CHAPTER 12.15

Gypsum

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Gypsum generally refers to the dihydrate form of calcium sulfate ($CaSO_4·2H_2O$). Anhydrite ($CaSO_4$) is the other principal calcium sulfate mineral. This chapter includes discussion on both calcium sulfate minerals because they are strongly related. Gypsum and anhydrite are often found in close association with one another and are formed primarily from the concentration of dissolved mineral constituents in saline water. Although a few notable underground mining operations exist, gypsum is most commonly extracted from near-surface deposits by quarrying methods.

Gypsum is also co-produced in significant quantities in many industrial processes and is chemically the same as mined gypsum. These commercial processes include acid neutralization from the production of some organic acids, fertilizer manufacture, and notably flue gas desulfurization (FGD) processes.

The most significant difference between gypsum and anhydrite is that gypsum is often calcined to the hemihydrate form of calcium sulfate ($CaSO_4·½H_2O$) through the application of a modest amount of heat (i.e., calcination). Common names for calcium sulfate hemihydrate include *stucco*, *plaster of Paris*, *molding plaster*, and *plaster*. Stucco is an intermediate product and is used in more than 90% (based on value) of all calcium sulfate products. Anhydrite, conversely, is inert at the relatively low amounts of heat applied during calcination, and its uses are limited to those few cases where calcium sulfate in the anhydrous form has an advantage.

Gypsum has a high place value. A large part of a deposit's value results from its geographic situation relative to the market area, inexpensive modes of transportation, utilities, and services. Conversely, gypsum has a low unit value. The widespread occurrence of raw gypsum gives it a low value per ton. In addition, almost 100% of extracted material is usable for manufacturing more than 400 products. Its value can be greatly increased by additional processing required for certain products.

Gypsum and anhydrite are used in many different industries. The predominant use of gypsum and anhydrite is related to construction products, including portland cement and wallboard manufacture. However, significant quantities of the minerals are also used in various agricultural applications and industrial products including glass manufacture, food and pharmaceuticals, pottery, sanitary ware, and dental plasters.

GEOLOGY AND MINERALOGY

Natural Gypsum

Gypsum and anhydrite are formed from diverse origins. Gypsum ($CaSO_4·2H_2O$) is primarily formed as a chemically precipitated sedimentary rock in basin or sebkha environments, but it may also form as the result of solutional, karst, hydrothermal, and volcanogenic processes. Anhydrite ($CaSO_4$) is the anhydrous form of the calcium sulfate family of minerals. Anhydrite may form as a primary mineral in a sebkha depositional environment or deep-basin environments. The terms *gypsum* and *anhydrite* are commonly used interchangeably for the minerals and rocks that are composed primarily of these minerals.

Gypsum and anhydrite may be deposited simultaneously in a sedimentary environment and are easily converted from one to another under varying conditions of heat, pressure, and the presence of water. The occurrence and relationship of anhydrite and gypsum in a deposit is complex. Mineralogical, textural, crosscutting relationships, and microscopic examination may be necessary to determine the ultimate origin of anhydrite in a deposit. Some deposits exhibit multiple episodes of conversion from gypsum to anhydrite and vice versa (Sharpe and Cork 2006).

Gypsum forms monoclinic crystals with a perfect {010} cleavage and distinct cleavages along {100} and {101}. It is distinguishable from anhydrite by its lower Mohs hardness (2.0 vs. 3.5) and specific gravity (2.24 vs. 2.97 g/cm^3). Pure gypsum is colorless, but may be tinted yellow, red, and brown because of the presence of impurities. Twinning is common along {100}, forming "swallowtail twins." Gypsum is relatively soluble in fresh water (~0.2 g/100 g H_2O) and is easily dissolved or eroded in conditions of high humidity or rainfall.

Anhydrite forms orthorhombic crystals with perfect cleavages along {100} and {010} and a good cleavage along

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Table 1 Gypsum lithology

Crystal Type	Lithology
Alabaster	A compact, fine-crystalline, translucent variety of primary gypsum that has been used by artists to produce statuary for thousands of years. Typically found in a variety of colors depending on the type and amount of impurities present, alabaster generally occurs as zones within larger gypsum deposits.
Anhydrite	Massive or granular texture. Scattered gypsum crystals commonly occur in the anhydrite groundmass and increase near the gypsum–anhydrite contact. Anhydrite is similar in appearance to rock gypsum, but usually slightly darker, with denser, finer crystals.
Gypsite	An earthy, pulverulent variety of gypsum that forms a surficial deposit in shallow saline lakes, playas, and salt pans in arid environments. The calcium and sulfur required to form gypsum are derived from the erosion and weathering of rocks and transported in surface and groundwater to closed basins. Gypsum precipitates at the surface by capillary movement and evaporation of groundwater. Gypsite is often contaminated by windblown sand or silt and clay from periodic flooding of the playas. Often called *gypsum sands*.
Satin spar	A fibrous variety of needle-shaped gypsum crystals filling fractures or along bedding planes. The needle-shaped gypsum crystals form with the C-axis oriented at a steep angle or perpendicular to the vein walls in fractured rocks undergoing deformation. It is important to recognize that satin spar is not an asbestiform mineral.
Selenite	Characterized by large, clear, euhedral crystals of gypsum. Bladed selenite crystals commonly form in fluid-filled cavities. Selenite may also form along fault zones. Cleavage fragments may be mistaken for muscovite mica. Poikilitic masses of selenite crystals, commonly known as *gypsum roses*, are formed by the crystallization of gypsum from interstitial pore fluid in unconsolidated sand.
Rock gypsum	Rock gypsum commonly consists of aggregates of gypsum crystals interbedded or mixed with mudstone, shale, siltstone, limestone, or dolomite. Gypsum rock and anhydrite may be nodular, massive, laminated, or bedded. Most rock gypsum has a medium to coarse crystalline texture, and this is the most common crystal variety of the mineral.

Source: Sharpe and Cork 2006

{001}. Anhydrite has a Mohs hardness of 3.5 and a specific gravity of 2.97 g/cm^3. Pure anhydrite is colorless, but the color is variable from colorless to dark gray (Sharpe and Cork 2006).

Commercial deposits of gypsum may be almost 100% pure or contain variable amounts of syndepositional impurities such as limestone, dolomite, clay, anhydrite, and soluble salts of potassium, sodium, and magnesium. Primary gypsum deposits consist of rock gypsum and alabaster. Selenite, satin spar, and gypsite are secondary varieties of gypsum. Anhydrite may occur as either primary or secondary minerals in a deposit, depending on its geological history. Table 1 provides the lithology of common varieties of gypsum.

Synthetic Gypsum

Synthetic gypsum originates from several industrial processes. Mainly, it is a product resulting from industrial acid neutralization processes or FGD of fossil fuel combustion in power plants and can be as pure as 98% $CaSO_4 \cdot 2H_2O$. By far, the largest amount of synthetic gypsum is obtained from the production of wet phosphoric acid from phosphate rock (phosphogypsum). However, high levels of impurities and often low levels of radon render most phosphogypsum useless (Henkels 2006).

Over the last 25–30 years, synthetic gypsum gained in popularity and use worldwide. It often replaces mined natural gypsum. In 2014, ~50% of the gypsum consumed by U.S. wallboard manufacture was from synthetic sources, primarily FGD (Crangle 2014). FGD gypsum use in the United States is expected to stabilize or decline in coming years as power companies convert electrical generation plants to natural gas to take advantage of inexpensive and plentiful shale gas. Also, as environmental concerns about coal combustion by-products are raised, leading to increased regulation, the cost of coal-fired power plants may increase, prompting reduced operating hours or closure.

Synthetic gypsum is usually available in a "wet cake" granular form (30–60 µm) with free moisture content varying from 6% to 15%. The product is normally dried by the consumer to less than 1% moisture content prior to calcining, and then handled in the same manner as natural gypsum throughout the manufacturing process (Henkels 2006). There are no significant advantages or disadvantages to using synthetic gypsum versus natural gypsum other than cost. The decision is one of economics; the cost of transportation is usually the determining factor. The increased prevalence of synthetic gypsum during the past 30 years in the United States has helped to keep the price of gypsum low (<$10/t [metric ton]).

Anhydrite

Anhydrite is considered an impurity where gypsum is the sought-after mineral. It is a common impurity in deposits of gypsum and may occur as a primary depositional mineral or the product of dehydration of deeply buried gypsum. Anhydrite can be found as a massive rock or as a mixture of gypsum and anhydrite in partially hydrated deposits. Soluble salts, such as sodium, magnesium and potassium chlorides, and sulfates are commonly concentrated in a halo in gypsum adjacent to the anhydrite contact. The soluble salts are leached from the anhydrite during hydration and precipitated in tensional features, such as fractures, many of which form during the volumetric expansion during hydration. As a contaminant, the anhydrite is harder and denser than gypsum and contains higher levels of soluble salts. Anhydrite increases the weight of finished wallboard products and is abrasive to grinding and processing equipment (Sharpe and Cork 2006).

EXTRACTION METHODS

The majority of gypsum rock is produced by surface mining operations. In North America, surface mining is by far the most common method. Only five active underground gypsum mines were in operation in 2014. Two are located in Indiana (United States), and one each in Iowa, Michigan (both in the United States), and Ontario, Canada (Sharpe and Cork 2006). In Europe, underground mining is the more commonly used extraction method.

Quarrying

Gypsum is extracted from near-surface deposits by quarrying methods. Overburden, consisting of glacial materials (till, sand, clay), shale, mudstone, siltstone, sandstone, sand and gravel, or limestone, is removed from the gypsum by various stripping methods. Stripping is performed by pan scraper, truck and excavator, front-end loader or hydraulic excavator and truck, dragline, and bulldozer. The maximum economic stripping limit (thickness) is approximately 30 m and depends on the method of stripping and the thickness of the underlying recoverable gypsum.

Final cleanup of the stripped gypsum surface is important and is determined by the final products to be manufactured. If the quarried rock is to be used as agricultural products, portland cement rock, or wallboard, then much of the impurities can be removed in the finer fractions during crushing and screening. Conversely, gypsum used for high-quality, high-value-added products requires more stringent cleaning. For example, articulated hydraulic excavators with multiple, interchangeable bucket widths scrape clay from the gypsum surface and fractures that extend deep into the gypsum.

Drilling and blasting is the primary method of quarrying gypsum. Quarry benches are generally about 8 m in height. Hydraulic rotary drilling and auger drilling are commonly used. Gypsum is soft, and penetration rates up to 7 m/min are possible. Blastholes are generally 50–100 mm in diameter and spaced relatively close together to distribute the explosive forces throughout the rock mass. The blasting components used include ammonium nitrate and fuel oil blasting agent, cast boosters, and nonelectric blast initiation systems. Bagged emulsion is used in wet holes. Approximately 1 kg of blasting agents per ton of broken gypsum is an average tonnage factor. The elastic nature of gypsum, the presence of solution-enlarged fractures, and the possible presence of water contribute to poor and inefficient rock fragmentation. An incorrectly designed blasting pattern may result in irregular fragmentation, including excessive oversized rock requiring secondary breakage, excessive fines, or irregular floor conditions that are detrimental to the efficiency and maintenance of mobile equipment. Quarry haulage trucks or over-the-road dump trucks transport the quarry-run broken gypsum from the quarry site to the primary crusher.

Another method of extracting gypsum from quarries that is gaining acceptance is the use of a surface miner. This is an adaptation of highway-resurfacing technology in which a horizontally rotating mandrel with cutting teeth chips away at the asphalt and either discharges the broken material in a windrow or directly into a haulage truck. Specialized machinery using this technology is being developed to quarry coal, gypsum, and limestone. The size, spacing, and arrangement of the cutting teeth on the mandrel are important factors in the efficient production of gypsum rock. The following are advantages over standard quarrying techniques (Sharpe and Cork 2006):

- Elimination of drilling and blasting
- Elimination of primary crushing
- Direct removal of interbedded thin waste beds or low-purity zones
- Increase in recovered gypsum purity by removal of off-specification material from windrows
- Maximization of the overall recovery of the gypsum near structures or utilities

There will be more and more use of surface miners in the future as these machines have the ability to easily avoid stripping undesired low-purity, contaminated areas and better control quality and purity compared to conventional mining methods (drill and blast).

Underground Mining

Underground mining of gypsum is far less common than quarrying. There are currently only five active underground gypsum mines in North America. The mines are located at a depth of <30 m (Hagersville, Ontario) to ~200 m (Iowa and Indiana). Access to the mine workings for workers, supplies, ventilation and escape, and production is by either vertical shafts or inclined adits (tunnels). The mined interval varies from 1.1 m (Hagersville) to 3.7 m (Iowa, Michigan, and Indiana).

Gypsum is extracted in most cases using the room-and-pillar method, in which pillars are left in place to support the roof strata, and the gypsum is removed in a checkerboard pattern. The extraction ratio, which is the proportion of material mined to material left in the supporting pillars, varies from 65% to 80%.

Drilling and blasting of gypsum in underground mines is similar to the methods used in gypsum quarries. The blasthole pattern, however, is drilled horizontally into the advancing face of a mine heading. The number of drill holes, orientation, depth, and sequence of blasting are designed to maximize breakage of the gypsum and to maintain the integrity of the adjacent pillars and immediate mine-roof strata. The roof strata are reinforced by roof-control fixtures, generally epoxy resin-grouted bolts, up to 1.5 m long. The resin-grouted bolts bind the roof strata together to form an integral beam that is stronger than the individual strata.

Continuous miner technology, popular in coal-mining operations, is also currently being deployed in a few specific instances. Although more capital investment intensive, continuous miners eliminate the need for drill and blasting and so forth and lower extraction costs.

Underground gypsum mines are generally very stable. For example, long-term measurements of roof and pillar convergence (vertical closure) at the USG Corporation mine at Sperry, Iowa, indicate that the structure should be stable for hundreds of years. An underground gypsum mine near Grand Rapids, Michigan, is currently being used as a computer network security center (Sharpe and Cork 2006). Table 2 shows a generalized list of mines by state groupings.

Rock Processing

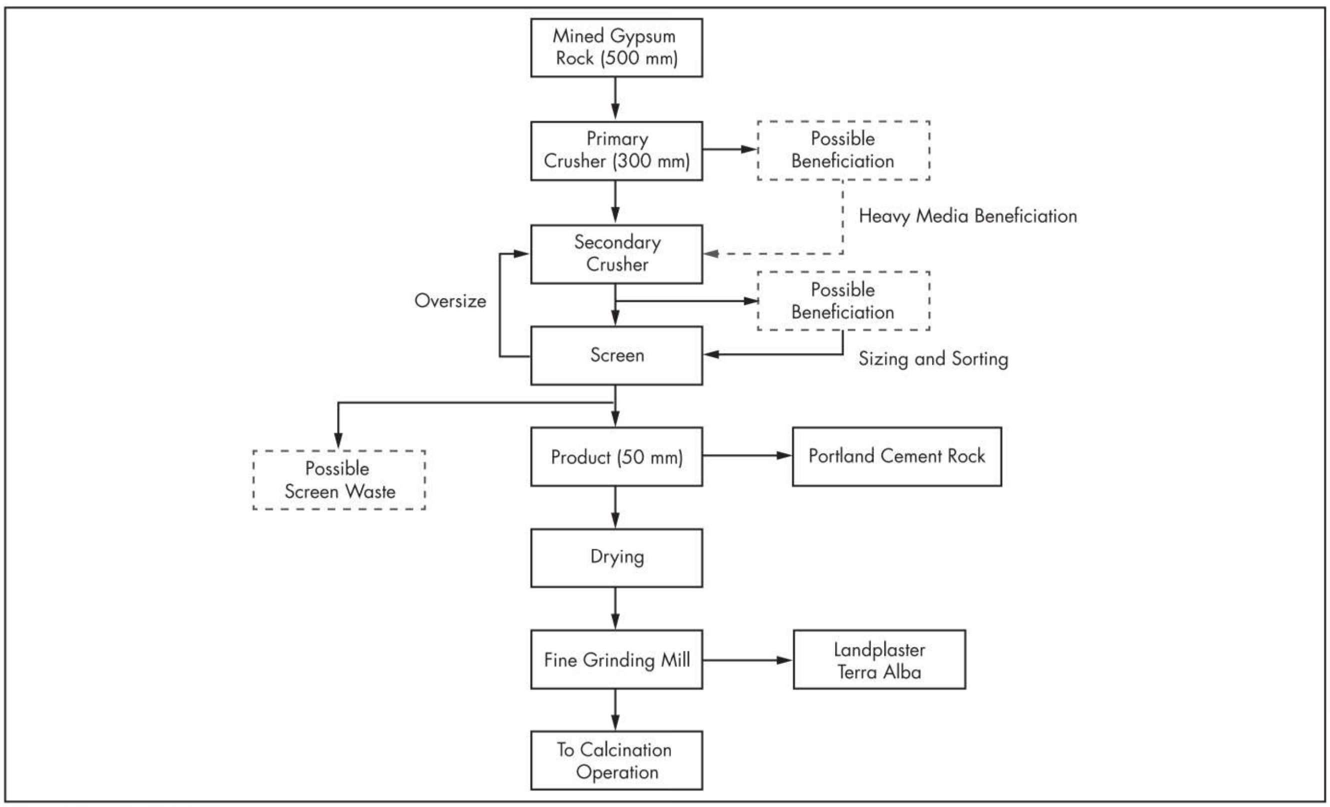
Figure 1 shows the processing steps for gypsum rock. After mining, gypsum rock is moved through a primary crushing operation. The primary crushing is accomplished by gyratory, jaw, roll, or impact crushers, depending on the size of the mine run rock, the desired throughput, and the type of subsequent processing. Secondary crushing is done with a variety of standard units, but hammer mills, roll-type, and cone-type crushers are most commonly used. Fine grinding of uncalcined gypsum is generally accomplished by air-swept roller mills fitted with integral air separators for better particle size control, although high-energy impact mills with air classifiers also have been used.

Both primary and secondary crushing steps are usually conducted with vibrating screens in the circuit, in part to maximize crushing efficiency and to reduce the production of ultrafines, but also to recover portland cement rock, the first marketable product of gypsum processing. The particle size of portland cement rock will vary with the requirements of each individual cement plant, but in the United States, it most often falls within a range of 38–51 mm top size by 6–13 mm bottom size.

Table 2 Location of gypsum mines in the United States*

State	2014 Active Mines	2014 Quantity, thousand t	2014 Value, thousand $	2015 Active Mines	2015 Quantity, thousand t	2015 Value, thousand $
Arizona, Colorado, and New Mexico	7	1,210	10,900	6	1,040	9,300
Nevada and Utah	6†	W‡	W	9	2,110	25,200
Arkansas and Louisiana	2	W	W	2	W	W
California	5	689	6,030	4	690	5,930
Iowa and Indiana	5	1,410	12,500	4	995	8,550
Michigan	3	233	2,050	2	W	W
South Dakota and Wyoming	3	W	W	3	W	W
Kansas, Oklahoma, and Texas	20	8,300†	73,300†	20	8,780	71,500
Total	**51†**	**14,900†**	**132,000†**	**50**	**15,200**	**135,000**

Source: Crangle 2016
* Data are rounded to no more than three significant digits; may not add to totals shown.
† Revised.
‡ Withheld to avoid disclosing company proprietary data; included in "total."



Adapted from Henkels 2006
Figure 1 Gypsum rock block flow diagram

In many cases, the purity or quality of gypsum as mined is sufficiently high that it can be used without upgrading; however, beneficiation techniques are sometimes used to meet the required specifications. The most common form of beneficiation is simple classification by particle size with dry screening, air separation, or other means wherein a size fraction containing a significant portion of impurity is discarded. In general, this method is used to reduce clay or sand (soil) impurities. In some cases, impurities that are harder than gypsum, and hence tend to concentrate in the coarser size fractions after crushing, can also be reduced by screening.

Drying (the removal of free moisture) may occur either before or after the secondary crushing stages, depending on the amount of free moisture in the mine run rock. Crushed gypsum is difficult to handle. Material measuring 5 mm is not free-flowing, particularly if wet, so drying is often required to assure the free flow of material in subsequent steps. This most often is accomplished in rotary dryers and must be carefully controlled so that the temperature of the rock does not exceed 49°C, the point at which dissociation of combined water begins to take place.

Beneficiation. Washing and/or wet screening is used in a few cases, particularly where the need for whiteness exists. Heavy media sink–float separation for the removal of impurities is currently employed at one operation in Canada. In many cases, gypsum is amenable to other gravity methods of beneficiation including froth flotation. In general, the relatively high cost of these methods and the availability of high-quality deposits and synthetic gypsum usually eliminate the need for beneficiation. Nevertheless, lower-cost beneficiation techniques continue to be investigated based on narrow rock sizing and adapting color-sorting techniques popular in waste recycling centers.

GYPSUM CHEMICAL AND PHYSICAL CHARACTERISTICS

Chemical Properties

Gypsum and anhydrite are able to undergo repeated dehydration and hydration, depending on the depth of burial and availability of water. Gypsum will begin to thermally decompose into the metastable species, calcium sulfate hemihydrate ($CaSO_4 \cdot ½H_2O$), in heated air higher than 70°C and at 1 atm of pressure. Differential thermal analysis curves show two endothermic peaks between 100° and 200°C (Deer et al. 2013). The first peak represents the loss of 1½ molecules of water during the formation of calcium sulfate hemihydrate. Further heating totally dehydrates gypsum, forming dead-burned (anhydrous) anhydrite ($CaSO_4$), which is used as a filler in plastics and as a moisture absorbent. The second decomposition peak occurs when the remaining one-half molecule of water is removed. Calcining processes for the manufacture of gypsum wallboard and plasters involve heating gypsum to ~155°C for 1–3 hours, during which time calcium sulfate hemihydrate forms.

Heating gypsum liberates water vapor, which helps hinder the spread of fire. Specialized types of wallboard are formulated and manufactured for use as a firestop between multifamily housing units, in the lining of elevator shafts, and in the walls and ceilings between living spaces and garages.

Gypsum's solubility in fresh water is approximately 150 times greater than that of limestone. This chemical characteristic provides a source of calcium and sulfur when gypsum is used in agricultural applications. The ionic exchange capability of calcium for sodium prevents the buildup of alkali in soils.

Although gypsum is a very soft mineral, specialized methods of calcining have been developed to manufacture denser, harder crystals. For most uses, the gypsum is ground to a powder and heated in a continuous kettle or batch kettle at 1 atm of pressure. This method of calcining produces anhedral, rough, splintered crystals known as *beta calcium sulfate hemihydrate*. This product is used in the manufacture of wallboard and industrial and construction plasters. The calcination of 12–250-mm sized, high-purity gypsum in an autoclave at elevated pressure produces dense, euhedral crystals of *alpha calcium sulfate hemihydrate*. This product is used in specialized plasters and cements for art and statuary, architectural applications, industrial prototype modeling, and road and floor repair (Sharpe and Cork 2006).

Physical Properties

The softness of gypsum is its most prominent physical feature. It is distinguished by its softness (Mohs hardness of 2) and three distinct cleavage planes. Anhydrite is distinguishable from gypsum anhydrite and has a hardness of 3.5 on the Mohs scale. Anhydrite rock is usually darker in color than gypsum rock (Sharpe and Cork 2006).

MINERAL USAGE

The earliest known use of gypsum plaster dates back some 8,000 years with the discovery of its use in Anatolia. Around 3,700 BC, Egyptians observed that gypsum rock, when exposed to fire, broke down into a powder that, when mixed with water, would form a putty that could be plastered on a rough mud brick or stone wall to make a smooth finish. Iranians, Babylonians, Greeks, and Romans were familiar with the art of gypsum plasters as well. Examples of its use include the walls of Jericho, the pyramid of Cheops, the palace of Knossos, and the decorated interior walls of Pompeii.

Gypsum was used in a limited way for ornamental purposes down through the centuries. Gypsum plaster did not achieve wide acceptance because of its quick (25–30 minutes) setting or hardening time that made it difficult to use. The first real understanding of gypsum chemistry was developed in France about 1760, and the gradual growth of its present utilization dates from that time. However, a craft so firmly steeped in tradition was slow to accept scientific inference, so that only in the last relatively few decades has gypsum manufacture developed into a modern industry. Today, a worldwide industry has been built on the mining and processing of this versatile mineral.

The primary use of gypsum worldwide is in the manufacture of construction plasters and portland cement. However, the principal use of gypsum in North America is in various types of wallboard panels. For example, ~90% of the total gypsum produced in the United States is used in wallboard and construction plasters (Sharpe and Cork 2006).

Gypsum is a very versatile mineral that can be used in the manufacture of several hundred products. Processing methods vary from simply crushing and sizing of quarry-run gypsum to specialized methods of calcination in closed pressure vessels.

The following sections describe in more detail the process steps and various mineral uses of gypsum in general order of added-value processing.

Uncalcined Gypsum

Gypsum that has been processed only by grinding and sizing is known as *land plaster*, *portland cement retarder*, and *terra alba*. Land plaster is used for agricultural gypsum and a raw feedstock for manufacturing wallboard and plasters. Portland cement retarder is used in the manufacture of portland cement. Terra alba is used in food and pharmaceutical applications.

Uncalcined gypsum is principally used as a retarder for portland cement, soil conditioner, mineral filler, and in other minor industrial applications. Approximately 25% of the gypsum mined in the United States is used in these markets. In countries where building practices differ from those in the United States and Canada (poured concrete, block, or brick), however, the relative usage of gypsum varies widely.

Although calcium sulfate deposits are the world's largest sulfur resources, only minor quantities of gypsum and anhydrite have been used to produce sulfur or sulfur compounds. This use is accompanied by a unique, site-specific set of economics, because sulfur is generally available from nongypsum sources at lower cost.

Portland Cement Rock

Quarry-run anhydrite or a blend of gypsum and anhydrite may be used as a portland cement rock product. Portland cement manufacturers use a variety of products from gypsum, anhydrite, or an anhydrite–gypsum blend, depending on the manufacturing process. The primary function of gypsum or anhydrite in portland cement is to control the setting time of the finished product. The SO_3 content of the portland cement rock is the most important quality parameter.

Adding calcium sulfate also controls the early strength characteristics of cement and product shrinkage during drying and curing. Approximately 3–5 wt % of calcium sulfate compounds are ground with clinker to form portland cement.

Gypsum also aids in the grinding of clinker by reducing the tendency of fine particles to agglomerate and adhere to the walls of the mill and grinding media (Hansen et al. 1988). Gypsum is much softer than clinker, is easier to grind, and has a much greater fineness (surface area) than clinker. Portland cement rock is typically ground to a particle size of 6–65 mm. Calcium silicates and aluminates that constitute clinker have negatively charged oxygen ions on the crystal surfaces. The hydrogen ions in the water molecules of the gypsum particles bind to the negatively charged clinker particles. The neutralization of the electrical charges by the attraction of the gypsum to clinker particles reduces the tendency for agglomeration.

Road Rock

Where alternate economical sources are limited, mixtures of anhydrite and gypsum rock (–19 mm and –51 mm are the typical grades sold) are used (e.g., in northwest Oklahoma) for temporary roads needed for energy exploration. Temporary roads are needed to access drilling sites for natural resources (oil and natural gas) and in the development of wind farms.

Glass Batch

Relatively pure uncalcined gypsum, depending on glass-batch chemistry, can also substitute for salt cake (sodium sulfate) in glass manufacturing. Thermal decomposition of gypsum in the glass melt produces sulfur dioxide as well as oxygen. The oxygen reacts with any free or reduced sulfur to form additional sulfur dioxide. Increasing the amount of gypsum in the glass batch decreases the sulfur content in the melt and results in a lighter-colored glass. Iron pyrites and carbon or blast-furnace slag are commonly added to the melt to manufacture amber-colored glass. Green-colored glass has a natural amber hue. Adding gypsum provides a source of sulfate in soda–lime glass. Decomposition of gypsum produces sulfur dioxide, which, in low concentrations, removes seeds and forms a clear glass. Surface scum can form on molten glass because of improper flow conditions in the furnace, especially near the bridge wall. The presence of coarse sand and stratification of the raw materials in the batch may result in selective melting and the formation of a surface scum. Gypsum added to the glass melt reacts with sodium carbonate to form sodium sulfate. The sodium sulfate melts and reacts with free silica to form sodium silicate, which in turn separates from the molten glass and floats on the surface. The gypsum sold for this application is normally sized at about 1.6 mm.

Agricultural Gypsum

Gypsum provides several benefits in agriculture. The specifications of agricultural gypsum are primarily related to the degree of fineness (particle size and surface area). As gypsum dissolves, it is a source of elemental calcium (25% by weight) and sulfur (20% by weight). Gypsum has a neutral pH (7.0) and is 150 times more soluble than ground limestone. Finely ground agricultural gypsum permits rapid dissolution and absorption by plants. Long-term availability of these elements during a growing season can be accomplished by applying agricultural gypsum of multiple particle sizes. Finely ground gypsum (100% passing through a 425-mesh screen) can also be dissolved in irrigation water for easy application. Generally called land plaster, this material can be produced from either gypsum or anhydrite and is usually ground in air-swept roller mills. The principal purposes for applying gypsum on agricultural land are to

1. Improve the structure or physical condition of soil by breaking down compacted clays, which, in turn, increases porosity and aids drainage;
2. Supply neutral, soluble calcium for peanuts, tomatoes, and other crops;
3. Supply sulfur quickly from available sulfate;
4. Neutralize alkaline soils;
5. Reduce high sodium salt content in irrigation waters;
6. Improve availability and utilization of nitrogen;
7. Act as a flocculating agent to clear up muddy farm ponds; and
8. Stimulate growth of soil microorganisms.

In other agricultural uses, land plaster, either in the dihydrate or anhydrous form, is often added as an ingredient in formulating feeds and feed premixes for beef cattle, dairy cows, and sheep. As a feed supplement, it supplies total sulfur requirements in safe, easy-to-mix form; increases the efficiency of nonprotein nitrogen in urea feeds; is an ideal supplement for ensilage enhancers; and is an effective regulator for self-feeding stock on the range.

Terra Alba

Terra alba is white, high-purity, uncalcined gypsum that has numerous uses in the food and pharmaceutical industries. It is made by fine grinding and air separation of gypsum with a purity of greater than 97%. Terra alba has a minimum calcium content of 23% (by weight). It is used to buffer the pH and reduce the hardness of water in brewing beer; as a calcium supplement and enrichment in baked goods including bread; as a diluent and inert extender in pharmaceutical products such as aspirin tablets; and in canned vegetables, cheeses, and artificially sweetened jellies and preserves. Terra alba gypsum is also used as a carrier for insecticides and micronutrients; granulated and pelletized gypsum is produced in limited quantities for these purposes.

Food- and Pharmaceutical-Grade Products

Gypsum is an approved additive on the Food and Drug Administration "Generally Recognized as Safe" listing of food additives. The use of gypsum in specific food products is described in Title 21, Part 184 of the Code of Federal Regulations (21 CFR 184.1230). The permitted amount of gypsum allowable in different types of foods is defined in the Food Chemical Codex in the United States and the National Formulary in the United Kingdom (Sharpe and Cork 2006).

Calcined Gypsum

The greatest utilization of calcined gypsum is in the manufacture of wallboard and the formulation of plasters for building markets. Beta hemihydrate gypsum or stucco is by far more common than alpha hemihydrate. Beta stucco is calcined at atmospheric pressure conditions and is suited for the construction applications where high early strength development is necessary. Alpha hemihydrate is normally calcined under pressure, and it makes a denser, higher strength cast; it is preferred for industrial uses where these characteristics are important. Other factors considered in the utilization of these two forms are cost (beta is considerably less expensive to make) and water demand (alpha requires less excess water, over and above that necessary for rehydration, to make a slurry of equivalent consistency or viscosity) (Henkels 2006).

Gypsum that is chemically transformed by heat or pressure to remove three-fourths of the water of crystallization is known as calcium sulfate hemihydrate, stucco, and plaster of Paris. The chemical reaction is the same for both alpha and beta stucco and is reversible at atmospheric temperatures and pressures:

$$CaSO_4{\cdot}2H_2O + \text{heat} = CaSO_4{\cdot}\tfrac{1}{2}H_2O + 1\tfrac{1}{2}H_2O$$

Many different products may be manufactured from alpha or beta hemihydrate or a mixture of both. The products are further mixed with portland cement, fiberglass, plastic resins, and other materials to produce products with high strength and density, fire and water resistance, and other specialized characteristics.

Alpha Hemihydrate

Alpha hemihydrate represents less than 1% of all gypsum hemihydrate produced. It is made by one of two methods and produces dense, euhedral crystals of calcium sulfate hemihydrate:

1. Relatively large-sized rock, anywhere from 12 to 250 mm, is loaded and calcined batchwise in an autoclave at elevated pressure (generally between 1 and 6 bar).
2. Finely ground land plaster or synthetic gypsum is mixed with water, and the resulting slurry is fed batchwise or continuously into a pressurized reactor. Reactor pressure is maintained between 1 and 4 bar. The calcined gypsum is then de-watered and dried with a filter belt or centrifuge and heated dryer.

Alpha hemihydrate is used in highly specialized plasters and cements for art and statuary, architectural applications, industrial prototype modeling, road repair, and flooring underlayment plasters.

Beta Hemihydrate

See Figure 2 for a flow diagram of a gypsum mill/beta calcination operation. Beta hemihydrate is by far more common than alpha hemihydrate and is produced by a few generalized methods, including the following:

- Finely grind gypsum (95% –100 mesh) in a roller-style mill and then calcine at temperatures between 140° and 160°C in vertically oriented, cylindrical steel kettles at atmospheric pressure. The calcination can be a continuous process or a batch process. Continuous calcining of land plaster is predominantly used for producing stucco for wallboard. Batch calcining is usually used for manufacturing construction and industrial plasters. The beta hemihydrate calcining process produces rough, fractured, fragmented particles.
- Calcine sized rock (–50 mm) in a long horizontally oriented rotary style vessel at ~150°C exit temperature and then fine grind (98% –100 mesh) the calcined rock. This is a continuous method and the stucco is generally used for construction plasters.
- The preceding calcining methods involve two separate unit operations. Another general approach involves one unit operation where the fine grinding and calcining occur simultaneously. Sized rock (typically 50 mm) is fed to an air-swept heated hammer- or roller-style grinding mill. Calcination takes place as the material is being ground and conveyed to a receiving dust collector. Control temperatures in the heated air stream after grinding are

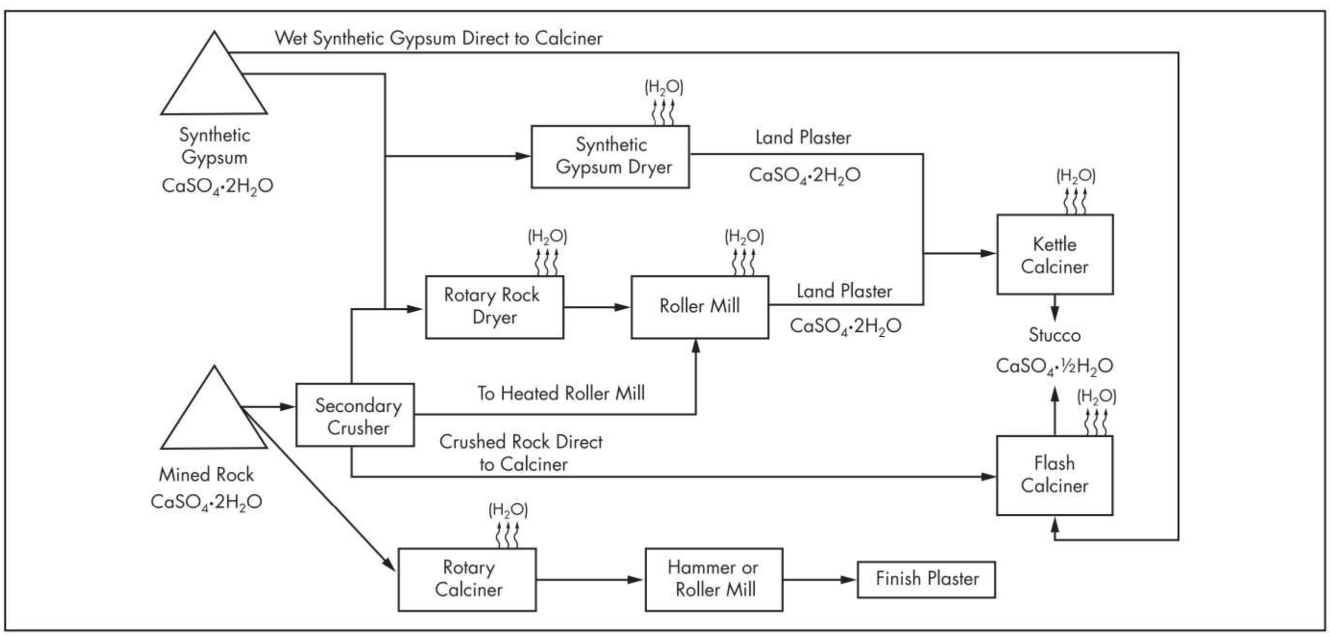
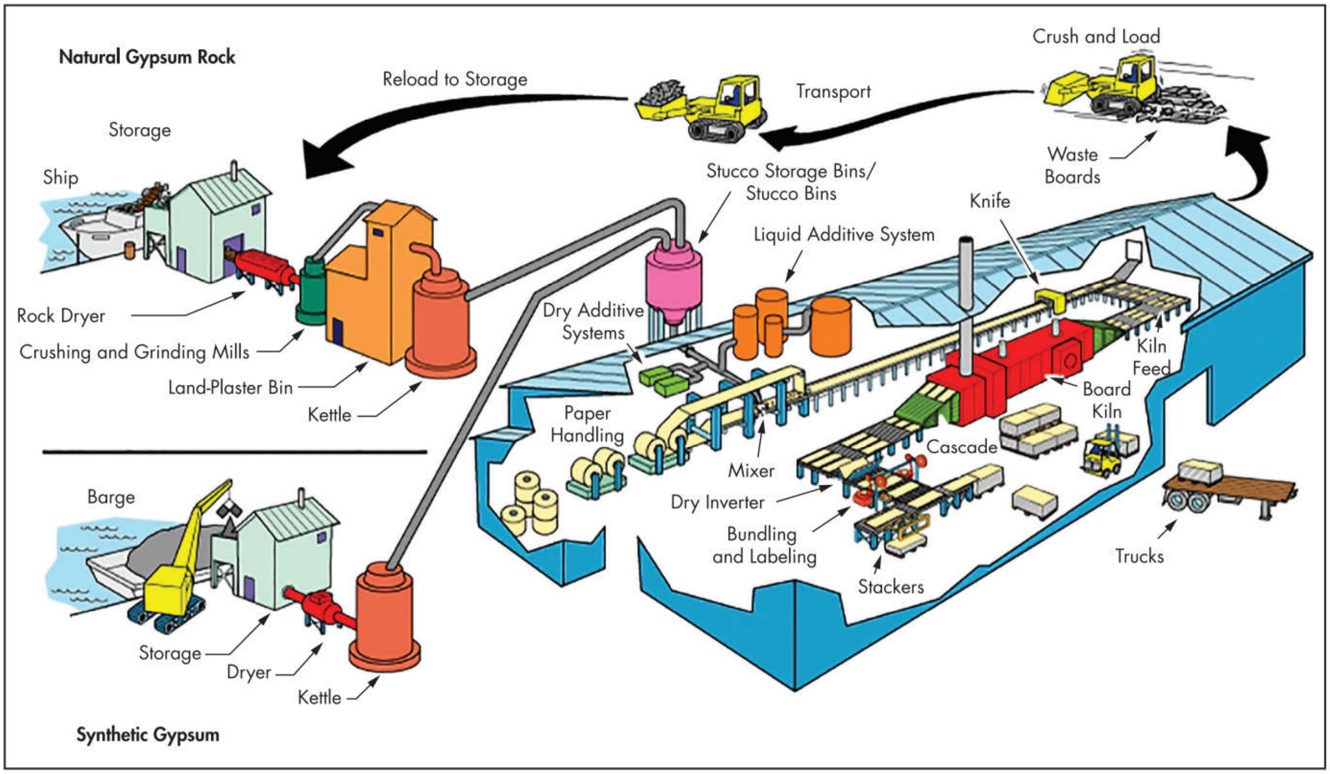


Figure 2 Gypsum mill/beta calcination operation



Source: Henkels 2006

Figure 3 Conceptualized drawing of a wallboard operation

typically in the 150°–165°C range. This is a continuous process and referred to as *flash calcination*.

In all beta calcination cases, as the molecular water is removed during calcination, it is released in the form of steam vapor.

Plasters. Plaster may be alpha hemihydrate, beta hemihydrate, or a mixture of both crystal phases. White art plasters used in schools or arts and crafts classes are made from beta hemihydrate.

The process of manufacturing pottery and ceramic products involves several steps from preparation of an initial model to the final product. An original block mold is manufactured from the finished model of the product to be manufactured. Then a case mold is made from the block mold. The case mold becomes a die for fabricating multiple working or production molds. The block and case molds are typically manufactured from alpha hemihydrate. The use of alpha hemihydrate allows for the production of dense, hard, strong, and durable molds that can be intricately detailed. Working molds, which are used for mass production, are manufactured from a blend of alpha and beta hemihydrate or from alpha hemihydrate. Although most construction plasters are made from beta hemihydrate, in certain cases, blends of beta and alpha are used, especially where higher compressive strengths are required.

Gypsum wallboard. Wallboard is also commonly known as *plasterboard* in markets outside of North America. Figure 3 is a conceptualized drawing of wallboard production. Three possible sources of raw material are shown: (1) natural gypsum rock delivered from an on-site quarry or an underground mine, (2) synthetic gypsum delivered from a nearby power plant or by barge, and (3) off-specification wallboard recycled into the manufacturing stream. The dry components are mixed with water and other liquid additives in a high-energy mixer designed for a continuous flow-through of material. The resulting slurry is dropped on a moving strip of paper, the edges of which are turned up to form a wide, shallow trough. This mass then moves under a second strip of paper, and the roughly formed board moves between edge guides and under a forming plate, which precisely controls the specified board thickness. The edges of the bottom paper are turned over to form square or rounded corners, and an adhesive is added to bond the top paper to the lower paper along its edges. The thickness of the board can be varied by raising the forming plate. The now fully formed board moves along on a flat conveyor belt up to a few hundred meters long. The length of the board line is designed to provide sufficient time (2–5 minutes) for the stucco to set. At that point, the moving strip is cut at specific intervals by a rotating knife to produce individual boards for drying in a kiln to remove excess free moisture. The speed of the board line normally varies between 0.5 and 3.0 m/s depending on machine design and the wallboard type being made.

Anhydrous Gypsum

In addition to the hemihydrate industrial plasters described earlier, several products are made from calcium sulfate with no water of crystallization. In this process, gypsum is calcined at higher temperatures past the hemihydrate stage, and all the chemical water is removed. The chemical reaction can occur in one step:

$$CaSO_4{\cdot}2H_2O + \text{heat} = CaSO_4 + 2H_2O$$

Or the reaction can happen in two steps in which first the gypsum is calcined to hemihydrate:

$$CaSO_4{\cdot}2H_2O + heat = CaSO_4{\cdot}½H_2O + 1½H_2O$$

Then more heat is added to convert the hemihydrate to anhydrite:

$$CaSO_4{\cdot}½H_2O + heat = CaSO_4 + ½H_2O$$

As in beta hemihydrate calcination, the molecular water removed during calcination is steam vapor.

Soluble anhydrite. Soluble anhydrite is made when the calcining temperature has been increased to ~200°C. This material has a high affinity for water, making it an efficient drying agent. It is sold in gradational particle sizes for use as a desiccant in laboratory and commercial applications.

Insoluble anhydrite. When the calcination process is carried to a temperature of ~600°C, a dead-burned or insoluble anhydrite product is formed, which is used for industrial filler. Dead-burned gypsum is preferred for some filler uses over uncalcined gypsum, particularly where the temperature of the product in which the filler is used exceeds 50°C, which is the point at which natural gypsum begins to release water of crystallization. Dead-burning usually produces a whiter product and is preferred where color is important.

Dead-burned gypsum fillers are used as a source of calcium in food products, and for yeast and beer processing. They also serve as diluents or extenders in such compositions as pharmaceutical pills, rubber, artificial wood, paper, and pigments. Dead-burned gypsum is used as filler in thermoplastics such as polyvinyl chloride (PVC) products: vinyl siding, window frames, moldings, conduit, and pipe. The filler imparts acid resistance and low electrical conductivity. It is also used in food packaging and as an additive in specialty portland cement compounds.

Keene's cement. A generic name for dead-burned construction gypsum plasters, additives are used to set and harden Keene's cement after mixing with water. The usual set specifications fall in the range of 4–12 hours. Its major use is in a wall plaster where extra density, strength, and hardness are desired. It is made in only a few locations and only in small quantities.

QUALITY ASSURANCE AND QUALITY CONTROL ISSUES

The manufacturing processes for wallboard can be adjusted for a wide range of gypsum purity. Wallboard can be made from relatively low-purity (low 80s) or very high-purity (high 90s) gypsum. The key is that the purity of the gypsum supplied from the mine or quarry, as well as the calcined gypsum stucco, should be consistent. Formulating calcined stucco with air-entraining agents can decrease the weight of the finished wallboard, enhancing its purity.

Most gypsum contains 10%–15% impurities, although some deposits may be exceptionally pure (i.e., +95%) or somewhat impure (i.e., 80%). In general, the amount of impurity that can be tolerated depends on (1) the type of impurity, (2) the product being manufactured, and (3) the competitive situation. Impurities are usually separated into three categories, based on their effect on the manufacturing process and finished products:

1. Insoluble or relatively insoluble minerals such as limestone, dolomite, anhydrite, anhydrous clay, silica minerals
2. Soluble evaporite minerals, including chlorides (halite, sylvite, etc.) and sulfates (mirabilite, epsomite, etc.)
3. Hydrous but insoluble minerals (e.g., the montmorillonite group of clays)

PRODUCT GRADES AND SPECIFICATIONS

Gypsum is used in highly diversified industries and products. Therefore, grades and specifications vary according to the industry and end-use requirements of customers. Gypsum used in construction products, food, and pharmaceutical products must meet stringent regulations.

Construction Products

ASTM International defines the specifications for testing uncalcined gypsum and construction products manufactured from gypsum. ASTM C471M-17 defines the testing methods for the chemical analysis of gypsum. ASTM C472-99 defines the standard testing methods for the physical properties of gypsum, gypsum plasters, and gypsum-based concrete. In 1999, ASTM began to phase in a new international standard for interior and exterior gypsum wallboard products and veneer plasters that combined nine separate earlier standards. ASTM C1396 eliminated inadvertent inconsistencies in the separate standards.

Packaging

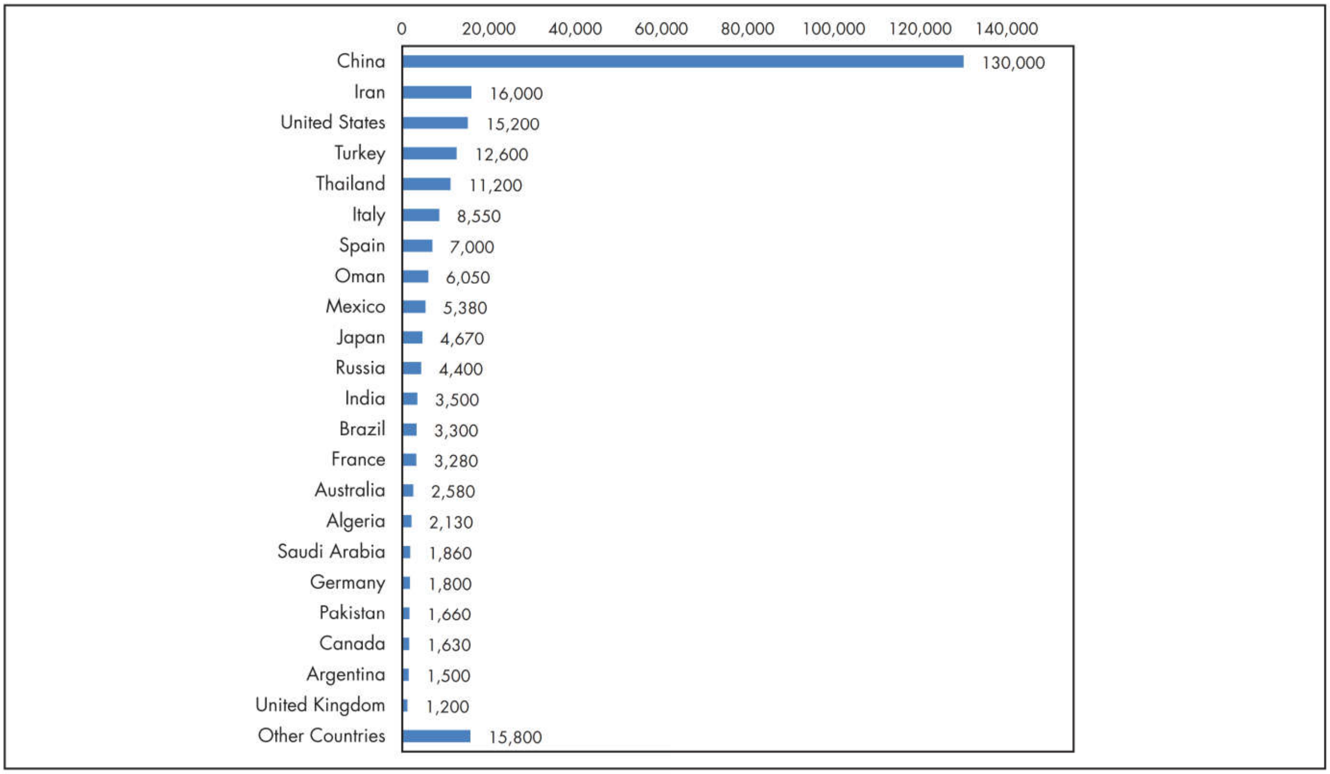
Gypsum is used in more than 400 products, and therefore many different forms of packaging are used for distribution to customers. Raw ground gypsum (land plaster) for agricultural uses and portland cement rock is distributed primarily by bulk truck. Wallboard panels are loaded onto trucks or railroad cars for distribution. Construction and industrial plasters are packaged predominately in paper valve bags in weights varying from 1 to 45 kg, but are also packaged in intermediate bulk containers, flexible intermediate bulk containers, and in certain instances, bulk trucks.

ECONOMIC IMPORTANCE AND OUTLOOK

Gypsum is normally mined in open pit operations from deposits widely distributed throughout the world and tends to be consumed within the many countries where it is produced. Less than 20% of the world's crude gypsum production is estimated to enter international trade. Only a few countries, such as Canada, Mexico, Spain, and Thailand, are major crude gypsum exporters. Of these, Canada and Mexico are significant exporters because of their large deposits in proximity to gypsum-consuming facilities in the United States.

Pricing

By far, China produces the most gypsum in the world. China produced more than 129 Mt (million metric tons) in 2013, and an estimated 132 Mt in 2014. The United States is the world's second-ranked producer and consumer of gypsum. Production of mined crude gypsum in the United States during 2014 was estimated to be 17.1 Mt, an increase of 5% compared with 2013 production. The average price of mined crude gypsum was \$9/t. Synthetic gypsum production in 2014, most of which was generated as an FGD product from coal-fired electric power plants, was estimated to be 13.2 Mt and priced



Source: Crangle 2016

Figure 4 Crude gypsum production by country in 2015, in thousand metric tons

at approximately \$1.50/t. In 2014, 47 companies mined gypsum in the United States at 118 mines with plants in 17 states. U.S. gypsum exports totaled 70 kt (kiloton), and imports were 3.5 Mt (Crangle 2014). Figure 4 lists the top 22 gypsum producers by country.

Gypsum is a low unit-value, high place-value industrial mineral, and its ultimate value is based on value-added processing. The lowest prices are for ground gypsum used for portland cement and agricultural gypsum. Calcining gypsum for use in manufacturing wallboard or construction and industrial plasters increases the price significantly. The most valuable products include specialty dental, orthopedic, and industrial plasters; food and pharmaceutical-grade gypsum (terra alba); and industrial gypsum cement. Table 3 lists the average crude gypsum prices in the United States between 1994 and 2014.

There is no recognized commodity value of a ton of raw gypsum. Although mining costs are relatively low, the energy-intensive post-mining processing and ultimate end use add significant value to the products made from the gypsum. Freight costs are a significant factor in marketability of a gypsum deposit.

Gypsum deposits are distributed throughout much of the world, and gypsum is produced in more than 90 countries (Crangle 2014). The value of a deposit of gypsum depends on geological, mining, engineering, and other factors.

The utility and value of a gypsum deposit can change over time as technological innovations in mining and manufacturing occur and new products are developed. Factors that must be considered when evaluating a gypsum resource for potential development, mining, manufacturing, and marketing include the following:

- Proximity to market area—because gypsum has a low unit value, an ideal deposit of gypsum would be located within the heart of a growing metropolitan area.
- Transportation—this includes the shipment of raw and finished materials by truck, train, ship, or barge; the import of paper used in wallboard manufacturing; transportation of finished products to jobsites, distributors, and retail outlets; and the potential for backhauls of raw materials or finished products.
- Fuel and utilities including water—wallboard manufacturing is highly energy intensive and requires an infrastructure of electrical service and a source of fuel for calcination and drying of wallboard panels.

There is no foreseeable shortage of either gypsum or anhydrite resources in North America or the world. However, there are instances where it may be difficult to find gypsum that can be considered economic at a given time and location, a problem that has its roots in place value.

Because of its widespread occurrence and huge potential reserves, and also because its uses are such that it is not basic to survival in a national emergency, gypsum is not considered a strategic mineral. This has permitted natural economic factors to prevail in the development of the mineral worldwide, which overall is a healthy situation that should continue to prevail.

Gypsum mining does not result in some of the environmental issues that are commonly associated with mining, such as acid-mine drainage, heavy metal contamination of surface water or groundwater, or the use of cyanide in heap leaching. Gypsum mines and quarries are regulated by numerous local, state, and federal agencies for compliance with environmental and safety regulations (Sharpe and Cork 2006).

Table 3 Average gypsum price in the United States

Year	Average Crude Rock fob* Mine Price, $US/t
1994	6.70
1995	7.29
1996	7.10
1997	7.11
1998	6.92
1999	6.99
2000	8.44
2001	8.44
2002	7.31
2003	6.90
2004	7.21
2005	7.48
2006	8.83
2007	7.50
2008	8.70
2009	7.40
2010	6.90
2011	8.20
2012	7.70
2013	7.50
2014	8.00
2015	7.80
2016	8.00
2017 (estimate)	8.20

Data from USGS 1995–2018
*fob = free on board.

The use of synthetic gypsum is expected to continue to climb worldwide and negatively impact the demand for mined rock. In the United States, however, the availability of inexpensive natural gas is reducing the number of operating hours for coal-fired power plants and synthetic gypsum production. In addition, increased environmental regulations on coal combustion by-products may impact the availability of synthetic gypsum. It is expected that synthetic gypsum usage has reached a plateau or will decline modestly in the coming few years in the United States. These two factors should increase the need for mined rock in the United States in the future.

The use of recycled wallboard will continue to grow. Off-specification wallboard is commonly recycled back into the manufacturing stream. Environmental regulations often require the plants to be zero discharge. Therefore, all off-specification wallboard is recycled. Also, it is expected to become more commonplace for wallboard plants to accept customer waste from new construction. This will also have some impact on reducing demand for mined gypsum.

A North American trend toward reducing wallboard weight will continue and is expected to expand into construction markets worldwide. This will reduce the gypsum used per sheet of wallboard. However, as emerging markets continue adopting Western construction practices and increase gypsum wallboard use, it will more than compensate for lighter wallboard products.

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