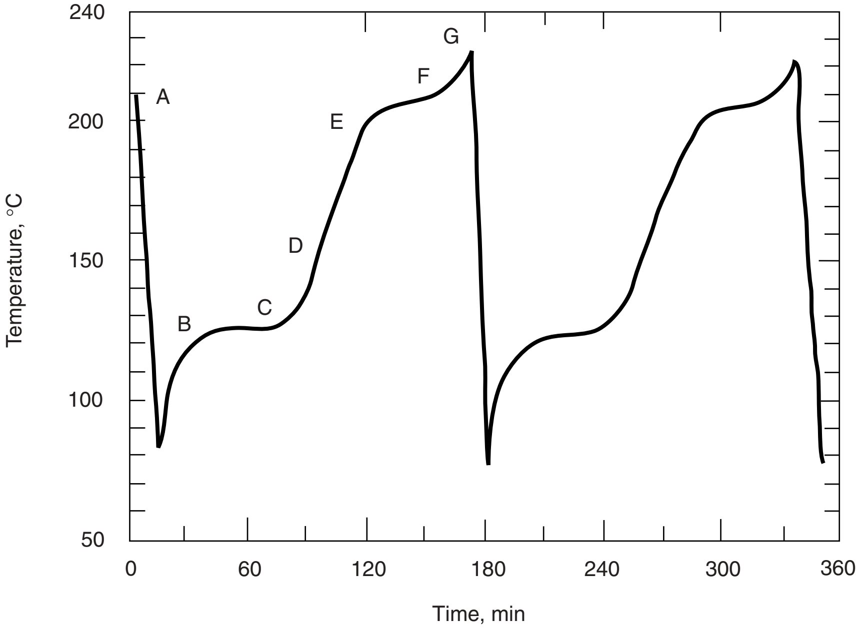

Fig. 5. Time–temperature profile for kettle calcination. Points A–B represent the fill period; B–C, is the boil or drag; C–D is the falling rate or cook-off; D is the discharge for hemihydrate. Points D–E show firing rate to second boil; E–F is the second boil; F–G is the second cook-off; G is the second-settle discharge.

continues for ~1 h, then subsides. Heating continues for a short time period to allow moisture release and the mass temperature increases to ~150–155°C if the hemihydrate form is desired, after which firing is reduced and the contents are dumped. In practice, owing to the inability to heat all particles of gypsum adequately, the discharged mass often contains small percentages of dihydrate, soluble anhydrite, and at times insoluble anhydrite.

If soluble anhydrite is desired, firing is maintained until a second boil occurs accompanied by a second temperature plateau at ~190°C. Virtually all the water of crystallization has been removed at 215°C. Soluble salts are impurities that increase the vapor pressure within the kettle. Aridized stucco refers to kettle-calcined hemihydrate that has been made with the intentional addition of 0.55–1.1 kg NaCl or $CaCl_2$ per metric ton of land plaster. The stucco characteristic of lower water demand permits higher density and higher strength casts. The hygroscopic nature of the chlorides prevents the use of aridized stucco for some applications.

5.3. α-Hemihydrate. The α-form of hemihydrate is prepared by dehydration of gypsum in water at temperatures >97°C and by dissociation in an atmosphere of saturated steam. Three processing methods are used for the production of α-hemihydrate. One, developed in the 1930s, involves charging lump gypsum rock 1.3–5 cm in size into a vertical retort, sealing it, and applying steam at a pressure of 117 kPa (17 psi) and a temperature of ~123°C (15). After calcination under these conditions for 5–7 h, the hot moist rock is quickly dried and pulverized.

Another method (16), first reported in the 1950s, has lower water demand. The dihydrate is heated in a water solution containing a metallic salt, such as $CaCl_2$, at pressures not exceeding atmospheric. A third method (17), developed in 1967, prepares very low water demand α-hemihydrate by autoclaving powdered gypsum in a slurry. A crystal-modifying substance such as succinic acid or malic acid is added to the slurry in the autoclave to produce large squat crystals.

Anhydrite. In addition to kettle calcination (Fig. 4), soluble anhydrite is commercially manufactured in a variety of forms, from fine powders to granules 4.76 mm (4 mesh) in size, by low temperature dehydration of gypsum.

Insoluble anhydrite is manufactured commercially by several methods. Where large rock gypsum is the starting material, beehive kilns are used and 24-h processing times are not unusual. Rotary calciners or traveling grates are often used for small rock feed. Fine-ground gypsum is calcined to the insoluble form in flash calciners. Temperature control is somewhat critical in all methods; low temperatures result in soluble anhydrite being present and too high temperatures dissociate the $CaSO_4$ into CaO and oxides of sulfur.

5.4. By-Product Calcium Sulfate. There are many industrial chemical processes that produce by-product calcium sulfate in one of its forms. Whereas the most common is the neutralization of spent sulfuric acid, many of those processes do not produce a commercially useful by-product because of contaminants, particle size, or volume produced. There are, however, six chemical processes that do produce sufficient volume to have potential commercial value. Each is named after its chemical process.

The two names commonly given to the by-product gypsum are desulfogypsum or FGD–gypsum which are produced by scrubbing sulfur dioxide out of flue gases (see SULFUR REMOVAL AND RECOVERY). There are three general types of scrubbing processes that produce by-product gypsum: limestone, lime, and dual or double alkali.

The process for limestone scrubbing can be generally described by

Absorption

$$SO_2 + H_2O = H_2SO_3 \tag{7}$$

$$H_2SO_3 = HSO_3^- + H^+ \tag{8}$$

$$HSO_3^- = SO_3^{2-} + H^+ \tag{9}$$

Limestone Dissolution

$$2H^+ + CaCO_3 = Ca^{2+} + CO_2 + H_2O \tag{10}$$

Bisulfite–Sulfite Oxidation

$$HSO_3^- + \frac{1}{2}O_2 = HSO_4^- \tag{11}$$

$$SO_3^{2-} + \frac{1}{2}O_2 = SO_4^{2-} \tag{12}$$

Crystallization

$$Ca^{2+} + SO_4^{2-} + 2H_2O = CaSO_4 \cdot 2H_2O_{(S)} \tag{13}$$

There are several lime-scrubbing processes being marketed. The generalized process is described by

Absorption

$$2\ Ca(OH)_2 + 2\ SO_2 = 2\ CaSO_3 \cdot \frac{1}{2}\ H_2O + H_2O \tag{14}$$

Oxidation / crystallization

$$2\ CaSO_3 \cdot \frac{1}{2}\ H_2O + O_2 + 3\ H_2O = 2\ CaSO_4 \cdot 2H_2O_{(s)} \tag{15}$$

In the dual or double alkali process, an alkali salt that is considerably more soluble in water than limestone is used. The alkali salt is then regenerated using a second alkali, $CaCO_3$. There are several alkalis used in the absorber; the most common are magnesium sulfite, sodium sulfite, and ammonium sulfite. A typical process using magnesium sulfite is

Absorption

$$MgSO_3 + H_2O + SO_2 = Mg^{+2} + 2\ HSO_3^- \tag{16}$$

Oxidation–crystallization

$$2\ HSO_3^- + 2\ CaCO_3 = 2\ CaSO_3 \cdot \frac{1}{2}\ H_2O + 2\ CO_2 + \frac{1}{2}\ O_2 \tag{17}$$

$$2\ CaSO_3 \cdot \frac{1}{2}\ H_2O + O_2 + 3\ H_2O = 2\ CaSO_4 \cdot 2H_2O_{(s)} \tag{18}$$

Note that the dual alkali process is not competitive with respect to the limestone–gypsum process, since it requires a double step not needed in the limestone process. Moreover the limestone–gypsum process gives excellent results for SO_2 removal, and for this reason is the most widespread worldwide. As an example, in the United States the Northen Indiana Public Service Company (NIPSCO) R.M. Schahfer Station converted two FGD systems from dual alkali process to limestone forced oxidation process during the winter 1996–1997 (18). Since this conversion, the FGD systems have consistently produced high quality, wallboard grade gypsum.

Moreover, of all the by-product gypsums from chemical processes, desulfogypsum from coal-fired electric power utility plants has the greatest commercial potential because electric power plants are numerous and many are located near large population centers where there would be a ready market for by-product gypsum wallboard products (see COAL CONVERSION PROCESSES; POWER GENERATION). Utilization of gypsum is dependent on economically removing deleterious chemicals, viz, excess chlorides, water-soluble sodium and magnesium, and unoxidized calcium sulfite.

By-product gypsum made by neutralizing waste sulfuric acid from the sulfate process used to manufacture titanium oxide pigment is called titanogypsum (see TITANIUM COMPOUNDS, INORGANIC). This is commonly a two-industry process in that iron-rich ilmenite ore is first processed to obtain iron and the resulting slag is sold to the TiO_2 producers. There are a few locations where titanogypsum is produced in large enough quantities to be considered for commercial use. Limitations are the iron compound contaminants and their average particle size. Titanogypsum has become the second most important source of commercial by-product gypsum after desulfogypsum in the United States.

Phosphogypsum [13397-24-5] is the name given to the by-product gypsum residue when phosphate ore is acidulated to extract phosphoric acid. There are several processes commercially used. All of them digest or acidulate tricalcium phosphate.

$$Ca_3(PO_4)_2 + 3\,H_2SO_4 + 6\,H_2O = 2\,H_3PO_4 + 3\,CaSO_4\cdot 2H_2O_{(s)} \qquad (19)$$

In the United States, environmental considerations render by-product gypsum from all of the processes inappropriate for the building material industry. Radon and daughter radionuclides are retained in the by-product residue after acidulation as is the heavy metal cadmium (see HELIUM-GROUP GASES; CADMIUM AND CADMIUM ALLOYS). Phosphogypsum's commercial use in the gypsum wallboard industry in Europe and Japan has diminished as desulfogypsum has become more available.

Fluorogypsum is the name ascribed to by-product gypsum from fluorspar acidulation to produce hydrofluoric acid. The chemical reaction

$$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2\,HF(g) \qquad (20)$$

produces anhydrite. Over time, the anhydrite converts to gypsum. Contaminants in fluorogypsum, especially the heavy metal beryllium, render fluorogypsum a better road metal, ie, roadbed material, for which it is used, than as a building material product.

Citrogypsum and borogypsum are named after the respective processes and produce sizeable quantities of by-product gypsum in certain locations. However, contaminants preclude commercial use in the gypsum wallboard industry.

6. Scale Formation

Precipitation fouling or scale formation represents a problem frequently encountered in a variety of industrial applications; deposits are usually formed from those compounds whose solubility decreases with increasing temperature, such as calcium sulfates. Scale can be described as the deposition of a salt from aqueous solution onto surfaces. Scale occurs when an electrolyte solution, in this specific case containing calcium and sulfate ions, is concentrated as, eg, by evaporation; the salts (calcium sulfate anhydrous, hemihydrate, or dihydrate) will precipitate in a certain order depending on the concentration of the various ions and on the temperature. In particular, the solubility of all calcium sulfate

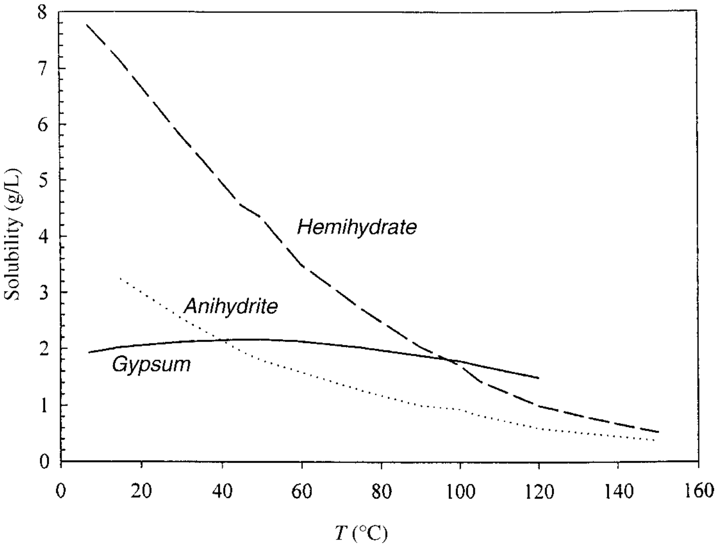

Fig. 6. Solubility of different forms of calcium sulfate.

forms decreases with increasing temperature starting from 40°C, as reported in Figure 6, a fact that is responsible for the formation of scale mostly constituted of a mixture of calcium sulfate dihydrate (gypsum), and calcium sulfate anhydrous (anhydrite). In this view, the comprehension of nucleation and crystal growth mechanisms that regulate the gypsum precipitation is fundamental to understanding processes in which gypsum formation is an unwanted occurrence. Water desalination (19), industrial water recovery in cooling tower technology, water distillation (20), and phosphoric acid production (21) are examples of calcium sulfate scale formation.

The best technique to inhibit gypsum scale formation is the addition of additives in solution, which retard calcium sulfate formation, ie, inhibit the nucleation kinetic mechanism.

Many substances, organic as well as inorganic, have been tested as additives for their capability of retarding the unwanted gypsum precipitation process. Regarding inorganic additives, aluminum ions are the most active among those studied (22,23), enhancing the degree of agglomeration of gypsum crystals and reducing the overall growth and nucleation rate. Moreover, experimental work has showed that chloride salts (NaCl and $CaCl_2$) influence gypsum nucleation by retarding nucleation kinetics (8). Among the organic species whose effect on gypsum precipitation was tested, polymeric additives were the most frequently used, eg, mainly polyelectrolytes (24,25), polyphosphates, and phosphonates (9,26,27). These authors agree that these polymeric species are effective in retarding the kinetics of gypsum crystal nucleation and growth, and their action depends on pH and polymer concentration. Recently, citric acid has proven to have a strong inhibiting effect on gypsum nucleation (28).

An industrially reliable method for calcium sulfate scale removal is the use of EDTA (ethylenediamine tetraacetic acid) and NTA (nitriloacetic acid), which form stable complexes with Ca^{2+} cations: The chelanting agents react with and dissolve solid deposits. As a matter of fact, the more insoluble calcium complex results and is disintegrated into a soft, pumpable slush (29). Moreover, various inorganic alkali solutions such as sodium hydroxide, potassium hydroxide, and ammonium and sodium bicarbonate have been effectively used to remove calcium sulfate, but they are usually referred to as converting solutions, since calcium sulfate is converted to calcium carbonate or calcium hydroxide, and these are in turn removed with acid (29).

7. Shipment

Gypsum and gypsum products are bulky and relatively low in cost. In North America, factors of varying regional supply and demand for building products not withstanding, the normal economic overland shipping range is ~500 km. For overland shipments, there has been a steady shift, starting in the 1950s, from rail-to-motor transport. In some cases, truck shipments are made from plants directly to building construction sites. For continental coastal and lake region markets, crude gypsum is most often transported in specially designed, rapid unloading ships that deliver from quarries to plant sites where the gypsum is then processed into finished products. During the 1980s, there were reports of increased intercontinental trade in both crude gypsum ore and manufactured goods.

As for synthetic gypsum, if the power stations are located on the coast so that economical loading facilities are available for ships, export of FGD gypsum via sea routes to neighboring states can be more advantageous than transportation to the domestic gypsum factories. This situation is encountered in Europe, where almost all power stations have harbor docking facilities (30).

8. Economic Aspects

Crude gypsum is the principal form of calcium sulfate shipped in international trade, although the 1980s saw an increase in the volume of fabricated products moved across international borders.

Figure 7 shows the gypsum usage by source, natural or synthetic, in the United States, showing that the production of synthetic gypsum has raised from 0 to 8.10 million tons from 1985 to the end of 1999 (31).

The quantity of FGD gypsum produced depends on the sulfur content of the coal and on the degree of desulfurization by the FGD plant. For example, a coal-fired power station with an output of 750 MW, an FGD plant efficiency of 95% and a sulfur content in the coal of 0.6–1% produces ~9–14 t of FGD gypsum hourly during full-load operation (32). In the year 2000, flue gas desulfurization plants with FGD gypsum as a by-product are in operation in several countries in Western and Eastern Europe (see Table 4). It has been estimated that in the year 2000, ~94,000 MW of power station capacity have been equipped with wet FGD

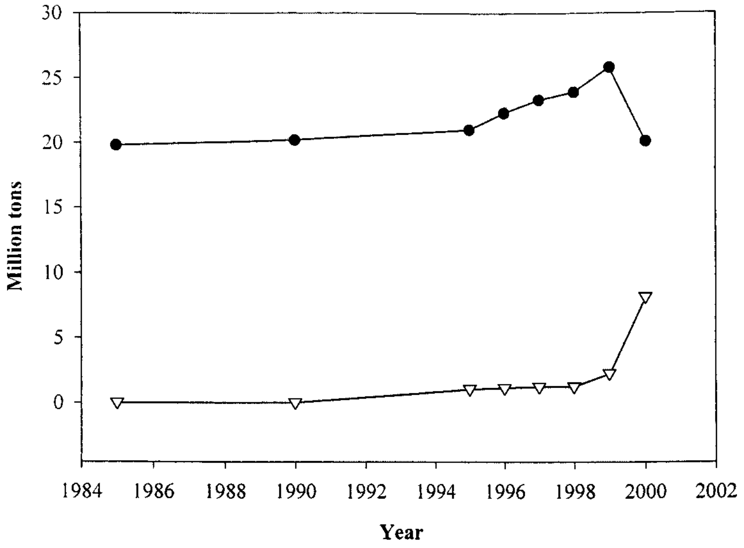

Fig. 7. Gypsum usage by source in the United States; △ synthetic gypsum; ● natural gypsum; (31).

systems and that a total of 15.8 million tons of FGD gypsum is obtained from them (30). It is expected that additional quantities of FGD will come after the installation of further desulfurization plants both in Western and in Eastern Europe, so that an increase of 22% more is expected in the quantity of FGD

Table 4. **FGD Gypsum Volumes in Europe**[a]

Country	Wet FGD systems installed (MW)	FGD gypsum volumes (tons)	
		year 2000 ($\times 10^{-3}$)	year 2005 ($\times 10^{-3}$)
Austria	1,500	100	100
Belgium	500	30	50
Croatia	210	30	110
Czech Republic	5,710	1,900	1,500
Denmark	4,200	330	400
Finland	1,800	170	170
France	1,200	60	90
Germany	51,000	6,200	6,500
Greece	450	120	190
Hungary	600	60	320
Italy	4,180	700	1,100
Netherlands	4,900	340	340
Poland	6,900	1,360	1,830
Slovakia	400	50	50
Slovenia	275	140	320
Spain	1,750	490	490
Turkey	2,670	3,160	4,700
United Kingdom	5,960	600	1,070
Total Europe	*94,205*	*15,840*	*19,330*

[a] Ref. 30.

Table 5. **Quality Specifications Set by the Gypsum Industry for FGD Gypsum Compared With Those of Natural Gypsum**[a]

	Units	Value for FGD gypsum	Value for natural gypsum
moisture content	%	<10	1
purity	%	>95	85
pH value		5–8	7
color (whiteness)	%	>80	
odor	neutral		
average particle size (sieve 32 μm)	%	>60	
minor constituents	%	<5%	
MgO	%	<0.10	0.010
Na_2O	%	<0.06	0.005
Cl	%	<0.01	0.003
$CaSO_3\ ½H_2O$	%	<0.50	
soot	%	<0.10	0.06
Al_2O_3	%	<0.30	0.30
Fe_2O_3	%	<0.15	0.20
SiO_2	%	<2.50	2.0
$CaCO_3 + MgCO_3$	%	<1.50	12
K_2O	%	<0.06	0.005
$NH_3 + NO_3$	%	0	

[a] Ref. 32.

gypsum up to the year 2005 as a result of retrofitting existing power stations. Therefore FGD gypsum quantity in the year 2005 would reach 20 million tons (30).

The properties of FGD gypsum have been drawn up on a European basis by EUROGYPSUM, the umbrella organization or the European gypsum industry, and has been adopted by all the interested European organizations. In the European view, FGD gypsum is a product and is identical to and of equal value with natural gypsum. FGD gypsum has now been legally accepted as a product in the European and International legislature, so for this reason FGD gypsum is no longer listed as waste in the waste catalogues (32). (See Table 5.)

9. Specifications

Formulated plasters utilizing specially processed calcined gypsum are packaged in multiply paper bags having moisture vapor–resistant liners. This type of packaging protects the contents from airborne moisture keeping the plaster more stable with respect to setting time and mixing water demand over longer periods of warehousing. Manufactured board products are most often bundled, two pieces face to face, stacked in units for transport to dealers' yards, and reshipped to individual job sites as construction schedules dictate. Specialized,

Table 6. **ASTM Gypsum and Gypsum Product Specifications**

ASTM method	Materials
	Gypsum and gypsum plasters
C22-91	gypsum
C28-91	gypsum plasters
C35-89a	inorganic aggregates for use in gypsum plaster
C59-91	gypsum casting and molding plaster
C61-91	gypsum Keene's cement
C317-91	gypsum concrete
C587-91	gypsum veneer plaster
	Test methods
C265-91	calcium sulfate in hydrated Portland cement
C471-91	chemical analysis of gypsum and gypsum products
C472-90a	physical testing of gypsum plasters, etc
	Gypsum board products
C36-91	wallboard (general)
C37-91	lath (base for plaster)
C79-91	sheathing
C442-91	backing board and coreboard
C588-91	base for veneer plasters
C630-91	water-resistant backing board
C931-91	exterior soffit board
C960-91	predecorated board
	Test method
C473-87a	physical testing of gypsum board products

labor saving, power driven handling equipment has been developed for stocking boards on construction sites. The ASTM specifications for gypsum and gypsum products are given in Table 6.

10. Uses

10.1. Uncalcined Gypsum.

Calcium sulfate, generally in the form of gypsum, is added to Portland cement (qv) clinker to stop the rapid reaction of calcium aluminates (flash set) [see ALUMINUM COMPOUNDS, ALUMINUM OXIDE (ALUMINA)]. Also, gypsum accelerates strength development. For this reason, gypsum is more properly termed a set regulator, rather than a retarder, for Portland cement. When it is used in proper amounts, it also minimizes volume change. Normal gypsum addition to clinker is 5–6 wt%. Another notable use of uncalcined gypsum is in agricultural soil treatment, wherein it is commonly called land plaster. For this use it is finely ground.

10.2. FGD Gypsum.

In countries with many years of gypsum tradition and with a well-developed market for gypsum-based building materials, such as in the United States, Japan, Austria, Belgium, Denmark, Finland, France, Germany, The Netherlands, and The United Kingdom, the gypsum industry

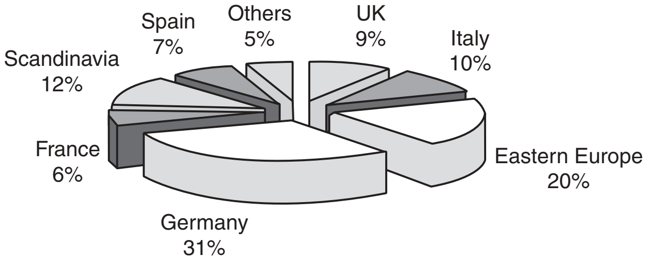

Fig. 8. Estimate of the extra capacity of gypsum required in Europe between 1998 and 2009 (33).

uses more raw gypsum than the amount produced by the FGD plants. This enables complete utilization of FGD gypsum by substitution of a part of the natural raw gypsum that occurs, eg, in Germany, or by substitution of a part of the imported natural raw gypsum, as in the case of The United Kingdom. Figure 8 shows an estimate of the extra capacity of gypsum required in Europe between 1998 and 2009, as estimated by Rumph (33) that could be satisfied by using FGD gypsum.

10.3. Calcined Anhydrite. Soluble anhydrite has physical properties similar to those of gypsum plaster. It hydrates to the dihydrate rapidly in water. Its outstanding property is its extreme affinity for any moisture, which makes it a very efficient drying agent (see DESICCANTS). In ambient moisture-laden air, it readily hydrates to hemihydrate. Soluble anhydrite, under the trade name Drierite, is widely used as a desiccant in the laboratory and in industry. A small amount is also used as an insecticide carrier. Small amounts of soluble anhydrite are unintentionally produced in most commercial calciners during hemihydrate production.

Keenes cement is produced from calcined anhydrite (dead-burned), finely ground and intermixed with special accelerator(s). Although the volume of its use has declined greatly since the 1960s, it is available for job-site mixing with hydrated lime as a composite, hand-finished plaster applied generally over an aggregated, gypsum-base (conventional) plaster.

10.4. Hemihydrate. The ability of plaster of Paris to readily revert to the dihydrate form and harden when mixed with water is the basis for its many uses. Of equal significance, is the ability to control the time of rehydration in the range of 2 min to >8 h through additions of retarders, accelerators, and/or stabilizers. Other favorable properties include its fire resistance, excellent thermal and hydrometric dimensional stability, good compressive strength, and neutral pH.

Upon setting, gypsum expands slightly and this property can be used to reproduce the finest detail, down to ~1 μm, as is done in certain dental and jewelry castings employing the lost wax process. Normal linear expansion upon setting of gypsum plaster is 0.2–0.3%, but by using additives, expansion may be controlled for special uses in the range of from 0.03 to 1.2%.

The calcination procedures and processing techniques produce a family of base stuccos best described by the amount of water, in wt%, of the plaster, which must be added when mixing to obtain standard fluidity. The range of fluidity permits casting neat plaster in the dry range of specific gravity of ~0.85–1.8 and consequent dry compressive strength of ~3.5–70 MPa (35–700 atm). Frequently, these stuccos are formulated with set and expansion control additives as well as many other materials to meet the needs of a particular application. Properties that limit gypsum plaster usage include plastic flow underload, which is increased under humid conditions, strength loss in a humid atmosphere, and dissolution and erosion in water. Thus gypsum is not normally used for permanent performance structurally or in exposed, exterior locations. To prevent long-term calcination, gypsum products should not be used where temperatures exceed 45°C.

The largest single use of calcined gypsum in North America is in the production of gypsum board. Gypsum wallboard replaced plaster in the United States during the 1960s as the main wall cladding material. During that same time period, new veneer plaster systems were developed as an alternative to gypsum board (drywall) and the classic plastering systems, all of which are specified in building construction (see BUILDING MATERIALS, SURVEY). The veneer plasters are highly proprietary and specially formulated composites that provide good wear-resistant interior wall and ceiling surfaces. They are applied on the construction site either by a one- or two-coat procedure at thicknesses of ~0.19–0.32 cm. As reported in Figure 9, in terms of volume and value, wallboard is the dominant market for gypsum not only in North America but also in those markets where wallboard is well established, such as Western Europe and Japan. Cement is the other main source of demand for gypsum; since the cement production was ~1.6 billion tons in 2000, the cement industry consumed ~5–6% of that quantity, or ~100 million tons of gypsum (33).

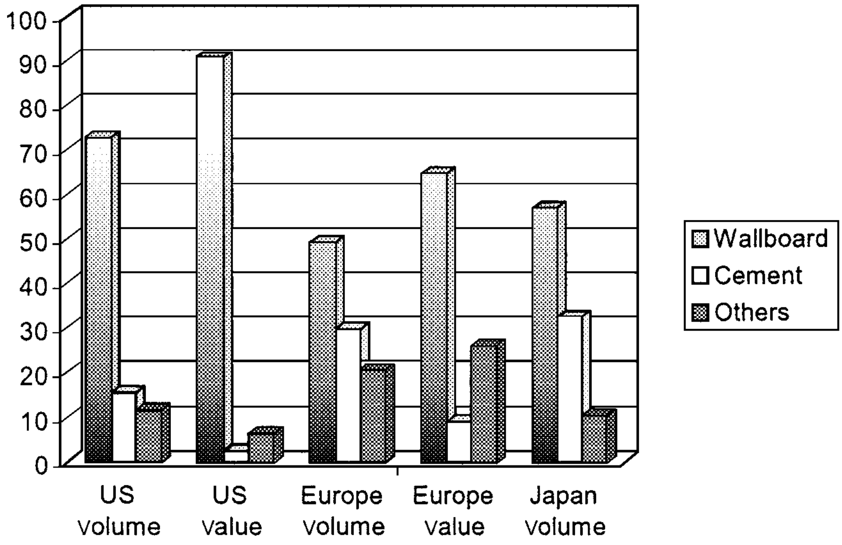

Fig. 9. Gypsum market (billion tons) and value in the United States, Europe, and Japan; (33).

Molding plasters have been used for centuries to form cornices, columns, decorative moldings, and other interior building features. Molding plaster is a good utility plaster where expansion control, high hardness, and strength are not needed. Its miscellaneous uses are numerous. Art plasters are essentially molding plasters modified to increase surface hardness, chip resistance, and to reduce paint absorption of casts made from this material. Orthopedic plasters are used by hospitals and clinics for all types of orthopedic cast work.

A moderate amount of plaster is used in making impressions and casting molds for bridges, and by dental laboratories. Both α- and β-plasters are used by the dental trade (see Dental materials). The α-plasters are also tailored to meet the needs of modern industrial tooling, where they are used for master patterns, models, mock-ups, working patterns, match plates, etc. They are the accepted material because their use results in great time and labor saving costs, as well as the excellent accuracy and stability of cast dimensions. Also, the material is adaptable to intricate, irregular shapes, complex intersections, and quick modification.

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