Gypsum

Connecting Science and Technology

Richard A. Kuntze

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Gypsum:
Connecting Science and Technology

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Preface

The purpose of this manuscript is to close a perceived gap between the academic and applied aspects of gypsum science and technology since a textbook covering these subjects is not available. Moreover, academic publications seem to deal with relatively narrow subjects and are concerned with cataloguing research results with little applied interpretation. In contrast, the practical literature is dispersed over a wide range of sources and gives the distinct impression of being unfocused. It is hoped that closing this gap will help to solve problems or to clarify situations that technologists and engineers may encounter and that may not necessarily be well understood.

Therefore, it is the intention to interpret the essential literature on gypsum and to place the information provided into its proper context. To achieve this, the characteristic properties of gypsum and cementitious materials derived from it have been discussed in terms of their strength and weaknesses, taking into consideration both historical and modern points of view. In any case, this manuscript is written in a manner which should make it acceptable and accessible not only to a specific audience but also to others generally interested in this subject.

An equally important reason for preparing this manuscript is the fact that misconceptions continue to resurface on key issues and these are unusually persistent. They touch on all categories from ancient history to modern properties such as dehydration, α-hemihydrate formation, water demand, aging and disintegration, rehydration and setting, as well as physical characteristics such as strength and gypsum board nail pull resistance. This has been the case since the time of Lavoisier and Le Chatelier in the 18th and 19th century, who first dealt with the dehydration and rehydration of gypsum in a modern scientific manner. A contributing factor has been the recent replacement of scientific research with current issues. Process research has become a most diluted and misquoted phrase. To a degree, the decline of gypsum research reflects the shift from gypsum plaster applied in the field to the manufacture of gypsum board in plants.

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It is obvious that a publication of this nature cannot be considered without recognizing the many people who have generously aided me during my involvement with gypsum research since 1955. Otto Schierholtz of the Ontario Research Foundation in Toronto introduced me to the subject of gypsum in general and to plaster retarders in particular. Also, Gil Gillespie of Gypsum, Lime and Alabastine Company in Caledonia, Ontario, as well as Barney Nies and Jack Summerfield of the United States Gypsum Research Center in Des Plaines, Illinois, have shared their knowledge over many years while I carried out contract research for their respective companies. I remember with particular gratitude that they encouraged publication of scientific papers, which was not common practice at the time. The members of the ASTM Committee on Gypsum made available their vast and detailed experience of gypsum and its application and who permitted me to serve as chairman from 1972 to 1985. I should also mention Graham Thayer who convinced me to function as chairman of several conferences on Natural and Synthetic Gypsum in Toronto from 1988 to 2000. Over most of these periods I have greatly benefited from a professional association with Franz Wirsching of Knauf Gypsum in Iphofen, Germany, with Bob Bruce of Bob Bruce and Associates, Nanaimo, British Columbia, and Peter Mayer of CertainTeed Gypsum. Peter Mayer also reviewed the manuscript and made many suggestions. I am indebted to all of them and many others for their insight and generosity. Of course, I alone am to blame for any errors and omissions that undoubtedly occurred with the preparation of this manuscript despite every attempt to avoid them.

Terminology

It is fairly well known that the English term gypsum is of Roman origin based on the Greek term *gypsos* for which various definitions exist. It is less well known that gypsum is also defined by archaic terms based on ancient usage, for example the location from which it is obtained such as alabaster, on descriptive terms such as the fibrous *satin spar*, or the specific application for which it is intended such as *selenite* and its transparent variety *Marienglas*. Since gypsum is a legitimate mineralogical term an attempt is being made in this manuscript to use it exclusively for the naturally occurring rock as well as synthetic gypsum and materials obtained from it by grinding, etc.

However, a distinction has to be made between the mineralogical term gypsum and the chemical term *calcium sulfate dihydrate*. Both are identical neglecting the impurities that may be present. *Calcium sulfate dihydrate* or just *dihydrate* is being used whenever purely theoretical concepts are being considered. It is therefore not uncommon to find the term *gypsum* used interchangeably with *calcium sulfate dihydrate*, even in modern scientific literature. This situation is being avoided in this manuscript and definitive terms are used wherever possible. This means that *gypsum* refers to practical considerations and *calcium sulfate dihydrate* to chemical or physical processes.

A similar situation exists with respect to the calcination of gypsum, that is, a heat treatment to produce stucco (first calcination stage) which consists largely of *calcium sulfate hemihydrate* or just *hemihydrate*. It should be noted that the term *stucco* is non-specific since it is also used for other cementitious materials based on hydrated lime or cement. If the heat treatment involves theoretical considerations of dihydrate the term dehydration is being used instead of calcination. This means that the term *dehydration* applies specifically to *dihydrate* whereas *calcination* is used for *gypsum*.

It should be noted that the term plaster is non-specific as well since it is being used for other materials such as hydrated lime, cements and a variety of other materials. However, for this manuscript, the term is used for plaster based on gypsum. Gypsum plaster is suitable for non-structural *interior* surfaces. In contrast to other materials it is not suitable for structural use or for *exterior* applications. Additives such as retarders and stabilizers are added to stucco to form *hardwall plaster*, which is mixed with perlite and vermiculite at the factory or sand and water in the field. In all these cases the term plaster is used, whether the material is dry or mixed with water. In addition, the term *plaster* applies to α-hemihydrate used for molding and medical/dental applications.

It is also common practice, particularly in Europe, to calcine gypsum completely to the second calcination stage which means that *insoluble anhydrite* is being produced. This dry material is referred to as *anhydrite plaster*, which is often blended with *stucco*. Additives, sand and water are added when this material is to be used as finishing plaster for various construction applications. The term *insoluble anhydrite* is employed mostly when this chemically active component is referred to specifically.

More importantly, most of the *stucco* being produced in North America is presently used as plaster for the manufacture of paper lined gypsum board (plasterboard). For this purpose it is mixed with additives, water and foam. The term *slurry* is used for this type of *plaster* because a larger quantity of mixing water (i.e. *gauging* water) is employed than that required to produce a plaster of normal consistency (ASTM C472-99). Therefore, *gauging* water is the amount of water mixed with stucco to produce a plaster with a flow property that is desirable for a specific application.

1

Introduction

1.1 Natural Gypsum

NATURAL GYPSUM CONSISTING MAINLY OF CALCIUM SULFATE DIHYdrate is a well-known common non-metallic mineral that occurs as a deposit of fairly soft and often impure rock. It was deposited from shallow seas as they evaporated about 200–300 million years ago, mostly during the Permian period. This deposition depends on pressure, temperature, and the concentration of other salts in solution. It is found in most areas near the earth surface and can be recovered relatively easily using quarries or shallow underground mines. Natural gypsum is normally white or light gray but depending on the impurities present can also be pink, dark gray, or almost black. The English term gypsum is taken from the Roman usage of the Greek "gypsos," apparently describing a material that does not burn, although there are other interpretations. The term may be based on the Arabic "jibs" or "jass," or the Akkadian (Mesopotamian) "yasser" or the Persian "gatch." (The hemihydrate mineral, called bassanite is found infrequently.)

It is common practice to classify gypsum according to its appearance because it is an ancient material and has been identified by rather archaic terms, allowing for sub-varieties that are often based on applications. For example, it can be identified as granular/massive, as satin spar (fibrous) or selenite (layered). Carving of statues, vases, and other artifacts were often carried out with a white and nearly translucent variety of fine-grained massive gypsum, called alabaster probably after one of its sources, Alabastron in Upper Egypt. The colorless, transparent variety of layered gypsum is cleavable. It can occur in relatively large plates that were used as window glass. When viewed through it, the sun gives the appearance of the moon and hence this variety of gypsum was called selenite. Again there are different interpretations. Similarly, the same variety of gypsum was used to protect religious images of Mary, originating the term "Marienglas" (Fig. 1.1). There are also non-commercial ornamental varieties of gypsum known as desert rose, rams horn selenite, etc.

1.2 Synthetic Gypsum

Synthetic gypsum is identical to natural gypsum from a chemical and crystallographical point of view. The difference between the two varieties of gypsum sources lies primarily in their physical state, which in turn depends on the origin or the manner of their formation. Synthetic gypsum is generally obtained as the final stage of industrial processes, where sulfuric acid is neutralized by a calcium salt, often $CaCO_3$. Most frequently, however, it is obtained as flue gas desulfurization (FGD) gypsum during the desulfurization of flue gasses from coal-fired power plants as FGD gypsum by the reaction of sulfur dioxide with a calcium salt. Normally calcium carbonate ($CaCO_3$) is used for this pur-

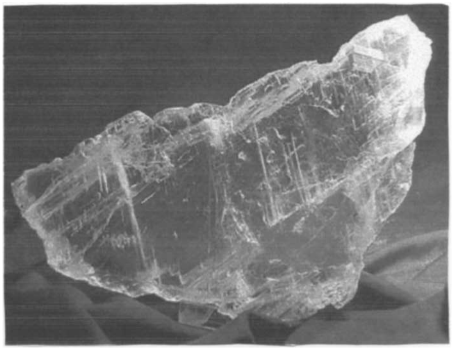

Fig. 1.1—Marienglas version of selenite gypsum.

pose or to a lesser extent calcium hydroxide ($Ca(OH)_2$). In these cases, gypsum is obtained as a filter cake in the form of wet, fine particles containing usually about 10 % water.

Therefore, the difference between synthetic gypsum and natural gypsum lies initially in the original physical condition, which dictates the subsequent process steps necessary for a particular application. That is, natural gypsum exists as solid rock, which must be crushed, ground, and dried prior to its subsequent calcination. In contrast, synthetic gypsum is already finely divided but it contains more free water than natural gypsum, which must be removed by drying. Sometimes synthetic gypsum is being agglomerated to facilitate storage, transport, or further processing. It may also be ground after drying, with or without agglomeration, to change crystal shape and size distribution.

Another significant difference between synthetic gypsum and natural gypsum can be the type and amount of impurities that must be closely monitored when they occur. For example, *p*H, chloride content, and carry-over carbon may be of concern if either FGD gypsum is to be used for gypsum board manufacture. The presence of crystalline silica, present in both natural and synthetic gypsum that may be of concern can best be determined by differential thermal analysis or differential scanning calorimetry. Phosphoric acid byproduct gypsum has been largely eliminated from further processing because of the presence of residual phosphates that interfere with the setting of calcined gypsum (stucco). However, the limiting factor for some types of phosphogypsum is the presence of radium-226.

1.3 Insoluble Anhydrite

It is currently accepted that gypsum, mainly calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$), is deposited initially and that insoluble anhydrite ($CaSO_4$), the anhydrous analogue of gypsum, is formed in situ from that gypsum by subsequent dehydration. This dehydration involves a rearrangement of the crystal lattice with complete loss of water that can occur when the temperature rises due to increases in pressure. However, this subject has always been controversial and numerous theories have been proposed to explain the mixed occur-

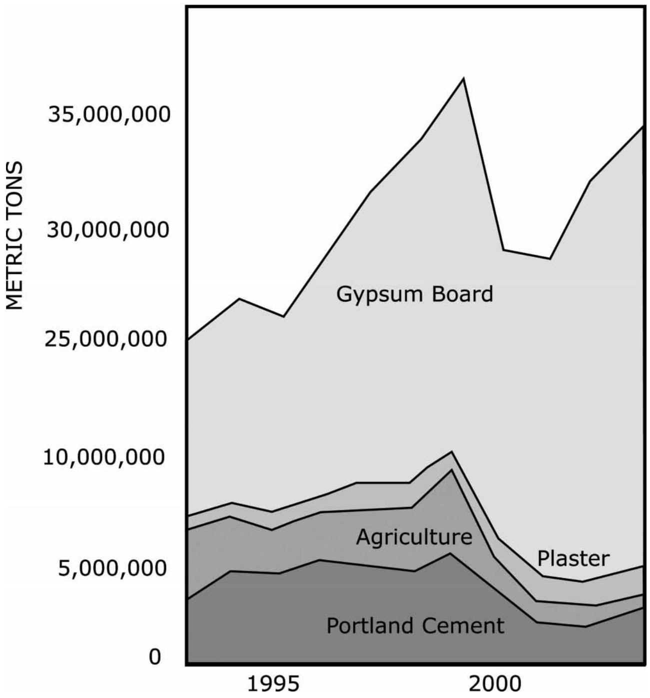

Fig. 1.2—End use of gypsum.

rence of gypsum and anhydrite in layers, lenses, etc. These views are being complicated since it is possible that natural anhydrite changes back into gypsum by subsequently reacting with groundwater or water seeping in from the surface. In any case, insoluble anhydrite occurs in the same deposit as gypsum, sometimes distributed unevenly and in substantial amounts.

Insoluble anhydrite can also be produced by heating gypsum at about 350°C (662°F) and above. This material is identified as thermal insoluble anhydrite to differentiate it from the natural variety although both materials are virtually indistinguishable. However, thermal insoluble anhydrite may exhibit longer setting times depending to the temperature employed during production and the length of exposure time. Synthetic insoluble anhydrite is obtained as fluoroanhydrite in the production of fluoric acid. In at least one situation, this material is being hydrated and used as gypsum.

1.4 Utilization

Natural gypsum has been used over the ages in an uncalcined form as blocks for construction purposes similar to ashlars and as the raw material to carve statues, vases, etc. More recently, utilizations of uncalcined gypsum have involved application as setting time regulator for Portland cement, as fertilizer, and for soil amelioration. Smaller amounts are used as functional filler for paints, polymers or paper (Fig. 1.2). These applications are discussed further in

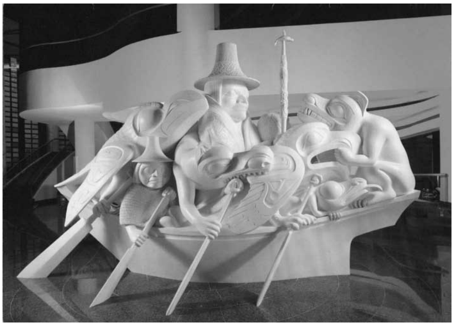

Fig. 1.3—Haida Gwaii by Bill Reid. Gypsum plaster pattern for a bronze cast at the Canadian Embassy in Washington, DC. (Canadian Museum of Civilization, Ottawa).

the video "Gypsum—The Miracle Mineral" [1-1] prepared by the Gypsum Association of Washington, DC.

However, most utilizations of gypsum are based on the fact that it can be calcined when subjected to heat treatment at fairly low temperatures. This results in the formation of either stucco as the first calcination stage or insoluble anhydrite as the second calcination stage. North American technology is based almost entirely on stucco. In Europe, both materials are sometimes produced separately and are then mixed together in certain proportions. When mixed with water, they rehydrate to gypsum by crystallization, that is, they are cementitious. In the case of stucco, this takes place in a relatively short time and in the case of insoluble anhydrite activators are normally used to speed up the process. Relatively minor quantities of plaster are used as molds for metal castings (Fig. 1.3) and for dental and surgical applications.

The most modern utilization of gypsum, both natural and synthetic, is for the manufacture of gypsum board on a large scale [1-2]. Gypsum board originated in the United States, which produces about 45 % of the total amount. Gypsum board is now produced almost everywhere (Table 1.1). Significantly,

TABLE 1.1—2007 World Capacity for Gypsum Board.

Region/Country	Capacity in Million Square Feet	Number of Plants
USA	37640	81
Canada	3821	13
Mexico and South America	2270	18
Europe	22250	73
Middle East and Africa	194(?)	11
Australia and New Zealand	2325	13
Japan	7368	23
India and China	8838	29
Total million square feet	84938	246
Total million square meter	7891	

the manufacturing process is based on stucco alone and does not involve insoluble anhydrite.

Both dehydration and rehydration phenomena are the basis for much of the gypsum science and technology.

1.4.1 Dehydration

Under atmospheric conditions, the dehydration of calcium sulfate dihydrate involves exposure to increasing temperatures with corresponding stepwise loss of water. It essentially passes through the process indicated below. Dihydrate, hemihydrate, and insoluble anhydrite are distinct and separate phases since they have individual crystal structures as illustrated by x-ray deposition techniques [1-2]. Soluble anhydrite, $CaSO_4$ (sol.) is a special case but not a separate phase. It has the same crystal structure as hemihydrate and may be considered an extension or an anhydrous variation of hemihydrate. Moreover, soluble anhydrite is unstable and reverts rapidly into hemihydrate when exposed to water vapor or when coming into contact with liquid water.

Dihydrate→	Hemihydrate→	Soluble Anhydrite→	Insoluble Anhydrite
$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot (1/2)H_2O$	$CaSO_4$ (sol.)	$CaSO_4$ (insol.)
Phase I	Phase II	Anhydrous Phase II	Phase III
Stable	Metastable	Unstable	Stable

Depending upon the dehydration conditions, two variations of hemihydrate are produced, α-hemihydrate and β-hemihydrate. The β-hemihydrate is formed under normal atmospheric conditions independent of the water vapor pressure present. This is the original variety also known as stucco in practice. The more recently developed α-hemihydrate is formed in an autoclave or in salt solution between 97°C (207°F) and about 160°C (500°F). This variety is mainly used for medical or dental applications to prepare molds as well as in self-leveling floor screeds.

An inordinate amount of work has been carried out on the difference between these two hemihydrates. In one instance this was done because it was assumed that the various and changing consistencies (water demands) of stucco calcined in a kettle were due to different ratios of α-hemihydrate to β-hemihydrate and that this ratio changed towards α-hemihydrate on aging. The current view is that there is no α-hemihydrate formed in the kettle. The aging of β-hemihydrate is due to adsorption of water vapor, which results in a decrease of the consistency due to the loss of its ability to disintegrate, that is, to separate into smaller particles when mixed with water. The differences between the two hemihydrates are now correctly viewed as being mainly due to the considerably larger size and the uniformity of the crystalline particles of α-hemihydrate. This variety of hemihydrate has a low consistency to begin with and does not disintegrate when mixed with water or age. Consequently its water demand is not influenced by the adsorption of water vapor.

1.4.2 Rehydration

The rehydration of hemihydrate and of insoluble anhydrite to dihydrate refers to the solution of these materials in water and subsequent crystallization. This process consists of the following steps with incorporation of water during crystallization and release of heat.

$$\text{Hemihydrate} + \text{water} \rightarrow \text{Dihydrate} + \text{heat (rapid process)}$$

$$CaSO_4 \cdot (1/2)H_2O + H_2O \rightarrow CaSO_4 \cdot 2H_2O$$

$$\text{Insoluble Anhydrite} + \text{water} \rightarrow \text{Dihydrate} + \text{heat (slower process)}$$

$$CaSO_4\ \text{(insol)} + H_2O \rightarrow CaSO_4 \cdot 2H_2O$$

1.4.3 Limitations for Utilization

The utilization of gypsum is affected by several overall technical factors, which play a key role in limiting its application.

1. Structural Effects: Rehydrated gypsum is not a structural material such as other cementitious materials, e.g., set limestone or Portland cement, because it is not physically stable. To a large extent, this is due to the high porosity of set gypsum caused by the evaporation of a larger amount of mixing or gauging water that is not used for hydration. The gypsum crystals are considered to be flexible but not elastic, which means that they can be bent but that is difficult or impossible to straighten them out. Also, some of the contacts between gypsum crystals are formed by relatively weak hydrogen bonds. As a consequence, rehydrated gypsum undergoes deformation, such as creep, when subjected to compressive, tensile, or flexural loads over time. This can be illustrated by the Instron® "bond"—test where a load is applied to below the breaking point to a plaster specimen cast in a dumbbell shape. The applied load diminishes over time, depending on the amount of moisture absorbed by the specimen and the resulting creep of the specimen. This process can be repeated several times, which is indicative of a high degree of creep. The original gypsum rock, which is solid and non-porous, does not show this behavior.

2. Effects of Water: Rehydrated gypsum loses strength in the order of 50 % when absorbing liquid water, which is much greater than that of other cementitious materials. It is also sensitive to adsorbed moisture in excess of true water of crystallization. This is partially due to the higher solubility of gypsum exacerbated by high porosity and the hydrogen bonding between gypsum crystals. For this reason, rehydrated gypsum is used primarily for non-load bearing applications for interior walls and ceilings of buildings. The same limitation applies when manufactured panels, such as gypsum board or cast blocks, are employed. However, there are certain advantages associated with this characteristic. For example, it is possible to bend gypsum boards to a certain degree, particular with prior wetting, when applying them to curved surfaces such as pillars. The allowable degree of bending of the wetted board varies with its thickness whereby thinner boards permit greater bending.

3. Effect of Hydrated Lime: Hydrated lime is often used in combination with calcined gypsum (stucco) for a variety of reasons. Historically, it was difficult or impossible to differentiate gypsum from limestone, particularly since both often occur in mixed deposits. To a degree, this explains the use of these materials in applications for which gypsum alone is not suited. At a latter stage, when the differences were better understood, both materials were mixed intentionally to improve the properties of gypsum. This tends to hide the characteristics of gypsum, such as inadequate load bearing properties and poorer resistance to water. The approach of intentionally using mixtures of hydrated lime with dehydrated gypsum continued almost to the present day.

4. Effects of Hydration Stage: Insoluble anhydrite rather than hemihydrate was the product obtained during the early approaches of manufacture. This is due to the fact that large pieces of gypsum were used for calcination, which makes it virtually impossible to notice or to stop at the intermediate hemihydrate level. Also, insoluble anhydrite was actually preferred since it has a lower water demand and produces longer times to set and harden, which may have been the intention at an age when set controlling additives were not available. The conscious use of hemihydrate alone is dependent upon the calcination of finely ground gypsum, which involves keeping the material in motion by boiling and stirring. This involved technology such as the shallow pan kettle that was introduced during the Baroque or Rococo periods in Europe. The relatively recent application of hemihydrate as plaster produced in larger kilns or kettles in North America and to a lesser extent in Europe usually requires the addition of retarders and other additives to control the setting process.

5. Plaster versus Gypsum Board: A switch from interior gypsum plaster to gypsum board occurred gradually in North America since the 1950s. This was less labor intensive and more cost effective. To a large extent it was also caused by the desire to obtain earlier occupancy of buildings by avoiding the relatively lengthy drying time required for plasters. In some locations, the change was also due to the lack of skilled plasterers. However, the key factor making this change possible was that North America practices a different type of building method that is based on stud wall construction rather than solid block or cement walls. Europe, South America, and Asia have lagged initially behind in gypsum board usage because of their primary residential building method is based on the latter.

1.5 Published Information

Most recent publications appear to be confined to specific scientific issues and, consequently, they are dispersed over a wide variety of sources. There seems to be no recent publication that covers gypsum science and technology in a comprehensive manner. Undoubtedly, this is due to the conviction that gypsum is a well-established building material and that the scientific and technological points are adequately understood. Needless to say that is not the case. Also, gypsum research is not considered to be a glamorous field. It is surprising, however, that the gypsum research that did take place has often itself contributed to the confusion of specific issues rather than clarifying them. In fact, certain schools of thought were customarily maintained as if existing in isolation and to the almost total exclusion of information from other research groups. To a large extent, this is also due to the fact that academics in general do not consult practitioners.

This situation has been summarized as follows in 1941 by Kelly, Southard, and Anderson: “To explain existing data several varieties of these three types of compounds have been postulated: two forms of $CaSO_4 \cdot 2H_2O$ and at least three varieties of $CaSO_4 \cdot (1/2)H_2O$ and four varieties of $CaSO_4$. Moreover, these varieties after being postulated were often confused because of lack of adequate means of identification. Some varieties were so ill-defined that an unsympathetic critic might claim that a new species of some compound had been postulated to accompany each set of discordant results.” [1-3]. Almost 25 years later, the situation had changed very little. Kirk and Othmer in 1964 stated the following: “This substance is probably the subject of more confused and discordant statements, misinterpretations and persistent lack of exact information than any other compound in the category of inorganic materials.” [1-4].

Against this background, gypsum has been used extensively where it is locally available. This has occurred despite its natural shortcomings that have limited its application to interior applications where it does not serve a structural purpose. From its initial discovery as primitive cementitious material to its present-day paper lined gypsum board, gypsum technology was advanced by empirical approaches depending on the particular application. Science has only played a minor role over the last 200 years.

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2

History

2.1 Scientific Aspects

A NUMBER OF EXAMPLES FOR THE UTILIZATION OF PLASTER ARE reported in the literature from around 7000 to 4000 B.C., such as Catal-Huyuk in South Central Turkey. However, all these applications are from pre-recorded history and they are difficult to place into proper perspective primarily because the available information is non-specific and often contradictory. There is considerable doubt that the plaster used at any of these locations was based on gypsum alone, but rather mixed with limestone or limestone alone. The difference between these two materials was poorly understood until Roman times.

A similar picture emerges for the utilization of gypsum in Egypt from 2500 B.C. Limestone and mixtures of limestone and gypsum were converted jointly and used as floor screed or to repair the exterior of natural stone structures. This is apparently the case for the pyramid of Cheops, the Sphinx, and subsequently the Minoan palace of Knossos on Crete (2000 B.C.).

Gypsum was used in Greece in about 700 B.C. to carve statues and for various artistic applications. The technology of using the cementitious properties of gypsum was apparently obtained either from Egypt directly or via Crete. It is not clear to what extent they understood the difference between limestone

Fig. 2.1—Antoine Lavoisier and his wife and assistant Marie-Anne in a painting by Jacques-Louis David

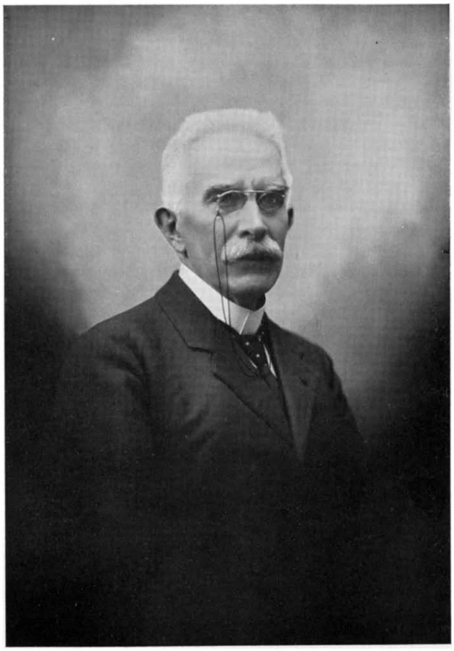

Fig. 2.2—Le Chatelier

and gypsum as original material or as plaster. They obviously noticed that gypsum was warm to the touch and had a higher solubility as compared to limestone, which was cold to the touch and did not suffer from solubility problems. Unfortunately, the Greeks failed to leave written records about their uses of gypsum, which is unusual since they pondered the nature of everything around them.

As mentioned by Plinius the Elder (23–79 A.D.) [2-1] in his *"Natural Science,"* the Romans acquired gypsum technology from the Babylonians and Greeks, and it was recognized that that there was a difference between lime plaster and gypsum plaster. The Romans were the first to recognize the limitations of gypsum plaster and used it exclusively for non-structural applications and for interior purposes such as the interior walls of Pompeii. However, they differentiated between these two materials by selecting appropriate deposits. They developed a multilayer gypsum mortar whereby the amount and the particle size of sand decreased from the bottom to the top layer. This apparently modern approach tends to reduce shrinkage cracks, a decided advantage when mortar is used as a base for frescoes or paintings. Unfortunately, the Romans also left few records about their gypsum technology except for a brief mention of gypsum by Vitruvius (80–70 B.C.) in his ten books on architecture [2-2].

Gypsum technology was supposedly lost completely with the dissolution of the Roman Empire in 476 A.D. For this reason, not much is known about the use of gypsum plaster during the Middle-Ages. For example, mortar based on insoluble anhydrite was used in the Harz mountain region during the early Middle-Ages for the construction of city walls, etc. and to cover interior walls of buildings. The major construction projects of the 9th to the 13th century were concerned mainly with monasteries, cathedrals, and palaces. For these gypsum plastering became more of an art form during the Renaissance period. Towards the end of the 15th century, towns and cities were built or enlarged. Therefore, it can be assumed that gypsum technology had been rediscovered at that time. In any case, it became the special knowledge of a few artisans according to the custom of the day. Gypsum plastering gained further in popularity during the Baroque and Rococo periods again mainly for the interior of palaces and churches. To deal with the increased demand for sophisticated gypsum plasterers, a school was established in Wessobrunn, Bavaria, and a similar school existed in Italy [2-3]. The fire resistive properties of gypsum used for interior wall covers were recognized early during fires at Basel (1457) and London (1212, 1666, and 1794). King Louis XIV in 1667 decreed that wood structures had to be covered inside as well as outside with gypsum plaster to resist the action of fire.

The modern science of gypsum began with the discoveries by Antoine Lavoisier (1743–1794) outlined in his two papers on gypsum presented to the French Academy of Sciences in 1765 and 1766. He explained that the heat treatment of gypsum resulted in the loss of about a fifth of its weight as water vapor to leave an anhydrous material. He also stated that this material when mixed with water would form gypsum again by crystallization. It is remarkable that the reviewers of the Academy praised his work for the "ingenious explication by which it reduces the phenomenon of the hardening of plasters to the laws of crystallization" [2-4].

In contrast to his compatriots, Lavoisier employed meticulous experimentation involving weight gain and weight loss of every part of a material when subjected to heating, which was an established method at the time. He also combined this process with the novel so-called solvent (water) method. This was a tremendous advancement primarily because it set aside the concept of phlogiston (inflammable) proposed by alchemists. They believed that the loss of weight of a material on heating was due to the irretrievable loss to the air of phlogiston, an unidentified "component" of that material. Using their preoccupation with metals as an example, this can be expressed by the following formulae: (1) metal (containing phlogiston) → metal calx (metal oxide) + phlogiston; (2) charcoal (containing phlogiston) → residue + phlogiston, and (3) metal calx + charcoal → metal + ashy residue. This hypothesis which was originated by J. J. Becher (1635–1682) and modernized by the German alchemist Stahl (1660–1734), was accepted throughout most of the 18th century even by eminent scientists. Some claim that the phlogiston concept although erroneous was the first unifying and comprehensive "scientific" theory whereas others maintain that it held up scientific development for about 100 years. It is difficult not to be critical of alchemists but it should be remembered that their attitudes were by no means uniform and that they were guided by convoluted concepts such a transmutation of metals, the philosophers' stone, etc.

Lavoisier also helped to set aside Aristotle's (384–322 B.C.) concept of fire, air, earth, and water as basic "elements," as well as the numerous modifications and opposing views proposed at the time. For this work and other accomplishments as outlined in *Méthode de nomenclature chimique and Traité élémentaire*, Lavoisier is rightly known as the Father of Chemistry. As indicated by the quantity of the weight lost when heating gypsum to about 300°C (572°F), Lavoisier of course obtained insoluble anhydrite. But he observed that 3/4 of the water of crystallization was easier to remove than the last 1/4 and that the first 3/4 of the material had a faster hydration than the last 1/4 of the material [2-5]. As an extension of Lavoisier's work, Le Chatelier (1850–1936) described hemihydrate as the intermediate material and reported that its rehydration to gypsum involves supersaturated solutions with respect to gypsum [2-6]. Possibly this is the reason why hemihydrate and not insoluble anhydrite became identified as Plaster of Paris. There is no doubt that this was a further tremendous accomplishment based on insight and accurate experimentation.

The physical-chemical foundation for the gypsum technology was provided by J. H. van't Hoff (1852–1913) [2-7] as corrected by Davis (1907) [2-8]. Considerable confusion had to be subsequently overcome because of the introduction of the then fashionable colloid theory for the setting process, which was advanced by quite a number of scientists such as Michaelis (1893), Cavazzi (1913), Desch and Traube (1919), Ostwald and Wolski (1920), and Baykoff and Neville (1926). However, the work of Weiser et al. in 1936 [2-9] showed that colloidal processes, however defined, were not involved. This meant that water in hemihydrate occupied specific locations in a crystal lattice. This also meant that hemihydrate is not a zeolite, which would have water occupying spaces in a random fashion. The need for clarification concerning hemihydrate and soluble anhydrite resulted in the work of Kelly, Southard, and Anderson in 1941 [2-10]. Unfortunately, they followed suggestions by Riddell, which led to a misinterpretation of the origin and role of α-hemihydrate and β-hemihydrate [2-11].

It is difficult to establish when and where stucco based on hemihydrate alone was prepared and used separately from insoluble anhydrite. However, it certainly occurred during the 19th century. The common procedure of calcining gypsum was to place fairly large pieces of gypsum on a grate with an open fire underneath. This produces primarily insoluble anhydrite because it makes exact temperature control rather difficult and takes no account of the water vapor released. In contrast, stucco was produced at the same time by finely grinding gypsum and heating it in shallow pans such as the Harz mountain kettle. Under these conditions, the water vapor released has a two stage fluidizing effect. The end of the first effect can be used to determine the end of the calcination process to hemihydrate. However, it should be realized that there is some overlap of the phases so that stucco usually contains a few percent of dihydrate and soluble anhydrite.

2.2 Practical Aspects

Stucco based primarily on hemihydrate was prepared in the above manner and introduced as a modern plastering material. There are many cases in Europe where this material has been used for the decoration of interior of walls and ceilings. However, for the normal coverage of walls the plastering industry in Europe continued to preferred mixtures of hemihydrate and anhydrite such as the building plaster (*Surcuit*) in France and a similar product (*Putzgips*) in Germany. There are several reasons for the preference of these mixtures over hemihydrate plasters. The most important one seems to be that less water is used to prepare these plasters and their strength is correspondingly higher. Also, a desirable delay of the hardening process is achieved without or with small amount of retarding additives, such as tartaric acid and hydrated lime. In some instances, hemihydrate plasters were employed as mortars, mixed with various quantities of sand or lightweight aggregates. Stucco based on hemihydrate was used exclusively for the manufacture of blocks and tiles.

The development in North America was quite different. To a large extent, this can be explained by the difference in construction practices, which are based on stud wall construction in North America versus solid brick or block wall construction in Europe. Lime plaster was used initially to finish interior walls and ceilings. This material hardens slowly but it requires a wood lath for mechanical keying. Waste lumber from saw mills cut into strips and nailed to wood framing became the standard plaster base. However, around 1885, it was discovered that retarders based on soluble keratin could be used to control the setting of hemihydrate and to make gypsum plaster with a quicker hardening process than lime plasters. The ability to retard plaster based on stucco was the breakthrough required for its widespread application. For example, gypsum plaster in North America, and to some extent in Britain, consisted of a two or three coat application containing sand, with a final finishing coat of neat (unsanded) lime/gypsum plaster instead of the European one coat application. (Except for Keene's cement, anhydrite plaster is unknown in North America.)

Because of the many shortcomings of wood lath it was replaced by a gypsum lath patented by Augustine Sackett in 1894 [2-12]. This lath or Sackett board consisted of four plies of paper and three layers of stucco plaster. Despite some problems with this lath, plants were built in several places in the United States. In 1909 these plants were purchased by U.S. Gypsum who developed Sackett board further by introducing a variety of new developments such as the paper folded edge. Subsequently, an Adamant board was developed consisting of a gypsum core faced with top and bottom paper. To meet increasing construction demands, further changes were made in 1926, which adopted the round edge and introduced foam and fiber into the gypsum core. This product has become known as Rocklath and it exists today in various adaptations.

The conversion from lath to gypsum board started in the early 1950s. It was driven primarily by two issues: (1) Avoiding the drying time of plaster which allowed earlier occupancy of buildings and (2) the lack of skilled plasterers in many locations. Gypsum board in its many manifestations has now replaced plaster almost entirely except for special applications. About 1 % of the calcined gypsum produced in the United States is used to manufacture plaster while nearly 26 million tons were used in 2005 to produce 36 000 billion square feet of gypsum board. The consumption of gypsum board has been increasing

Fig. 2.3—Augustine Sacket

substantially since in 2000 only 21 million tons of calcined gypsum was used to produce 26 000 billion square feet of board. North American gypsum board systems have also been accepted in Europe, Asia, and South America particularly for high rise and institutional construction.

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3

Origin

3.1 Natural Gypsum

AS MENTIONED BEFORE, GYPSUM WAS DEPOSITED ABOUT 200–300 million years ago during the evaporation of seawater that was probably repeatedly cut-off from the main body. This crystallization process is influenced by many factors but essentially it takes place in brine of various concentrations and not in plain seawater. In Europe gypsum deposits formed primarily during the Permian, Triassic, and Jurassic periods. They occur in France, Spain, Germany, and Italy whereas the one near Paris is best known because of the name Plaster of Paris. In North America gypsum was deposited during the Ordovician and Silurian periods as well. The best known deposits in Africa are the Adrigat formation in the Blue Nile Valley, which dates from the Jurassic period, and the deposit of the Ethiopian plateau (Danakil depression) [3-1]. Smaller deposits of gypsum are abundantly present almost everywhere except in areas of volcanic origin. Gypsum formation takes place by crystallization following the relative solubilities of the other salts present. Accordingly, gypsum is deposited after calcium carbonate and prior to sodium, magnesium, or potassium chlorides and other sulfates. Natural gypsum deposits often contain primary impurities in various quantities, such as calcium sulfate anhydrite, calcium carbonate, dolomite, or various types of clay. Minor amounts of primary impurities that are found less frequently are silica, bitumen, glauberite ($Na_2Ca(SO_4)_2$), and syngenite ($CaSO_4 \cdot K_2SO_4 \cdot H_2O$). Secondary impurities are introduced after deposition by materials in solution seeping into cavities or by contamination during the mining process.

Gypsum usually forms a solid nonporous rock near the Earth's surface and consequently the mining of gypsum ore is generally carried out in quarries or shallow underground mines. Gypsum can be pure white, gray, or reddish if clay is present or if it contains iron oxide, or nearly black if bitumen is present. Based on differences in appearance or structure that reflect crystallization patterns and crystal size, gypsum is also known by a variety of sometimes archaic terms, such as massive including alabaster (fine grained/translucent), selenite (sheet-like/transparent), or satin spar (fibrous). Because of its white color, it is also known as terra alba or as landplaster because of its use for agricultural purposes. Earthy gypsum or gypsite forms as a secondary deposit when gypsum is remixed with other material after the original deposition. Gypsum sand is usually contaminated with Glauber's salt, $Na_2SO_4 \cdot 10H_2O$, or Glauberite.

Both physicochemical and geological factors have to be taken into consideration when trying to explain the nature and configuration of the gypsum deposits, in particular those that are stratified repeatedly with insoluble anhydrite. Physicochemical factors are the result of short term laboratory exercises that study primarily the effects of various salt concentrations and temperature.

Geological factors on the other hand try to take into account long term geological events as well. These involve periodic flooding of seas that may be only partly or temporarily isolated, subsiding basins, and tectonic lifting that occurred repeatedly over millions of years. Not surprisingly, the two factors disagree in many respects.

However, none of the salt concentrations and ratios studied in the laboratory is found under evaporite conditions in the field. Accordingly, there has been no success in reproducing real geological situations with laboratory experiments. For example, if one assumes an average salinity of sea water, only about 1.5 % of the original volume is deposited on evaporation. This means that for a depth of 1000 m, only 15 m of salt is deposited. Of these 15 m only 0.55 m are gypsum. This contrasts with deposits that can be as much as 600 m thick.

Dihydrate forms double salts with alkali-metal and ammonium sulfate, some of which occur in nature, such as syngenite, $CaSO_4 \cdot K_2SO_4 \cdot H_2O$. An example for a triple salts is the polyhalite, $CaSO_4 \cdot MgSO_4 \cdot K_2SO_4 \cdot 2H_2O$, which is also found in nature. A variety of other triple salts exist that involve divalent ions of iron, zinc, manganese, copper, and magnesium, as well as alkali metal and ammonium.

3.2 Natural Insoluble Anhydrite

The problem of deposition is highlighted when considering the occurrence of insoluble calcium sulfate anhydrite within gypsum deposits. This is a complex proposition involving salt concentration and temperature as well as other factors. Anhydrite is found as layers with various thicknesses on top, at the bottom or between layers of gypsum. It is also found intermingled and as lenses within gypsum deposits apparently without indication of differential precipitation. According to physicochemical consideration the precipitation of gypsum or anhydrite is a matter of the $CaSO_4$ concentration depending on the temperature intervals and taking into account the stabilities of the two phases. For example, during sea water evaporation at 30 °C (86 °F), gypsum will always precipitate when the salinity lies between 3.35 and 4.48 times the normal salinity of the sea water. Anhydrite is deposited above this concentration. On the basis of this and other considerations, it is also postulated that anhydrite will be deposited above 42 °C (108 °F). Unfortunately it is doubtful that this concept can be used to explain the occurrence of anhydrite in gypsum deposits since it is improbable that 42 °C (108 °F) was reached and exceeded over the required long periods of time.

The Blaine formation in Oklahoma was studied microscopically and petrographically and it represents an opposite view. According to the results, the gypsum deposit in the area was formed near the surface by the hydration of anhydrite. It follows that the anhydrite was the initial precipitate in an evaporating basin. Unfortunately there is no other supporting evidence available. For example, no consideration is given to the volume increase when anhydrite is changed into gypsum, which would stop it at a certain depth.

An interesting case is the formation of giant crystals (up to 11 m) of gypsum in a limestone cave at the Naica mine near Chihuahua, Mexico. These gypsum crystals were apparently formed from anhydrite during long term exposure to 58 °C [3-2].

However, considering the available data and opinions, it becomes obvious that there is no easy answer to the question of whether gypsum or anhydrite was deposited first. Nevertheless, the current view is that gypsum was the original material deposited and that anhydrite was formed from it at a later time.

3.3 Synthetic Gypsum and Synthetic Insoluble Anhydrite

Synthetic gypsum is being produced by a variety of industrial processes. Most of these obtain synthetic gypsum by a neutralizing reaction between sulfate and calcium ions such as in the manufacture of phosphoric acid or titanium dioxide. Most processes that use sulphuric acid to digest rocks must be neutralized before they can be used or safely discarded. Limestone is the best case of a neutralizing agent. As mentioned previously, synthetic gypsum is chemically identical to natural gypsum and has the same crystal structure. Although it has usually a higher dihydrate content (purity) than most natural gypsums, its impurities are different and that can be of concern [3-3].

Despite the availability of synthetic gypsum, there has been an initial reluctance in North America to use this material in the gypsum industry. These concerns are often based on costs for transportation and drying. However, the key reason for this reluctance was the question as to whether these materials would perform as well as natural gypsum, particularly for the manufacture of gypsum board. There was also a question of sufficient supply in appropriate locations. Nevertheless, over the past 20 years, there has been a considerable change toward the use of synthetic gypsums that were obtained by the desulfurization of flue gases at coal fired power plants. Because of the slow start in the North America to use these materials, the industry in Japan and in Europe was initially more advanced. (FGD gypsum is known as *Desulpho-Gypsum* in Britain and as *REA-Gips* in Germany.) For example, in 1983 Japan used 2.5 million tons per year of FGD gypsum whereas the total combined consumption in Europe and North America was only 0.3 million tons per year. In 2005 this has risen in North America to over 9 million tons per year or 34 % out of a consumption for gypsum board or plaster manufacturing of 26 million tons per year. With the exception of the relatively small amount of titanogypsum and flouroanhydrite, other synthetic gypsums or synthetic anhydrites are still not being used.

A number of circumstances have contributed to make the acceptance of some synthetic gypsum a reality in North America. The greatest impetus was provided in the United States by the Clean Air Act of 1963, its 1970 Extension, as well as similar provisions. This led to the production of considerable quantities of acceptable quality synthetic gypsum primarily from coal fired power plants using the limestone or lime process. The other main reasons were the consolidation of the gypsum industry, the tendency toward the building of larger plants for the production of gypsum board rather than plaster. In some

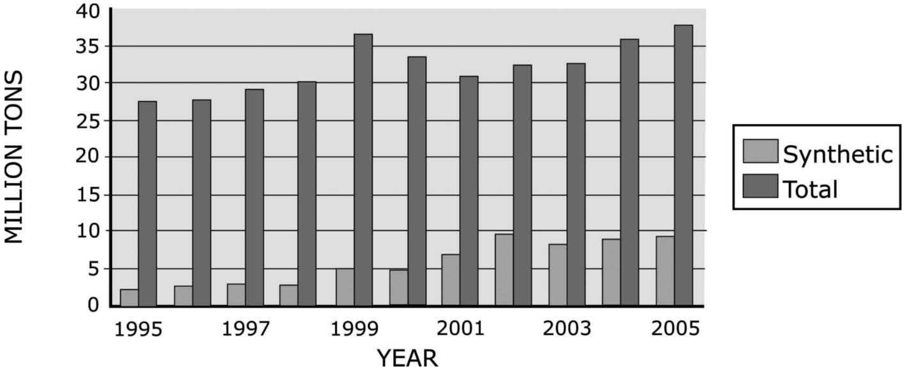

Fig. 3.1—Consumption of total gypsum and synthetic gypsum in the United States.

cases, the depletion of suitable natural gypsum supply played an important role (Fig. 3.1).

3.3.1 Flue-Gas Desulfurization Gypsum

The largest quantities of so-called FGD gypsum are presently obtained from the desulfurization of flue gases from power stations and other large production plants that use fossil fuels such as bituminous coal. Almost all of these operate by the counter current washing of flue gas with an aqueous suspension of limestone or lime to remove the sulfur dioxide (Fig. 3.2). Numerous other processes have been developed for this purpose but only a few have been industrialized.

For limestone scrubbing the net reaction is represented by

$$SO_2(g) + CaCO_3(s) + (1/2)O_2(g) + H_2O \rightarrow CaSO_4 \cdot 2H_2O(s) + CO_2(g).$$

The first step takes place at a *p*H of 7–8 and produces an almost insoluble calcium sulfite

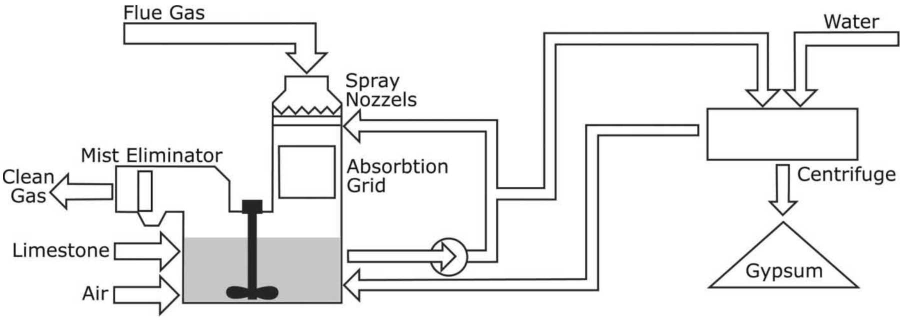

Fig. 3.2—Desulfurization of the gases in a coal fired power plant.

$$(1)\ SO_2(g) + CaCO_3(s) + (1/2)H_2O \rightarrow CaSO_3 \cdot H_2O(s) + CO_2(g).$$

In the second step the suspended calcium sulfite is converted at pH 5 to soluble calcium bisulfite

$$(2)\ 2CaSO_3 \cdot H_2O(s) + 2SO_3(g) + H_2O \rightarrow 2Ca(HSO_3)_2\ \text{(solution)}.$$

In the third step the calcium bisulphate is oxidized at pH 5 to calcium sulfate dihydrate, the so-called FGD gypsum

$$(3)\ Ca(HSO_2)_2\ \text{(solution)} + H_2O \rightarrow CaSO_4 \cdot 2H_2O(s) + H_2SO_4.$$

The remaining sulfuric acid produced reacts with the remaining limestone, thus forming additional gypsum

$$(4)\ H_2SO_4 + CaCO_3(s) + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2(g).$$

Large and uniform gypsum crystals normally form in the aqueous suspension. These crystals or crystal clusters are separated from the aqueous suspensions by dewatering in hydrocyclones and vacuum belt filters or by centrifuges. This produces a filter cake of gypsum having a free water content of slightly less than 10 %. Characteristically, FGD gypsum has a high purity (high percentage of calcium sulfate dihydrate) and an off-white color. The fineness and the crystal shape of the gypsum are important factors for the manufacture of gypsum board and they may require corrective steps. As always the quality of the gypsum is of concern. Problems in that respect are generally centered on the pH of the material, its chloride content, and in some case the flyash and residual carbon content. About 4.5 tons of gypsum is produced per ton of sulfur in the fuel. Apart from small quantities used in Portland cement, all of the FGD gypsum currently produced is consumed by the gypsum industry primarily for the manufacture of gypsum board (Fig. 3.2).

3.3.2 Phosphogypsum

Worldwide about 130 million tons per year of phosphogypsum are currently produced. This constitutes the largest quantity of any type of synthetic gypsum and it is expected to increase as the demand for fertilizers increases. In any case, the quantity of phosphogypsum produced per year exceeds by far the demand on gypsum and anhydrite, which is only about 75 million tons annually.

Usually phosphogypsum is produced during the production of wet phosphoric acid from phosphate rock (apatite) and sulfuric acid: $Ca_5(PO_4)3F + 5H_2SO_4 + 10H_2O \rightarrow 5CaSO_4 \cdot 2H_2O + 3H_3PO_4 + HF$.

Normally about 1.7 tons of dihydrate are produced per ton of raw phosphate. This corresponds to 5 ton of dihydrate per ton of phosphorus pentoxide produced.

The phosphogypsum is obtained as a moist fine powder with a free water content of 20 %–30 %. Considerable amounts of impurities are usually present depending on the source of the rock and the particular process used. Of major concern is the radioactivity of the phosphogypsum as produced, which again depends to some extent on the rock source. For this reason Florida rock is much less suitable for utilization than rock from Morocco or Kola. For example, during the decay of radium-226 into radon-222 and its other decay products, an increase in the dose rate occurs in the inside of buildings. For this reason, the utilization of phosphogypsum from Florida is banned since it contains approximately six times the limits set by EPA.

In North America, technical difficulties in removing radioactive materials are the main reason why currently only about 4 % of the phosphogypsum produced is utilized mostly in agriculture or as road base. No phosphogypsum is used in any construction material such as gypsum board or Portland cement. It is an extremely expensive and involved process to remove unwanted substances from phosphogypsum. The other principal difficulty preventing the use of phosphogypsum is its high content of free water and subsequently high drying costs.

Another serious problem that is often overlooked is that isomorphic incorporation of chemical constituents into the dihydrate lattice can occur during the wet phosphoric acid process. Most commonly calcium hydrogen phosphate, $CaHPO_4 \cdot 2H_2O$, is incorporated because it has almost the same lattice spacing as dihydrate. It is also possible to incorporate monosodium phosphate, Na_2HPO_4, or fluorophosphates, FPO_3, into the dihydrate lattice. Hemihydrates produced from phosphogypsum of this type are characterized by abnormal set times and poor strength development. This is the main reason for the failure of the Giulini process for α-hemihydrate. The process did not remove sufficient phosphate to improve the properties of the hemihydrate even with recrystallization in solution.

3.3.3 Other Synthetic Gypsum

Small quantities of calcium sulfate are formed during the production of organic or inorganic acids, such as tartaric acid, citric acid, oxalic acid, boric acid, or titanium dioxide. Larger quantities of synthetic gypsum are expected to be produced because of the treatment of sulfate-containing waste waters and the neutralization of dilute sulfuric acids that occur during the processing of minerals such as zinc ore. However, for various reasons these gypsums are difficult to utilize. The exception is the relatively small amount of synthetic gypsum which is obtained during the manufacture of titanium dioxide pigment. This material is characterized by a small particle size, high purity, and a white color.

Attempts continue to be made to utilize gypsum scrap from the ceramic industry and metal foundries. Again, the largest problems are created by the removal of impurities and water introduced during slip casting. Although gypsum processing is known to be forgiving, it cannot tolerate certain soluble impurities or impurities in large quantities.

3.3.4 Synthetic Fluoroanhydrite

This is the only representative of insoluble anhydrite which is being manufactured by reacting fluorspar with sulfuric acid during the production of hydrofluoric acid. This process results in the formation of fluoroanhydrite according to the following reaction:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF.$$

1 ton of fluorspar produces about 1.75 tons of anhydrite. The total production of this material is about 2–3 million tons per year. Fluoroanhydrite is being utilized only in Europe primarily for self-leveling floor screeds. If aluminum sulfate is used as accelerator, hydration to gypsum is often difficult, which to a large extent is due to isomorphism that may occur between ions of aluminum fluoride (AlF_5^{--}) and sulfate (SO_4^{--}).

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4

Basic Properties

4.1 Phases

THE $CaSO_4$–H_2O SYSTEM IS REPRESENTED BY THREE SOLID PHASes that exist at room temperature in air containing water vapor, namely calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$), calcium sulfate hemihydrate ($CaSO_4 \cdot (1/2)H_2O$), and insoluble anhydrite ($CaSO_4$-insol.). In these cases a phase is identified and characterized by an individual and distinct crystal structure. Soluble anhydrite ($CaSO_4$-sol.) is not a phase because it has the same crystal structure as hemihydrate. In fact, it is considered to be the anhydrous state of hemihydrate. However, because of its theoretical and industrial importance, it is discussed together with the above three phases.

Two underlying factors are always evident when discussing these substances and in particular the changes from one into the other. They are (1) dehydration of the dihydrate and (2) rehydration to the dihydrate. Dehydration refers to the stepwise loss of water of hydration that is accomplished by increasing the temperature of dihydrate for the purpose of obtaining one of its dehydration products, i.e., hemihydrate, soluble anhydrite, and insoluble anhydrite. The temperature ranges given for the individual dehydration steps depend on whether the process is static or kinetic. In general, static conditions appear to proceed at a lower temperature but they require more time. For example, dihydrate begins to dehydrate at about 46°C (115°F) but conversion takes months or even years to complete.

Rehydration is the exposure of these dehydrated materials (hemihydrate, soluble anhydrite, and insoluble anhydrite) to liquid water for the purpose of obtaining the dihydrate again at standard conditions. This process proceeds by the crystallization of the dihydrate in water. If the starting material is hemihydrate, a supersaturated solution with respect to dihydrate is formed prior to crystallization. In the case of insoluble anhydrites as the starting material, the influence of activators and dehydration temperature shows that the rate of conversion to gypsum is affected by these parameters in addition to solubility.

The solubilities of dihydrate, hemihydrate, and insoluble anhydrite are important consideration for a variety of reasons but primarily because they allow a distinct separation between the three phases on a theoretical basis. Their approximate solubility curves are shown in Fig. 4.1. The intersection between two curves gives the equilibrium temperature below which the less soluble phase is stable. For example, the curves show that above 40°C (104°F) (point A) insoluble anhydrite is the most stable phase. Above this point, dihydrate when in contact with water does not convert to insoluble anhydrite. In practice, it may do so but at a very slow rate. Below 100°C (212°F) (point B) dihydrate is more stable than the hemihydrate. Therefore, saturated solutions of hemihy-

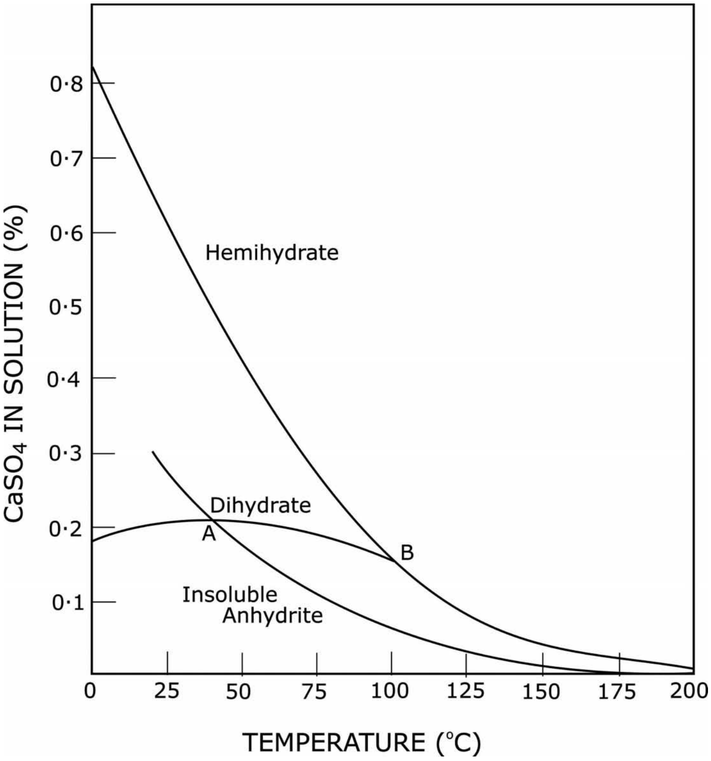

Fig. 4.1—Solubility of calcium sulphates.

drate are supersaturated with respect to dihydrate, and dihydrate precipitates from that solution.

This dehydration-rehydration process appears to be relatively simple but there are a number of significant circumstances to be considered. For example, water vapor plays a significant role in the dehydration and rehydration of soluble anhydrite (Fig. 4.2). Also, hemihydrate occurs in the α-form and β-form depending on the method of dehydration (Fig. 4.3). Insoluble anhydrite can be produced by dehydration but it also occurs as the natural material. High temperature anhydrite exists only above 1180°C (2166°F) and is not discussed further because it is not of interest for the purposes of this manuscript.

Exposure of hemihydrate to water vapor in the atmosphere results in the adsorption of the water to a maximum of slightly less than 2 % of the material depending on its surface area. Dihydrate is not formed under these conditions unless the amount of adsorbed water vapor exceeds about 2 %, which leads to capillary condensation. This nonstoichiometric water can be completely removed by drying below 46°C (115°F).

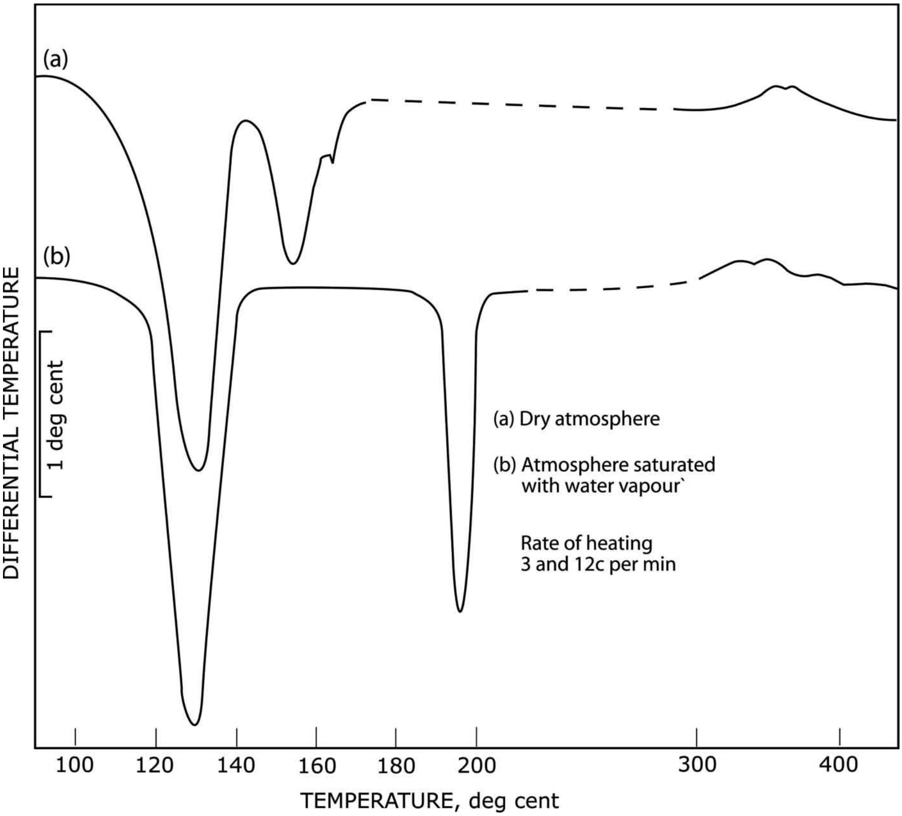

Fig. 4.2—Effect of water vapor pressure on soluble anhydrite formation.

4.2 Dihydrate and Dehydration Products

4.2.1 Dihydrate

Dihydrate is the basic phase in the $CaSO_4$–H_2O system. Its crystal structure reflects a ratio of one molecule of calcium sulfate to two molecules of water, hence its chemical name. It occurs as monocline crystals with four molecules per unit cell: $a = 5.67$ Å, $b = 15.15$ Å, $c = 6.51$ Å, $\beta = 118°23'$. The unit cell structure is a lattice layer, in which calcium ions (Ca^{2+}) and tetrahedral sulfate ions ($SO4^{2-}$) form strong double sheet that remain essentially unchanged during phase changes. These sheets are completely separated by double layers of water of crystallization. This means that the water is embedded in planes between the calcium sulfate layers which allows for easy cleavage. It also means that the water of crystallization is essential for the integrity of the entire structure and to some extent explains the ease with which dihydrate is converted to hemihydrate.

The water constitutes about 21 % of the total mass of the dihydrate but it represents almost 50 % of its volume. This condition also contributes to the

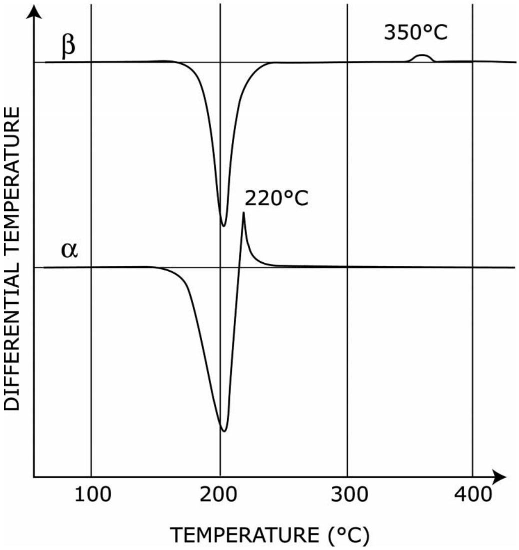

Fig. 4.3—Differential thermograms of *α*- and *β*-hemihydrates.

ease with which dihydrate is converted to hemihydrate by heating (Table 4.1). Flörke provided the most modern version of the crystal structure of dihydrate, hemihydrate, and insoluble anhydrite, including corrections of earlier work [4-1] [Fig. 4.4].

The thermodynamical stabilities of dihydrate and its dehydration products are classified as follows: dihydrate = stable, hemihydrate = metastable, soluble anhydrite = unstable, and insoluble anhydrite = stable. This classification refers

TABLE 4.1—The $CaSO_4$–H_2O system.

Characteristics	Dihydrate	Hemihydrate α-hemihydrate	 β-hemihydrate	Soluble Anhydrite	Insoluble Anhydrite
Formula	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot (1/2)H_2O$		$CaSO_4$ (sol.)	$CaSO_4$ (insol.)
Molecular mass	172.17	145.15		136.14	136.14
Thermodynamic stability	Stable <46 °C	Metastable		Unstable	stable >46–1180 °C
Water of crystallization	20.92	6.21		0	0
Density, g/cm^3	2.31	2.76	2.62–2.64	2.58	2.9–3.0
Hardness, Mohs	1.5				3–4
Solubility in water at 20 °C, g/L	2.1	6.5	≈8.8	Hydrates to hemihydrate	2.7
Lattice symmetry	Monoclinic	Rhombohedral		(Deleted)	Orthorhombic
Refractive index	1.522				

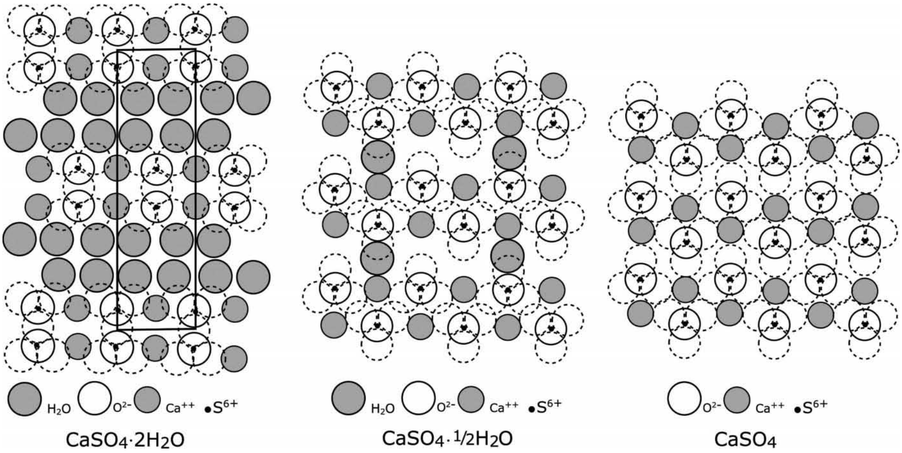

Fig. 4.4—Crystal structure of dihydrate, hemihydrate, and insoluble anhydrite.

to conditions at room temperature in air that contains water vapor. Under these conditions, only the dihydrate is stable below 46°C (115°F). Above this temperature only the insoluble anhydrite is stable. Hemihydrate is metastable since it changes relatively rapidly into dihydrate in the presence of liquid water. Soluble anhydrite is unstable because in the presence of water vapor or liquid water it converts to hemihydrate almost instantaneously.

The solubilities of dihydrate and the various dehydration products have a major effect on the characteristics of these substances. For example, solubility determines the general behavior of dihydrate in comparison to other cementitious materials that are much less soluble in water. Specifically, the high water solubility of dihydrate makes it unsuitable for external applications or any situation where exposure to water is a possibility. In addition, the solubility difference between dihydrate (~2 g/L) and that of hemihydrate (~8 g/L) is the major reason for the crystallization of the latter at room temperature. Insoluble anhydrite has a lower solubility than dihydrate above about 46°C (115°F), which is reflected in its hydration behavior.

The solubility of dihydrate is influenced greatly by acids, especially sulfuric acid, phosphoric acid, and nitric acid. Dihydrate is readily soluble in glycerol and in aqueous solutions of chelating agents, such as EDTA. The solubilities of the other forms of calcium sulfate are strongly affected by the presence of other compounds.

A larger number of papers have been published that deal with the reaction of acids, salts, etc., and the formation of compounds with calcium sulfate. This work is not covered here because it is largely of academic interest.

4.2.2 Dehydration

Dehydration is the first of the two key features of dihydrate science and technology. When carried out under normal atmospheric conditions, hemihydrate, soluble anhydrite, and insoluble anhydrite are produced from the

TABLE 4.2—Heats of dehydration.

Phase change from dihydrate	J/mol	kJ/g
To β-hemihydrate	86,700	597,200
To α-hemihydrate	84,600	582,700
To β-anhydrite (sol.)	121,800	895,700
To α-anhydrite (sol.)	117,400	863,100
To anhydrite (insol.)	108,600	798,000

dihydrate at progressively increasing temperatures. Examples of the formation of the phases and states are given below. The temperature ranges are based on a variety of practical considerations and are approximate

$$\begin{array}{lclclcl} \text{Dihydrate} & \rightarrow & \text{hemihydrate} & \rightarrow & \text{soluble anhydrite} & \rightarrow & \text{insoluble anhydrite} \\ & & 100-180^{\circ}\text{C} & \rightarrow & 180-350^{\circ}\text{C} & \rightarrow & 350-1180^{\circ}\text{C} \end{array}$$

The dehydration mechanism shown reflects a kinetic or dynamic process. It does not take into account long exposure times or slow rates of conversion. For example, as a result of the high water content and the sandwich structure, dehydration of dihydrate occurs at fairly low temperatures. The lowest temperature at which dehydration can proceed is 46°C (115°F), but it does so at a very slow rate. Also, insoluble anhydrite is formed from the other phases above 46°C (115°F) but its conversion requires a very long time.

These processes can be described as follows:

Dihydrate	→	**Hemihydrate**	→	**Soluble Anhydrite**	→	**Insoluble Anhydrite**
		(requires liquid water, rehydrates relatively fast converts into dihydrate)		(converts with water vapor or liquid water to hemihydrate)		(requires liquid water, rehydrates relatively slow converts into dihydrate)

The dehydration kinetics of the dihydrate substantiates these reaction processes. Kelly et al. made a thorough study of the thermodynamic properties of the $CaSO_4$–H_2O system. Table 4.2 gives the heats of dehydration of the various phase changes that are of significance. However, all the hypothesis concerning reaction mechanisms, activation energies, and orders of reaction have not yet been proved. The problems are that the kinetics of the phase changes is often inhibited and that the test conditions have not been precisely defined.

4.2.3 *α*- Hemihydrate and *β*-Hemihydrate

When the temperature of dihydrate is raised, the first phase obtained is hemihydrate. As the name implies, it has a ratio of one molecule of calcium sulfate to 0.5 molecule of water. During dehydration the volume is decreased and channels are created that run parallel to the $CaSO_4$ chains. As a result, this dehydration step involves a change in crystal structure from a sandwich to a honeycomb format. This honeycomb structure is unique in that water molecules are not essential for its integrity. That is, the water molecules occupy

TABLE 4.3—Technological properties of α- and β-hemihydrates (ASTM C26 or DIN 1168).

Consistency (mL/100 g)	35 (alpha)	42 (alpha)	66 (beta)	90 (beta)
Linear expansion on setting (m/m)	0.0028	0.004	0.0021	0.0016
Setting time (min)	15–20	15–20	20–40	25–35
Flexural strength—dry (kg/cm^2) [psi]		125 [1778]	49–50 [697–711]	
Tensile strength dry (kg/cm^2) [psi]	66 [931]		13	[185]
Tensile strenght—1 h—wet (kg/cm^2) [psi]	35 [499]			6.6 [94]
Compressive strength—dry (kg/cm^2) [psi]	560 [7965]	450 [6400]	100–130 [1422–1849]	56 [797]
Compressive strength—1 h—wet (kg/cm^2) [psi]	280 [3982]			28 [398]

specific spaces stoichiometrically but they do so without being strongly bonded. This means that hemihydrate is not a zeolite, which is characterized by the absence of a stoichiometric arrangement.

When hemihydrate is obtained under normal atmospheric conditions, it is referred to as β-hemihydrate to differentiate it from α-hemihydrate. The latter is a form obtained from dihydrate either by autoclaving or by solution processes. An inordinate amount of work has been carried out to establish the differences between these two forms using most available instrumental methods.

In the past, this has led to the proposition that both forms represent two limiting states whereby intermediate states can be prepared by changing the water vapor pressure existing during dehydration. From a practical point of view this work was done because α-hemihydrate has a considerable lower water demand than β-hemihydrate when preparing a plaster with a standard consistency. It was believed, therefore, that the different consistencies of kettle calcined stucco could be explained by different ratios of α- to β-hemihydrate or alternatively by a species that lies between the two extremes. Moreover, it was erroneously believed that aging, that is, the irreversible lowering of the consistency of kettle calcined stucco when exposed to adsorbed water, could be explained by a change of β-hemihydrate into α-hemihydrate.

Of the techniques used to identify the difference between α- and β-hemihydrate (heat of hydration, stacking order index, DTA, consistency), only a few still remain valid. The chief difference seems to be due to the fact that the α-hemihydrate particles consist of relatively large uniform mono-crystals. In contrast, the β-hemihydrate particles consist of clusters of micro-crystals that have the ability to undergo aging. That means that in the presence of adsorbed water vapor they lose the ability to disintegrate (change into individual micro-crystals) which gives the appearance of a change towards α-hemihydrate.

The data given in Table 4.3 show that at the first approximation the compressive strength of α-hemihydrate and β-hemihydrate depends largely on the amount of water used to prepare specimens, such as cubes, and not on the modification. The data also show that the compressive strengths of wet specimens are about a 50 % lower than that of dry specimens. This is a much greater effect than obtained for other cementitious materials such as Portland cement.

TABLE 4.4—Heats of hydration.

Phase Change to Dihydratte	J/mol	J/g
From β-hemihydrate	19,300±85	111.9±0.50
From α-hemihydrate	17,200±85	100.0±0.50
From β-anhydrite (sol.)	30,200±85	173.3±0.50
From α-anhydrite (sol.)	25,700±85	149.6±0.50
From anhydrite (insol.)	16,900±85	98.0±0.50

Differential thermal analysis clearly shows the difference between the two forms (Fig. 4.3). The thermograms indicate that the conversion of α-hemihydrate to insoluble anhydrite takes place immediately following the dihydrate to hemihydrate conversion rather than at 350°C (662°F) [4-2]. However, this difference may be lost when grinding the α-hemihydrate. Frequently quoted differences in heats of hydration are given in Table 4.4.

4.2.4 Soluble Anhydrite

Soluble anhydrite is obtained by removing the water molecules from the honeycomb structure of the hemihydrate, usually on further heating. This occurs without changing the original crystal structure. However, this process is dependent on the water vapor pressure present. That is, for each temperature up to about 200°C (392°F), a threshold water vapor pressure exists above which soluble anhydrite does not form. However, soluble anhydrite does form almost instantaneously when the temperature exceeds this threshold water vapor pressure. This is due to the unique characteristic of the hemihydrate, which allows water molecules to leave and re-enter its structure with relative ease despite the fact that they occupy specific stoichiometric positions. There appears to be no difference between α- and β-hemihydrate in this respect. However, above about 200°C (392°F) even saturated water vapor does not prevent soluble anhydrite formation. Below about 350°C (662°F) the dehydration-rehydration process is reversible and repeatable so that soluble anhydrite or hemihydrate can be obtained whenever either the temperature or the water vapor pressure is changed [4-3].

Since the soluble anhydrite is simply the anhydrous state of hemihydrate, the cumbersome term “dehydrated hemihydrate” is sometimes used to describe it. Care must be taken during its preparation because it reacts rapidly with water vapor at room temperature and even at elevated temperatures up to about 200°C to form hemihydrate. Also, insoluble anhydrite begins to form above 100°C (212°F) within a relatively short period of time. Therefore, soluble anhydrite must be prepared within certain limits of time, temperature and water vapor pressure. Significantly, soluble anhydrite converts rapidly to hemihydrate when exposed to water vapor or to liquid water. This characteristic is utilized industrially and in the laboratory when Drierite® (soluble anhydrite) is used to remove water from liquids and gasses. Spent Drierite® (hemihydrate) can be restored by heating at appropriate temperatures.

4.2.5 Insoluble Anhydrite

The third phase, insoluble anhydrite, is obtained by raising the temperature of hemihydrate or soluble anhydrite beyond about 350°C (662°F). As mentioned before, it must also be kept in mind that insoluble anhydrite can form slowly at lower temperatures. This dehydration step involves a further change in crystal structure from the honeycomb format of β-hemihydrate into a compact format of the insoluble anhydrite. Consequently, its structure lacks channels and for this reason it is the least reactive phase of the calcium sulfates. It exhibits the closest packing of ions, which makes it the densest and strongest of the calcium sulfates. The crystal structure becomes more compact with increasing temperature and time of exposure, which results in increasingly longer times of reacting with water.

Insoluble anhydrite produced by heat treatment is often called *thermal* insoluble anhydrite (or “dead burn” in industry) to differentiate it from natural insoluble anhydrite. Both varieties of insoluble anhydrite have the same crystal structure. Also, both varieties are similar in appearance and are being used in similar applications.

4.3 Rehydration to Dihydrate

Rehydration is the second key feature, which refers to the addition of liquid water to the hemihydrate or insoluble anhydrite. As mentioned before, soluble anhydrite converts instantaneously to hemihydrate and behaves thereafter as hemihydrate.

4.3.1 From Hemihydrate

For the rehydration process, hemihydrate dissolves to form a supersaturated solution with respect to dihydrate. It crystallizes as dihydrate from this solution and solidifies when the appropriate amount of water is used, producing only a slight expansion. The solidification appears to involve three types of bonds: (1) true crystalline intergrowth where ions are shared, (2) network formation by growing past each other into water filled spaces, and (3) hydrogen bonding where crystals touch. The time of conversion of hemihydrate to dihydrate is dependent on the calcination method but is usually in the order of 20 min. This time can be lengthened to several hours by the addition of retarders or shortened to less than 3 min by using suitable accelerators. The utilization of hemihydrate plasters depends to a large extent on these two characteristics. That is, in the past hemihydrate plastering technology required the use of retarders and stabilizers (retarder/accelerator combinations) whereas the present technology of manufacturing gypsum board relies mostly on the use of accelerators to achieve the required short setting times.

4.3.2 From Insoluble Anhydrite

Insoluble anhydrite crystallizes directly into dihydrate without forming a solution that is significantly supersaturated with respect to dihydrate. An increase in volume of about 60 % has been estimated for this process. This means that the process is essentially governed by the rate of solution of insoluble anhydrite rather than its solubility. Conversion normally takes place in a matter of days. This time can also be shortened to hours by the addition of activators such as K_2SO_4 but it is difficult to obtain setting times in the range of minutes. Obviously, this confines the use of insoluble anhydrite to certain applications such as mining mortars.

4.3.3 Acceleration and Retardation

The setting times of hemihydrate and of insoluble anhydrite are shortened or lengthened by the addition of accelerators and retarders. Both effects are absolutely essential for their application or to the manufacture of products, such as hardwall plaster and gypsum board. Accelerators reduce the time required for hemihydrate to form dihydrate whether or not retarder has been used previously to lengthen the setting time. This demonstrates again that gypsum is resilient and forgiving under certain circumstances.

The most common accelerator is gypsum itself by providing homogeneous nucleation points. This effect is noticed most often in the field when plaster is contaminated with freshly set gypsum. (Heterogeneous nucleation occurs when acceleration takes place with a material other than gypsum.) Ground gypsum treated with sugar, starch, or a surfactant is used for the manufacture of gypsum board. So is potassium sulfate, which represents a chemical type of accelerator by initially providing a large amount of sulfate ions. Aluminum sulfate in the presence of lime is used to accelerate and stabilize the set of hardwall plaster in the presence of retarder [Fig. 6.22(4)]. A common retarder in the past was soluble keratin, which was obtained by hydrolyzing animal hoof or horn material by treatment with sodium and calcium hydroxide. This process provides relatively long chain molecules with carboxyl, sulfo, amino, and amide groups. However, during a study of the mechanism of retardation [4-4], it was shown that short molecules are quite effective if the functional groups are in a preferred position. Carboxyl groups are always absolutely essential as shown by octric acid (1, 1′, 3, 5, 5′-pentane pentaacetic acid), which is an extremely potent retarder. For the manufacture of gypsum board, soluble keratin has been largely replaced by diethylene triamine pentaacetic acid (DTPA) [4-5]. This type of retarder represents a series of synthetic materials, which have demonstrated the function of amino groups if carboxyl groups are in the correct position. DTPA can be fed directly into the gauging water just ahead of the pin mixer and results in better control of retarder addition. The above retarders are characterized by a delay of the onset of the hydration with a minor effect on the rate of hydration itself. Another type of retarder performs differently in that it delays the rate of hydration with a minor effect on its onset. This type of retarder is represented by natural tartrate, which is activated by the presence of calcium hydroxide. Interestingly, it can be used with insoluble anhydrite either alone or mixed with stucco. In addition, several chemical species which represent small molecules are being used to retard the rate of hydration of plaster. This includes some phosphates which must be handled with a certain degree of care because of their potentially negative effect on the strength of plaster.

4.4 Misconceptions

4.4.1 Soluble Anhydrite “Prime”

Various materials have been characterized by x-ray analysis, differential thermal analysis, scanning electron microscopy, mercury porosimetry, and measurement of the specific surface area. On the basis of the values obtained, the existence three limiting states for soluble anhydrite were postulated: β-anhydrite, β-anhydrite prime, and α-anhydrite. An α-anhydrite prime was considered as well. In particular, it was claimed that β-anhydrite prime is produced at very low water vapor pressures when the water vapor is released rapidly and the particle size is small. Under these conditions, β-soluble anhydrite “prime” forms directly from the dihydrate without formation of an intermediate hemihydrate. Not surprisingly the β-anhydrite “prime” was shown to have a much higher specific surface area than either the β-anhydrite or α-anhydrite [4-6].

However, it should be obvious that soluble anhydrites and hemihydrates can be prepared in the laboratory with vastly different properties and characteristics. Consequently, this work merely identifies one method of preparing a β-soluble anhydrite. It must be emphasized that it does not constitute a separate phase but simply another condition since both hemihydrate and soluble anhydrite have the same crystal structure. This is a classic example of how confusion can be created about the existence of the various phases, states or forms in the $CaSO_4-H_2O$ system. Moreover, it would be necessary to use a different nomenclature for hemihydrates obtained from the soluble anhydrite prime by absorption of water vapor. For example, if this material differs in their physical properties from conventional hemihydrate it should be designated as β-hemihydrate prime.

4.4.2 2/3-Hydrate

Attempts are being made repeatedly to claim the existence of a calcium sulfate 2/3-hydrate. The last proposal was made in the late 1990s by studying the structure of dehydration products [4-7]. Specifically, it was claimed that both hemihydrate and the 2/3-hydrate were obtained during the dehydration of dihydrate and the crystallographic particulars of the 2/3-hydrate were identified. However, on closer examination of the data presented, it turns out that only the possibility of the existence of 2/3-hydrate was originally claimed, not the existence of the material itself [4-8]. Therefore, its existence cannot be accepted without considering additional evidence.

4.4.3 Colloidal Hydration

Cavazzi [4-9] and several others proposed a colloid theory according to which the hydration of hemihydrate to dihydrate proceeds via an intermediate colloidal or non-crystalline state. This concept is based primarily on the observation that hemihydrate plaster passes through a “plastic” state during the very early hydration stage where no dihydrate is yet detectable. The colloid theory has also been modified to include a topochemical reaction, which

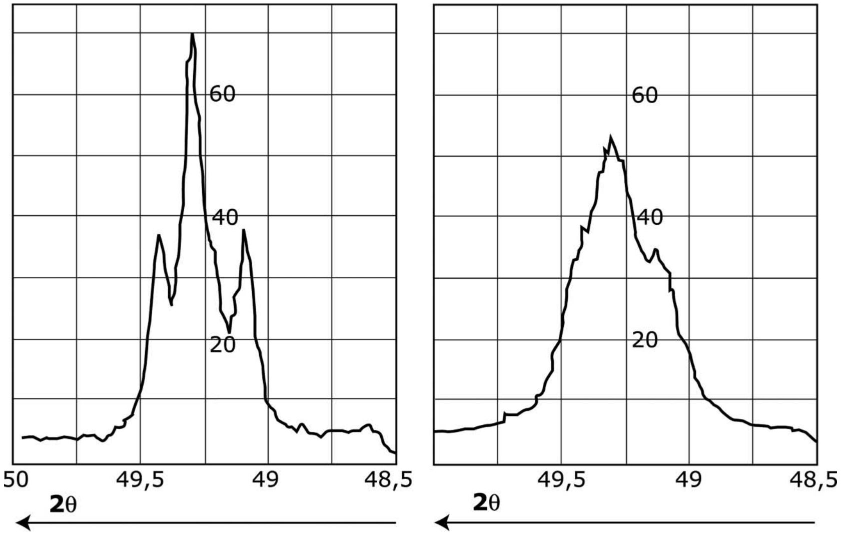

Fig. 4.5—Stacking order indices of α- and β-hemihydrate.

includes a hydration of the hemihydrate particles taking place over very short distances.

There are several other explanations for the behavior of the hemihydrate plaster, such as dispersion or disintegration of particles. The most likely explanation, however, is that that microcrystalline substances with a particle size smaller than 1 μm can behave as a colloid. This is due to the fact that below that particle size the surface of the substance determines its properties instead of its mass.

4.4.4 Formation of α-Hemihydrate in Stucco

To explain the differences in the water demand and setting time of kettle stucco, it has been postulated that α-hemihydrate and β-hemihydrate are formed in stucco during calcination. In principle, it was postulated that the ratios of these two forms were dependent upon the water vapor pressure surrounding the particles during the calcination process [4-10]. Heat of hydration measurements were used to support this hypothesis [4-11]. An inordinate amount of work was carried out subsequently to study the effect of water vapor on the formation of α-hemihydrate or β-hemihydrate. This led to various other hypotheses including the existence of a range of hemihydrates exhibiting intermediate properties between the two forms. The most interesting concept was advanced by Morris [4-12] who found differences in stacking order indices (Fig. 4.5).

However, none of these hypotheses have stood the test of time. Consequently, it is currently believed that only β-hemihydrate is formed during kettle calcination or at any atmospheric condition. The differences in properties between various stuccos produced and the changes with time are more properly assigned to differences in the reactivities of the stucco particles, as exhibited by the degree of dispersion, aging, etc.

4.4.5 Aging

Aging of stucco is a process that over time causes the drastic reduction in water demand (consistency) and the increase of setting time due to the absorption of water vapor [4-13]. The reduction of water demand is due to the loss of ability of stucco particles to disintegrate seemingly forming larger particles as the aging process proceeds [4-14]. Initially, this process has been assumed to be due to the conversion of soluble anhydrite to hemihydrate, which occurs very quickly in the presence of absorbed water vapor. However, it has been demonstrated that two separate processes occur and that aging of stucco proceeds long after all of the soluble anhydrite has been converted.

It was further assumed, following a suggestion by Riddell [4-10], that the loss of water demand on aging involves the conversion of β-hemihydrate into α-hemihydrate. The foundation for these assumptions was again provided by Kelley et al. based on heat of hydration measurements. However, it was shown by Lane's work that exposure to absorbed water vapor leads to a reduction in water demand, which is due to the loss of stucco particles that can be disintegrated. The increase in setting time over the same period is caused by the same changes of the apparent reactivity of the stucco crystal aggregates. Dihydrate is formed only when the amount of adsorbed water exceeds 2 %. This is a somewhat contentious issue because dihydrate can form after long periods of time (days and weeks) at moisture levels below 2 %.

A newer version of aging has been introduced through the work of Bold [4-15], in which stucco is exposed for a short period of time (minutes) to steam to lower its consistency.

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5

Calcination Processes

GYPSUM PROCESSING CAN BE CONSIDERED TO ENCOMPASS TWO separate stages. The first consists of the preparation of the raw gypsum and covers such steps as receiving and storage, drying, crushing, and grinding. The second stage involves the calcination of this material using a variety of equipment, such as kettles and kilns. Obviously, the essential feature of the first stage is to prepare the raw gypsum so that it is acceptable by the calcination unit. There are many procedures to accomplish this but it is always necessary to control moisture content and particle size distribution. For this reason, the procedures discussed below should be considered as examples to accomplish these tasks.

5.1 Natural Gypsum Preparation

Natural gypsum is mined in quarries using drilling and blasting at several levels or by underground mining using chamber blasting. This rock consists of large pieces usually containing up to 4 % free moisture. The coarse rock is conveyed to the crushing plant often located at the gypsum plant site. Impact crushers, jaw crushers, and single roll crushers with screens and oversize returns are all suitable for coarse size reduction. Impact pulverizers or roller mills are used for intermediate size reduction, and hammermills, ball mills, and ring-roll mills are used for fine grinding. The mined and crushed gypsum rock is sometimes homogenized before being calcined. This is done in homogenization plants, with capacities of about 1 week production. Cleaning or beneficiation of gypsum is done infrequently at the present time. A possible exception is the removal of Glauber's salt ($Na2SO_4 \cdot 10H_2O$) by washing.

5.1.1 Receiving and Storage

Conventional gypsum processing is considered to begin when the raw material is received by the plant. For example, 35,000 ton self-unloading ships, 100 ton rail cars, or 25 ton trucks, generally supply gypsum rock with a maximum diameter up to about 6 in. Conveyors generally move rock delivered by ship to a storage site. Because natural rock is relatively coarse, rain and snow does not materially increase its moisture content. This material has usually a density of 90 lb/ft^3 (1442 kg/m^3) and an angle of repose of 38°, which is given by the angle between the base of the material and its slope. This angle can be increased to 45° if the rock is dried and its particle size is reduced. Outdoor stockpiles of 1,200,000 ton are not unusual while storage buildings usually have a maximum capacity of about 40 000 ton. The intention is to provide a supply of 14 days for the plant. If transport to distant gypsum or cement plants is necessary, the gypsum is reduced to the size required by those plants.

Rock supplied by ship is often transferred by conveyor belt from the storage site to drying and crushing section of the plant. Rock supplied by rail car or truck may be stockpiled or fed through a grizzly into a hopper to be conveyed to the plant. Other feeders, such as apron conveyors or vibrating pans, may be used to assure an even feed to the belt conveyor.

5.1.2 Drying

If the free moisture content of the gypsum rock is below 3 % it can usually bypass the dryer and move directly to the crushing stage. However, for rock with moisture content above 3 % some drying may be necessary. Rock obtained from outdoor storage often contains a higher moisture content, which must be removed or reduced prior to crushing. The drying of rock can be obtained with a directly heated rotary dryer operating at 180°F (82°C). This type of dryer is usually 6 ft (1.8 m) in diameter by 50 ft (15 m) long and is capable of reducing the moisture content of the rock from 8 %–10 % to 2 %–3 % at a rate of 50 ton/h (45 metric ton/h).

5.1.3 Crushing

Natural rock is usually reduced in size to about 3/8 to 1 1/2 in. (0.95–3.81 cm). In many plants, the rock passes through a screen and only material larger than 1 in. (2.54 cm) is crushed. This approach allows the use of a lower capacity mill because only about one-third of the rock is larger than 1 in. in size. Both fractions are then combined and transported by bucket or screw conveyors to a crushed rock storage bin.

Excessive amounts of dust can be produced by high-speed impact crushers and by overloading of crushers. Crushers should therefore be operated at the lowest possible speed. For this reason, conveyors are normally enclosed for dust control and hoods leading to baghouses are located at each transfer point. Electrostatic precipitators or cyclones are used in some plants but they are considered inferior to baghouses. Magnets may be provided before and after crushing to remove ferrous materials (nails, wires, etc.). The bucket elevators or screw conveyors generally supply the crushed rock to several storage bins. Vibrators or air blast systems maintain proper flow. The bins typically have a capacity for a 24-hour operation of the plant. In some plants, facilities are provided to allow intermediate storage of the crushed rock. This provides more flexibility if other uses are contemplated. For example, the crushed rock can be homogenized if necessary at this stage. Also, the rock can be screened and the appropriate fraction used in rotary kilns or flash calcining mills. Further, it is possible to supply rock for Portland cement from these sources.

5.1.4 Grinding

Crushed rock is fed into a roller mill system, which is designed to reduce the rock to an appropriate size range. As a general guide, 90 %–95 % passing a 100-mesh (150 μm) screen is normally obtained. A variety of other mills can be used for this purpose as well. At this stage, it is possible to further reduce the moisture content of the rock by drying. In a more specific example, dried rock is passed through a Raymond roller mill to produce “landplaster” with a fineness of 0-trace on a 40-mesh screen (0.425 mm) and 60 %–65 % through a 325-mesh (0.045 mm) screen. Retention on a 100-mesh screen is then established to meet the 325-mesh criteria. Both 40-mesh and 100-mesh values are then measured frequently. The use of a 50-mesh screen is common as well.

The ground gypsum is often called landplaster because of its traditional use as fertilizer and soil conditioner. It is collected in cyclones and fed by screw conveyors to the kettle feed bins. These bins should contain enough material to fill the calcination kettle several times. High-speed hammer mills and single roll crushers normally produce higher proportions of fines than slow-speed hammer mills, ring roll mills or gyratory, jaw or double roll crushers.

5.2 Flue Gas Desulfurization (FGD) Gypsum Preparation

In North America quite a number of companies are now using synthetic gypsum as a complete replacement of natural gypsum. In 2006, about 46 % of the total consumption of 35 million tons of gypsum consisted of synthetic material. In almost all cases, this involves FGD gypsum. Titanogypsum is used in only a few locations in combination with other types of gypsum to compensate for the small particle size of this material. Large quantities of FGD gypsum are now available at power plants that are often located near population centers. One reason for accepting synthetic gypsum is its high purity (dihydrate content) combined with a low level of deleterious impurities. This makes these materials suitable for the manufacture of gypsum boards. Also, FGD gypsum can be processed into conventional stucco, multiphase plasters as well as α-hemihydrate plasters. In some cases, the plaster may require additional preparation or blending to obtain the required plasticity as a slurry.

In general, the potential for substitution of natural gypsum by FGD gypsum in a specific location depends on many factors including gypsum quantity and quality, proximity to power plants, lack of disposal sites, disposal costs, environmental concerns, and government regulations. In addition, the relationship of the user of the gypsum to the utilities is of major importance. However, after overcoming some initial problems, it seems that FGD gypsum has now found general acceptance.

FGD and natural gypsum differ in the chemical composition of their impurities. They also have different physical properties that may require special attention. In general, FGD gypsum has a higher purity and a lower level of major impurities such as limestone or dolomite. However, it may have a higher content of potentially deleterious impurities such as sodium, magnesium, and chloride salts as well as calcium sulfite, $CaSO_3 \cdot (1/2)H_2O$, flyash and residual carbon. It may also have a higher pH than 8, which can produce a poor bond of core to paper. It is important that impurities are below a specified level.

FGD gypsum requires a somewhat different handling procedure because of a number of differences between the two materials. The key difference is the fine particle size and narrower particle size distribution of the FGD gypsum. It also has a moisture content that is higher, usually just below 10 % as compared to natural gypsum about 4 %.

5.2.1 Initial Drying

Primary dewatering is the separation of the solid gypsum from the scrubbing slurry, which is the first step of preparing FGD gypsum for subsequent use.

Gypsum crystals obtained in a forced oxidation system are relatively large, which allows hydrocyclones to be used rather than thickeners that are less efficient. The hydrocyclones normally concentrate the solids from the slurry at the scrubber outlet from about 10 % to about 40 %.

Horizontal vacuum filters or vertical basket centrifuges are used for secondary dewatering by the majority of the recently constructed forced oxidation FGD plants. A cost analysis for this type of equipment and its operation should include the cost for chloride removal by washing and subsequent treatment of the wash water. Different types of dewatering equipment require different quantities of wash water and different auxiliary equipment for washing the filter cake.

The free water content of the filter cake from a horizontal vacuum belt filter is typically 10 %–12 %. A basket batch centrifuge produces free water content of about 6 %–8 %. FGD gypsum treated by both types of dewatering systems can be handled by dump trucks. Dust problems may arise when the moisture content falls below 5 %.

5.2.2 Receiving and Storage

FGD gypsum requires a covered storage because the amount of moisture held or adsorbed is a function of the particle size. Consequently, rain or snow may increase the moisture content of FGD, which will make subsequent processing difficult and more costly.

FGD gypsum is generally supplied as a wet filter cake or alternatively as a dried and agglomerated product or reclaimed from wet or dry storage stocks. It is seldom received as a completely dry powder or wet agglomerate. If the material is supplied as a wet filter cake, additional facilities will be required for unloading and subsequent handling. However, extensive modification of equipment and facilities is required if the material is supplied as a dry powder. Material that is dried and agglomerated requires the same equipment as natural rock because of the similarity in size.

5.2.3 Final Drying

In general, drying of FGD gypsum is carried out prior to most calcination processes. The rotary dryer employed for drying natural gypsum rock can possibly be used in some cases. However, it may require the same modification as carried out for the cage mill or the Williams mill because of the higher water content and the fine particle size of the material. Therefore other drying equipment such as the fluidized bed dryer has been used. This type of equipment can also be used for the combined drying and calcining.

The fluidized bed dryer is similar to the Hazemag rapid dryer or the Babcock flash dryer used in Europe. It consists essentially of a closed vessel with two rotating shafts in the lower part. The FGD gypsum is fed into the dryer behind the hot gas inlet. The hot gases entering the vessel has a temperature of about 400°C (752°F) and exits at about 90°C (194°F). The gypsum is moved upwards and forward by the rotating paddles with the hot gases to the end of the dryer. The residence time of the gypsum ranges from 8 to 13 s. The dried gypsum is then calcined in kettles and the stucco produced can be used without additional grinding for the manufacture of gypsum board or blocks. However, the particle size of the gypsum is too small to produce stucco to be combined with anhydrite to form plaster. One of the directly heated, co-current dryers for non-agglomerated FGD gypsum is shown in Fig. 5.1 as part of a drying-agglomeration plant.

5.2.4 Grinding

The grinding of FGD gypsum may be necessary if modification of its crystal shape or its particle size distribution is required. This improves the handling characteristics of the gypsum or the properties of the stucco after calcination. For example, changes in the size distribution of the gypsum may be required to change its fluidization and flow properties, which are important properties during the calcination process. This can possibly be achieved by increasing the $<10\ \mu m$ proportion of the gypsum, either by grinding or addition of fine gypsum or limestone. Also, the shape and size of the FGD gypsum crystals can be permanently modified by briquetting at $100\ kN/mm^2$ and subsequent grinding. This suggests that briquetting is a suitable process to prepare FGD gypsum with poor crystal shape for conventional calcination.

The small particle size of the FGD gypsum makes it particularly suitable for kettle calcination. It may also be suitable for special rotary kilns that use ground gypsum, but these are not common. One such rotary kiln, manufactured by Schilde (now part of Grenzebach BSH), is used in North America. Other exceptions are indirectly heated tube kilns also provided by Babcock-BSH.

5.2.5 Agglomeration

For conventional calcination in the rotary kiln or the conveyor kiln, FGD gypsum must be agglomerated before it is suitable as feed material. Various agglomeration processes have been developed for FGD gypsum that primarily supply, with subsequent grinding, larger particles for specific calcining processes. Similarly, certain Portland cement plants can be provided with this material.

Of the agglomeration methods such as granulating, extrusion, pelletizing, and briquetting, the latter has proved to be the most effective and is the most widely accepted. In this process, the FGD gypsum must be dried prior to compacting without the use of binders or other additives. This produces a 2 cm thick (3/4 in.) and 6 cm long (2 1/2 in.) briquette. Grinding of the briquettes also provides the means of modifying the crystal shape and size distribution of the FGD gypsum. However, this involves a high cost of about $10/ton. Dried and agglomerated FGD gypsum can be handled by conventional equipment in the same way as natural gypsum rock; assuming that fine particles created by excessive attrition do not create unforeseen difficulties.

The briquettes have mechanical properties that do not differ substantially from those of natural gypsum. They have a hardness of 500 N, an apparent density of $\approx 2.15\ g/cm^3$ and a bulk density of about $1\ ton/m^3$ ($68.6\ lb/ft^3$). Also, they are exceptionally abrasion resistant and they can be stored in the open since they do not disintegrate when exposed to rain or frost. For this

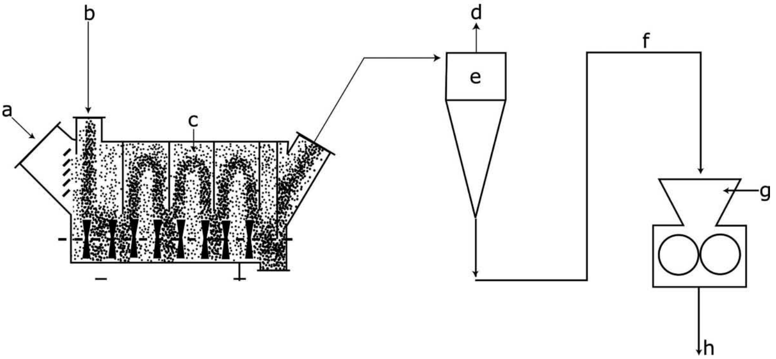

Fig. 5.1—FGD gypsum drying and briquetting: (a) hot as inlet; (b) moist FGD gypsum inlet; (c) rapid dryer; (d) hot gas outlet; (e) cyclone; (f) dry FGD gypsum inlet; (g) compacting press; (h) briquettes.

reason, FGD briquettes can be processed in conveyor kilns to multiphase plasters in the same manner as natural gypsum. They can be used alone or mixed with natural gypsum.

Figure 5.1 shows a flow diagram of a plant for processing FGD gypsum by drying and briquetting. The extra energy required to dry one tonne of dry FGD gypsum consists of 550,000 kJ of thermal energy and 12 kWh of electrical energy. Agglomeration by briquetting requires 10 kWh.

5.3 Preparation of Other Gypsum and Anhydrite

5.3.1 Phosphogypsum

The utilization of phosphogypsum is problematic mainly because it contains a high proportion of deleterious impurities such as phosphates, silicofluorides, and organic substances. Also, the small particles size of the phosphogypsum results in a high water content of 20 %–30 %. More importantly, there are also significant differences between European phosphogypsum and North American phosphogypsum since they are derived from different phosphate rock. European phosphogypsum is usually derived from Moroccan (sedimentary) or Kola (magmatic) phosphate rock whereas Florida rock is the source in North America. Moroccan rock contains small amounts of radioactive uranium, which is present in larger quantities in Florida rock. For this reason, great care must be exercised when interpreting results obtained in Europe.

Many approaches have been investigated to process and utilize phosphogypsum over the past years. However, most of these have been met with mixed results at best. It must be concluded therefore that the chance of phosphogypsum ever being utilized on a large scale is extremely remote. For this reason they are not discussed further in this publication.

5.3.2 Titanogypsum

This material is available in limited quantities in North America and Europe. It is obtained by the neutralization of dilute sulphuric acid by calcium carbonate under specific conditions such as *p*H. Characteristically, it has a white color and a high purity. The only known problem is its fine particle size and needle like crystal habit that requires blending with other types of gypsum or agglomeration.

5.3.3 Insoluble Anhydrite

The only material in this category is fluoroanhydrite, which does not require calcination. Instead, it is neutralized with calcium hydroxide and ground for use as anhydrite plaster. Activators to promote setting are potassium sulfate, zinc sulfate together with calcium hydroxide, or Portland cement. These are usually mixed with the anhydrite at the plant. There are a number of problems associated with the utilization of this material. It is slow setting despite the use of activators and it may have a latent acidity, which depends on the manner in which the occluded fluoric acid is released from the anhydrite crystals. Fluoroanhydrite also has a different crystal shape from natural anhydrite. It consists of very small primary crystals that have been combined to secondary particles with a high surface area and a high reactivity. In contrast, natural anhydrite consists of very large primary particles, which must be processed further by grinding.

5.4 Calcination Methods

Little is known about the beginning of ancient calcination methods. The earliest descriptions given by the Egyptians refer to the placing of hand-sized pieces into an open fire. The temperature of these fires could be raised by blow tubes or bellows. Contamination with ash was minimal since the chunks did not disintegrate. This method of calcination was changed very little over time and the Romans appear to have calcined gypsum in a similar manner although their facilities were larger. It is also not known to what extent they differentiated between limestone and gypsum. There was some improvement, which probably took place in the 15th century when large pieces of gypsum were placed on a grate in a furnace to separate it from the ash. It is obvious that for all these processes, a control over the calcination process was incidental. The materials produced resembled insoluble anhydrite.

A major departure from the above procedure took place with the advent of equipment such as the Harz Mountain kettle, probably in the 17th century. This kettle resembled a shallow pan in which ground gypsum was heated indirectly. Since this took place under more controlled conditions, it allowed the production of stucco instead of anhydrite. Significantly, the calcination process gave the impression of a mechanism akin to boiling due to the release of steam. This was an essential feature for more modern processes since release of steam caused fluidization of the gypsum and maintained a high water vapor pressure surrounding the individual particles. Modern, larger kettle processes, whether continuous or not, makes use of this concept.

Calcination is obviously the most critical operation of the gypsum plant. If the gypsum is under-calcined, the residual gypsum may reduce the setting times. If present in large enough quantities, it will also lead to lower strength. If the gypsum is over-calcined to contain soluble anhydrite, the energy consump-

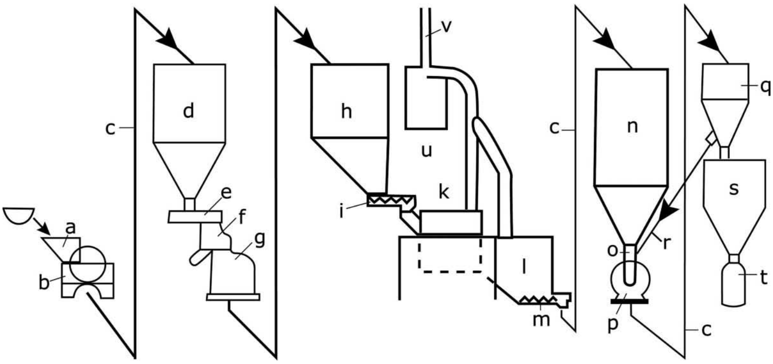

Fig. 5.2—Calcination process for grinding before and after calcination: (a) inlet; (b) breaker; (c) transport arrangement; (d) intermediate silo; (e) feeder; (f) magnet drum; (g) hammer mill; (h) silo; (i) transport screw; (k) kettle; (l) hot pit; (m) transport screw; (n) silo; (o) cell feeder; (p) grinding mill; (q) classifiers; (r) large size return; (s) silo; (t) bagger; (u) dust collector; (v) exhaust pipe.

tion is increased and the setting properties of the stucco may be affected.

Chloride levels can affect the calcination of gypsum through a process known as aridization. This generally results in lower water demand of the stucco produced and it is more noticeable with batch calcination. For this reason, it is sometimes referred to as artificial aging. Chlorides can lower the calcination temperature and thereby result in undesirable phase distributions of the stucco. Most importantly, chloride salts interfere with the bond between the core and the paper of gypsum board. Therefore, specifications for chloride levels are quite stringent. However, efficient washing techniques have been developed, which can reduce chloride to acceptable levels, usually below 100 ppm.

Although many industrial processes for the calcination of gypsum have been developed, only a few have been used extensively. They are usually characterized by simplicity of design and by robust equipment combined with low capital and operating costs. The intention is to manufacture as uniform a calcination product as possible. This calcination product is always based on stucco, that is, β-hemihydrate.

At the present time there are various calcination processes in use in North America and in Europe. The main processes, however, are based on the Ehrsam Kettle and to a lesser extent the Rotary kiln. Possible exceptions are systems that grind and calcine at the same time such as the flash calcining Raymond impact mill (imp mill) and the Claudius-Peters ring ball mill. Grenzebach BSH produces similar impact mills and roller mills that are nearly identical to the Claudius-Peters ring ball mill. The term flash calcining is used to define processes that produce stucco rapidly, that is, in terms of seconds or minutes rather than hours. Similarly, Calcidyne operation involves rapid calcining of gypsum that is ground prior to feeding.

The conventional kettle and other equipment used for the calcination of ground natural gypsum are also suitable for the calcination of FGD gypsum. Agglomerated material is normally required for units that require coarse natural gypsum such as rotary kilns, conveyor kilns, impact mills, or roller mills. Flash calciners without grinding capabilities, such as the Calcidyne and the Holoflite units, are also suitable for FGD gypsum. Moreover, the Raymond cage mill, which was converted to a dryer/flash calciner for moist gypsum, has been used successfully in several plants.

In Europe, continuous and conical kettles with capacities of up to 45 tons have been use for some time. Some difficulties in conveying and mixing have been experienced because of the unusual flow properties of the dry FGD gypsum. This can result in material flowing out of gates that retain natural gypsum. Similarly, dry FGD gypsum may consolidate (bridge) and resist mixing under certain conditions.

Kettle calciners operate most efficiently when the calcining mass is well fluidized by the steam generated by the calcination process. Often, smooth fluidization is dependent on a relatively broad particle size distribution. This can be accomplished by grinding or the addition of $<10\ \mu m$ material. The relationship between size distribution of FGD gypsum and calcination properties has not been investigated. Consequently, the details of the modifications of the distribution to improve calcination properties are not known.

A typical arrangement for a calcination process is shown in Fig. 5.2.

5.4.1 Batch Kettle

The batch kettle was initially the process adopted by the gypsum industry for the production of stucco that was intended for the manufacture of so-called hardwall plaster. This kettle consists of a steel shell 3/8 in. (0.95 cm) thick and a convex bottom 1 1/2 in. (3.2 cm) thick, heated indirectly at the bottom. The earlier kettles were pierced by four flues about 14 in. in diameter, normally arranged two above two but sometimes with four in one line. Kettles are usually about $12 \times 12\ ft^2$ ($3.7 \times 3.7\ m^2$) in size with a capacity of about 20 ton of gypsum. Other kettles can have capacities as low as 7–10 ton and as high as 40–45 ton. The example discussed below is based on a 20-ton kettle.

Kettles are normally fitted with burners that allow a low and high firing rate. The combustion chamber should contain most of the flame to reduce radiation to the kettle bottom. Also, minimum excess air should be used to accomplish complete and clean combustion. Leakage of air into the system should be avoided. Baffles are provided in the combustion chamber to direct hot gases against the bottom. If the equipment is suitable the hot gases should also pass up the sides, down the back and through the flues of the kettle to the stack. The heat transfer surface of both the kettle bottom and the cross flue tubes should be cleaned periodically in order to maintain maximum efficiency. The fuel used for heating is usually gas but oil and coal may be used as well (Fig. 5.3).

Originally, batch kettles were operated with a calcination cycle of about 2–3 h. In this process, the dried gypsum is ground to <2 mm (0.08 in.) and added to the kettle over a period of approximately 15–30 min. The stirrer is in operation at that time and the kettle is heated according to a specific program.

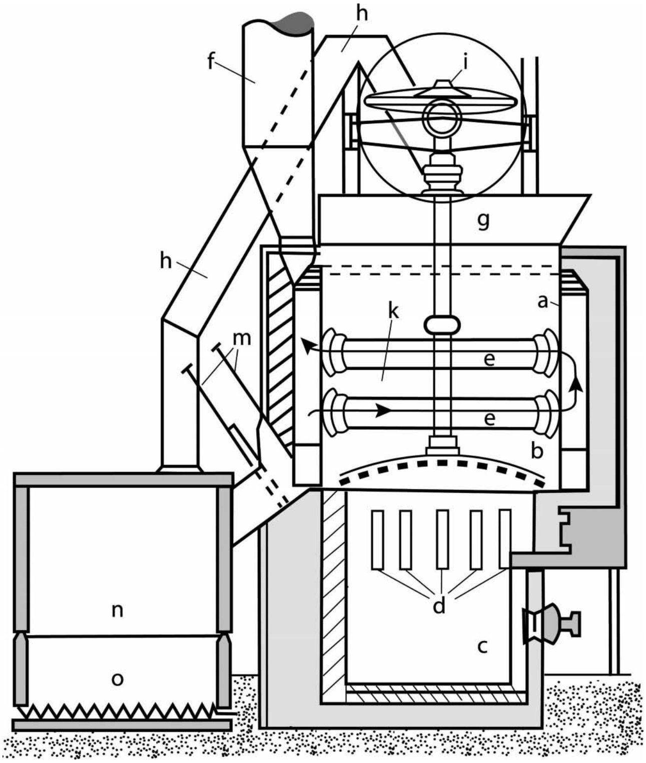

Fig. 5.3—Batch kettle with four transverse flues, usually oil or coal fired. (a) Kettle; (b) kettle bottom; (c) furnace; (d) baffles; (e) flues; (f) stack; (g) exhaust lid; (h) exhaust pipe; (i) stirrer motor; (k, l) stirrer; (m) dumping slide; (n) hot pit; (o) transport screw.

The calcination temperature (drag) is about 125°C (257°F) and the dump temperature is normally about 160°C (320°F). For a hot kettle, filling takes place immediately following the dumping. The total thermal efficiency (energy including electrical energy) of batch kettles is low at about 55 %. (Table 5.1)

When starting with a cold kettle, heat is supplied for about 3 h using the low firing setting. This is intended to minimize thermal shock of the refractory materials within the kettle. While the stirrer is operating, a small sealing charge of about 2 tons of gypsum is then fed into the kettle and is allowed to come to a boil with the burner still at a low firing rate. Feeding about 5 tons into the kettle follows the sealing charge and the burner is set at the high firing rate. The remainder of the gypsum is then added at a rate to maintain boiling.

At the end of the calcination cycle, the stucco is "dumped" within 30 min from the kettle into the hot pit, a silo built from concrete or steel. The stucco is normally cooled to about 125–140°C (257–248°F) and post-calcination grinding often takes place. This is a critical step because the stucco ages on exposure to water vapor in the hot pit. Also, both the rheological properties (e.g., consistency or water demand) and the setting characteristics can change.

In extreme situations, liquid water is formed in the hot pit when the water vapor condenses. This leads to the formation of dihydrate and very short irregular setting times.

Stirring of the batch kettle contents is provided primarily by the steam released during the calcination. Additional mechanical stirring is necessary for the filling and cook-off periods (time just prior to dumping) when the steam release is slow. The standard mechanical stirring is provided by a central shaft approximately 1×6 in.^{2} (2.5×15.2 cm^2) and sufficient in length to reach within less than 6 in. (15.2 cm) of the kettle wall. The blade of the paddle is set at an angle of 45° so as to plow the material in the kettle upward and towards the center. Stirring is of particular importance for the bottom arm that has a different shape and conforms to the bottom of the kettle. The material in this area must be constantly moved to maintain efficient heat transfer and avoid overheating. Drag chains are added to the bottom arm for this purpose. There are numerous arrangements for stirrer and drag chains in use, all intended to move the calcining material away from the kettle surfaces.

To ensure constant stucco quality, it is essential to maintain all operational steps as constant as possible. This requires diligent operation if the kettle is operated manually. However, many of these problems can be overcome by an automatic operation.

The batch kettle in general has a lower rate of production than the continuous and submerged combustion kettles discussed subsequently. This is mainly due to extra time required by the emptying and refilling of the batch kettle. However, optimization of operation can be achieved by controlling the following parameters: Stacks, filling systems, kettle top openings, kettle gates, hot pits, scalping screens, aridization (lowering of the consistency through chloride additions), and instruments for kettle temperatures, firing control, control panels, and interlocking systems. In that context, it is most important to establish a calcination plan with appropriate control functions for such operating steps as cold and hot start ups, kettle filling control, drag, and cook-off and dumping. To avoid creating dust, the kettle should not be filled too high.

5.4.2 Continuous Kettles

The conventional batch kettle used to compete with the rotary kiln, particularly since the latter operated on a continuous basis and provided nearly instantaneous turn-on and shut-off means. This has changed since the kettle has been modified to a continuous operation. BPB Canada (Westroc), now CertainTeed Gypsum, developed the continuous process in the late 1950s and it is now used almost universally. The key change consisted of the introduction of mechanisms that allowed simultaneous adding of gypsum and removal of stucco. This led to an increase in the rate of production and the thermal efficiency. The increase in the rate of production relates to the batch kettle, primarily because of time saved through fewer start-up and dumping steps. About 10–12 ton/h can be produced in a 20 ton kettle. Also, continuous kettles are fitted with up to 18 flues and the gases are passed though the flues more than once. The partial recirculation of combustion gases tends to increase

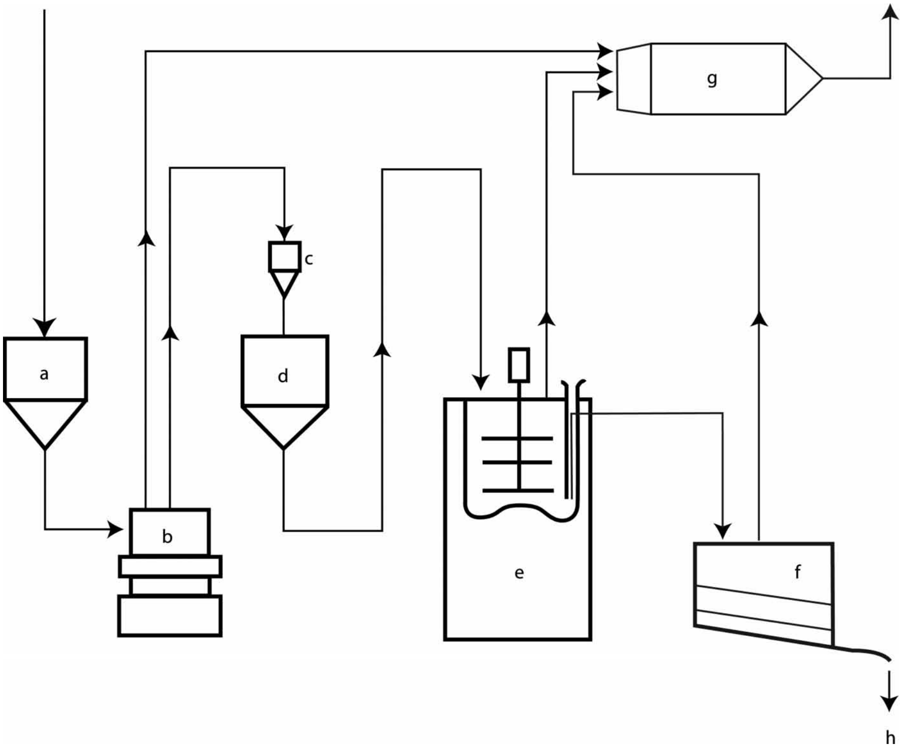

Fig. 5.4—Continuous stucco production: (a) gypsum silo; (b) drying-grinding unit; (c) cyclone; (d) feed bin; (e) continuous kettle; (f) hot pit; (g) electrostatic precipitator; (h) stucco outlet.

thermal efficiency, which is about 65 %, considerably better than that of the batch kettle.

The initial start-up for continuous operation is similar to that used for the batch kettle. This consists of filling the preheated kettle with raw gypsum while heating and stirring is maintained. When the kettle contents reach the required control temperature, the addition of the gypsum is balanced with the discharge of the stucco to the hot pit. During the calcination of gypsum the developing water vapor fluidizes the material, as in the case of the batch kettle. The stucco settles to the bottom and it is continuously discharged near the top through a pipe connected to the inside of the kettle (Fig. 5.4).

The operation of the continuous kettle has a number of advantages over the batch kettle such as a more constant product, easier operation, less wear, more efficient utilization of dust collectors, and constant waste heat from burners.

In some plants, the gypsum is ground ahead of the calcination instead of or in addition to grinding the stucco after calcination. However, these procedures do not have the same effect. Grinding gypsum before calcination broadens primarily the particle size distribution of the gypsum in order to change

TABLE 5.1—Total energy efficiency and rate of production of kettles.

		10 ton kettle		20 ton kettle	
	Operating Temperature, °C	Energy Efficiency, %	Production Rate, ton/h	Energy Efficiency, %	Production Rate, ton/h
Batch process	125	35–45	3–5	45–65	8–10
Continuous process	>140	40–45	4.5–5.5	55–75	9–12
Submerged combustion	>140	55–60	6–9	63–83	16–19
Conical kettle	140–170			90	20

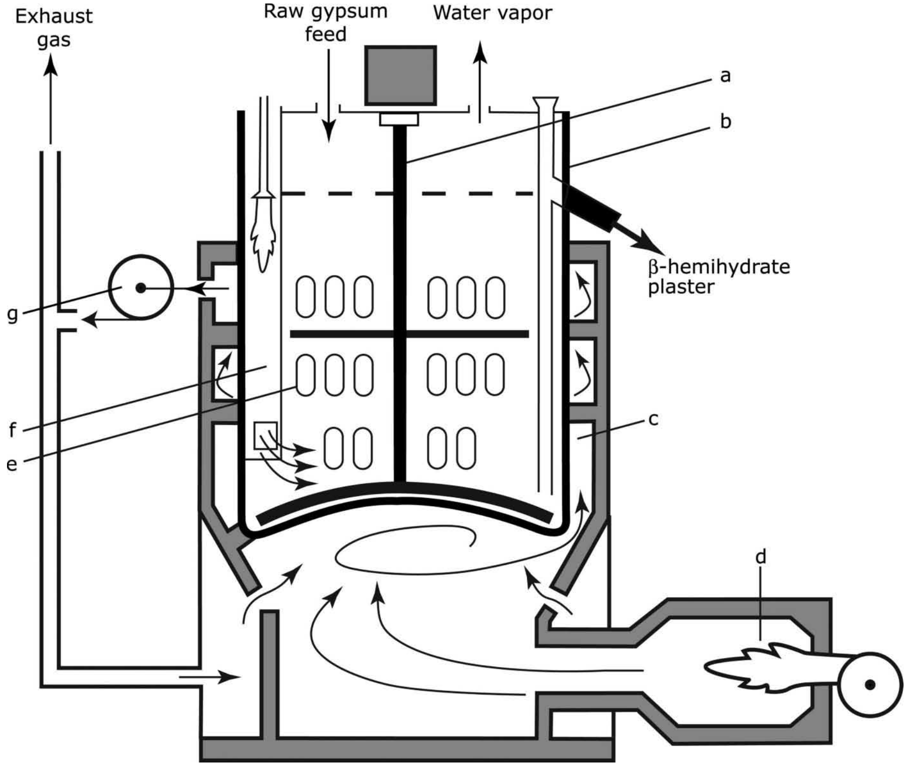

Fig. 5.5—Kettle with submerged combustion: (a) stirrer; (b) outer casing; (c) pipe for stucco discharge; (d) combustion chamber; (e) cross flues; (f) pipe burner for submerged combustion; (g) recirculation fan.

primary the flow properties of the gypsum. Grinding of the stucco produces new surfaces that can.materially change the rheological and the setting properties of the stucco.

5.4.3 Submerged Combustion Kettles

This technique has been developed as a means of further increasing the rate of production of existing kettles. As a result, a number of kettles are now equipped with submerged combustion providing about 35 % of the energy consumed (Table 5.1). The production rate of both the batch and continuous kettle is limited by the quantity of heat, which can be transferred to the material to be calcined mainly through the bottom of the kettle and to a lesser extent through the flue tubes. Above a given temperature limit, there is the possibility of more frequent kettle damage.

Therefore, the submerged combustion technique was developed for the purpose of providing a more efficient method of direct heat transfer. The obvious advantage of the process is that extra heat can be supplied directly to the material being calcined without raising the bottom temperature of the kettle.

The material in the kettle is fluidized primarily by the steam generated during calcination. The heat transfer in a fluidized bed is very high and the heat contained in the combustion gases is passed directly to the kettle content. Therefore, the submerged combustion system increases the fuel efficiency of the continuous kettle. The efficiency is increased to approximately 75 % excluding the normal bottom burner. The gases leave the bed about 5–10°C (41–50°F) higher than the kettle control temperature, which contributes to the high thermal efficiency of the system. When using natural gas, the burner is adjusted to operate with only 10 % excess air, which also adds to the fuel efficiency.

Typically, when an existing kettle is fitted with a submerged combustion unit, there is also a saving in electrical energy in addition to the increase in rate of production. When using submerged combustion, the amount of dust passing the dust collector is obviously increased. To reduce the dust loading to the collector, a level control device is used for the kettle as a standard feature (Fig. 5.5). When properly operated, the quality of the stucco produced changes little. However, there is some reduction of setting times, which is an advantage if one considers the manufacture of gypsum board.

5.4.4 Conical Kettle

The conical kettle is the logical extension of the experience obtained with the continuous kettle having submerged combustion. The kettle consists of a cylinder with a conical bottom and a cylindrical upper portion. All the calcining heat via the combustion gases is passed directly into the calcining material. This is done from the top of the kettle through a tube reaching almost to the bottom, which is protected from the heat of the flame by a ceramic or concrete cone. Gypsum is added continuously to the top of the kettle and stucco is removed through an overflow arrangement located at the conical part of the kettle. Significantly, the conical kettle does not have a stirring mechanism.

Fluidization and stirring of the calcining material is achieved by a combination of steam being generated during calcination and the flue gases being supplied by submersed combustion. This mixing effect is assisted by the conical bottom of the kettle (Fig. 5.6).

The greatest savings in energy consumption is claimed for this process because of the direct contact of all of the flue gases with the calcining material as well as the absence of an electrical mechanism for stirring. In this manner, a 20 ton kettle produces about 20 ton/h of stucco with an energy efficiency of 90 %. However, care must be exercised for this process since the material is exposed directly to the heat of the burner flame operating at a relatively high temperature. For all kettles, it is characteristic that at the end of the normal calcination procedure both soluble anhydrite and dihydrate are present in small amounts. This can be exacerbated in the conical kettle. Moreover, insoluble anhydrite can be formed in substantial quantities when this kettle is being operated incorrectly.

Complete and accurate tests are essential for all kettle operations to develop and maintain good calcination practices. A testing program should be developed for each particular plant to show the properties of materials at all stages of the process. However, the complete control of quality requires more than just the testing itself. It requires intelligent interpretation of the test results to determine where and when changes should be made. Therefore, other observations of the performance of the entire system should be taken into consideration (Table 5.2).

5.4.5 Rotary Kilns

A typical modern rotary calciner is basically a ceramic lined steel cylinder, 8 ft (2.4 m) in diameter and 130–155 ft (39.6–47.2 m) long that is installed at a slope of 1/2 in. per foot (3.9 cm per meter). The speed of rotation is about 1–2 rpm. In North America, direct heat is normally supplied in a counterflow manner, that is, with the heat entering the shell at the stucco discharge end. The feed for the rotary kiln is relatively coarse with a size range of 0–1 in. (0–25 mm), which often does not have to be dried prior to calcination. This feed is heated by direct contact with the flue gas as well as by radiation from the shell. The internal design of the shell must provide uniform distribution of feed and heat supply. In addition it must provide sufficient air to allow proper combustion and to remove the steam released during calcination.

Earlier versions of the rotary kiln calciners were shorter and did not contain distribution diaphragms. They were used with co-current flow by introducing the feed and the heat at the front end. Difficulties such as maintaining a uniform flue temperature led to changes in design that are commonly used in North America. In Europe, co-current rotary kilns, as shown in Fig. 5.7 are still in use.

Rotary kilns are more energy efficient than average size batch kettle or simple continuous kettles with a capacity of 20 ton/h. Continuous kettles with a capacity of 40–45 ton/h are almost equal to rotary kilns and only conical kettles are more efficient. Primarily, this is due to the higher production rate of kilns producing up to 25 ton/h of stucco and the corresponding fuel savings.

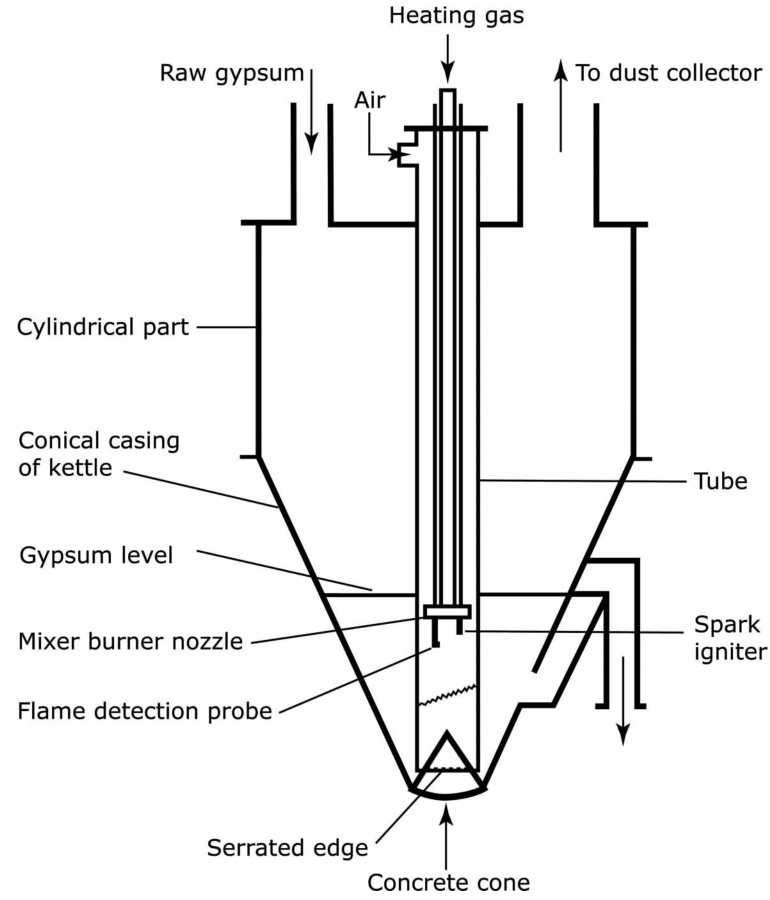

Fig. 5.6—Conical kettle.

For these reasons and because the kiln has almost instantaneous start-up and shut-down capabilities, rotary kilns were at one time the calciner of choice for some companies in North America.

Grenzebach BSH manufactures a co-current rotary tubular kiln, which is

TABLE 5.2—Analysis of stuccos produced.

	Dihydrate, %	Soluble Anhydrite, %	Insoluble Anhydrite, %	Water Demand, mL/100 g	Setting, Time min.
Batch kattle	3	11	2	64	25
Continuous kettle	4	6	2	65	18
Submerged combustion	4	6	2–4	65	15
Conical kettle	4	6	3–4	65	15

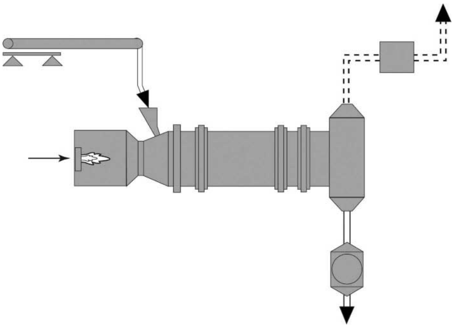

Fig. 5.7—Co-current rotary kiln.

fitted with several flues along the length of the kiln to increase the heat exchange. This type of kiln requires a feed of about 2 mm (0.08 in.) instead of the usual 25 mm (1 in.).

If properly operated, the rotary kiln can produce stucco similar in uniformity and quality to kettle stucco, both for the manufacture of hardwall plaster and gypsum board. This can be achieved only by feeding the proper size gypsum at a uniform rate through the rotary kiln and by heating the gypsum uniformly. Various mechanical methods are used for this purpose. For example, a diaphragm is used to spread out the feed that may be damp and to provide more surfaces for heat transfer.

However, since the feed to the rotary kiln consists of particles ranging in size from fine dust to about 1 in., there is a tendency to over-calcine the fine dust to a water-of-crystallization content as low as 1 %. Conversely, the centers of the very large particles tend to be under-calcined to a water-of-crystallization content as high as 10 %. A feed with a fines content of less than 10 % through a 100-mesh screen is satisfactory because it tends to roll over itself while passing through the shell. This brings the coarse particles to the top and protects the finer particles in the center.

The dust from the collector is the least desirable part of the product. It forms a significant part (5 %–10 %) of the stucco produced. Since the dust is collected from the entire length of the calciner, it contains a mixture of gypsum, hemihydrate, and soluble anhydrite. The material is further calcined by the hot gases that carry it to the collector. Consequently this material is usually soluble anhydrite and insoluble anhydrite. Insoluble anhydrite remains unchanged and constitutes an impurity, which may be significant. Also, the dust can have a high *p*H because of the possible decomposition of the insoluble anhydrite to CaO and SO_3.

FGD gypsum must be agglomerated prior to calcination using this type of calciner. Rotary kilns that use a powdered gypsum feed are not common, except the tubular rotary kiln produced by Grenzebach-BSH. A possible advantage of such a technique is that drying and calcining may be carried out in one step.

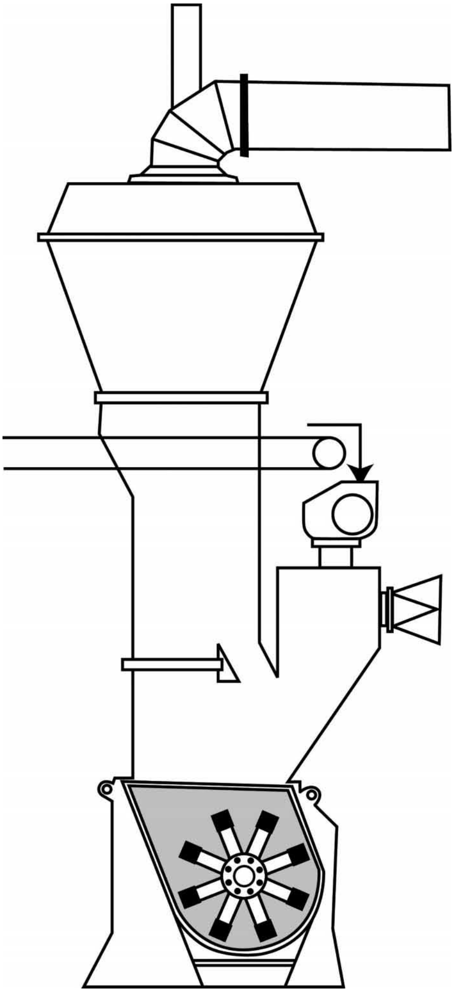

Fig. 5.8—Imp mill calcination.

5.4.6 Impact Mill Calciner

Some flash calciners (e.g., impact mill and ring ball) grind and calcine the gypsum simultaneously. The feed for these operations is generally in the order of 3/4 in. (1.9 cm). Agglomerated FGD gypsum can be used for these calciners, which has the added advantage of modifying shape and size distribution. Alternatively, the hammers can be removed from the imp mills to process the FGD gypsum in a dry or wet state. For either approach, calcination parameters and the effect of size distribution require further examination.

A well known flash calcination system in North America is based on the impact hammer mill (imp mill). It grinds and calcines gypsum simultaneously using the same Raymond impact hammer mills that are used to pulverize gypsum. The large version of this mill produces about 12 ton/h with a fineness of 96 % passing a 100-mesh (150 μm) screen or <0.2 mm. The gypsum is generally pre-ground to pass 3/4 in. (1.8 cm) screen. A smaller version of this mill is in use producing approximately 2 1/2 ton/h or less.

Hot gases, generated in a burner outside the mill, are blown into the grinding chamber of the mill while the gypsum is being pulverized. The ground and calcined material is carried out of the mill by the hot gases and collected in cyclones. As in conventional calcining, the hot stucco is transferred to a hot pit for cooling. Attempts have been made to make this a truly start-up and shut off process by avoiding the hot pit. This has not been successful since the hot pit appears to be needed to produce uniform stucco by calcining residual gypsum and converting soluble anhydrite to hemihydrate. Very fine material remaining in the gas stream is removed by bag houses and combined with the calcined gypsum. The hot gases are recycled to the burner, which is one reason for the relatively high-energy efficiency of this process (Fig. 5.8).

5.4.7 Ring Ball and Roller Mills

These flash calcining systems originated in Europe. The Claudius-Peters ring ball mills are similar to roller mills except that balls are used instead of wheels as in the Grenzebach-BSH calciner. Both are often used for simultaneous grinding and drying of coal. Therefore, the move to a combined grinding and calcining of gypsum was a logical step. The operation of the ring ball grinder/calciner is very similar to that of the imp mill calciner, except that gypsum up to 1 1/2 inch (3.8 cm) can be used as feed material. The stucco produced has a particle size of approximately <0.2 mm (100-mesh or 150 μm) (Fig. 5.9). Exact thermal and electrical energy requirements are difficult to establish. Thermal energy consumptions of similar devices were found to be between 940 and 1312 kJ/kg (890,000−1,234,000 Btu/ton). The corresponding electrical energy requirements are generally between 34 and 53 kWh/ton.

5.4.8 Calcidyne Unit

This flash calciner accepts pulverized feed intended for a single pass. It resembles a vertical rotary kiln, directly heated, with baffles to control the movement of material through it. The gypsum and flue gases enter the unit at the bottom and the stucco is collected at the top. The flue gases and the water vapor from calcination are recycled into the bottom of the calciner. The Calcidyne unit is suited for FGD gypsum because it accepts material with a narrow feed size distribution (Fig. 5.10).

There are various other calcining units in use in North America and elsewhere, such as the Holoflite. These are not discussed further here because of their similarity to other units or because they are not significant.

5.4.9 Anhydrous and Multiphase Plaster

Anhydrous plasters are produced with dry calcining processes between 300 and 900°C (572 and 1652°F). Usually three reaction stages are being considered, i.e., <500°C so-called slowly soluble anhydrite, 500–700°C (932–1292°F) insoluble anhydrite and >700°C floor screed plaster. Specific ratios between

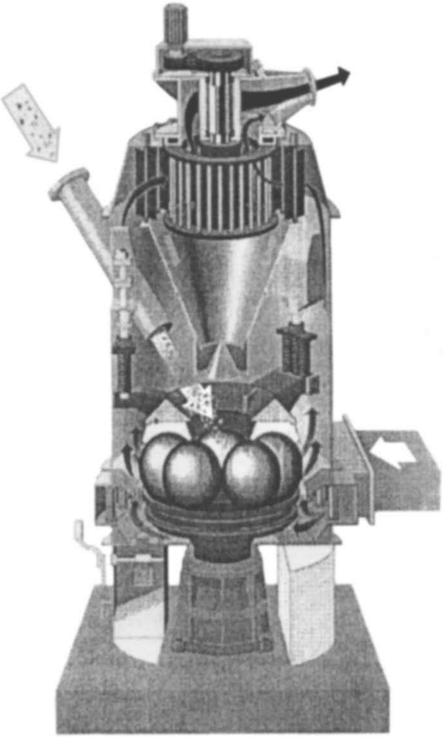

Fig. 5.9—Claudius-Peters ring ball calciner with classifier.

the reaction stages are required, which are determined by both the raw material and the calcination process. Finally, these plasters are mixed with conventional stucco to obtain multiphase plasters.

A modern calcining process for anhydrite plasters is the conveyor kiln. Capacities of 1200 tons per day are usual and the thermal efficiency of the conveyor kiln is believed to be greater than 70 %. Before being fed into the conveyor kiln, the gypsum is crushed to pass a 60 mm (2.4 in.) screen and split into several sieve fractions, i.e., 7–25, 25–40, and 40–60 mm (0.2–1, 1–1.6, and 1.6–2.4 in.). The fractions are placed in layers onto a moving grate, the smallest size on the bottom. The grate moves at a speed of 20–35 m/h underneath a calcining hood from which the hot gases are drawn through the gypsum by fans. There is little dust being created because the gypsum is not moved during calcination and therefore no dust collection is required. About half of the gases at approximately 270°C (518°F) are recirculated to the combustion chamber and mixed with air at about 230°C (446°F), which is then drawn through the plaster bed for cooling (Fig. 5.11).

For the production of multiphase plaster, intended for spray application, the anhydrite is mixed in approximately equal portions with conventional stucco. This stucco is produced in a rotary kiln using the 0–7 mm fraction,

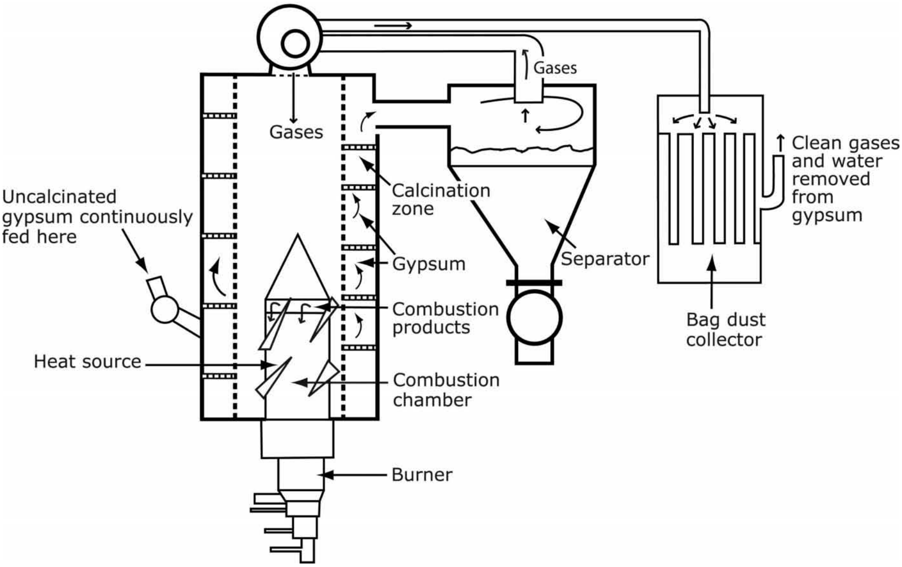

Fig. 5.10—Calcidyne calcining system.

which is subsequently ground before being mixed with the anhydrous plaster. The multiphase plasters produced differ in their setting properties from each other as well as from stucco.

Multiphase plaster intended for spray application has been produced since 1965 by incorporating chemical additives. These spray applied plasters differ from similar North American plasters because they are mixed with water at the spray nozzle rather than being mixed with water and pumped prior to spraying. Multiphase construction plasters without additives (Saarland Construction

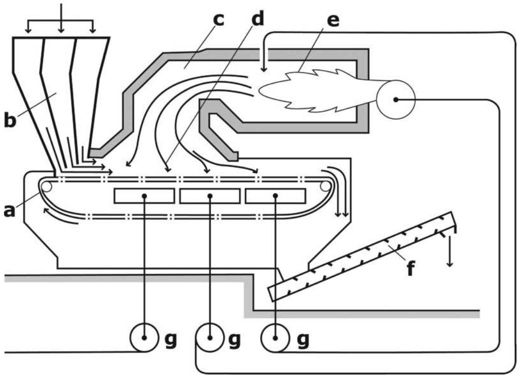

Fig. 5.11—Conveyor kiln for anhydrite production: (a) conveyor grate; (b) feed hoppers; (c) calcining hood; (d) gypsum; (e) combustion chamber; (f) discharges; (g) recirculation and cooling fans.

Plaster, Southern German Double Calcined Plaster), which are prepared in these types of plants, have declined in use recently.

Other calcining plants produce anhydrite in a counter current rotary kiln (Vernon). For example, *Surcuit* is produced in France as Paris Building Plaster by mixing anhydrite with stucco. In this type of kiln the gypsum reaches a maximum temperature of about 500°C (932°F) just before discharge. These kilns, with capacities of 15–30 ton/h, are sometimes linked together to produce first anhydrite followed by the production of stucco. This improves their thermal efficiencies since it provides for cooling of the anhydrite. The problem of cooling has also been solved by using the planetary cooling system of the cement industry.

Anhydrite can also be produced by grinding natural anhydrite rock in tube mills or impact mills to a particle size of below 0.2 mm. Activators to promote setting are added together with the gauging water. These activators are mixtures of alkali metal or heavy-metal salts and calcium hydroxide. They are being used in quantities of up to 2 % by weight based on the anhydrite. Acid activators such as potassium hydrogen sulfate or iron (II) sulfate can also be used.

5.4.10 α-Hemihydrate Plasters

Calcination by steam autoclaving originates with the 1933 patent by Randel and Dailey [5-2]. In this patent the term alpha-gypsum was coined and that term was adopted in the scientific literature as α-hemihydrate. This led to the term β-hemihydrate produced either in the laboratory or as stucco in a kettle. In essence, the patent describes the process of calcining gypsum in an autoclave for approximately 6 h at a temperature of 235°F (113°C) and a pressure of 15–17 psi. The resulting plaster was capable of producing a cast of gypsum with unusually high strength due to the low water demand of 42–45 mL/100 g. This process became the basis for α-plaster production in North America.

For this process, gypsum rock, 1/2–2 in. (1.27–5.08 cm) in size, was preferred because of ease of handling and drying. Because of the size of the material used, it is sometimes called the lump process. It is also called the dry process to distinguish it from the slurry autoclaving or solution processes developed at a later time. The patent specifically states that ground gypsum or synthetic gypsum may be briquetted and used as well. This concept has been developed further in Europe, for example, by autoclaving pressed bricks of FGD gypsum using sand/lime brick manufacturing facilities.

The first practical batch process for slurry autoclaving was developed by Schoch and Cunningham in 1940. They found that autoclave calcination in concentrated magnesium chloride solutions produced short rod-like crystals having a water demand of 45 mL/100 g. The water demand could be reduced by ball milling to 35 mL/100 g. A pilot plant based on this process established the cost for commercial production as US$8.82 per short ton.

Haddon and Cafferata describe the use of crystal habit modifiers such as succinic acid and a relatively low temperature of about 120°C. Commercial processes have been developed on the basis of this invention which typically

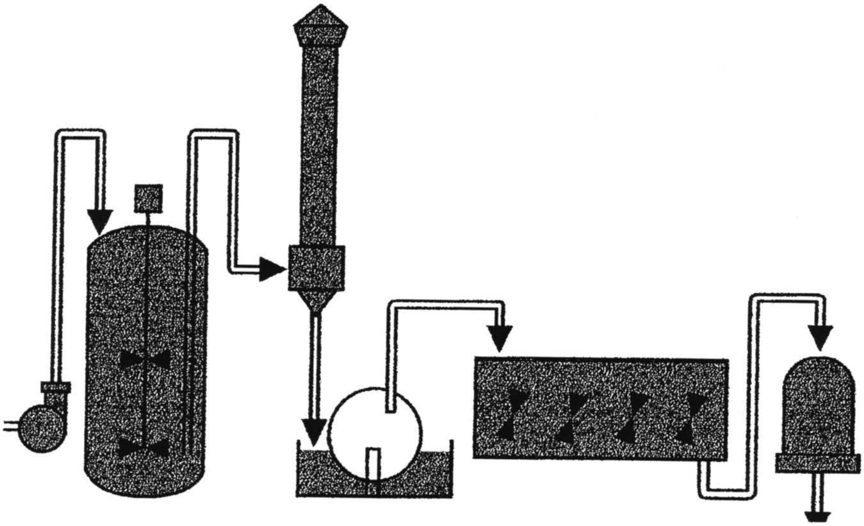

Fig. 5.12—Autoclave for α-plaster production.

produces α-plaster with a water demand of less than 35 mL/100 g.

A continuous autoclave process developed by Giulini is aimed at synthetic gypsum from the phosphoric acid manufacture. This process uses salt solutions and crystal habit modifiers as well as a relatively low temperature and a low *p*H. The process was not entirely successful mainly because of the isomorphic phosphate impurities, which interfere with subsequent gypsum crystallization.

Another continuous autoclave process has been developed by Knauf using FGD gypsum [5-3]. Calcination takes place in the presence of crystal habit modifiers at approximately 125°C and at 2–3 bar pressure. The α-plaster produced has a low water demand and is suitable for floor screed applications. Production costs for this type of process are usually given as about $60 per short ton, mostly because of high-energy costs (Fig. 5.12).

Finally, Eastroc in Pennsylvania, a subsidiary of BPB North America, now CertainTeed Gypsum, had developed an elegant and interesting process, which uses an autoclave to convert the calcium sulfite from the scrubber directly into α-hemihydrate. To a large extent this process utilizes the exothermic condition of this reaction. At the present time this plant is not in production [5-4].

Considering the above mechanisms it becomes obvious that α-hemihydrate consists of fairly large, single crystals that have a low aspect ratio. The essential key is a low water demand and, consequently, a higher strength. In most cases the α-hemihydrate plaster has different rheological properties from regular plaster based on stucco. Calcining “lumps” or briquettes in an autoclave can produce this material. Alternatively, it may be obtained in slurry-autoclaves or with slurries at atmospheric pressures using inorganic or organic crystal habit modifiers. If these crystals are needle-like they produce a high water demand.

Under certain conditions it may be possible to achieve a low water demand by subsequent grinding all or part of the material [5-5].

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6

Properties of Stuccos and Plasters

6.1 Stucco Requirements

STUCCOS PRODUCED BY ONE OF THE CALCINATION PROCESSES ARE generally formulated by adding a variety of materials at the mill to control or adjust their properties. Formulation usually means that at least retarders are added to lengthen the set time of the plaster. Often, stabilizers, such as a combination of aluminum sulfate (papermakers' alum) and hydrated lime, are added to make the setting of the plaster less sensitive to freshly set gypsum or other accelerators inadvertently added at the job site. Other additives are used to adjust various functions of the stucco, such as water retention. If lightweight aggregates, such as expanded perlite, are involved, they are usually added at the mill as well. After the addition of these materials, stucco is called (dry) plaster.

The dry plasters are then normally mixed with sand and subsequently with water at the job site to be used as (wet) plasters for specific applications. At this stage the wet plaster resembles hydrated lime or cement mortar, which have a similar historical development to gypsum plaster. In North America, the prime example is hardwall plaster, which is stucco that is retarded to about 3–5 h. It is also stabilized so that freshly set gypsum has a minimal effect. This material is applied in two or three coats to a plaster base, such as gypsum lath that is fastened to studs. Finally, a neat (not sanded) finishing coat consisting of a mixture of stucco and hydrated lime is applied over the last coat. As mentioned before, this process has been largely replaced by "drywall" applications.

The corresponding material in Europe consists either exclusively of regular stucco or of finishing plaster, which is a combination of insoluble anhydrite and stucco. Finishing plaster differs from regular stucco in having a lower water demand and a more gradual setting behavior. Specifically, this means that it has an earlier initial set and a later final set. Dry plasters are prepared from these materials by the addition of retarders, fillers such as limestone, or aggregate such as expanded perlite. To prepare mortars, sand is added at the job site. Finishing plaster is primarily used for spray application by machine. All other plasters are usually applied by hand.

Other requirements for stucco are concerned with the minimum hemihydrate content as well as proper shipping and storage conditions. Additional requirements for plaster are concerned with number of coats, the effect of frost, and the absorption capacity of the plaster base.

For board manufacture, it is common practice to require that the stucco meets certain rudimentary particle size specifications. For stucco from natural sources these are generally expressed, for example, as 90 % passing a 100-mesh (150 μm) sieve. This takes into account a specific knowledge of the grinding processes that are used for both the gypsum prior to calcination and for the stucco by the so-called post-calcination grinding. In Europe, the specification calls for regular stucco to retain 10 % on a 0.2 mm sieve (approximately 100-mesh), and 40 % for finishing plaster.

The fineness of the gypsum can be significant because it affects the degree of calcination. Coarse gypsum may possess a high amount of insufficiently calcined material particularly in the center of large particles. Conversely, the exposed surfaces of some particles may be over-calcined, that is, it may contain soluble or insoluble anhydrite. Fine gypsum may be successfully calcined but the water demand of the board slurry may be increased. This may adversely affect the operation by requiring slower machine speed and more fuel to dry the board.

For single charge kettles and Holoflite units, the consistency of stucco is sometimes controlled by the addition of calcium chloride, the so-called aridization process. In general this lowers the water demand of the stucco by a mechanism akin to aging, i.e., by the prevention of disintegration. Caution must be exercised since chloride salts have a detrimental effect on gypsum crystal growth when used above 2 lb per ton of stucco produced.

Further grinding is sometimes required for FGD gypsum if these specifications are to be met. Grinding is necessary for materials that have a rod-like crystal shape and a bulk density of about 0.5 ton/m^3 (31 lb/ft^3). Because of its small particle size of 20–60 μm (maximum 200 μm) FGD gypsum is preferentially calcined only in kettles unless it is agglomerated. This type of kettle stucco may be difficult to use as plaster since it has a tendency to demonstrate peculiar consistency behaviors sometimes mistaken to be thixotropic. It may also lack plasticity, smoothness, and a volume yield that is too variable. Grinding is not required for materials with a cubic crystal shape and corresponding bulk density of about 1.2 ton/m^3 (75 lb/ft^3).

Aging is a factor that lowers the consistency whereby the rate and degree of this effect depends on the amount of water vapor absorbed by the stucco [6-1]. This in turn depends on the water vapor pressure (relative humidity and temperature) to which the stucco is exposed. It is significant that the consistency can be lowered rapidly within a day when the amount of water vapor absorbed is high, a condition which can occur in the hot pit. It should also be noted that the stucco continues to age once water vapor is absorbed. For this reason, plaster placed in bags continues to age if it was previously exposed to water vapor. The aging process can be terminated by drying but it is not possible to reverse this process.

For board manufacture, this property is important since under certain condition the stucco may remain in the storage bin for longer than intended. This can lead to a variety of situations and it is an example of how non-uniformity occurs. If the stucco remains hot, it is possible that soluble and even insoluble anhydrite is formed with the dihydrate being converted to hemihydrate. Under certain circumstances, prolonged storage is used to "finish off" the calcination resulting in a much slower set on the board machine.

Under normal conditions the stucco will cool and it will do so unevenly. This creates its own set of problems. Usually these bins are not properly ventilated so that the moisture (either present or generated) will condense at the coolest part of the bin to form dihydrate. However, the main effect of cooling in the bins is that the water demand of the stucco will be lowered drastically due to rapid aging. This often produces a slow set and generates peelers or splitters.

6.2 Wet Plaster Properties

The application of these materials as wet plaster involves certain plaster properties, mainly normal consistency, setting time, and volume change on setting. These properties influence each other to some extent.

6.2.1 Normal Consistency

This property of stucco is often referred to as water demand. It is usually expressed as milliliter of water per 100 g of stucco and is indicative of the water to stucco ratio, which produces a wet plaster with "normal" flow properties. This characteristic is intended to reflect the workability of the wet plaster and it is perhaps the most important and least understood of all plaster properties. It is usually measured by one of several methods such as the depth of penetration of a conical plunger into the plaster (ASTM C472)[1] [6-2], by placing plaster in a cylindrical mold and measuring the decrease in height when the cylinder is lifted (British Method), or by measuring the spread of plaster under its own weight after pouring (US Industrial Method). An interesting method is used in the German DIN 1168 procedures where stucco is added slowly to a fixed amount of water. The end point is reached when the water no longer rises to wet the plaster by adsorption. In this case, the normal consistency of plaster is expressed as a gram of stucco per 100 mL of water. For this test, it has not been established to what extent disintegration takes place.

The workability of plaster is usually considered without reference to its rheological or force/flow relationship. For example, it is seldom appreciated that the normal consistency of plaster represents only one aspect of the non-Newtonian force/flow curve, that is, the yield point. The examples given in Fig. 6.1 illustrate the behavior of plaster, which is characterized by the non-Newtonian curve. This curve indicates that a certain force is required before a flow is achieved and that this force corresponds to the yield point of the plaster. Once flow is attained, the curve beyond the yield point may be straight or it may have some other configuration that are indicative of other flow characteristic of the plaster. In contrast, the Newtonian curve starts at the origin and continues in a straight line.

Another way of demonstrating this difference is by placing a cylindrical weight on the surface of a Newtonian substance, petroleum grease for example, and of a non-Newtonian substance represented by plaster. In the first case, the

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[1] Standard Test Method for Physical Testing of Gypsum, Gypsum Plasters and Gypsum Concrete.

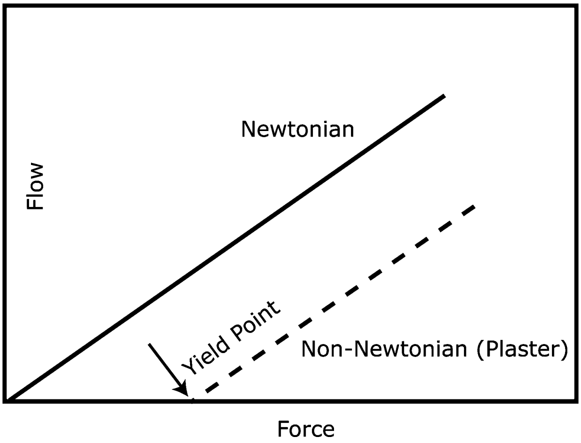

Fig. 6.1—Schematic force/flow diagram.

weight will penetrate immediately into the grease and will continue to do so at a slow but constant rate. For most plasters, the cylinder will rapidly penetrate the plaster to a certain depth and stop at that level provided the water. Solid ratio is appropriate.

These conditions are in reasonable agreement with the characteristics of hardwall plaster as experienced in practice. That is, on the trowel, the plaster is in a non-flow position because no force is applied and therefore it remains below the yield point. However, as soon as a certain manual force is applied through the trowel, the plaster begins to flow because the yield point is exceeded. When the plaster is applied to the wall and the force exerted by the trowel is discontinued, the plaster returns to its non-flow position. For this reason, the plaster does not “slough off” the wall and this is obviously an important characteristic. It also may give the erroneous impression that plaster is thixotropic. Similar conditions exist during spray application.

It should be realized that the consistency (water demand) and other rheological properties of plaster depends primarily on the particle size distribution of the stucco. In the past, this was a difficult subject because there was apparently no simple correlation between these two parameters. For example, grinding of relatively uniform stucco can lower the consistency instead of raising it. This is due to the production of small particles that fill the interstitial spaces between the larger particles. Therefore, attempts to use density instead of particle size distribution give only a first approximation of the situation. Other factors, such as the surface conditions of the stucco particles, and substances, such as surface-active agents, do play a role, sometimes to a significant extent. In addition, consistency is affected by aging, that is, of decreasing with time after absorption of water vapor.

The understanding of these factors have changed with the work of Lane [6-3] who showed that exposure to liquid water in conjunction with mechanical action produced the expected correlations between particle size distribution

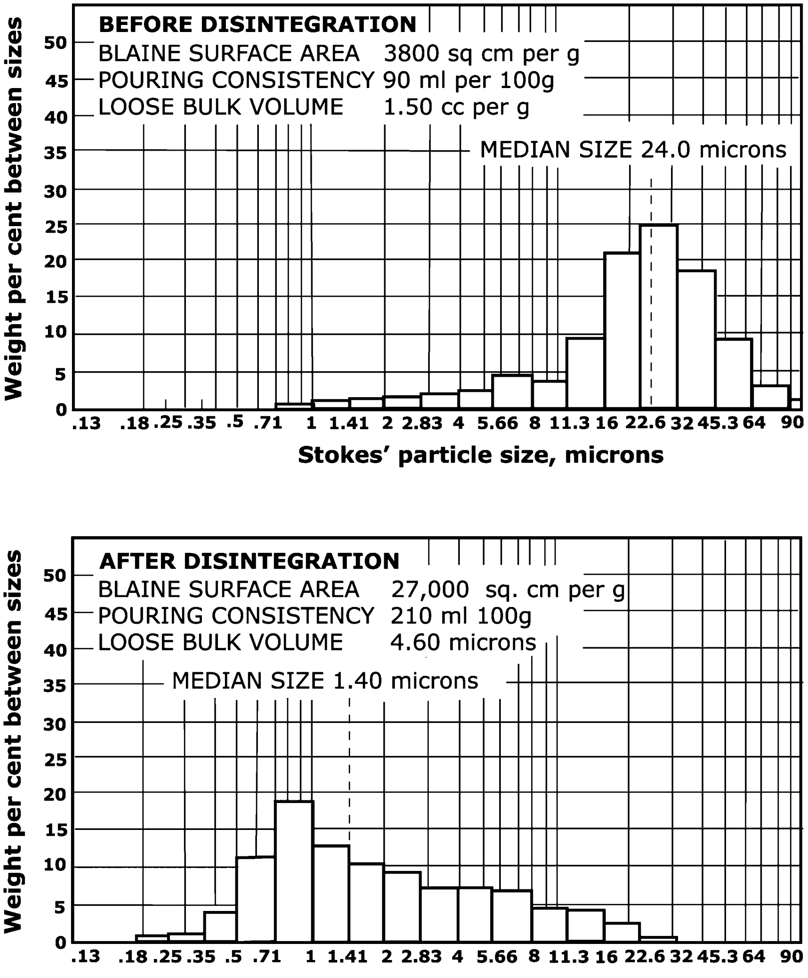

Fig. 6.2—Particle size of stucco before and after disintegration.

and consistency. This means that particle size distributions carried out in liquids other than water produce different particle size distributions that are of limited usefulness in this context (Fig. 6.2).

Specifically, the work of Lane shows that mechanical mixing of the stucco with water for 60 s produces complete disintegration, which changes its median particle size distribution from 24 to 1.4 μm and the Blaine surface area from 3800 to 27,000 cm^2/g. This has the effect of changing the pouring consistency from 90 to 210 mL per 100 g, a very high value. Further work by Wirsching also showed that the largest size fraction of the stucco disintegrates preferentially whereas the smaller size fractions remain largely unchanged.

Of course, this indicates only the potential of disintegration since complete

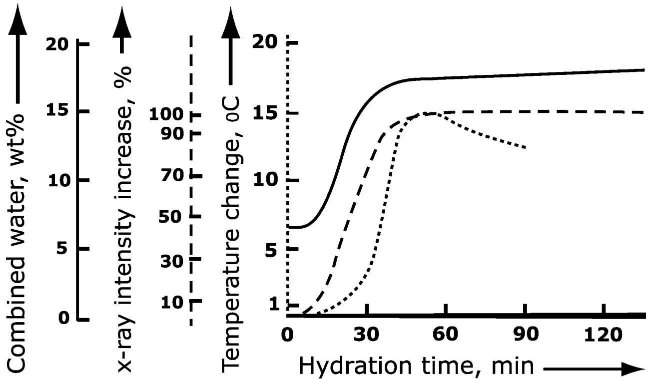

Fig. 6.3—Methods for the determination of the rate of setting.

disintegration is seldom if ever reached under practical conditions. However, mixing of plaster always produces some disintegration. For any practical application, the degree to which this occurs should be established.

6.2.2 Setting Characteristics

Plaster dissolves and precipitates to form a solid mass of interlocking gypsum crystals, provided its consistency is within a normal range. This process is known as setting and it must be kept in mind that the actual process is affected to some extent by the type of rock and the calcining procedure used. It is, however, possible to follow its progress by measuring the degree of gypsum formation by a variety of methods [Fig. 6.3]. The most practical way is to measure the heat that is released during hydration. These methods have the advantage that they can produce a continuous temperature-time curve from start to finish. They have the disadvantage that cooling affects the temperature-time curve somewhat. It is also possible to measure the percentage of gypsum formation by x-ray diffraction, differential thermal analyses (DTA), or differential scanning calorimetry (DSC), or by weight loss determinations, which necessitate the removal of samples at intervals.

The rate of hydration can also be followed by mechanically measuring the degree of hardening or solidification. This is a relatively slow process and requires that the stucco and water is in the proper proportions, that is, be at normal consistency. For this purpose, the Vicat needle (ASTM C472) is generally employed. In some plants the Gillmore needle (ASTM C266)[2] is the preferred procedure. A 1/4 lb (113 g) needle indicates the initial set on the board machine at which the board can no longer be disturbed. This means that all mechanical action such as forming the edges with shoes must take place before the initial set is reached. A 1 lb (454 g) is used to determine the final set, which indicates that the board is sufficiently solidified to be cut by the knife.

For gypsum board manufacture, the temperature of the stucco slurry is significant. In general, the fastest final temperature rise is achieved at

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[2] Standard Test Method for Time of Setting of Hydraulic-Cement Paste by Gillmore Needles.

temperatures between 100 and 120°F (38 and 49°C). Higher or lower temperatures result in appreciably lower setting times. Maintaining the stucco slurry temperature at the appropriate level is not an easy process. It must take into account the cooling rate of the stucco, the water temperature, etc. In some plants the water can be heated particularly during the winter months. It is doubtful however whether water should be used to control the stucco slurry temperature other than by a small degree.

The characteristics of hydration or setting have been studied extensively over the years. One of the goals of this effort was to arrive at a formula for a sigmoid curve that would express the mechanism of the conversion of hemihydrate to dihydrate. An example of this attempt is the work of Schiller who assumes the existence of a classical sigmoid curve because the maximum rate of hydration occurs at 50 % [6-4]. On the other hand, Ridge assumes that the maximum hydration rate occurs at 60 % [6-5].

In the past, much of the stucco produced in kettles or kilns was used for the manufacture of so-called hardwall plasters, that is, plasters for application over lath or another plaster base. For this purpose, the stucco was cooled to room temperature and ground in a tube mill before adding the required additives and bagging the material. Tube milling improves the plasticity of the stucco when mixed with water. It should also be noted that grinding before or after calcination can lead to a reduction in water demand, for example, for a plaster with relatively coarse and uniform particles. Sand is normally added to the plaster at the job site. Instead of sand, lightweight aggregate such as perlite can be added at the mill.

As shown in Fig. 6.4, the setting time of hardwall plaster as determined by the temperature method is increased almost exponentially by the addition of retarder. In this condition, its setting time is very sensitive to the addition of accelerators such as freshly set gypsum occurring at the job site. Therefore, hydrated lime and aluminum sulfate are introduced that provide a relatively stable setting time in the order of 3–4 h. Gypsum itself is unsuitable for this purpose because its acceleration effect decreases with time and particularly with exposure to water vapor.

6.2.3 Volume Changes

These effects refer to expansion, shrinkage, and creep during the hardening process. All cementitious material experiences some volume changes that depend on the temperature and the condition of the material itself. For plasters an average thermal coefficient of $20 \times 10^{-3}\ \mathrm{K}^{-1}$ can be expected. This compares with a coefficient of about $10 \times 10^{-3}\ \mathrm{K}^{-1}$ for Portland cement concrete. Practical experience has shown that no problem exists for gypsum despite the larger value. However, a sudden temperature shock, such as exposure to freezing conditions, must be avoided.

Expansion is generally considered to be due to the growth of gypsum crystals in the plaster matrix but it does not include volume changes during the very early stages of the setting process. Expansions of 1 mm/m are possible under unrestrained conditions depending on the basic composition of the plasters. Shrinkage is expected to occur because of the water loss through

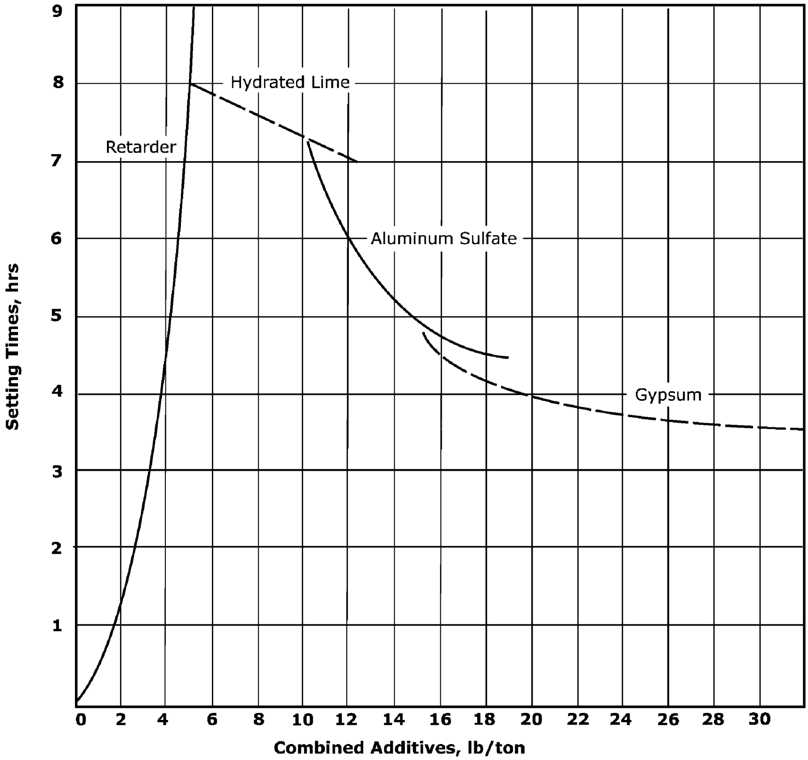

Fig. 6.4—Set time stabilization by combined retarder, hydrated lime, and alum.

evaporation after the plaster has set. This value is 0.3 mm/m according to practical experience. It appears that no damage is usually caused by the processes of expansion and shrinkage while the plaster is still in the plastic state. These processes are essentially completed when the plaster reaches its final hardened condition. Occasionally severe problems of expansion have been experienced for example when the setting takes place in two stages whereby the second setting occurs in a partially hardened plaster, such as floor screed.

This high degree of tolerance to expansion and shrinkage is obviously due to the larger pore volume and the ability of the plaster to creep. Creep occurs under conditions when the plaster is exposed to slow lateral loads particularly in the presence of adsorbed moisture. In fact, it is the main reason why few cracks appear in the plaster in practice when the load is applied slowly.

6.3 Properties of Hardened Plaster (Gypsum)

A key consideration is the type of internal bond formed when plaster solidifies during the process of dihydrate formation. These bonds represent three mechanisms: (1) Formation of a true bond between crystals when ions are shared, such as twinning; (2) crystals growing past each other into available spaces and forming a mechanically interlocking network; and (3) hydrogen bonding be-

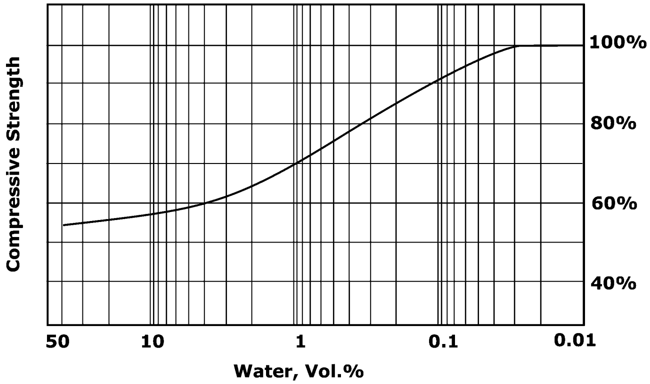

Fig. 6.5—Effect of water on compressive strength.

tween crystals where they touch. Mechanical interlocking is similar to the keg-of-nails effect where the nails "agglomerate" by friction. However, the gypsum crystals grow into empty spaces and therefore cannot be disentangled as in the case of nails. It has also been speculated that the loss of hydrogen bonds are the reason for the relatively large loss of strength of gypsum plaster, up to 66 %, when exposed to liquid water.

It should also be taken into consideration that sand or other aggregate is usually added to the plasters to be applied in the form of mortars. This method employed first by the Romans using several plaster coats for the base of painting and frescoes. The Roman approach of using decreasing particle size and decreasing amount of sand for successive coats towards the surface is not followed in North American practice. Instead the same type and amount of sand is used for each successive layer. In any case, this means that the physical properties of the sanded plaster can be significantly different from those of neat plaster. This is the case particularly when the amount of sand added exceeds specifications or is too fine, which is not unusual.

For the manufacture of gypsum board it is obviously an essential feature that the gypsum crystals bond to the paper fibers of the liner. A variety of hypotheses are offered to explain this mechanism. For example, they attempt to explain the role of the starch, which was originally not necessary when the board was dried slowly.

6.3.1 Drying Conditions

It is often not realized that the physical properties of hardened plaster are mainly dependent upon the amount of water that evaporates after setting. In that condition, the set plaster (gypsum) behaves quite different to non-porous or solid gypsum found in nature. This effect is relatively large since the amount of water evaporating after setting is also relatively large. For example, wet gypsum has less than 60 % of the strength of dry gypsum (Fig. 6.5). In comparison, Portland cement loses only about 10 % of its strength on wetting. The plaster as applied to walls and ceilings normally requires several days to

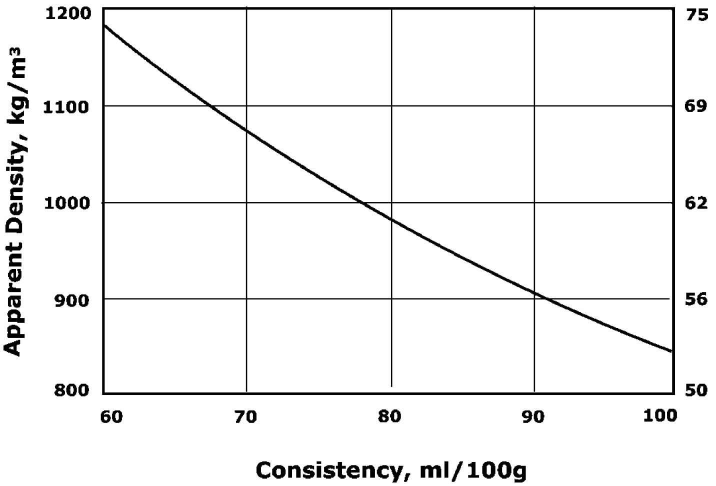

Fig. 6.6—Relationship between apparent density and consistency.

dry. In practical terms, this means that the physical properties of the plaster, such as strength and hardness, improve considerably during this process.

Prolonged exposure of set plaster to water, such as delayed drying, should be avoided since it may lead to permanent changes of the structure of the plaster due to recrystallization of the gypsum. This condition, called brownout in the field, is extremely difficult to reproduce in the laboratory. This picture is being complicated by the fact that subsequent drying will often restore the original physical properties in many instances even when wetting and drying takes place repeatedly.

6.3.2 Apparent Density and Porosity

Density is dependent almost entirely on the water to solid ratio or the consistency of the plaster. Specifically, it is dependent upon the amount of water that evaporates as excess water after setting, i.e., water that is not used for hydration. Figure 6.6 shows that the apparent density has nearly a straight-line relationship with the consistency ranging from about 1200 kg/m^3 (74.9 lb/ft^3) for 60 mL/100 g to about 850 kg/m^3 (53.1 lb/ft^3) for 100 mL/100 g.

Porosity is closely related to apparent density, that is, the pore volumes of gypsum created by water in general lie between 50 % and 60 % depending on the gauging water used. However, the effect of the configuration of the pores and their structure can be quite significant. For example, hardened and dried gypsum consists of two continuous phases, the solid phase consisting of gypsum crystals and a gaseous phase consisting of air. This means that both the solid phase and the gaseous pores are interconnected and for this reason the structure of gypsum resembles that of a sponge rather than foam. Moreover, the gaseous pores act as capillaries and this also has the effect that they absorb and transport liquid water rather quickly.

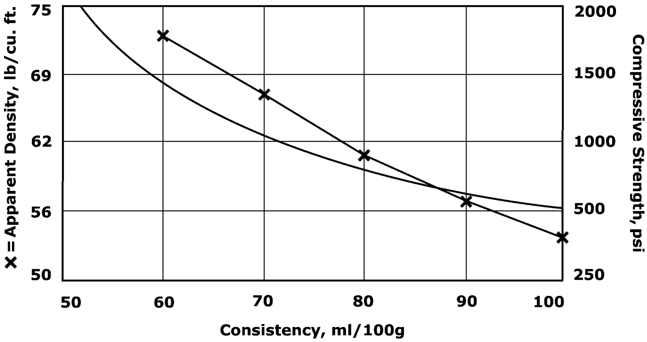

Fig. 6.7—Consistency versus apparent density and compressive strength.

6.3.3 Strength

It is perhaps not surprising that there is a close relationship between density and the compressive strength of hardened and dried gypsum. The effect of decreasing density on the compressive strength is relatively large (Fig. 6.7). Obviously both are caused by the water demand of the stucco, that is, its consistency. The effect of the density on the flexural strength of gypsum is similar but less well understood since flexural strength is a poor property of gypsum.

6.3.4 Temperature Tolerance

A long-term exposure to temperatures above 46°C (115°F) leads to strength losses and must be avoided because gypsum converts into hemihydrate and soluble anhydrite. It is often believed that the staying below 100°C (212°F) is a safe procedure. This misunderstanding about the calcination behavior of gypsum and the difference between long and short-term exposure has led to severe problems in practice, for example, with certain electrical heating devices.

6.3.5 Fire Protection

Gypsum has been used for a long time to protect buildings from fire. A case in point is the edict by Louis XIV stipulating that all wooden buildings must be covered inside and out with a layer of gypsum. It is doubtful the mechanism of fire protection by gypsum was fully understood at the time but considerable protection of the building was certainly obtained. At the very least, it leads to compartmentalization of the fire, which must be considered a tremendous advantage. The more modern concepts of fire protection are referred to in the next section.

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7

Gypsum Board

GYPSUM BOARD IS UNDOUBTEDLY THE PREMIER PRODUCT MANUfactured by gypsum companies in North America. In 1996, about 88 % of the nearly 40 million tons of the total consumption of gypsum in the United States was used for the manufacture of gypsum board. While approximately 3.3 million tons were used as set regulator (retarder) for Portland cement, very little was used for the manufacture of other products such as plaster or gypsum fiber board (GFB). In Europe, plaster and GFB play a larger role.

A modern plant for the manufacture of gypsum board bears only a superficial resemblance to the plant to manufacture board or lath patented by August Sackett in 1894 [7-1]. Following the usual pattern of development, the manufacturing process as well as the composition and structure of the board has been reinvented on several occasions since that time. In fact, since its inception, the process is being constantly improved by the introduction of various changes at most key points of the process. Among other things, the purpose of these changes was to increase line speed, improve core to paper bond, and to make the drying process more efficient. For this reason, the discussions of the individual steps of the process emphasize the reason for the various functions rather than describing fixed process requirements. The descriptions of the various process steps, whether they refer to additives or mechanical devices, are given only as examples.

7.1 Essential Manufacturing Features

The single most important factor in the manufacture of gypsum board is uniformity. This means uniformity of production rates, uniformity in feed rates and raw material usages, and uniformity in stucco, water, and raw material quality. The key to uniformity lies with satisfactory process control, equipment maintenance, and adequate testing.

Stucco used for the manufacture of gypsum board has properties that are similar to those of conventional stucco. However, there are three significant differences with respect to both temperature and setting behavior. Stucco for board manufacture is normally used at an elevated temperature between 100 and 120°F (37 and 49°C) whereas conventional stucco remains at ambient temperatures. Also, stucco in the board slurry is accelerated to less than 3 min whereas conventional stucco is used with a stabilized setting time of 3–5 h. The third significant point is the larger amount of gauging water used, that is, about 90 mL/100 g whereas normal wall plaster requires about 55–65 mL/100 g. Board stucco can be produced from natural rock or from FGD gypsum or blends of both or with other synthetic gypsum. However, a number of different demands are made on this material. That it can meet these conditions shows again that stucco is a very accommodating substance. Features such as weight, fire resistance, strength, water demand, and setting behavior are briefly discussed below.

7.1.1 Board Weight

When discussing gypsum board for North America, a variety of developmental issues present themselves immediately. The most significant of these is the replacement of the weight for regular (non-type X) board by flexural strength. This was introduced by the ASTM Committee C11 on Gypsum and Related Building Materials and Systems, which constitutes a shift towards specific physical performance requirements. This move was not followed by jurisdictions in Europe and Japan where the weight replacement is apparently not a significant issue.

Subsequently, technology was developed in North America to reduce the weight of the board by maintaining compliance with physical performance requirements, which were considered to reflect demands in practice. An example of this situation is described in an article by R. Wenk [7-2]. In doing so it was shown that most physical requirements could be met relatively easily except nail pull resistance. In fact, nail pull resistance still remains the key requirement that prevents an appreciable lowering of the weight beyond the present level of about 1530–1700 lb MSF (7.2–8.2 kg/m^2) for 1/2 in. (12.7 mm) board.

7.1.2 Fire Resistance

Equally important, however, was the consideration that regular board with reduced weight would not meet the fire-resistance requirements when tested according to ASTM E119, which involves a specific test furnace producing a standard heating curve [Fig. 10.1]. The temperature of the unexposed side of the board when tested as an assembly using either load bearing wood studs or non-loadbearing galvanized steel studs, must not rise above a certain temperature after a described length of exposure time [7-3]. To meet these requirements, a special fire resistant board "type X" was developed for each of the board categories having a higher weight than standard board. This type of board has a core that is usually modified by the addition of unexfoliated vermiculite and glass fiber. Typically, a 1 h fire resistance-rating is required for type X wallboard with a 5/8 in. (15.9 mm) thickness and 3/4 h for board with a thickness of 1/2 in. (12.7 mm) [7-4]. For type X lath, coreboard and shaftliner board slightly different requirements apply apart from a higher weight. The reproducibility of this test remains an issue since values of one hour or less occur during the initial steep rise of the temperature curve.

It should be noted that assemblies using type X boards are listed in manufacturers' literature and by the Gypsum Association [7-4]. Where applicable these listings also cover sound transmission classification (STC) and surface burning characteristics. Most of these assemblies are certified by agencies such as Underwriters Laboratories. Random plant inspections are also carried out to ensure adherence to validated formulations to establish, for example, that type X board does not contain more than 2 % paper fiber inadvertently or intentionally added to the core.

7.1.3 Board Strength

It should also be pointed out that while weight is a major factor in influencing physical requirements, such as nail pull resistance, it is not the only one. Various attempts have been described to increase the physical performance of low weight board, usually by increasing the strength of its core. These attempts generally involved a change in the structure of the core of the board by producing larger foam bubbles and establishing layers with higher densities near the core to paper interface. Similar attempts have been made by increasing the amount of immobile starch that remains in the core [7-5].

For example, it is claimed that additives such as sodium trimeta-phosphate (STMP) increase the nail pull resistance of manufactured gypsum board and having a beneficial effect on other properties as well. A patent by U.S. Gypsum [7-6] states that STMP raises the compressive strength, rigidity, and dimensional stability, such as drying shrinkage and nail pull resistance. Rigidity in this context refers to humidified deflection, i.e., sag resistance in the presence of high moisture levels of 90 %RH/90 °F. Cubes cast in the laboratory with accelerated slurry showed a strength increase of about 10 %–20 % for 0.1 % STMP additions. Manufactured board samples met the ASTM sag resistance of 10/8 in. (32 mm) with STMP additions of only 0.04 %. Drying shrinkage, i.e., width and length changes on drying, was also eliminated completely by STMP additions of 0.04 %. About 0.08 % STMP was required to raise the nail pull from 88 to 96 lb for manufactured board. Perhaps somewhat surprisingly, 0.08 % STMP additions produced a slightly poorer bond failure. The addition of both non-pregelatinized starch (HI-Bond) and particularly pregelatinized starch (PF1000) was required to eliminate this problem, i.e., to obtain zero bond failure.

In another patent by the U.S. Gypsum Company [7-7], it is claimed that tetrameta-phosphate also imparts increased resistance to permanent deformation (humidified deflection or sag) and dimensional stability (drying shrinkage) when added in quantities of about 0.04 %–0.16 %. This is accomplished while maintaining or increasing strength. Specifically, it was shown with laboratory specimens that the sag is less than 0.03 in. with 0.1 % tetrameta-phosphate additions. It was also shown that there was no retardation but there was little increase in strength. The claim that there is a considerable improvement for drying shrinkage is questionable.

From a practical point of view it should be kept in mind that many factors may have a profound effect on the size of the final gypsum crystals and thereby the strength of the gypsum board. For example, a faster setting time produces generally smaller crystals potentially producing higher strength. The amount of water also affects the crystal size whereby short crystals and lower strength may be obtained if insufficient liquid water is available.

7.1.4 Water Demand

An essential difference between normal wall plaster and the board slurry is an increase in the water demand to increase its flow out of the mixer. The intention is to obtain free-flowing slurries that spread evenly over the entire

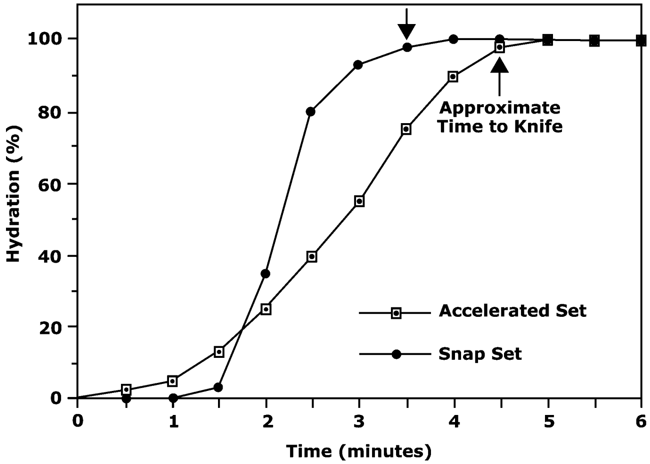

Fig. 7.1—Snap set versus accelerated set.

paper surface upon which it is placed. This is particularly important when only one main outlet is used for the mixer. An increase in the water demand of the stucco shifts the yield point towards the origin and moves both density and strength toward lower values. A similar effect is being produced by the addition of surface active agents, such as dispersants and wetting agents.

7.1.5 Setting Behavior

Obviously, the setting behavior of the gypsum slurry is a most important property and must be precisely controlled. The actual setting time will vary from plant to plant depending on the combination of accelerator and retarders used. To some extent, this is based on machine speed, the time of travel from the board formation (wet end) to the cut-off knife, and on the other additives used.

The key property is the acceleration of the setting time of the slurry in the time from the mixer outlet to the knife. In particular, short setting times in the order of less than 3 min are achievable. Different accelerating techniques are used but a combination of gypsum and potassium sulfate is common. The gypsum provides homogeneous and heterogeneous nuclei and potassium sulfate provides a large amount of sulfate ions immediately.

Schiller and Ridge have attempted to create formulas for the setting of stucco that are based on sigmoid curves. However, as mentioned before neither of these approaches captures the differences between the actual setting curves which express different setting behaviors. For example, curves of temperature rise versus time are given in Fig. 7.1 for a conventional accelerated setting behavior and for a snap-set. Since the board slurry is normally used at a higher than ambient temperature, this should be taken into consideration. The differences between the two curves are important because they affect not only the gypsum board manufacturing process but also the physical properties of the board core such as strength. For the snap-set curve, the essential

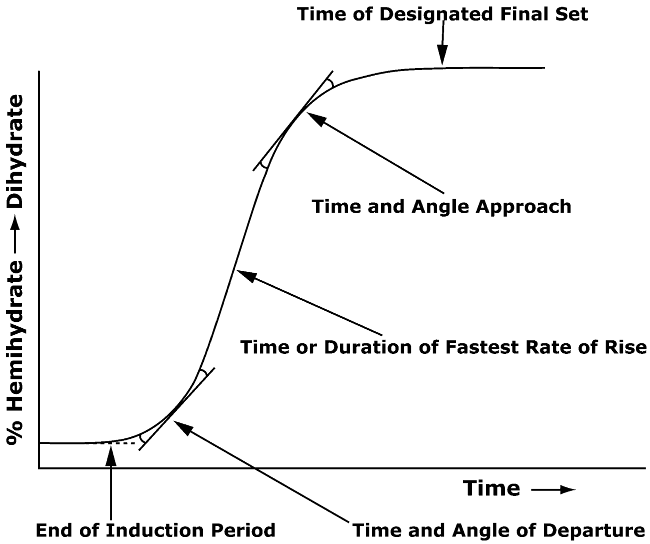

Fig. 7.2—Measuring points.

differences consist of a longer induction period, a faster rate of rise, and a sharp approach to a level that assumes complete hydration.

As shown in Fig. 7.2 the following points may be of importance when analyzing setting behavior: (1) Induction period (the time interval without measurable temperature development); (2) angle of departure from baseline; (3) time, duration, and fastest rate of temperature rise; (4) angle of approach to final degree of hydration; (5) and the time for the final degree of hydration. The final degree of hydration is often considered to be 95 % or 98 %. However, this conflicts somewhat with the notion that a hydration above 95 % does not translate into strength contribution to the board. It should also be kept in mind that not all of these factors have to be determined at all times. However, it should be established which factors are important for particular stuccos under specific circumstances and these should be determined on a regular basis.

7.2 Core Manufacturing

The process of manufacturing the board consists essentially of six segments: (1) Supplying the calcined gypsum containing additives to the mixer; (2) providing the paper liners to the forming table; (3) addition of water and foam to produce a slurry, which is then deposited onto the paper at the forming table, (4) forming the board on the forming table, (5) conveying the formed board to the knife to be cut and subsequently to the entrance to the dryer during which time the hardening of the slurry takes place, and (6) drying and subsequent handling of the dry board.

The viability of the process to manufacture board requires very fast setting rates. This is obviously the key function of the accelerator system, which consists preferentially of ground and treated gypsum and sometimes of potassium sulfate as well. Proper application of accelerators requires control over the amount of gauging water and plaster rheology. In addition, it is necessary to meet specifications of board properties, such as mechanical strength. Obviously, this requires accurate control of the structure of the gypsum formed as well as of the amount and distribution of air voids in the core before hardening.

Although each segment plays an important role, the mixer and forming table constitute the heart of the manufacturing process. The mixer is used to prepare the slurry, which is then placed onto the back of a face paper liner moving continuously over the forming table. At the end of the forming table, the slurry is covered by a second paper liner forming the back of the board. The edges of the face paper liner are then folded over twice forming an envelope.

After the stucco has hardened to a large extent, the boards are cut to the specified length so that the ends of the board are the only part not covered by the paper liner. The cut boards are then supplied to drying kilns where they are subjected to a quick drying process. This method produces a sandwich structure whereby the paper provides the tensile strength and the core provides the necessary compressive strength, hardness, and stiffness. A satisfactory bond between paper and core is absolutely essential.

Additives are incorporated into the stucco to aid in the manufacturing process, particularly with respect to water demand, air entrainment, rate of setting, and bonding between paper liner and core gypsum. Weight reduction is obtained by adding foam to the core. The water not required for hydration of the plaster in the slurry is removed by a drying process, generally carried out by kilns, which further reduces the weight of the board. It is essential to realize that for the board making process the setting time of the slurry has to be accelerated. Less than 3 min is the best time reached at present. Also, depending on the intended application of the board, materials are added to the core to improve its physical properties, such as water absorption, flexural strength, or brittleness. The paper is modified or laminated as well depending on the intended application.

A schematic representation of the production arrangement is given in Fig. 7.3. The normal width of the boards produced with this arrangement is 4 ft (122 cm), except when a smaller size such as lath is produced. The thickness of the board is created by the forming plate or, less frequently, the master roll. The length of the board is normally 7 or 8 ft (213 or 244 cm) but other lengths can be produced depending on limitations of the process. The thicknesses vary from 1/4 to 1 in. (6.4–25 mm) depending on the specific type of board being produced. Various edge configurations can be introduced as well (Fig. 7.4). This arrangement allows the manufacture of various types of board suitable for specific applications in the field such as wallboard and predecorated wallboard, backing board, coreboard and shaftliner board, soffit board, sheathing, base for veneer plaster, and lath and ceiling board [7-8]. The board is intended for application in the field as a panel without the use of water. For this reason, it is often called drywall in reference to the main difference to the use of wet wall plaster.

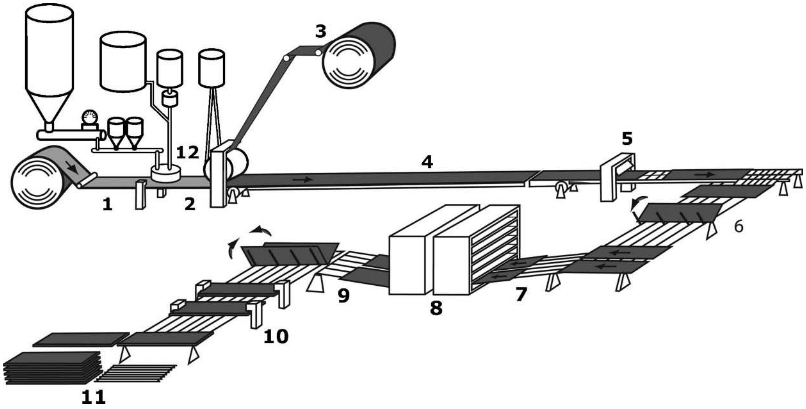

Fig. 7.3—(1) Face paper; (2) forming table; (3) back paper; (4) conveyor belt; (5) knife; (6) board inverter; (7) dryer inlet (tipple); (8) dryer; (9) booker; (10) transport; (11) bundles; (12) slurry preparation.

7.2.1 Stucco Supply

The initial step of board forming is the supply of satisfactory stucco to the mixer. It is often not appreciated that the board making process can only be optimized to produce a consistent quality if the stucco supplied to the board mixer is uniform in terms of its physical and chemical properties. Quite often the stucco handling system is responsible for introducing variability instead of reducing it to a minimum.

The process of supplying stucco may be considered to begin with the stucco supply bins, which are usually fed from the hot pit via a stucco supply screw. Most new plants operate two stucco supply bins, which hold a total supply of 8 h for the board line. They are designed for mass flow and incorporate a high capacity circulation system to continuously discharge, elevate, and blend the stucco with the fresh stucco from the cooling system before returning it into

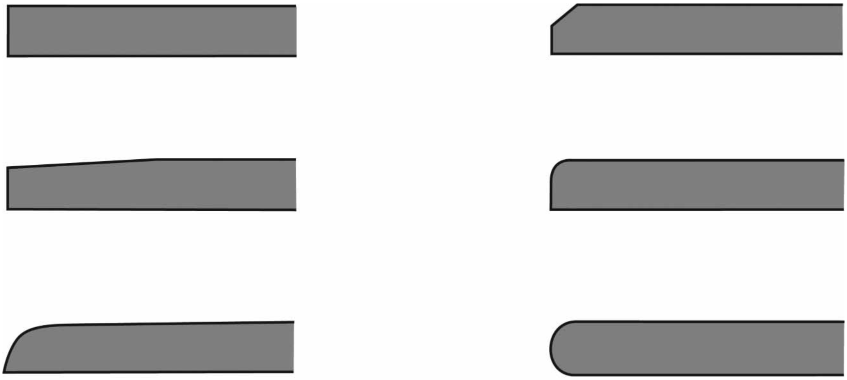

Fig. 7.4—Edge configuration of gypsum board.

the bins. This maintains a constant dynamic density, which is essential for consistent stucco metering. The most common technique in new plants is to introduce the hot stucco into a vertical airlift to directly flash cool and to elevate it simultaneously. In some plants, a grinding mill is used as well.

Board core quality is enhanced with the correct slurry temperature and a circulation system. This is intended to assure that the temperature of the stucco is reduced to about 110–125 °C (230–257 °F) and that the system is properly vented to release excess water vapor. For this reason, most new plants are equipped with a stucco cooling system ahead of the supply bins. This system is considered ideal to produce the necessary uniformity of the stucco properties. It is not recommended practice to use the stucco cooler to eliminate the supply bin. Depending on the nature of the calcination process, it may be desirable to keep the stucco briefly hot to achieve more complete calcination. Insulated screw conveyors, hot pits, or short-term storage bins are often used for this purpose.

7.2.2 Volumetric Feeder

The stucco is transported by a bucket conveyor from the supply bin to the volumetric feeder. This feeder uses a variable speed drive to meter the correct amount of stucco into the pin mixer. About 25 %–30 % of stucco fed to the volumetric feed system is returned to the supply bin via another bucket conveyor.

The mixing screw conveyor transporting the stucco to the pin mixer also receives the dry additives from other conveyors. These materials are blended by the mixing screw conveyor using cut and folding flights and mixing paddles. They are then fed directly into the pin mixer of the board line.

If the board line is momentarily shut down, the dry mix conveyor is also shut down and the metered stucco that normally feeds into the mixer is returned to the recirculation system. This arrangement assures that fresh stucco is immediately available for the mixer when the board line starts up again. This is an important prerequisite for maintaining tight board weight control and for high-speed board lines where clean start-ups are essential.

7.2.3 Additive Systems

In high-speed board plants, most wet and dry additives are received and stored in bulk and material handling is kept to a minimum. Emphasis is placed on feed rate accuracy and reliability. For example, stand-by pumps are usually provided to allow maintenance flexibility and minimum down time. It is important for the successful operation at high line speeds that very high quality accelerator with uniform potency be precisely fed into the board slurry mixer. Finely ground gypsum produced in water-cooled ball mills with an additive and often being directly fed into the mixer is considered standard practice. This is often augmented by potassium sulfate considered to be a chemical accelerator to achieve the shortest set times.

7.2.4 Pin Mixer

Slurry mixing is technically the most critical aspect of the board plant, especially at high line speed. A pin mixer is normally used for this purpose. It is

Fig. 7.5—Three-port mixer depositing slurry onto back of face paper. Note: slurries from edge mixers.

produced in two sizes, 42 in. (107 cm) and 60 in. (152 cm). It mixes the stucco plus additives that are received from the mixing screw conveyor with the gauging water. A key problem is the build-up of freshly set gypsum inside the mixer, which can be avoided by using a small amount of retarder such as diethylene triamine pentaacetic acid (DTPA). An essential feature of the pin mixer is its role of incorporating foam into the water: Stucco slurry. The pin mixer is often modified for a variety of reasons. For example, pins may be replaced by feeding tubes or by plows. In some plants, mixers of different designs or sizes are used. The main outlet from the mixer is a most important feature and a single discharge is often utilized for this purpose instead of three outlets shown in Fig. 7.5.

7.2.5 Roll Coater

Placing slurries with higher densities at the face paper interface is the technique now generally used in the production of lightweight board. For this purpose, separate mixers are provided to accept slurries from the pin mixer and to remove foam from these slurries. They are then transferred to a paper roll coater that places them onto the back of the face paper prior to depositing the regular board slurry by a so-called foam placement technique. Tangential edge mixers to reduce the quantity of foam from the slurry to be placed at the edges of the board are no longer in use.

7.2.6 Forming Table

This is one of the most difficult operations of the board making process. Board forming tables with top and bottom plates are often used. Control of the slurry in front of the forming plates is a special problem due to the relatively violent action at very fast line speeds. A forming plate or master roll is located at the end of the forming table to control the initial thickness of the board. This occurs when the back paper liner is placed onto the slurry that is already spread onto the back of the face paper. The side edges of the face paper are then folded over twice to form the edges of the board and creating an envelope for the slurry. This process may be assisted by mud dams to contain the slurry as

TABLE 7.1—Approximate gypsum board formula

Ingredients	Weight Percent
Stucco	100
Water	94–98
Accelerator (HRA, heat resistant accelerator, sugar coated)	1.1–1.6
Starch (HI BOND, acid modification starch, non-pregelatinized)	0.5–0.7
Dispersant (DILOFLO, napthalene sulfonate)	0.20–0.22
Paper fiber (hammer milled)	0.5–0.7
Set retarder (Versenex 80=DTPA)	0.07–0.09
Foaming agent (Witcolate 12760)	0.02–0.03
Recalcination inhibitor (Cerelose, dextrose)	0.13–0.14

well as by edging shoes in addition to the forming plate. The paper edges are then glued to the back of the back paper liner after buffing to reduce thickness and obtain a better paper to glue bond. The edges of the board are reduced in thickness and modified to meet certain demands of application in practice.

Figure 7.5 shows an older type of mixer to illustrate the edge mixer arrangements. Newer type of mixers have in most cases only one outlet, and they may or may not have edge mixers.

7.3 Core Composition

To achieve this, the gypsum board manufacturing industry relies heavily on chemical additives. They are intended to optimize the manufacturing process (slurry workability, setting rate, and drying rate) and to ensure appropriate physical properties of the hardened board (density, strength, and water resistance). Most gypsum board processes now typically include water reducers (dispersants), foaming agents, and air entraining agents in addition to set modifiers (accelerators/retarders). While each additive is introduced for a specific function, many of them will also influence the hydration process and each other's performance. Combination of additives can therefore interact in complex and unpredictable ways to modify the setting process and the properties of the resulting gypsum board.

Various slurry formulations exist depending upon the type of board to be manufactured and various other requirements. A variety of components can be combined to produce board with specific properties. Table 7.1 gives an example of the ingredients used for the board formula. The relatively high amount of water should be noted.

Table 7.2 gives an example of a board formula for a 1/2 in. (12.7 mm) type X board with a weight of 1700 lb MSF (thousand square feet). The board is produced at a relatively slow speed of 250 ft/min which amounts to 1000 ft^2/min.

7.3.1 Gauging Water

The gauging water is obviously a key component of the board slurry. Theoretically, it should meet all requirements for potable water. However, for

TABLE 7.2—Approximate formula for 1/2 in. type X board, 1900 lb MSF

	Consumption per MSF	Weight
Stucco	1745 lb	45 lb/ft^3
Starch	7 lb	30 lb/ft^3
Potassium Sulfate	~3 lb (if required)	90 lb/ft^3
Gypsum Accelerator	10 lb	95 lb/ft^3
Retarder (dry basis)	0.2 lb	95 lb/ft^3
Vermiculite	15 lb	55 lb/ft^3
Foaming Agent	0.05 gal	8.70 lb/gal
Foam	300 gal	1.7 lb/gal
Lignosulfonate	0.25 gal	9.85 lb/gal
1/2 in. Glass Fiber	2.5 lb	95 lb/ft^3

economic or logistic reasons, other sources, such as deep wells or local streams, may be used. In any case, care should be taken that they do not contain components that are detrimental to board manufacture, such as sodium chloride or sodium sulfate.

The water is usually heated so that the slurry is at 100°F (38°C) or higher. It should be noted that the amount of gauging water used is relatively high with about 95mL/100 g. This exceeds the normal consistency of plaster which is in the order of about 65mL/100 g.

7.3.2 Foam System

The objective of introducing foam into the board slurry is to create voids to further reduce the final weight of the board without the use of water. Foam addition also improves the physical properties of the board by making it less brittle whereby a possible reduction in strength is minimal. It is also claimed that foam improves the wet bond between core and paper of the board. In contrast, large voids of collapsed foam are sometimes unintentionally generated at the paper to core interface where this usually leads to strength problems mainly because it interferes with the sandwich structure of the board. The lack of stability of the foam is generally blamed for this situation. However, it can be caused by a variety of other circumstances.

Foam is usually produced by a separate foam generator consisting, for example, of either a disk type churn generator or a pump-type generator, which mixes water containing a foaming agent with compressed air. The preferred procedure is to dilute the foaming agent with water to about 5 %–10 % and metering this solution to the foam generator. The feeding of the foaming agent directly into the foam generator for a variety of reasons should be avoided.

In the past, foaming agents consisted of commercial soaps, such as rosin soap, which characteristically produce dry foam. Dry or light foam is difficult to feed homogeneously into the stucco slurry. However, soaps have been largely replaced by synthetic material, which produces wet foams. These are known by trade names such as Millifoam (alkyl ether sulfate) or Cedepal (ammonium alkyl ethoxy sulfate). The foam is usually pumped directly into the pin mixer where it is blended with the slurry. In some plants, the foam is combined with the gauging water or alternatively the entire gauging water is fed through the foam generator producing very wet foam. The stability of the foam generated in a particular manner must be considered.

The production of foam with a consistent density and volume requires that the make up water for foaming agent, and air be uniformly metered. A density of 16 $\mathrm{lb/ft^3}$ (256 $\mathrm{kg/m^2}$) has been suggested but there are other densities in use. This process requires that the metering pumps be accurately calibrated and that information is available showing the consumption of each constituent at various machine speeds. This is necessary because the drying characteristics of the board would otherwise vary. However, the mix head should not be controlled by varying the foam constituents other than in a minor manner.

In the past, it was considered that small and uniform bubbles uniformly distributed throughout the core were required to obtain optimum strength of the board. This view could be maintained as long as each bubble was surrounded by core gypsum as in heavy board. However, this view had to be changed as more foam was added to the core to reduce board weight further. Bubbles began to touch each other and the core gypsum between them was reduced significantly or disappeared at those points. In that way, the core resembles a lightweight bone of a bird. For this reason, different theories have been advanced recently regarding the size distribution of the foam bubbles and their location to produce optimum properties of the board (Fig. 7.6).

For example, gypsum board is now being produced that does not have foam bubbles uniformly distributed throughout the core. In controlled density (CD) board, the layers adjacent to the paper have fewer large bubbles and consequently a higher density. To maintain the same board weight, larger or more bubbles are being confined to the center of the core. When mounted on a ceiling, this type of board has greater resistance to sag than regular gypsum board. Other boards have a more sophisticated core structure in terms of bubble distribution while maintaining a dense layer on one or both paper core interfaces. The original work on this subject was carried out by Bob Bruce (Nanaimo) et al. by demonstrating that lighter board with superior properties can be obtained by controlling foam distribution in such a way that denser layers occur at the gypsum core to paper interfaces. This is achieved by selecting the stability of the foam to control the rate of collapse of the foam which is caused by the rate of shear at the interface between the paper and the gypsum core [7-9]. Subsequently, a similar effect was obtained by using blends of two foaming agents that are chemically different and are classified as stable and unstable [7-10].

7.3.3 Accelerator System

The main purpose of the accelerator system is to shorten the setting time of the board slurry from the mixer to the knife although it affects the entire setting behavior of the board slurry. The time of set is usually the maximum point as given by a time/temperature curve. Gillmore needles, thumb test, etc., are not sufficiently accurate because they depend on the judgment of the operator.

Gypsum block accelerator is commonly composed of calcined gypsum that

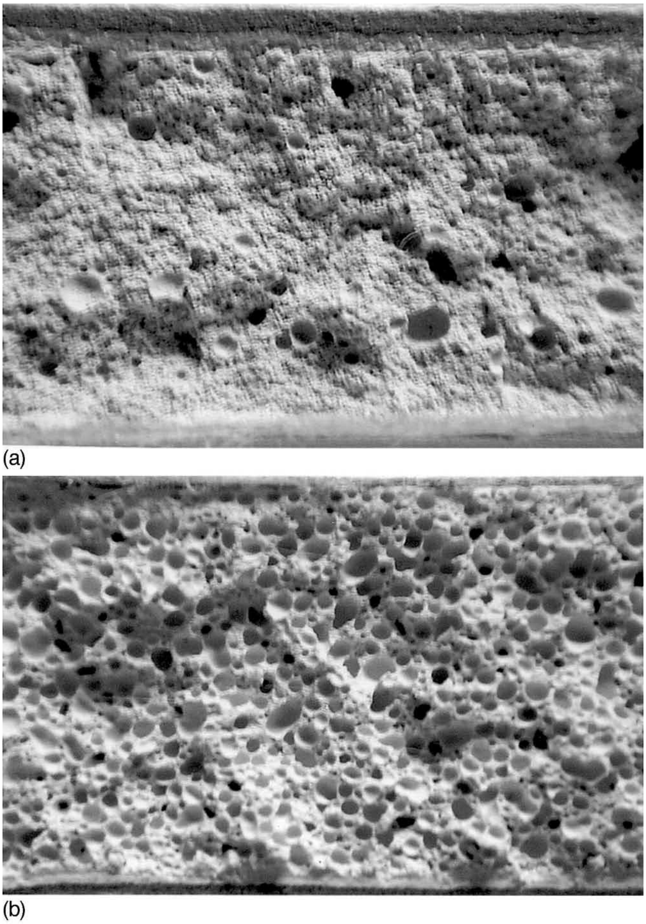

Fig. 7.6—Micrographs of original and improved gypsum board core.

has been cast in 25 lb blocks and allowed to hydrate. For a less recommended method, the gypsum block is obtained from the board slurry. The gypsum is then ground just prior to board manufacture and added to the stucco slurry. Immediate addition to the slurry is necessary because ground material, which has been to be exposed to moisture for any appreciable time is noticeably less efficient as an accelerator. In any case, the performance of the gypsum accelerator should always be verified experimentally when it appears that it has lost potency.

Another problem can arise with the block methods when the gypsum is partially calcined during grinding because of the heat being generated. Partial calcination reduces the acceleration capacity of the accelerator. One method to solve this problem in practice involves an increase of the grinding speed to produce more fine gypsum within a given time. This achieves exactly the opposite effect since, under these conditions, the gypsum is dehydrated more instead of less.

It should be kept in mind that increasing gypsum additions may decrease the set time only to a certain point because the set is governed primarily by the rate with which the stucco dissolves. This rate in turn is affected by such factors as the temperature of the slurry, the fineness of the stucco, and the rate of shear in the pin mixer. Therefore, additional usage of gypsum does not have the desired increase of the acceleration effect when the fastest feasible setting time of the core slurry is reached.

Gypsum accelerator is manufactured by passing ground gypsum or landplaster through a ball mill and blending it with an additive. The most modern acceleration systems involve ball milling in the presence of sugar (USG), starch (National Gypsum), or a suitable surface-active agent (CertainTeed). USG produces HRA (heat resistant accelerator) and CSA (climate stable accelerator). The additives adhere to the surface of the gypsum particles and in the case of sugar or starch prevents loss in acceleration potency through partial calcination. In other cases, additives can also prevent aging, that is, the loss of accelerating potency by moisture adsorption. Therefore, these accelerators can be stored for a period of time or shipped in bags to be added to the stucco as required. Protection from moisture is prudent even under these circumstances.

The other common accelerator is potassium sulfate, which when added to the board slurry quickly supplies sulfate ions (SO_4^{--}). It is considered a chemical accelerator and as such is not affected by aging. It is generally used in addition to the ground gypsum and it is considered to have a greater accelerating effect. Ground gypsum has the tendency of creating initial stiffening and a slow final set. In contrast, potassium sulfate does not promote initial stiffening and it creates a snappy final set. Under certain circumstances, potassium sulfate appears to form large gypsum crystals. This behavior is used for sheathing type boards where it will often permit a reduction in asphalt/wax emulsion.

Potassium sulfate is added to the stucco in the mixing screw or alternatively it is added directly to the pin mixer. In some modern high speed plants, the potassium sulfate is added just ahead of the single outlet port. It is essential to provide means to immediately shut off the accelerator should the board slurry stiffen prematurely. Attempts have been made to add potassium sulfate to the pulp tank. However, this practice has the disadvantage that is not possible to shut off the accelerator independent of the pulp.

7.3.4 Retarders

These materials are added to the board slurry to assure that no premature setting occurs either in the mixer or on the forming table. Setting in the mixer would lead to material build up that restricts flow and requires frequent cleaning. Lumps may be formed in the slurry or a stiffening of the slurry may occur, which produces cavities in the board core. These cavities appear often at the core to paper interface and can result to poor bond to the paper. The use of retarders also tends to minimize the initial setting action in the mixer caused by minor quantities of gypsum that has not been calcined. It may also promote correct accelerator use. Under these conditions, the retarder may enhance slurry fluidity, provide for better incorporation of foam into the slurry, and maintain a cleaner mixer. If optimum retarder usage is maintained, the wet bond will also be increased. However, no amount of retarder will correct a situation that is caused by severely under-calcined stucco.

In the past, dry retarders consisting of soluble keratin were added to the mixing screw. Soluble keratin was obtained by hydrolyzing animal hoof or horn material by treatment with sodium and calcium hydroxide. However, soluble keratin has been largely replaced by sodium solutions of DTPA [7-11]. DTPA is fed directly into the gauging water just ahead of the pin mixer and results in better control of retarder addition. It also makes it possible to increase, decrease, or shut off as required by the setting behavior of the slurry.

In board manufacture, a combination of retarders and accelerators are typically used to produce a snap set [Fig. 7.1]. This type of set is characterized by the lengthening of the induction period during where no noticeable temperature is generated. This is followed by initial setting period and subsequently by a more rapid setting as compared to the usual accelerated setting. This also results in an earlier completion of the setting process. Therefore, a snap set avoids setting in the mixer or on the forming table and it assures complete hydration (95 %–98 %) prior to cutting and drying. Also, snap set maximizes the strength of the board core, which is particularly desirable for the manufacture of lightweight board.

7.3.5 Starch

Starch is used in several industries primarily because of its high water-retaining capacity. In the past, starch for lath or board manufacture was dissolved in water by heating or cooking. However, modern board starches are modified to be cold-water soluble and can therefore be added as a dry material to the stucco in the mixing screw. A less desirable method of adding starch to the slurry is by using the hydropulper of the pulp system, which results in less control.

The major sources of starch are wheat, corn, tapioca, and potato. In nature, starch exists in the form of granules whereby their shape and size is determined by the starch source. Chemically, starch is a long chain polymer consisting of glucose units in the form of amylose as a straight chain and amylopectin as a branched chain molecules. The amylose molecules consist of 300–600 glucose units with an average molecular weight of 50,000–100,000. Amylopectin has a molecular weight of over 1,000,000. The starch granules are formed through hydrogen bonding.

Unmodified starch is insoluble in cold water. However, a process called gelatinization starts at a temperature of 55–60°C (131–140°F) when the starch is heated in water. During this process, which continues until about 95°C (203°F), the hydrogen bonds between the molecules begin to weaken and the starch granules start to absorb water. This is indicated by an increase in viscosity as measured by an Amylograph viscometer. Subsequently, the granules start to swell until they are completely hydrated and they subsequently collapse. As the result, the molecular chains are liberated, which is indicated by a decrease in viscosity. Upon cooling, these molecules repolymerize by retrogradation, which causes again an increase in viscosity. Despite this effect, gelatinization is irreversible.

Physical modification leading to pregelatinized starches includes the classification of granules into different sizes. This is done to increase the solubility and the rate of migration during evaporation in the dryer, as well as to reduce the cooked starch viscosity or to reduce the temperature of gelatinization. It also involves drum drying of pregelatinized starches, extrusion, and the formation of expanded foams. Chemical modification which produces non-pregelatinized starches includes the reduction of the molecular weight of starch by acid thinning with H_2SO_4 or HCl or oxidation by forming carboxyl carbonyl groups. It also includes esterification, etherification, cross-linking, as well as the formation of copolymers.

Various hypotheses have been advanced in support of concepts to explain the bond between gypsum crystals and paper fiber. To a large extent, these hypotheses are based on the fact that in the past gypsum board was produced with slow drying and without the use of starch. However, it was found subsequently that pre-gelatinized (cooked) corn starch allowed much higher drying temperatures without breaking the paper to core bond. This was the discovery that allowed the high speed manufacture of modern gypsum board.

Despite these efforts, the question of how starch bonds the core to the paper remains largely unanswered. The most common of these hypotheses assumes that when the board enters the dryer the core begins to heat up and the starch (or a fraction of it) will dissolve in the free water of the core slurry. As the board dries, both the water and the dissolved starch move towards the surface paper of the board. The starch then precipitates at the point where the water turns into steam at or near the core/paper interface. It forms a gel at this location covering the gypsum crystals. Since this gel has a high water holding power, it will maintain liquid water around the gypsum crystals protecting them from calcination. This assumes that the bond between core and paper is formed by gypsum crystals interlocking with the paper fibers of the inner ply of the liner with the starch playing a protective role.

A different hypothesis attempts to take into account the performance of new types of paper. It suggests that starch alone bonds the gypsum core to the paper. The starch produces the bond because modern papers have lower water absorption than older paper and therefore absorb less water that is supersaturated with respect to gypsum from the board slurry. For this reason, it is unlikely that gypsum crystals form within the paper to create a bond. For this, it is visualized that the starch bridges the paper fibers with the gypsum crystals.

Regardless of which hypothesis is correct, starch is essential for obtaining a good bond between core and paper particularly when board is produced at high speeds and high dryer temperatures. Good starch migration profiles exist when 75 %–85 % is found within the paper and at the core/paper interface. About 65 %–75 % of this quantity is obtained through migration from the center of the core. This migration depends to a large extent on the degree of modification, which increases the mobility of the starch as well as the cold and hot water solubilities. For example, a migration of 45 % is obtained at a Brookfield Viscosity of 900 cps (12 % solids, 80 °C) whereas the migration is 80 % at a viscosity of 20 cps.

Other factors influencing starch migration are the water to stucco ratio of the board slurry, that is, the free water available to act as the carrier for the starch. For example, a migration of 70 % is obtained at a ratio of water: stucco of 82 mL/100 g, whereas the migration is only 30 % at a ratio of 92 mL/100 g. For a similar reason, an increase in foam voids reduces starch migration.

Starch migration is also affected by the sizing and porosity of the paper. Starch will migrate following the path of least resistance thereby accumulating greater amounts at the more porous interface. The face and bottom papers should have similar properties in order to accumulate equal amounts of starch. Likewise, the drying process is often variable from deck to deck and from left to right. In general, a faster rate of water evaporation results a lower migration level. Similarly, different drying rates will cause disproportionate starch migration to the interfaces.

Starch is particularly important when chlorides are present in the board slurry that can interfere with the bond to the paper. This is presumably due to the lowering of the calcination temperature of the gypsum during drying. Because starch raises the calcination temperature, it can offset the negative effect of the chlorides.

It has also been found that due to its molecular weight distribution, a certain amount of starch remains within the core providing adhesion between gypsum crystals. This results in an increase of the compressive strength of the core. However, the quantity of starch used to produce this effect considerably exceeds the normal amount of starch used. Increased quantities of starch can lead to various problems including long drying time because of the water holding capacity of the starch.

In summary, the principal function of the modern starches is to protect or create the bond and to a degree to increase the strength of the board. For this reason, starch is often increased as a cure-all for bond problems. However, this may require an increase in the drying temperature because the board becomes harder to dry, which usually compounds the problem. Obviously, the stucco quality should be improved and maintained so that the lowest amount of starch can be used instead of fixing a problem with an expensive additive.

7.3.6 Other Additives

7.3.6.1 Boric Acid

Boric acid has been used in the manufacture of gypsum board for about 60 years to increase sag resistance particularly of ceiling board, which sags both under its own weight and the weight of added insulation. In addition, boric acid has been used to prevent paper bond failure caused by calcination in the dryer. The manufacture of lighter board has led to an increase in the use of boric acid, as sag and calcination on overdrying become more problematic. Other uses have been for increases in flexural strength, edge and core hardness, and nail pull resistance. Most manufacturers use boric acid at levels between 0.06 % and 0.3 %. If the level of boric acid addition is much higher, the board is more brittle and stiffer. Consequently, the breaking load is concentrated over a short span at the center of the board when the board is lifted on one end during handling, which results in easier cracking and breaking.

Examinations of the effects of boric acid have shown that it decreases the rate of calcination substantially but not the onset of the calcination. This effect on the rate of calcination is indicated by the increasing peak temperatures of differential scanning calorimeter curves of set stucco to which increasing amounts of boric acid has been added. This should not be confused with a shift of the onset of calcination, which remains the same as shown by the incipient temperatures of the DSC curves. The protective effect of boric acid on the calcination of the board in the dryer must therefore be considered in terms of time as well as temperature.

It has also been shown that boric acid migrates easily and rapidly to the surface of the board. It was further shown that it appears to modify the crystal habit at the surface of the board but not within the interior of the core. There is no explanation for this effect since boric acid migrates to the surface after the plaster has set.

As expected, boric acid increases the humidified strength of the bond between paper and core and it does so at a lower concentration than starch. There appears to be a beneficial effect in the presence of chlorides. Also, boric acid has a noticeable effect in improving the humidified deflection (sag) of the board.

Boric acid improves the edge hardness and nail pull resistance of board particularly in the presence of chloride concentrations that are above specifications (e.g., 200 ppm). For unknown reason, this effect seems to be dependent upon the origin of the stucco used.

7.3.6.2 Water Reducing Agents

Dispersing agents or wetting agents are often added to the board slurry to reduce the water requirement of the stucco or to increase the fluidity of the stucco slurry maintaining the water solid ratio. The use of these agents is considered a valuable tool in reducing the quantity of water used for the slurry because it results in faster machine speeds and reduced manufacturing costs. At the same time, it is recognized that these materials may change the yield point or the other rheological properties of the slurry. It is estimated that a reduction of 1 % in gauging water can lead to an energy saving of approximately 1 % through reduced drying requirements. Obviously, the water saved had to be replaced with foam.

The most common of the dispersion agents are calcium, ammonium, or potassium lignosulfonate (Lignosol). Most are available as solids and they can be added to the stucco in the mixing screw or as both solid and liquids to the pulp tank. Care should be exercised when using these materials since some have retarding properties and may affect the gypsum crystal formation and lead to a weaker core or a poorer core-to-paper bond.

More modern materials or superplasticizers, such as sodium salt of polynaphthalene sulfonic acid (PNS), polymelamine sulfonates, or polyacrylates are used in place or in addition to lingnosulfonates. They are available in liquid form and hence are added directly to the pin mixer or the gauging water. Addition through the pulp tank is possible but the previously mentioned loss of control can occur. In general, these agents are water-soluble organic polymers that have ionized groups as well as hydrophobic groups (side chains) and a molecular weight from 103 to 105. It has been stated that PNS at a concentration of 0.1 % by weight of the stucco has the same effect as increasing the water by 10 %. This is based on a similar increase in patty size when water or PNS are added to a stucco paste with a normal patty size [7-12].

A variety of theories have been advanced to explain the mechanism of water reduction by dispersion or wetting, such as adsorption, electrostatic repulsion, or steric repulsion. In the presence of calcium ions on the surface of the stucco surfaces, the most likely of these is adsorption. However, it should be noted that electrostatic and steric repulsion could seldom be eliminated entirely. Also, superplasticizers have side effects in many cases such as lengthening the setting time and modifying crystal growth and crystal morphology. It is also significant that they may interfere with or have synergistic effects on other additives such as foaming agents.

7.3.6.3 Paper Pulp

Paper fiber is considered to improve some of the physical properties of the final board, particularly brittleness and nailability. For special fire rated type X board, 2 % by weight must not be exceeded to meet UL inspection. In this case, paper fiber is usually introduced through recycled board. For regular board, however, paper pulp is produced by dispersing used newsprint or waste board paper in a hydropulper on a batch basis for about 60 min. The hydropulper or similar equipment pulps the paper under high shear, forming a homogeneous suspension. The aqueous pulp slurry is then transferred to a holding tank (chest) holding about two to three batches. This tank is fitted with a stirring mechanism to prevent settling of the paper. From this tank, the pulp suspension is pumped continuously into the pin mixer or the gauging water line if it is free of foam. In some plants, this suspension may also include retarder, core starch, potassium sulfate, and water reducing agents. Obviously, a much preferred procedure would be to meter the materials separately into the pin mixer.

Usually the pulp tank supplies the major part of the gauging water but in some plants only a small volume of water is incorporated with the dispersion. In this case the remainder of the gauging water required for the slurry mix is supplied by a separate water source. This is a preferred procedure since the gauging water is metered directly into the pin mixer.

7.3.6.4 Hydrophobes (Asphalt Wax Emulsions/Silicones/Siloxanes)

It is a definite characteristic of the core of untreated gypsum board that water is adsorbed by positive capillary action. This is due the fact that the core of gypsum board consists of a continuous solid phase (gypsum) and a similar continuous phase existing of empty space. Capillaries are formed in this space as the water evaporates, that is not needed for hydration, and these capillaries are clad by gypsum. This can be demonstrated by placing the board horizontally in contact with water whereby the board will show a wicking effect, that is, the board becomes wetted above the water level.

Consequently, the purpose of hydrophobes is to create a negative capillary action (negative meniscus) to avoid penetration of water into the core of the board for a predisposed time. ASTM C473-07,[1] Section 20, addresses this situation by specifying that the Water Resistance of Core-Treated Water-Repellant Gypsum Panel Products be determined by submerging a specimen of board in water for 2 h with a 1 in. hydrostatic head.

It is an accepted hypothesis that asphalt/wax emulsion functions by forming a coating over the gypsum crystals, which surround the capillaries within the core structure. Microcrystalline wax crystallizes on the surface of the asphalt in the dryer. This creates a negative meniscus for these capillaries and prevents the water from entering the core for a certain period of time. There is a trend towards replacing the asphalt portion in the emulsion by wax that contains a non-microcrystalline portion, which improves its handling properties but otherwise achieves the same effect.

In the production of water resistant core for interior backing board (base for tiles, etc.) or exterior sheathing, asphalt wax emulsions are added to the board slurry. An example of the consumption of asphalt/wax for a 1/2 in. (12.7 mm) board is given as 13.2 gallon (50 L). The ratio of asphalt to wax ranges from 2:1 to 4:1. The paper of this type of board is also water repellant.

The asphalt/wax emulsion is generally supplied in heated tank cars and is often fed from these cars into the pin mixer using heated lines. Alternatively, heated tanks are available at the plant for storage. Attempts to add these emulsions directly to the pulp tank have led to problems. Avoiding this practice would make changeover easier and avoid foaming of the pulp system. Needless to say, all pump, piping, and related equipment should be flushed with water after completion for the board run so that fouling can be avoided.

The total emulsion usage and the quality of the emulsion largely determine the water resistance obtained. However, there are other conditions that influence this property. For example, water resistance decreases with the amount of pulp fiber added. Also, water resistance depends on the amount of foaming agent used whose efficacy is reduced by most emulsions. Finally, water adsorption is decreased by the accelerators used. This has led to an increase of potassium sulfate as compared with ground gypsum.

Apart from water resistance, asphalt/wax emulsions or wax emulsions alone do not improve the other physical properties of the board and in fact they may

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[1] Standard Test Method for Physical Testing of Gypsum Panel Products.

be detrimental. In particular, core treated boards have poorer sag resistance than regular board. Initially it was suspected that this was due to the presence of the organic material. It is now believed that this is due to larger amounts of potassium sulfate being added to the board slurry to obtain the required setting time. Potassium sulfate produces large gypsum crystals, which may be the reason for the poorer sag resistance of the board.

Most of these problems can be avoided when silicones or siloxanes are used instead of asphalt/wax emulsions. These materials were first used in Europe, where heavier board is manufactured. For lighter board in North America, this approach was initially not very successful. However, these problems have been overcome as indicated by the steadily increased use of these materials for the purpose of manufacturing water repellant board.

Silicones or siloxanes create a negative meniscus; the requisite by which they are effective in increasing water repellency. They apparently do so to by adhering to the gypsum forming the inside of the capillaries. However, this is a questionable proposition and it raises the question of the adhesion of the asphalt/wax emulsion to the gypsum crystals, which so far was thought to be a necessity. Therefore, the asphalt may act merely as a diluents and the hypothesis of asphalt adhesion to the gypsum crystals should be revisited.

7.3.6.5 Glass Fiber, Vermiculite, and Clay

Glass fiber is added to the core of special fire rated type X board to change the crack formation of the board when it is subjected to fire. This results in a larger number of small cracks instead of fewer larger ones. For the same reason, glass fibers improve the mechanical strength of the board when the gypsum has been calcined on exposure to fire.

Increasingly, there is a tendency to replace pulp with glass fiber to increase the flexural strength of the board. This avoids the breaking of long board (10–16 ft or 3–4.9 m) that is often lifted in the field at one end. Glass fiber can be supplied to the plant as dry strands. These fibers are chopped to 1/2 in. (12.7 mm) and fed into the dry stucco in the mixing screw. This is not a recommended procedure because it is difficult to mix chopped fiber with dry stucco. A more suitable procedure is to add the glass fiber to a separate tank. In some plants, this is usually done for pre-chopped glass fiber that is treated with a wetting agent to aid dispersion in water.

Unexfoliated vermiculite is added to the board slurry when special fire rated type X board is produced. It is generally metered into the stucco in the mixing screw. Vermiculite ore exfoliates, that is, it expands resembling an open accordion when subjected to heat. On exposure to fire, this expansion compensates for the shrinkage of the core due to the calcination of the gypsum. As a result, the cracks and fissures formed in the core are fewer and smaller, which increase the fire resistance of the board. Additionally, the exfoliation process absorbs energy, which provides further protection from heat transfer through the board.

When special fire rated type X board is produced, some plants add clay to the board slurry in addition to vermiculite and glass fiber. Clay is generally added to the stucco in the mixing screw. The exact mechanism for the function of this material is not known but it increases the fire resistance of the board. However, clay should not be used unless absolutely necessary because of the negative effect on the setting characteristics and the water demand of the slurry.

7.4 Paper Liners

7.4.1 Paper Handling

For board manufacture two roll arrangements are available, one each for the face and the back paper of the board. The face paper is laid down first and face down on the forming table to receive the slurry on its back. The back paper is then placed on top of the slurry forming the top of the board as manufactured. Each of these paper roll arrangements consists of the following:

1. A paper roll stand.
2. Pull rolls to protect the paper from breaking.
3. Guides and tensioners.
4. Paper heaters to remove absorbed moisture.
5. Units to cut grooves along the inside of the face paper for easier folding.
6. Paper cutter if board with smaller width is to be manufactured.

Shaftless roll stands and automatic splicers are the standard equipment for new high-speed board lines. The roll stands are capable of handling roll diameters up to 84 in. (2.1 m) and all normal paper widths. Handling of rolls by fork trucks and manual handling is minimal. A system is generally provided that incorporates all controls for accurate positioning of the paper rolls, automatic splicing, and continuous automatic tension control. Splicing must be very accurate and reliable. Special features provide power assisted unwinding to facilitate paper thread-up and smooth start-ups.

These systems are relatively easy to operate and require minimum operator attention. The only other devices used are gas-fired heaters to condition the paper as well as web guides to precisely track the paper sheets into the forming station and creasers for folding.

The stand supplying the face paper is usually located immediately adjacent to the board forming table. This table provides support for the pin mixer and the vibratory roll. The vibratory roll, not used by all plants, is intended to assure that the slurry discharged from the pin mixer moves across the width of the paper.

7.4.2 Paper Liner Performance

Some plants still experience problems that should have disappeared with modern developments. For example, difficulties may be encountered because the paper shrinks and expands as it absorbs moisture. Most commonly, the edges of the paper expand when stored at a high relative humidity resulting in cockles near the edge of the board during manufacture. For this reason, most plants heat the edges of the paper to avoid this situation.

Once the board is formed, there are several factors that affect the performance of the paper. For example, gypsum board may be manufactured with face and back papers having different expansion characteristics. The expansion of paper will vary with the quantity of waste paper used, the saturation, the permeability, and the moisture of the paper. For this reason, it is not safe to estimate the expansion by saturation or permeability alone.

The wet bond as observed at the knife is another consideration. This bond is good when a fairly thick layer of paper adheres to the core. Again, there are many factors that influence this behavior, such as the temperature of the slurry, the type and amount of foaming agent, the saturation of the paper, the water to stucco ratio of the slurry, the setting time characteristics, and the amount of retarder/accelerator used. Surprisingly, it is not affected by the type and amount of starch in the core.

As the board enters the dryer, the permeability of the paper becomes a critical factor. If the paper has too low a permeability, entrapped steam will form under the paper. This may result in formation of blows or blisters when the steam pressure exceeds the wet ply strength. Conversely, if the permeability is too high, the board may dry too easily and peelers may result because of surface calcination of the board. For this reason, it is extremely important that face and back papers are balanced in terms of permeability as close as possible.

In recent years, the quality of the paper used has improved so that most of the problems experienced in the past have disappeared. For regular board, ivory or cream paper is used for the face whereas grey paper is used for the back of the board. For some face papers, only the top ply consists of cream or ivory material and the remaining plies are made up of gray stock. Ivory paper stock is processed to remove impurities. The total weight of the face and back paper is about 90 lb per MSF (0.5 kg/m^2). Water repellant paper used for sheathing is colored brown usually because of asphalt impregnation. Different producers use different colors for other types of board. For example, USG uses green water repellant paper for interior backing board whereas the National Gypsum Co. uses blue paper.

The main improvements are due to the use of fewer plies and the use of waste paper. These developments occurred despite a decrease in grammage from 380 GSM in 1965 to 190 GSM in 1996. Over the same time, the machine speed was increased from 110 to 650 m/min, which resulted in an increase of the production rate from 7 to 21 tph.

Modern papers consist of three to seven plies whether they are intended for the face or the back of the board. For the face paper, the first ply that forms the ivory exterior of the face is normally decorative. The grey back ply (normally one or two) is intended to bond to the board slurry. The center of the paper is formed from one to four middle plies. All these plies are held together by hydrogen bonding.

A typical paper liner consists of 87 % by weight of cellulose (paper) fibers, 10 % water to control paper expansion and paper handling, and 3 % chemicals of various types. These chemicals are intended to provide water repellency (sizing), color, anti-scuff properties (starch), anti-mold properties (fungicide), and additional strength (starch). For economic manufacture, the paper liner must have a low grammage to allow high productivity and consistent low cost of raw material.

The paper is produced by various machines including underfelt formers, ultra-formers, Manchester formers, and high-speed, multi-wire Fourdriniers. A typical papermaking machine has a 400,000 ton capacity and operates at speeds of up to 700 mpm. This equipment produces trimmed width of either 2.85 m (9.35 ft), 3.65 m (11.97 ft), or 4.44 m (14.56 ft).

To assure that a good quality gypsum board can be manufactured, the paper liners must meet the following requirements at the board plant: A good reel presentation (correct width, diameter, etc.), true and consistent unwinding (no slack edges, nicks, holes, or creases), ease of scoring and producing good edges, acceptable gluing properties at edges, predictable expansion in CD direction (no cockling or ridging), good wet bond at knife, resistance to water ingress to retain strength at turn over, easy to dry in board driers, excellent dry bond, and good scuff resistance.

In addition, the following properties are an issue in the marketplace: Presentation of attractive surface (flat surface, no creases, color, etc.), ease of decoration by paint or wallpaper, acceptance of joint compounds or joint cements and wallpaper, and good strength (handling without breaking).

7.5 Conveyor Section to Dryer

7.5.1 Board Conveyors

After the slurry is formed on the forming table and encased by the paper, the board moves automatically to a belt and subsequently to live roll sections. At this stage, the part of the face paper overlapping the back paper is often sprayed with water to improve the glue bond. The belt section generally consists of two belts that are supported by a series of precision rollers on a steel framework. Each belt is equipped with pulley terminals, AC motor drive for firm control in high speed plants, and belt washers. Their function is to maintain the board in flat position while it is moved from the mixer towards the knife. The live roll section consists of a series of AC powered stainless steel rolls that transfer the board, now sufficiently rigid, from the belt section to the knife. In newer plants, forming belt conveyors reach almost all the way to the knife. This is more economical than open roll sections and provides a better support for the gypsum board.

7.5.2 Knife

The cut-off knife with a digital control system is used to cut the board to lengths usually ranging from 4 to 16 ft (1.2–4.9 m). The requirements for accurate cutting of the wet board at very fast line speeds led to the development of a new rotary cut-off knife. The new design uses separate drives on the top and bottom shafts, which are synchronized electronically. Because of the low inertia design, the knife reaches an exact speed and position to produce a clean cut and precise board length. There may also be a feature to perforate the board at a specific length for breaking at the job site.

It is essential that the length of time from the mixer to the knife is sufficient for the board to develop the required strength and stiffness. This means that the stucco in the core must have hydrated sufficiently prior to cutting. A typical setting time of board slurry for new boardlines provides about 3 min between the mixer and the cut-off knife. Many older plants have increased the speed of manufacture and operate in the 3–4 min range. On the line, the degree of setting is generally tested by a thumb impression. This underscores the importance of the snap set, which allows a better control of the setting process. A serious flaw of the board plant design is that the boardline is often too short to allow speed increases in the manufacturing process. As a result, problems occur either at the mixer when the slurry sets too early or at the knife when the slurry has not hardened sufficiently.

The time required from the knife to the dryer is approximately another 4 min. Flexing of the board during that time period must be avoided. It is important that the stucco in the core of the board has fully hydrated when entering the dryer. This is often overlooked and it is assumed that sufficient strength at the knife guarantees complete hydration at the dryer entrance, which is not always the case. Shortly after entering the dryer, hydration of the stucco ceases because of exposure to high temperatures.

7.5.3 Acceleration and Transfer Section

Some high-speed plants designs are based upon cutting long wet boards and then sawing them to the desired final length after drying. The cut lengths of the board are 24 ft (7.3 m) minimum and 32 ft (9.8 m) maximum. They are fed two pieces at a time into the acceleration section. The purpose of this section is to quickly move the board away from the knife. In the transfer section, the boards are inverted so that they pass through the dryer in a face-up position to avoid staining of the face paper. Before entering the transfer section, the boards are inspected visually and any board showing sign of flaws or damage is rejected at the reject conveyor stage.

The boards are “degrouped” before feeding them into the inlet section of the dryer, which reduces the required length of this section. The overall length of the inlet section is usually selected to obtain a total of about 7 min of hydration time from the mixer to the dryer entrance. The inlet section is entirely belt driven for smooth, quiet operation and low maintenance. Fast and smooth motion as well as accurate positioning is achieved by special servo drives for the dryer tipple.

7.5.4 Bond between Core and Paper

The dryer and the drying process cannot improve board quality but it can have a negative effect. For example, improper drying may cause poor bond of the paper to the core. Two types of failures occur most often under these circumstances, commonly known as splitters or peelers. Splitters are distinguished from peelers by having some of the core material attached to the paper. In contrast, peelers are characterized by a clean paper surface with almost no core material attached. Although there are numerous hypotheses for the occurrence of splitters and peelers, their mechanism is not clearly understood. However, there seems to be a positive correlation between chloride content and paper-to-core bond failures. Other types of failure occur less frequently. For example “blows” refer to the lack of paper core bond over large areas of the board.

A number of hypotheses exist for the generation of a good or poor bond between gypsum crystals and the paper fibers of the liner. While some of these make sense, there is little evidence to support them. For example, it is claimed that the gypsum crystals interlock with the paper fibers protruding from the paper liners, thus bonding the paper firmly to the core by a mechanical bond as opposed to a chemical bond. This overlooks the role of the starch functioning under modern conditions (see Section 7.3.5).

Small gypsum crystals tend to form under unsatisfactory circumstances within the pin mixer. These will be broken by mechanical action and do not continue to grow and in severe cases produce a weak paper-to-core bond. In extreme cases it can also produce a soft core. Similarly, it is believed that if the crystals attain any appreciable length before the slurry contacts the board surface liner, the bond will be weak because the crystals are easily broken by mechanical action. More believable is the assumption that the strongest paper-to-core bond is obtained when the natural crystal growth does not begin until after the board has been formed. If lumps of set gypsum enter into the core, there will be no bond in the corresponding areas and this can lead to blisters and blows.

Other process factors such as accelerator-retarder combinations should be investigated as well. Apart from bond considerations, a slurry of stucco, which stiffens too quickly can result in blisters of the paper and splitters can occur on the face or back of the board. If stiffening is due to excess accelerator, side effects may include excessive shrinkage of the board during drying, as well as a “punky” hard drying core.

7.6 Board Drying and Handling

7.6.1 Board Drying

It is essential to control this process so that the gypsum slurry is not calcined again due to the high temperature in the dryer, which would lead to loss of core strength and loss of paper-to-core bond. Initially, the board is moved into the dryer by a feed tipple, a conveyor that is hinged on one end to allow vertical movement and access to all dryer deck levels. Most new plants in North America are built with board dryers that provide 35–40 min of drying time for 1/2 in. (12.7 mm) thick board. This is somewhat conservative considering that the typical drying time in older plants is 30 min or less. Board dryers are available that function in a longitudinal, a cross-flow format, or a combination of the two.

The dryers are either two or three boards wide. The wider type is recommended because they are more economical. They also provide significant timing advantage for the dryer feed system as well as the dry board handling equipment, which is an important benefit for high-speed plants. Most new dryers are 12 decks high, which reduces their overall length as compared to the typical eight deck dryers used previously. Each deck is individually driven and speed controlled. The fans are also speed controlled to adjust air volume and velocities.

Three zones are common but the largest dryers have four zones. For three zone dryers, the first zone operates at the highest temperature usually at about 600°F (315 °C); the second zone operates at about 400–450°F (205–232 °C); and the third zone at about 350°F (178 °C). For each zone, the inlet and outlet temperature of the hot gases is monitored. Typically, the first and second zones remove each about 40 % of the excess water. The board experiences a rapid rise in temperature in the first zone and a corresponding decline in the second zone. Removal of the remaining 20 % excess water in the third zone is carried out at the lowest temperature and it is therefore a somewhat slower process.

Most dryers are heated with natural gas, but oil heated and to a lesser extent coal heated dryers are in use. Standby fuel may be propane or light oil. The dryers are very energy efficient and some of the new dryers are therefore not equipped with heat exchangers. However, by optimizing individual zone exhausts the energy requirement can be improved from >1550 BTU/lb (>780 kcal/kg) to 1400 BTU/lb (710 kcal/kg). A further improvement can be obtained by exhaust heat recovery, which reduces the energy requirement to <1300 BTU/lb (<650 kcal/kg). For maximum efficiency, some dryers are analyzed in detail relying on real time balancing tools, automated dryer firing, etc.

To avoid calcination of the ends of the board, it is essential that they move through the dryer in close contact. Both the ends and edges of the board are subject to calcination when the temperature of the dryer is too high or the when the speed through the dryer is too slow.

7.6.2 Dry Board Handling

The take-off system is intended to be capable of dealing with all board width, length, and thicknesses at full production speeds. It should handle board that has the same finished lengths or two or three different lengths at the same time. After the take-off procedure, the boards are separated by another accelerator section. A subsequent transfer section moves the board at a 90° angle to the booker that places two boards face to face. Two separate systems are provided for transferring, booking, and sawing, each capable of processing the full flow of board. One system is intended for board rejects or length change transition and as stand-by.

The ends of the boards are subsequently cut to obtain the desired length. Long board are squared and clamped during sawing with traveling saws at slow traveling speed. This results in a cut of high quality and accuracy.

After booking, the boards are accumulated into stacks up to 4 in. (100 mm) high, which greatly reduce the time required for the downstream functions. Each bundler is equipped with an accumulator to collect two or three bundles before feeding them to the stackers. Two separate stackers are supplied for each bundler, which operate alternately and are capable of building multiple stacks to minimize forklift-handling time.

In North America, all board is fitted with end tapes. Since no sawing is being performed at the bundlers, a faster throughput can be achieved. In a separate operation, special boards are finished with vinyl sheet, paint, or fitted with aluminum foil to their back. Also, dunnage or spacer strips used to separate stacks of board are produced in a separate operation. Several reject stackers are provided to deal with problems as they arise. Reject board is sometimes fed back into the system during full production operation.

7.7 Joint Compounds and Cements

Proprietary joint compounds (drying types) and joint cements (setting types) are used to fill and finish the joints between the boards in the field. In North America this involves embedding a reinforcing tape, which usually consists of paper but glass tape is sometimes used as well. The joint cement is normally based on stucco that is retarded to a certain length of setting time, i.e., up to 90 min. Obviously, these preparations must adhere to the paper, they must not show shrinkage and they must be able to produce an extremely thin coat towards the edges of the joint. To achieve this, the materials used include latex binders, thickeners, and non-leveling agents. Examples of latex binders are polyvinyl acetate and polyethylene co-vinyl acetate. Thickeners may include ethyl cellulose, hydroxy propyl methylcellulose, methyl hydroxy propyl cellulose, hydroxy ethyl cellulose, and hydroxy propyl cellulose, hydroxy ethyl cellulose and hydroxy ethyl cellulose. Non-leveling agents include attapulgite, sepiolite, bentonite, and montmorillonite clays.

7.8 Recycling

In some plants, reject board is ground and used as accelerator. Care must be exercised for this procedure because of the presence of retarder and because ground gypsum board is a variable accelerator. Also, reject board is ground and added to the gypsum feed for the calciner. In recent years, small companies have emerged that take the rejected board, separate the paper from the core, and then return the core material to the board plant for use as raw material. The use of rejected board or otherwise recycled board can be controversial because it may raise the amount of paper present in the newly formed board to above 2 %, which is not acceptable for type X board.

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8

Glass Mat Gypsum Board

8.1 Sheathing

PAPER LINED GYPSUM BOARD SUCH AS EXTERIOR SHEATHING IS particularly sensitive to long term exposure to rain and snow in the field. These problems occur despite the use of a water resistant core and water resistant front paper. Sheathing is intended to be covered with a weather barrier but it is often installed and left uncovered. The same situation exists when the board is stored in the open without adequate protection. For this reason, attempts have been made to replace the paper with a glass fiber mat.

In North America, Georgia-Pacific (GP) was the first company to develop and market such a board. The mats are partially covered by a thin layer of core material pressed through the mat during the manufacturing process, which is very similar to the production of normal gypsum board. The core can be treated with hydrophobes, i.e., "water proofing agents," such as asphalt/wax emulsions, silicones, or siloxanes usually during the production process. The board meets ASTM C1177 specifications and it is manufactured as type X board as well [8-1]. This type of board is particularly suitable for applications in so-called exterior insulation and finishing systems (EIFS), where the board is often applied to the exterior of building and left exposed to rain and snow for some time. British Plaster Board had earlier developed a similar board made by a similar process. This board is now manufactured in North America and used for the same purpose. It differs from the GP board in that the fiber-glass mat is completely embedded and covered by a thin layer of gypsum. Because of the successful application of the glass mat board, attempts are underway to replace it for the paper covered sheathing as an EIFS substrate.

8.2 Backing Board

A similar type of board is used as a water resistant backing board for ceilings and walls in bath or shower areas. It meets ASTM C1178 and is designed as a base for the application of ceramic or plastic tile [8-2].

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9

Gypsum Fiber Board

FOR A VARIETY OF REASONS, ATTEMPTS HAVE BEEN MADE TO PROduce a different type of board by incorporating reinforcement material throughout the core rather than just applying it to the surface. A number of these boards have been described in the literature, but only a few have found application in practice. In general, they are characterized by a considerably lower rate of production.

For fiber reinforced gypsum board, fiber is usually incorporated throughout its core to provide improved tensile, flexural, and impact strength. A variety of fibers, such as paper, wood, glass, or mineral fibers, are normally used for this purpose. The proportion of paper fiber in this type of board can reach 15 wt. %, which results in a 1/2 in. (12.7 mm) board that is relatively heavy at 2100–3100 lbs MSF (10.2–15.1 kg/m^2). Although additional surface liners are normally not required, they are used in some cases. Most efforts to develop a gypsum board without a paper surface involve the use of paper fibers. Wood fiber or wafer-reinforced gypsum board is a relative newcomer to the industry, which was developed because of the need to replace formaldehyde-containing glue in particleboard. Synthetic polymeric fibers have found little application, probably because of their high cost.

All gypsum fiberboards are produced in a similar fashion. Differences between individual processes are related primarily to the methods of mixing, moistening, and densification the material. Generally the stucco is mixed with the paper fiber and a relatively small amount of water is added which produces a "semi-dry" or "wet" compound. This mixture is placed into molds of a very large sheet press, similar to those used in the manufacture of resin-bonded particleboard. After the stucco has hydrated, the resulting board is dried using a method similar to that used for regular gypsum board. The major advantage of this process is the lower cost for the paper, particularly if waste paper is used. In addition, drying costs are reduced significantly because the board contains less water, which results of course in higher weights. In regular gypsum board, drying cost is approximately 20 % while the cost of paper is about 40 %.

The development and application of paper or wood fiberboard occurred primarily in Europe with only a few operations in North America. There are a number of companies with very similar technologies. The Ferma Company in Germany originally developed gypsum fiberboard as Fermacell about 20 years ago. The technology has improved considerably since that time, but it is still essentially based on mixing waste paper with stucco. Also, there is always competition from traditional gypsum board companies. For example, Knauf produces an approximately 4×4 ft^2 (1.2×1.2 m^2) board for the do-it-yourself market.

In North America, Würtex and Schenk have provided technology for a plant constructed by Furman Lumber at East Providence, Rhode Island, and to

Louisiana-Pacific for a plant in Nova Scotia that was for a time operated by U.S. Gypsum. Total construction costs were estimated at U.S. $37 million as compared to U.S. $28 million for the plant of Louisiana-Pacific in Nova Scotia. Both plants are no longer in operation.

The Würtex and Schenk plants use less water than Fermacell by employing a continuous semi-dry process. This permits higher production rates that are achieved by a continuous operation rather than by pressing of board stacks. Also, excess water is not removed by the press and hence better dimensional tolerances are possible and final sanding is not required. Both plants also allow for the production of a board with a lightweight center of the core by incorporating expanded perlite. This approach recognizes that normal board from this process is too heavy for the North American market.

Specifically, the stucco is initially mixed with wetted waste paper supplied from the U.S. East Coast. Sufficient water is added prior to forming the board and the remaining water is subsequently spray applied. The plants are designed for two lines using various mixing and forming heads. The board travels through this section on a thin belt. Pressing is accomplished with continuous belt presses whereby one belt must be a sieve to allow for the removal of entrapped air. The press time ranges from 30 to 45 min. The wet board then passed through a jet dryer, which requires about 30 min for drying. The finished board has a thickness of about 1/2 in. (12.7 mm) and weighs slightly more than 2400 lb per MSF. This is considerably heavier than typical 1/2 in. regular gypsum board, which weighs less than 1700 lb per MSF. The capacity of manufacturing this type of board is relatively high amounting to approximately 45 ft/min based on a board 4 ft (1.2 m) wide.

The manufacturing of Knauf board is based on a process developed by Hatcheck, which originally used stucco and paper fiber and was later modified for the manufacture of asbestos cement. For this process, a thin film of stucco and paper fiber is formed and placed onto a continuous felt where the water is removed by suction. The film is then wound around a mandrel, which is stopped when the desired thickness is reached. It is then cut lengthwise to obtain a sheet and further curing and drying is carried out as appropriate. The product obtained is relatively dense but can be used for furniture and computer floor applications.

Gypsum fiberboard products meet gypsum board specifications. They are covered by a separate standard [9-1]. It is also claimed that the finishing of the joints can be accomplished without the use of reinforcing tape and for this reason it is faster than for regular gypsum board. However, this is in part a reflection of the differences in construction practice between Europe and North America, where reinforcing tape is used to finish gypsum board joints. Additionally, the surface of the fiber-reinforced board differs since it is composed of a mixture of fiber and gypsum instead of paper exclusively. Therefore, paints with especially good hiding characteristics are required for those boards. Gypsum fiberboard has a tendency to be more abuse resistant than regular gypsum board where the softer core is exposed when the surface paper liner is damaged.

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10

Testing, Analysis, and Installation

APPROPRIATE SAMPLING AND TESTING IS AN IMPORTANT CONSIDeration to obtain materials with consistent qualities throughout the entire manufacturing process, but particularly during and after calcination. Unfortunately this point is often overlooked or neglected as indicated by the absence of suitable sampling stations or ports in many locations. This can lead to difficulties particularly when problems are to be solved. Even under normal circumstances it amounts to an unsatisfactory situation.

In actual practice, these methods are a blend of procedures developed by a particular company and procedures published by standards writing organizations such as ASTM. To some extent, this allows testing of the behavior of the stucco produced during calcination as well as testing of the stucco slurry during board manufacture. For example, certain test methods are intended to cover situations where the stucco meets the requirements of the specifications but actually contains a small amount of non-calcined gypsum. The presence of this effect will not necessarily show up in routine laboratory consistency test where gentle hand mixing is employed. However, it will show up in actual plant operation due to the high mechanical action and shearing action of the pin mixer.

The detection of this behavior can be made in the laboratory by the use of a high speed mixer such as a "malted milk mixer." Normal stucco will not thicken and will pour from the container at the end of the test. However, if the slurry thickens within 15–20 s of mixing, the stucco probably contains considerable amounts of gypsum that has not been calcined.

Another method of gauging the initial characteristics of stucco slurry during actual plant operation involves measuring the slurry temperature. Temperature readings are taken directly beneath the pin mixer discharge boot and as close to the nip of the forming plate as possible.

In actual practice, a temperature rise of 1°F (0.7°C) is considered to be within acceptable limits. If the temperature rise between these two points exceeds that limit it shows that the setting occurs too early and that paper-to-core bond problem may result. Hence, the possibility of the presence of uncalcined gypsum should be determined. This can be done most easily by subjecting the stucco to DTA or DSC analysis [10-1]

To complicate matters, stucco may be calcined beyond the proper level so that it contains soluble or even insoluble anhydrite, which can cause problems with set control and paper to core bond. This characteristic will be noticed during routine quality control tests because its combined water will be below the specified range. However, if the stucco contains both over-calcined and under-calcined material, it may give the impression of being acceptable. Therefore, determinations of the hydration rate of the stucco should be carried out routinely.

Routine testing is generally carried out according to methods developed by standards writing organizations, such as ASTM, British Standards Organization, DIN, Canadian Standards Organization, and the Japanese Standards Organization. These organizations are responsible for establishing a consensus among a variety of participants prior to publishing the standards. They are seldom involved in the testing process itself. The standards are similar with the exceptions that they cover some materials or products that are not manufactured elsewhere. For example, DIN 18163 covers molded wall (partition) panels that are not mentioned by ASTM because this product is not produced or used in North America. Also, some locally developed test methods may be preferred, such as the DIN water wicking method instead of a normal consistency method.

Standards are usually subdivided into (1) Test Methods, (2) Specifications, and (3) Application or Installation Procedures. Accessories and related products are treated in the same manner and chemical analyses are normally included with test methods. A distinction is usually made between materials and products although that is not always easy. The test methods are intended to establish the significant performance characteristics or properties of the materials and products. These must meet specific criteria that are outlined in appropriate specifications usually in a prescriptive rather than a descriptive manner. Application or installation procedures serve as a best practice guide as to how the products are to be used in practice.

10.1 Materials Testing

ASTM C11 refers to the terminology related to gypsum and gypsum products whereas ASTM C22 provides the initial test methods for gypsum to be used to produce various products. Essentially it establishes that gypsum shall contain not less than 70.0 wt % of dihydrate, $CaSO_4 \cdot 2H_2O$. The chemical analysis of gypsum and gypsum products is covered by ASTM C471. ASTM C472 outlines the test methods for physical testing of gypsum, plasters, and gypsum concrete [10-2]. It covers methods for stucco, such as free water (drying), fineness (sieving), consistency (cone penetrometer), setting time (Vicat needle), compressive strength (2 in., i.e., 5 cm cubes), and density (weighing). It is emphasized that the available material must be tested in a dried condition and that all equipment must be kept free of freshly set plaster. Gypsum veneer plaster is a special case with ASTM C587 covering joint strength, bond strength, impact strength, and flexural strength.

10.2 Materials Specifications

The corresponding specifications for plasters are given in ASTM C28 [10-3], which stresses that the physical properties differ in the field when plaster is applied to lath or masonry and that they are affected by a variety of conditions experienced in practice. The specification covers neat plaster (stucco and water only) and plasters containing aggregate such as sand, perlite, vermiculite or wood fiber. Stucco must contain at least 66.0 wt % of hemihydrate, $CaSO_4 \cdot (1/2)H_2O$. The specification refers only to the setting time and compressive strength of these materials giving the permissible composition (ratios of stucco to aggregate) where applicable. Fineness is addressed only for gauging plaster intended for finishing coats. Other examples are specifications for Casting and Molding Plasters (C59), anhydrous Keene's Cement (C61), and Gypsum Concrete (C317). The latter covers density instead of fineness.

10.3 Product Testing

For board products, the test procedures are intended to outline sampling and the measurement of properties as they affect the entire product as produced by a specific manufacturing process [10-4]. These are outlined in ASTM C473.

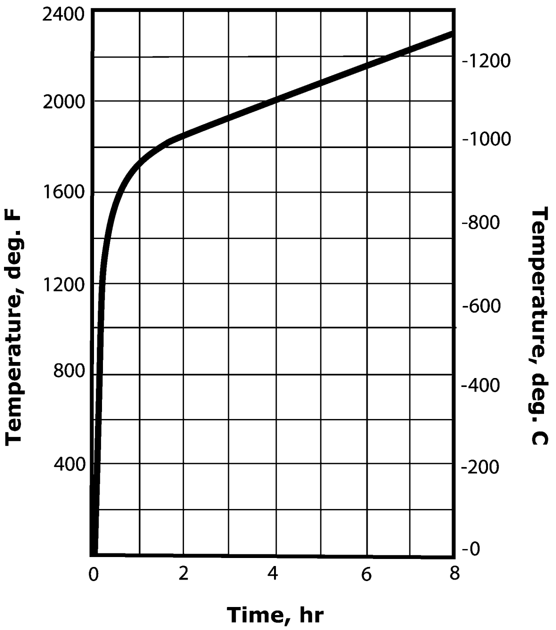
Fire protection is an example of product testing. It is an undisputed fact that there is a considerable delay for the back of hardened gypsum board to reach a failure temperature when it is exposed to an actual fire or a fire test. One of the hypotheses offered for this protective effect is the formation of a steam curtain at the front of the board that is created when the dihydrate in the gypsum dehydrates. This steam curtain allows the temperature to rise only very slowly. However, this hypothesis is difficult to maintain as the exclusive mechanism in the light of the magnitude of the temperature and length of exposure to which the board is subjected in a fire test [Fig. 10.1]. Other factors must be taken into consideration.

It should also be noted that the requirements for gypsum board normally lie within the first hour of the E119 test procedure, that is, failure occurs as the furnace temperature is still rapidly increasing. Therefore, it is more likely that the slow progression of the temperature into the gypsum is assisted considerably by the fact that the sponge-like structure of the board prevents crack formation. This assumption is supported by the observation that failure of gypsum board in a fire test usually occurs when a crack appears in the core through which hot gases reach the back of the board.

10.4 Product Specifications

In North America the overriding standard is ASTM C1396, which is a recent combination of several individual standards. Similar test methods are issued by other standards writing organization (e.g., DIN 18180). It should be understood that these are minimum requirements and consequently the boards exceed them in many instances. These tests are again considered routine affairs. The only contentious issue is the nail pull resistance of the board. For example, if the values given in C1396, Section 5.1.3 are plotted, a break appears at the 1/2 in. (12.7 mm) value. This requires correction since a straight line should be obtained for gypsum board. This means that the paper contributes to the nail pull value in a constant manner; say 5 lb (2.27 kg). The core on the other hand contributes a value which increases with its thickness (Fig. 10.2). It could be argued that the nail pull values for 5/8 and 3/4 in. board are too low. However, this would require exceptionally high nail pull values for both these boards.

The specifications cover the significant properties of a board such as flexural strength, humidified deflection, core-, edge-, and end-hardness, as well as



Standard Time-Temperature Curve
(ASTM E 119)

Fig. 10.1—Fire endurance test.

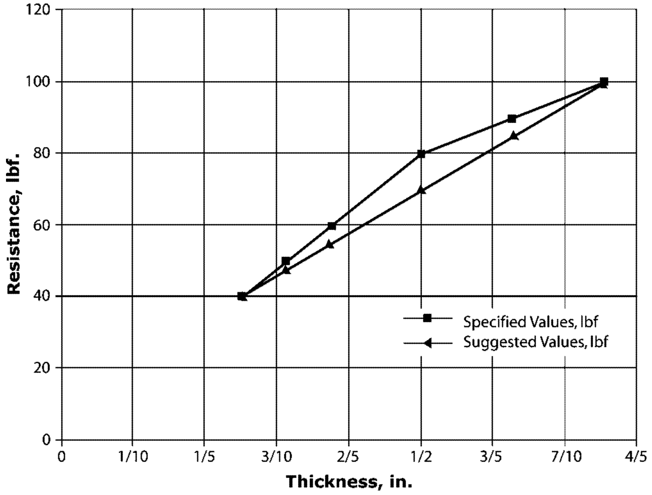


Fig. 10.2—Nail pull test specifications.

nail pull resistance. This includes dimensions and tolerances for thickness, width, ends, and edges of these boards. They also cover criteria which differentiate the type of boards primarily according to the intended use. For example, the following boards are now covered by ASTM C1396 [10-5]: gypsum wallboard and predecorated gypsum board with and without foil backing; gypsum backing board, coreboard, and shaftliner board; water resistant gypsum backing board; exterior gypsum soffit board; treated core and non-treated core gypsum sheathing board, gypsum base for veneer plasters; gypsum lath, and gypsum ceiling board. Gypsum formboard is a special case covering a permanent form for poured in place-reinforced gypsum concrete, which also addresses resistance to fungi. For water-resistant backing board and sheathing the specification also covers water resistance and surface adsorption. Where foil backed board is involved, water vapor transmission (permeance) is specified.

In most cases these boards are also produced as type X (special fire rated) board, which must meet the definition for fire resistance of type X board and type X lath (E119) and flame spread (E84). In practice, these tests are performed and listed by UL or other listing agencies for individual assemblies of which the board is a key component. This is intended to assure that type X board meets the requirements of Building Codes. Sound transmission situations are handled in a similar manner.

This situation gives the impression that there is a good perception of the fundamental parameters that define the performance characteristics of the gypsum board or one of its components. However, this is not always the case. It is characteristic for manufacturing to respond to observed shortcomings of the board by adding yet another additive. This is bound to be problematic in view of the presence of a large variety of these additives that are used for various purposes and whose interplay is not known. Little or no attention is being paid to the fundamental characteristics of the board or its core that make it stiff, strong, hard, or brittle.

10.5 Testing Problems

Nail pull resistance is a case in point for a remaining problem. As stated previously, it is the key property that prevents lowering the weight of regular board below a certain level. Based on fracture mechanics, a hypothesis was advanced to describe the failure mechanism that occurs when a load is applied to a test nail in the laboratory inserted into the board during the test leaving the nail head resting on its surface (Fig. 10.3). Essentially, radial cracking was noticed first at the bottom of the board at a load of about 30 lb (13.6 kg). Next, at a load between 30 and 50 lb (13.6 and 22.7 kg) a circumferential crack with a diameter of 1 in. (2.5 cm) was noticed at the back of the board in the core. This crack then propagates upwards with increasing load from the bottom of the board towards the edge of the nail head. Further increase in load causes shear failure to occur immediately under the nail head when a maximum load of 80 lb (36.3 kg) is reached [10-6].

This mechanism is difficult to reconcile with observation during the actual

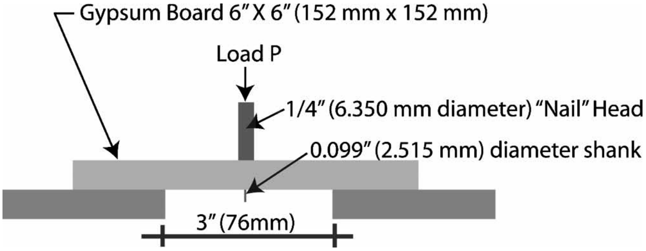


Fig. 10.3—Nail pull test assembly.

test on gypsum board and it is also at odds with observation on other brittle materials. For these materials, a cone is formed as well but it typically propagates from the top, where the nail head impacts the board, towards the bottom. This behavior has been confirmed for gypsum board by work carried out at the Research Laboratories of British Plasterboard [10-7]. It must be remembered that hydrated stucco forming the core of gypsum board is brittle and contains many cracks or fissures, which open under tension but "come up solid" in compression. As a consequence, gypsum board does not obey Hooke's law and it has a correspondingly low Young's modulus.

10.6 Analyses

The chemical analyses of gypsum and gypsum products are covered by ASTM C471, which covers gypsum, plaster, and a variety of products ranging from ready mixed plaster to gypsum board. The individual analytical procedures address not only the basic constituents such as calcium oxide and sulfur trioxide but also a number of impurities such as chlorides. Analyses of FGD gypsum are of course somewhat more involved. These points are discussed in the publication entitled "Analysis and Evaluation of Synthetic Gypsum" [10-8]. A German publication discusses the Analysis of FGD Gypsum in a more detailed manner [10-9].

10.7 Application and Installation Procedures

A variety of standards have been issued that are intended to cover the application of these materials, boards, and accessories in the field [10-10]. Testing, specification, and application/installation standards should therefore be considered an integral part of the entire process of production and construction. This assumes appropriate feedback from the field. While some testing according to specifications is carried out in the manufacturing plant, other tests are carried out by approved agencies and are performed according to installation standards.

On the surface this may appear to be a static procedure but in reality it involves new developments and changes on an almost perpetual basis. An interesting example of this is the fact that the paper liner for sheathing has been replaced by a glass mat, a significant change in the structure of this board. Also, the paper liner of the gypsum board can be wetted and the board can then be applied to cover rounded surfaces such as pillars and arches. In these cases the original strength is largely restored by drying [10-11].

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11

Health Considerations

GYPSUM IS CONSIDERED TO BE A NON-TOXIC MATERIAL WITH THE dust falling into the nuisance category. Natural gypsum (not synthetic gypsum) is recognized as calcium sulfate to be acceptable for human consumption and a wide variety of other uses by the U.S. Food and Drug Administration. It is a dietary source for calcium, it is used as color additive for drugs and cosmetic, it conditions water used for beer brewing, it controls the tartness and clarity of wine, and it is an ingredient in canned vegetables, flour, white bread, ice cream, blue cheese, etc.

As indicated by the term landplaster, gypsum is used as a fertilizer since it benefits a variety of crops where substantial amounts of sulfate sulfur are required. It is also used as soil additive to improve the workability, water penetration of soils, and to overcome the effect of alkalinity. It settles dirt and clay particles in turbid water, particularly ponds, without injury to aquatic life. Finally, surgical and orthopedic casts are often made from hydrated α-plaster, i.e., gypsum [11-1].

NIOSH requires a maximum REL of 10 mg/m^3 TWA and 5 mg/m^3 (respiratory), whereas OSHA allows a maximum PEL of 15 and 5 mg/m^3, using NIOSH methods 0500 and 0600. NIOSH also specifies first aid procedures in case of contamination of eyes, respiratory system, or by ingestion [11-2].

Of course, impurities of the gypsum have to be considered separately and individually. For example quartz (determined by DTA) must not be present in quantities that exceed EPA requirements.

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