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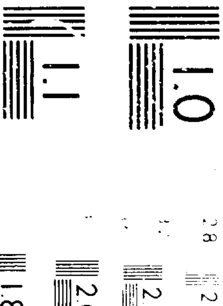
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PRESENT-DAY PROBLEMS OF UTILIZATION OF GYPSUM ROCK AND GYPSUM PLASTER IN THE BUILDING INDUSTRY

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May 1979

Ing. Lubomír Lejsek

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1. Introduction

Gypsum plaster and gypsum plaster products belong to those building materials which attract an ever growing attention and the utilization of which in the building industry is steadily growing.

Gypsum plaster exhibits from the point of view of prefabrication a number of highly advantageous properties - it sets rapidly, has a good workability, facilitates the attainment of smooth surfaces, accurate dimensions, can be made lightweight, etc. The rapid setting of the gypsum plaster makes possible, in comparison with cement, a better utilization of the moulds, since already 10 to 20 minutes after mixing the gypsum plaster with water, the products can be removed from the mould and dried. The finished products exhibit favourable sound insulating properties, they can be employed in the field of fire prevention. Additionally, prefabricated gypsum plaster elements are characterized by microclimate regulation capabilities; during the period of a higher relative humidity in the atmosphere they absorb moisture, in case of a decrease in humidity they, on the other hand, release moisture.

With regard to the properties of gypsum plaster - non-flammability, soundness, low density, low thermal conductivity - it can be appraised as a building material that is close to the ideal material for the construction of diverse unloaded building elements for interior purposes.

The application of gypsum can look back on a very long history. In the antiquity were manufactured gypsum mortars (Egypt, Assyria, Phoenicia, Palestine). Herodotos (approx. 450 B.C.) states that in Ethiopia the bodies of the deceased have been encapsulated in gypsum plaster. The knowledge of gypsum plaster has come from Egypt to Greece to Rome.

Already in the fourth century B.C. Theoprastos described the gypsum rock mineral and also in some detail the more significant properties of gypsum plaster. At the same time Litostratos described gypsum plaster masks. Around the year 100 A.D. Vitruvius and Plinius described stuccowork.

After the Migration of Nations we again come across a more pronounced utilization of gypsum plaster around the year 1000 A.D. (Anstett) and in the middle of the 11th century we can observe in Germany the manufacture of gypsum plaster floors. But the actual development of the production and utilization of gypsum plaster dates back to the beginning of the 19th century (Gay-Lussac, Payen, etc.) and gradually are then also appearing theoretical papers dealing with the clarification of processes that are involved both in the production and setting of gypsum plaster (Michaelis, Schott, Le Chatelier, van't Hoff, Le Chassevent, and others).

The gypsum plaster industry recorded an especially significant development in the period after the Second World War, mainly through the introduction of the manufacture of gypsum plaster products for the building industry which, as the main user of the products, plays the most significant role.

Also the physical and chemical research work recorded during this period extraordinary successes thanks to modern instruments which make possible the determination of the inner structure of the material.

2. Gypsum rock - starting raw material

Gypsum rock - $CaSO_4.2H_2O$ - is the natural form of calcium sulphate. The generally in nature concurrently appearing anhydrite is its waterloss form ($CaSO_4$). Both materials are genetically very close to one another and are often also similar in outer appearance. In a simple manner they can, as a rule, be differentiated according to their different hardness, gypsum rock can be scratched with the nail, but anhydrite can not. Anhydrite is generally finely crystalline, gypsum rock finely to coarsely crystalline. In the more fine-grained basic mass of the gypsum rock occur sometimes large scattered gypsum rock phenocrysts, mostly of a secondary origin. As long as gypsum rock crystalizes in argillaceous sediments, more rarely also in sandy sediments, there can occur also considerably large gypsum rock crystals and their phenocrysts. With regard to the closeness of the chemical composition of gypsum rock and anhydrite, also the conditions of their formation are very close. If the waters, from which the deposits of the two minerals as evaporite rocks are formed, do not contain sodium chloride, anhydrite crystalizes at a temperature above 42 °C, below this temperature gypsum rock is precipitated. In complex solutions, which include sea water, anhydrite crystalizes already at temperatures above 34 °C, and from the most concentrated salt brines anhydrite is liberated regardless of temperature. If from sea water crystallizes already halite (NaCl), then only anhydrite can be formed. The border between the regions of anhydrite and gypsum rock separation is thus temperature and concentration dependent.

In accordance with the appearance of gypsum rock or anhydrite it is not, however, possible to assess in a simple manner the physico-chemical conditions of sedimentation, since the two minerals are under certain conditions unstable and are converted into one another. The primary sediment is generally anhydrite. Numerous anhydrite deposits or at least parts thereof have in the vicinity of the surface been secondarily changed into gypsum rock. Anhydrite is namely converted by hydration into gypsum rock with a simultaneous change in volume by 30 - 50 %which often leads to considerable deformations both of the mineral itself and the strata in its vicinity. By secondary hydration can sometimes be converted to gypsum rock even entire mighty anhydrite strata, but often hydration afflicts only their marginal parts.

Gypsum rock formed through the effect of permeating waters sets up on the fringes of the anhydrite lens its gypsum rock border; an example of this is given in Fig. 1.

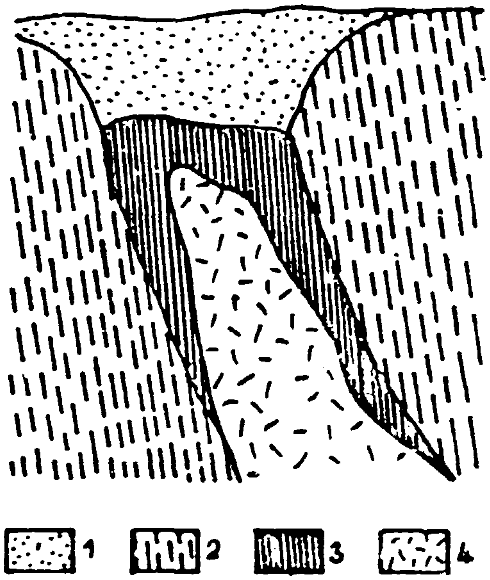

Fig.1. Gypsum rock deposit near Spišská Nová Ves (ČSSR) 1- weathered rock; 2-barren rock; 3- gypsum rock; 4- anhydrite;

A contrary process is the change of gypsum rock into anhydrite. This occurs during the contact of gypsum rock with concentrated salt brine in the centre of the basin or through the action of pressure. Thus e.g. the pressure of a 450 m thick rock cover is according to certain authors sufficient for the conversion of gypsum rock into anhydrite.

Both gypsum rock and anhydrite are thus formed above all through evaporation of sea water or the water of salt lakes. Generally it can be stated that under elevated temperatures - e.g. in a hot arid climate - prevailingly anhydrite is deposited, whereas under lower temperatures - especially in the mild climate - gypsum rock is deposited.

Through the evaporation of a 100 m thick layer of normal sea water is formed a calcium sulphate layer with a thickness of approximately 7 cm.

Calcium sulphate appears in nature also in less current forms. The highly fine-grained transparent form is alabaster; its fibrous form - selenite - fills various cracks and interstratal joints or forms, similarly to anhydrite, whole strata. Earthy gypsum rock formed by the evaporation of waters contaminated with argillaceous materials - e.g. under lake conditions - is called gypsite.

Beside the above natural forms of gypsum rock and anhydrite there occur huge quantities of gypsum rock as by-products in the manufacture of phosphoric acid and in other chemical processes (neutralization of sulphate waters, citric acid production, conversion of ammonium sulphate, etc.). A considerable part of these by-products is not being utilized at the present time, with regard to the present contamination. Even though the removal of the latter is technically feasible, it has proved itself in many cases as too costly and gives thus no chance to compete with the very cheap natural gypsum rock.

Gypsum rock and anhydrite appear in large quantities all over the world. There exist in fact few regions where no commercially interesting deposits are available. The raw material has a very low price; at the present time the price of 1 ton e.g. in Great Britain without transport costs from the mine is 3.5 - 4.0 £. With regard to the both technically and thermally not highly exacting production, also the price of gypsum plaster and gypsum products is relatively low which contributes to the popularity of those products in the building industry.

Even though the field of occurence of the deposits is great and the world reserves are large, the main factor which decides about the viability of the potential investment (i.e. mining, production and processing of gypsum plaster) is the distance from the potential markets and the ease of transportation. The US Bureau of Mines estimates that the world reserves have reached in 1977 approximately 2 billion tons. This figure apparently takes into account only the reserves that are being utilized at present. Significant exceptions are Japan and Skandinavia; this fact, on the other hand, made Japan a leading country in the utilization of by-product calcium sulphate in order to avoid high imports with the associated transportation costs.

Worth mentioning are large gypsum rock localities in the centre of the European part of the USSR (the region of Tula and Gorki), in the North in the Archangelsk Region, in the region of the central and southern Volga, in the North Causasus, in the Ural, the Far East (Irkutsk and Krasnojarsk Region), in the Ukraine, in Uzbekistan and Turkmenia.

The main European localities include deposits in Poland, the German Democratic Republic, the Federal Republic of Germany, France, Italy, Creat Britain, Austria, Greece, Spain and Cyprus.

On the American Continent, the main gypsum rock winning and processing countries include the Argentine, Brazil, Canada, the USA, the Dominican Republic, Mexico, Peru.

In Africa it is above all Southern Africa and in the remaining parts of the world above all Australia, India, Iran, Japan and Pakistan.

3. $CaSO_4$-H_2O system

Gypsum binders are obtained by dewatering gypsum rock at various temperatures. Dependent on temperature and the external conditions of hydration time, various modifications of both hydrated and anhydrous calcium sulphate are formed which mutually differ in the form and magnitude of the crystals, density, optical as well as other properties.

On heating, under various conditions the following compounds may be formed:

α-$CaSO_4 \cdot 1/2\ H_2O$
β-$CaSO_4 \cdot 1/2\ H_2O$
α-$CaSO_4$ III soluble anhydrite
β-$CaSO_4$ III soluble anhydrite
$CaSO_4$ II insoluble anhydrite
$CaSO_4$ I .

The first changes on heating $CaSO_4.2H_2O$ occur already at approximately 45 °C, pronounced changes than at 75 - 80 °C. A technically necessary gypsum rock dehydration rate is, however, attained only at such a temperature, at which the tension of the vapour released during the dehydration exceeds the atmospheric pressure.

The equilibrium temperature of the reaction (at a pressure of 0.1 MPa)

$$CaSO_4.2H_2O \longleftrightarrow CaSO_4.1/2\ H_2O + 11/2\ H_2O$$

is according to various authors 97 - 107 °C. This relatively great difference in the data for the dihydrate decomposition temperature is given by the fact that the dehydration temperature and rate of samples from various localities and even from various locations of the same deposit exhibit considerable differences. This is influenced by the different size and various forms of the gypsum rock grains; by different degrees of purity, methods of crushing and grinding, heating rate, etc. The optimum temperature is therefore often verified experimentaly with the aid of differential thermal analysis (DTA).

α- semihydrate is formed by heating gypsum rock to 115 - 125 °C under a mild overpressure (0.12 - 0.13 MPa) in an environment saturated with water vapour or even under normal pressure and a lower temperature in water or solutions of certain salts. This modification is formed when the water of crystallization escapes from the gypsum rock in a liquid form, so that it does not cause destruction and loosening of the individual particles. In this way can be explained the effectiveness of certain salts that are present in the solution which reduce the water vapour tension on the surface of the particles and make possible the escape of water in its liquid form. As effective salts are listed e.g. $CaCl_2$, $MgCl_2$, alkalic acetates, salts of aliphatic carbonic acids, etc.

In practical operations it often happens, especially during the production of β-semi-hydrate in cookers, that near the cooker bottom, where the pressure is higher than in the surface layers, a certain quantity of α-semi-hydrate is formed.

α-semi-hydrate is dense. It forms nice needle-shaped or prismatic crystals. Its density is 2.72 - 2.73 g/cm^3, whereas β-semi-hydrate is porous, has a density of 2.67 - 2.68 g/cm^3, its crystals are smaller and have no such clearly defined shape. Therefore the β-modification has for a practically identical grain size a larger specific surface than the α-modification. This manifests itself in practical operation by the fact that the α-modification requires for the same plasticity of the gypsum plaster paste a smaller quantity of water than the β-modification. The water-gypsum ratio of the α-modification is 0.35 - 0.45, of the β-modification 0.5 - 0.7. Therefore products from the α-modification have higher strengths than products from the β-modification.

The above modifications differ also in the quantity of the heat of hydration.

$$\alpha\text{-}CaSO_4.1/2\ H_2O + 11/2\ H_2O \rightarrow CaSO_4.2H_2O + (4100 \pm 20)\ \text{cal}$$
$$\beta\text{-}CaSO_4.1/2\ H_2O + 11/2\ H_2O \rightarrow CaSO_4.2H_2O + (4600 \pm 20)\ \text{cal.}$$

Conversely, the heat of decomposition for the formation of the two modifications does not differ too much.

$$CaSO_4.2H_2O + 19{,}850\ \text{cal} \rightarrow \alpha\text{-}CaSO_4.1/2\ H_2O + 11/2\ H_2O$$
$$CaSO_4.2H_2O + 20{,}350\ \text{cal} \rightarrow \beta\text{-}CaSO_4.1/2\ H_2O + 11/2\ H_2O\ .$$

β-semi-hydrate is formed on heating gypsum rock under normal pressure at a temperature of 100 - 160 °C. In the course of this reaction water is liberated from the lattice in the form of steam which leads to a mechanical disintegration of the grains. The particles are then more porous and have a rough surface.

α-anhydrite III - soluble anhydrite - is formed from α-semi-hydrate by the heating of the latter to 200 - 210 °C.

β-anhydrite III - soluble anhydrite - is formed from β-semi-hydrate by the heating of the latter to 170 - 180 °C.

Both soluble anhydrite forms are unstable and already under the action of atmospheric moisture they are converted to their semi-hydrate forms. In doing so the β-modification is less stable than the α-modification, with regard to the different porosity of the latter. The heat of hydration of the α-modification is 6,210 cal, that of the β-modification 7,210 cal.

The soluble anhydrites set more rapidly, require more water and exhibit lower strengths than the corresponding semi-hydrates. Industrial gypsum plasters should therefore as a rule contain the least possible quantity of those components.

By heating soluble anhydrite III to a temperature of 400 - 800 °C, $CaSO_4$ II - insoluble anhydrite - is formed. The properties of the insoluble anhydrite are very similar to those of the natural anhydrite. With water it combines very slowly; this reaction can, however, be speeded up by the addition of certain hydrogen as well as normal sulphates. This fact is utilized in practice in the manufacture of anhydrite binders. The heat of hydration is 4.030 cal.

By further heating the insoluble anhydrite to 800 - 1000 °C there already occurs a partial decomposition of the calcium sulphate with the formation of free CaO and SO_2. If the firing operation is conducted in such a way that the material contains 2 - 3 % CaO, by grinding the grains flooring gypsum plaster is obtained.

In the conclusion to this chapter should be stated that industrially produced gypsum plasters contain as a rule beside the main active ingredient - the main modification - an accompanying quantity of also other components. This is given by the variability of the raw materials as well as by the sensitivity of the hydration process.

The $CaSO_4$-H_2O system is a very complicated physico-chemical system and a number of authors are investigating it in great detail. In this chapter an attempt was made to provide at least a brief summary of generally accepted technical facts.

4. Gypsum plaster production

One of the oldest methods of quick-setting gypsum plaster manufacture is its dehydration in a cooker. A disadvantage is interrupted production (in recent years continuously operated cookers have been developed), but its advantage lies in the fact that β-semi-hydrate with the presence of a smaller quantity of α-semi-hydrate is obtained. This method therefore still maintains since its introduction (in 1870) a very important position in this field.

The latest newer designs include cookers made by Messrs. Büttner-Schielde-Haas (FRG). The general arrangement is shown diagramatically in Fig. 2.

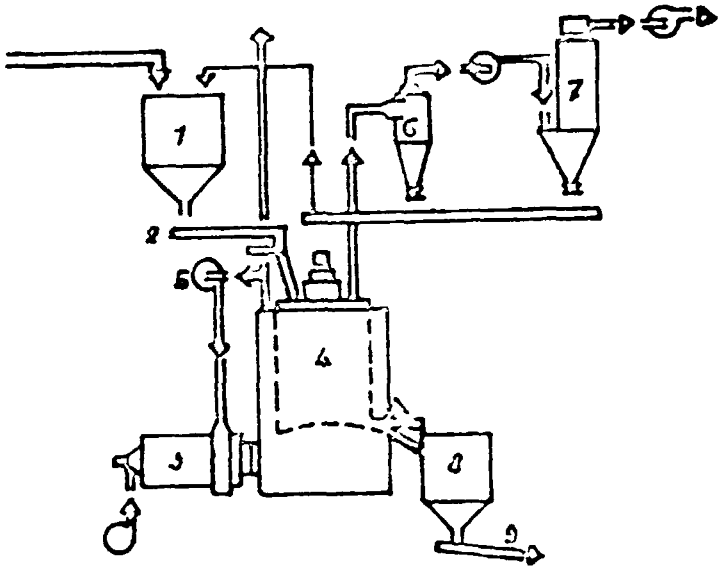

Fig.2. Büttner-Schielde-Haas cooker
1- raw material storage bin; 2- conveyor;
3- generator of hot gases; 4- cooker;
5- ventilator fan; 6,7- dust collector;
8- burned material storage bin; 9- conveyor

In this case has been eliminated the intimate contact of the flame with the cooker bottom which prevents the possibility of unwanted overburning. The technical and economical parameters of this system are improved by the combined grinding and drying of the gypsum rock before entering into the cooker; for this purpose is in a suitable manner being utilized the heat content of the waste gases. The dehydration period is 2.5 - 3.5 hours. The produced gypsum plaster is as a rule subsequently stored in a maturing bin and then ground as required. The temperature on entering the grinding mills should not exceed 80 - 82 °C.

A great advantage of the cookers is their simple construction which guarantees trouble-free operation. In the cooker can be produced all types of gypsum plaster with excellent properties, practically from all types of gypsum rock. Down times required for filling and emptying amount, however, up to 25 %. ~~Continuous~~ Discontinuous operation and the thus arising change in temperature conditions place exacting requirements on the control of the hydration process and dust extraction.

These disadvantages are overcome by the solution of Messrs British Plaster Board Ltd. which is characterized by the aspiration of the dewatered raw material through a separate pipe in an obliquely upward direction in such a way that the level in the cooker remains at a constant height. The rating of the continuous cooker is 25 - 40 % higher, the heat consumption and other indirect costs are lower. The gypsum plaster quality is equally good.

A further new type of production plant which at the same time grinds and carries out dehydration, is the grinding equipment of Messrs. Claudius-Peters (FRG) which is shown in Fig. 3.

This plant consists essentially of two rings, between which grinding balls are located; the bottom ring rotates and provides the grinding function. Adequate compression is provided by springs. Gypsum rock, precrushed to 0 - 30 mm, enters the grinding mill through a side feed opening into the grinding space. After grinding and dehydration, it is pneumatically aspired into the classifier; the corase fraction is returned, the fine fraction goes into the bin. Two of these grinding mills are as a rule connected into one

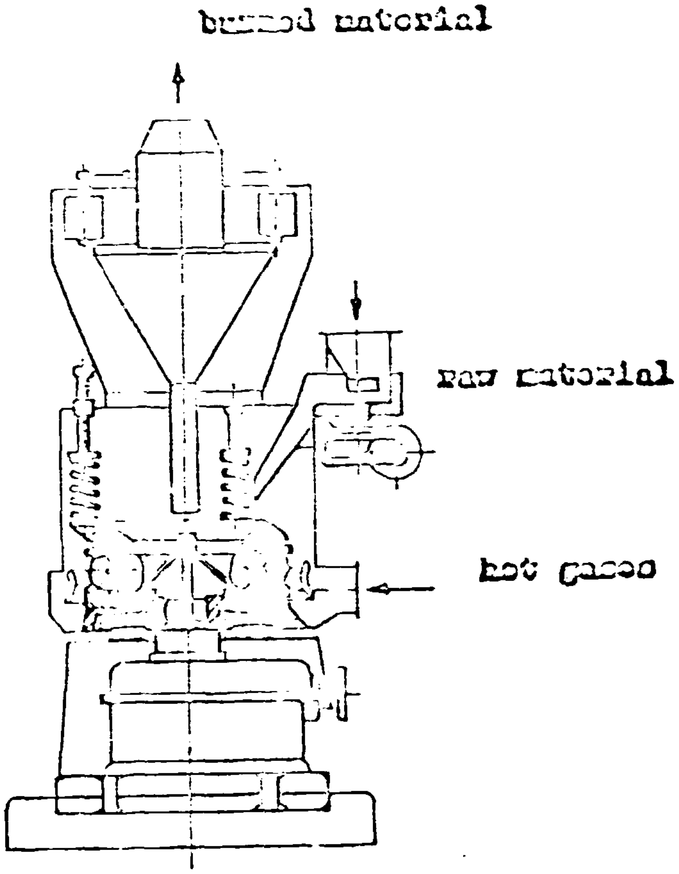

Fig.3. Grinding and dehydrating mill Claudius - Peters

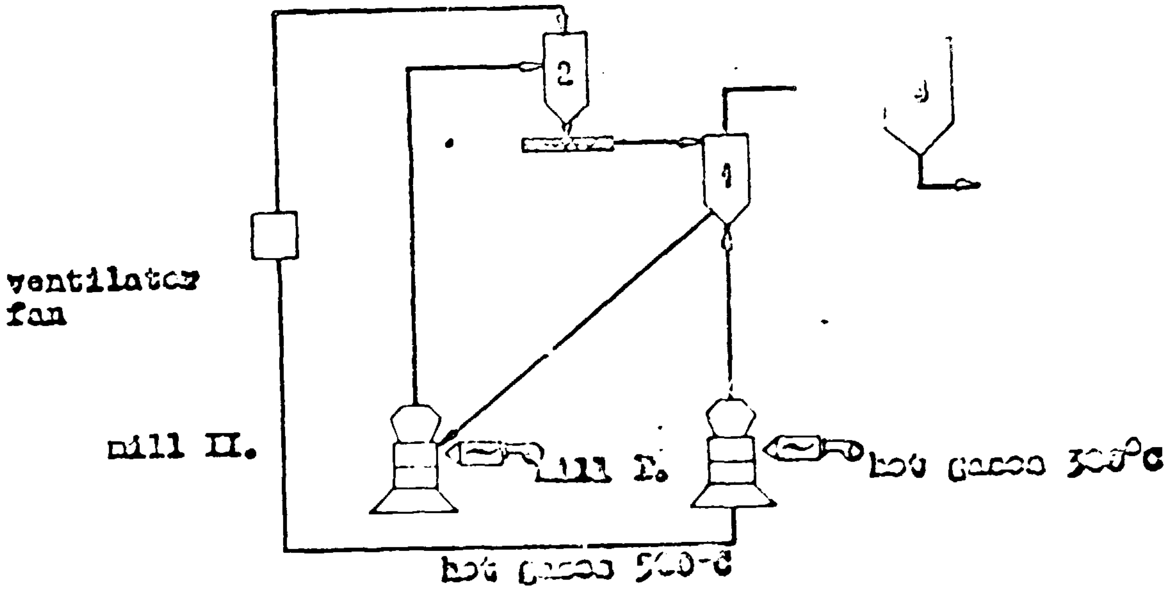

Fig.4. Connection of two Claudius - Peters mills for the production of mixed gypsum binders.
1- storage bin (hemihydrate); 2- storage bin (anhydrite);
3- storage bin (ready product).

technological line; one operates at a temperature around 300 °C (producing semi-hydrate), the other at a temperature around 500 °C (producing anhydrite). By intermixing in the relevant ratio, gypsum plasters with controlled properties can be obtained. An example of a connection is shown in Fig. 4.

On a similar principle operates the IMP-Mill system of Messrs. Raymond (Chicago). This system exhibits a 20 % lower electric power consumption with the same heat consumption, but a higher specific performance.

An interesting technological solution presents the rotary dehydration plant of Messrs. Büttner-Schilde-Haas (FRG) which is shown in Fig. 5: utilizing this equipment, all the main types of both gypsum plaster and anhydrite can be manufactured. The feed grain size is 2 mm max. By adapting the plant, both co-current and counter-current burning can be achieved, and by connecting two burning units with subsequent mixing, it is possible to obtain products with controlled properties. The exhausted gases can be utilized for drying the raw material in the course of the grinding process, and thus maximum utilization of the heat can be achieved. Dust is controlled with the aid of electrostatic precipitators. When using combined lines, the material flow circuit includes classifying equipment, on which the coarse fractions are separated that go via the overflow into the grinding mill and then back into the classifier. The fine fraction (undersize) goes into the bin. The technological arrangement makes also possible the addition of additives which control special properties. An example of this arrangement is shown in Fig. 6.

Another type of combined kiln is the double-shell kiln which makes firing possible in the inner space, directly heated at a higher temperature; the fired material overflows into the outer space where it is mixed with the raw material destined for firing at a lower temperature. By cooling down it hands over heat to the raw material which is to be dehydrated at a lower temperature. Thus heat is being utilized in an utmost manner. If required, also this outer space can be heated by additional equipment. It should be added that firing at the higher temperature is carried out counter-currently, firing at the lower temperature co-currently. The commercial [illegible] grinding mill [illegible] coarse fraction and equipment for [illegible] additives. An example of this arrangement is shown in Fig. 7.

The last alternative of a recent development [illegible], which is given in Fig. 8, is the feeding in two different locations in such a way that the counter-current firing of the raw material proportioned into the firing zone is carried out at a higher temperature and of the raw material proportioned at a point approximately 1/3 of the length from the end is carried out with the utilisation of the heat of ~~[illegible]~~ [illegible] of the primary raw material that has already been preheated in the firing zone. At the feed end the raw material is also ground and generally simultaneously dried with the aid of extra equipment which at the same time utilises part of the heat from the primary heating operation. With this arrangement, extra cyclones are sometimes introduced into the drying system. (see Fig. 9)

During the years many production systems for the burning of gypsum plaster have been developed; for the sake of completeness should be mentioned e.g. the [illegible] System, furthermore the [illegible] system grate kiln, fluid-bed firing systems, various systems for the production of β-gypsum plaster from by-product calcium sulphate ([illegible], ICI, Rhône Progil, etc.), and today already several systems that have been developed for the production of (α)-phospho gypsum plaster (e.g. Giulini), and others. Nevertheless it can, however, be stated that the cookers, especially the up-to-date continuous version of BPB Ltd., are still maintaining their important position.

As regards the firing to higher temperatures, e.g. 500 and possibly also more (900 - 1000) °C, especially rotary kilns with subsequent grinding are employed.

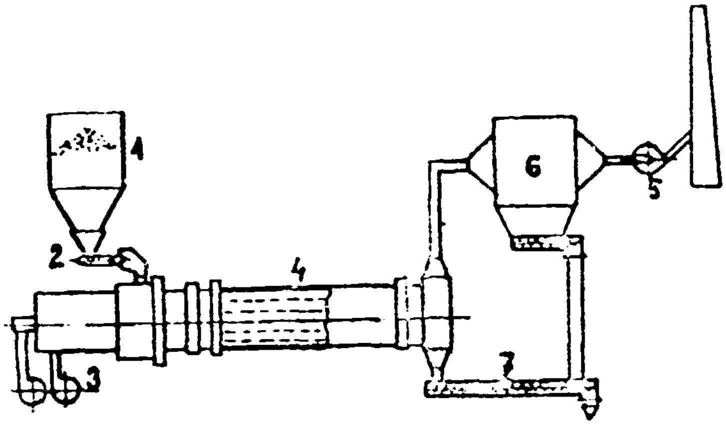

Fig.5. Rotary calcinator Büttner-Schilde-Haas

1- raw storage bin; 2- dosing device; 3- generator of hot gases; 4- rotary calcinator; 5- ventilator fan; 6- dust collector; 7- conveyor of ready product.

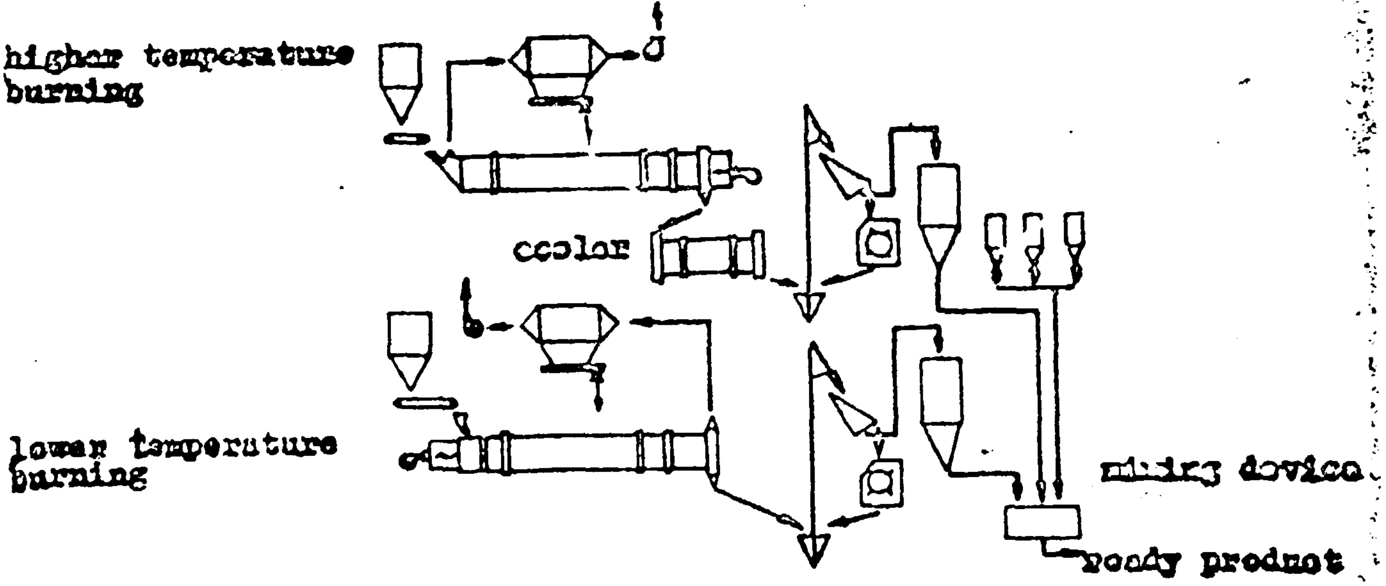

Fig.6. Technological line for the production of mixed binders with the utilization of two rotary calcinators (Büttner-Schilde-Haas).

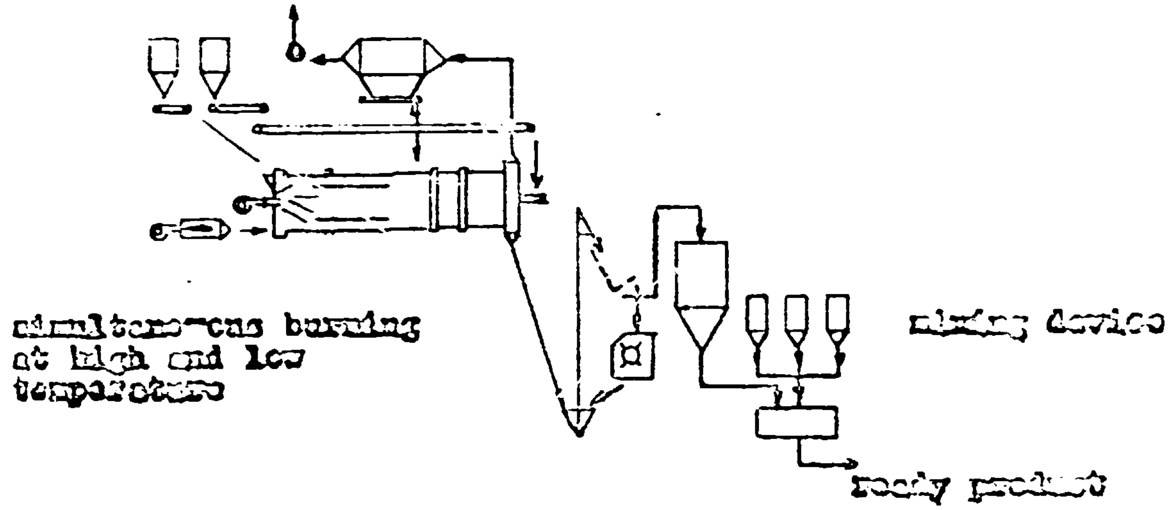

Fig.7. Double-shell calcinator (Büttner-Schilde-Haas).

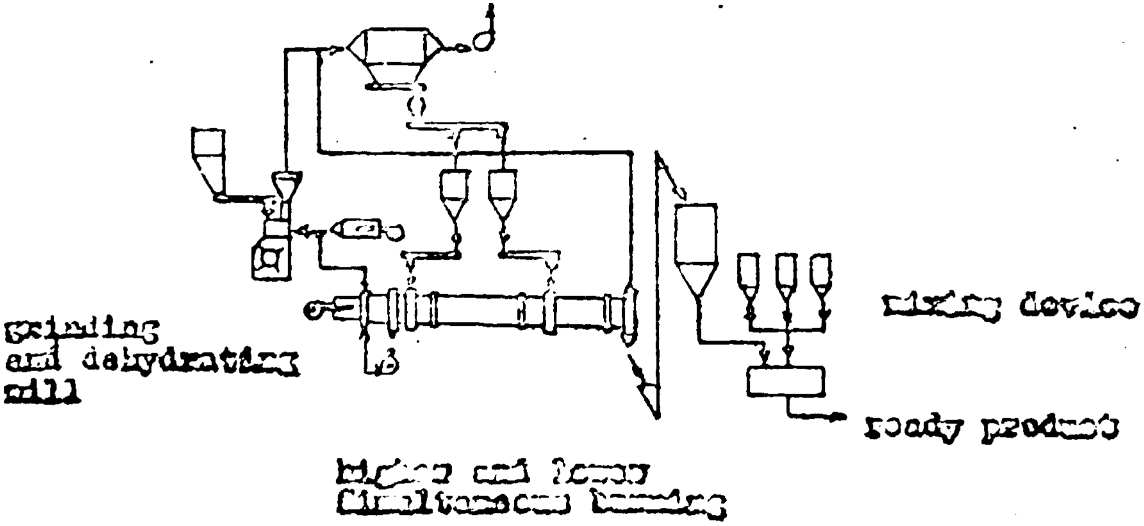

Fig.8. Rotary calcinator with the feeding in two different locations.(Büttner-Schilde-Haas).

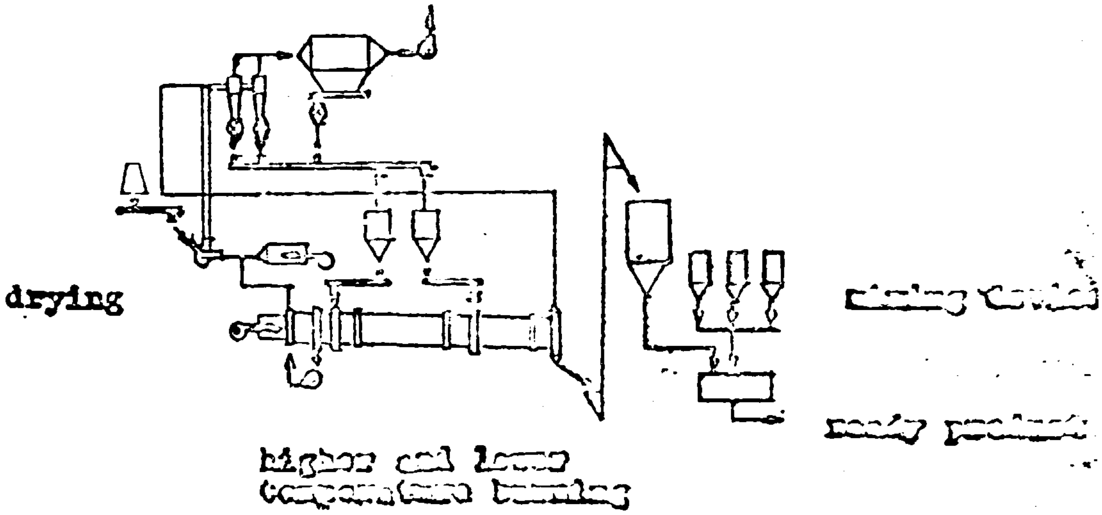

Fig.9. Technological line for the production of mixed binders with the feeding of rotary calcinator in two different location and with the simultaneous aplication of drying.

The technologically correct selection of the production plant must start out above all from the properties of the raw material from a concrete locality, furthermore from the purpose, for which the produced gypsum plaster will be used, and from the required capacities. For this reason the suppliers of machinery equipment have built their test plants and engineering consultation services; on the basis of these input data they are then generally capable of designing an optimum solution.

5. Utilization of by-product calcium sulphates

The world production of phosphoric acid via the decomposition of phosphate raw materials with sulphuric acid according to the equation

$$2\ Ca_3(PO_4)_2 + 6\ H_2SO_4 = 6\ CaSO_4 + 4\ H_3PO_4$$

has reached almost 20 million tons in 1975. In the course of this production is formed at the same time a by-product - calcium sulphate in quantities of approximately 4.5 tons per ton of produced phosphoric acid which represents a great total of 20 x 4.5 = 90 million tons. If we realize that the overall yearly world production of natural gypsum rock represented approximately 60 million tons in 1975, it can readily be seen that by-product calcium sulphate can in due course become a competitor of the natural raw materials.

This problem can not, however, be assessed from the point of view of a simple replacement, since here a determining role is being played by questions of a technical and economic nature; transport and environmental problems, etc. have to be also taken into consideration.

The primary problem is above all the question of the contents of contaminants such as fluorine, residual sulphuric as well as phosphoric acid, salts of uranium, radium, and many other impurities, the contents and character of which depends above all on the incoming phosphate raw materials and on the morphology of the calcium sulphate crystals that are formed in the course of the decomposition process. The solution of these technical problems, projected into their economic consequences, can then exert a limiting influence onto the utilization of this raw material.

A determining influence onto the solution of problems associated with the utilization of these by-products can have also environmental protection. When these by-products are stored in sludge settling lagoons, the soluble impurities can contaminate ground waters and thus infest and endanger wide areas in the vicinity. If then there occurs a drying out of the surface of those dumping grounds, the wind can also scatter the solid particles into wide surroundings and contaminate them.

Some production plants are situated on the sea shore and solve this problem by draining the wastes into the sea water. Also this method is already today in a number of cases not practicable and the production plants will in due course have to search for other solutions, even at the cost of having to finance research work and paying for new investments.

As an example can be quoted that in Florida, USA, the by-product gypsum dumping grounds contain more than 200 million tons; this quantity would be sufficient to cover the requirements of the USA for a period of 10 years. At the same time, the yearly waste in the USA represents approximately 21 million tons, out of which e.g. in 1977 only 600,000 tons have been utilized.

These problems have to be assessed from the point of view of the needs and conditions of the relevant country. Thus e.g. in Japan the total gypsum rock consumption in 1975 was 4.095 million tons, the mining of natural gypsum rock amounted to only 189,000 tons. The difference was covered by processing by-product gypsum, the ampunt of which (as waste) represented in the same year 5.02 million tons.

Since the natural gypsum rock resources in Japan are very limited, there was an endeavour to cut down on imports from abroad which was at the same time accompanied by activities in the investigation of the possibilities of utilizing by-product gypsum. With regard to the negative influences of impurities present in the by-product gypsum, research work was orientated above all on the development of such phosphoric acid production technologies which produce purer by-products. This procedure was considered to be more feasible than the secondary purification of contaminated by-product gypsum.

Thus was established e.g. the new Nissau Process which provides in the first phase semi-hydrate, in the second phase an already much purer dihydrate, already applicable for further processing. On a similar principle is also based the NKK Process. Another method which yields a product of greater purity, is the Central-Prayon Process. This process includes the recrystallization of dihydrate; its final product is semi-hydrate. Despite the fact that these combined processes are more costly in their operation, they have been applied on a broad industrial scale, since in this way was solved the problem of importing almost 4 million tons of gypsum rock into Japan. Only when there occurs a temporary drop in the phosphoric acid production, the lacking gypsum rock quantity is imported from Australia and Mexico.

In other countries, above all in Europe (Federal Republic of Germany, France, USSR, Great Britain) attention was given, on the contrary, to the processing of untreated by-products formed in the course of a single-stage decomposition. This naturally places more exacting requirements onto the entire production technology for the actual gypsum plaster.

At present there exist several different processes, the resultant product of which is semi-hydrate gypsum plaster which can be utilized above all in the building industry. Essentially we are concerned here with two basic dehydration systems - the dry process which produces β-semi-hydrate, and the wet process which produces α-semi-hydrate and/or a semi-hydrate slip which can be employed directly for the manufacture of gypsum plaster board or elements. The β-semi-hydrate manufacturing technology was worked out above all by Messrs. Gebrüder Knauf (Iphofen - FRG) and realized in a company owned plant in Castrop-Rauxel and at the Westdeutsche Gipswerke in Iphofen. This method consists of the following operations:

washing the by-product with water
↓
drying
↓
1st firing operation
↓
rehydration and neutralization with milk of lime
↓
2nd firing operation

A modification of the Gebrüder Knauf Method consists of a neutralization after the washing of the raw material with subsequent drying and firing.

The dry technologies also include a method worked out in the cooperation of the companies Rhône Progil, Air Industrie and Charbonnages de France Chimie; the technological arrangement realized by Messrs. Rhône Progil at the Douvrin Works includes thorough washing and separation of mechanical impurities on a sieve, then follows a passage through two hydrocyclones, filtration, drying, firing and, according to requirements, grinding with additives. The yearly production is 130,000 tons; the major part of the production is processed to gypsum plaster partition elements.

Messrs. Rhône Progil have built another plant for Donau Chemie, Pischeldorf (Austria) which produces 500,000 m^3 of partition elements per year.

Messrs. ICI have realized some time ago in Billingham in the North of England the firing of by-product gypsum in a multi-stage kiln. Despite the fact that very good results have been attained there, production was stopped for commercial reasons.

To the extraordinarily important methods of semi-hydrate gypsum plaster production from by-product calcium sulphates belongs undoubtedly the system realized in Ludwigshafen (FRG) by Messrs. Gebrüder Giulini GmbH. This method involves the continuous pressure dehydration of calcium sulphate in a suspension. Since the incoming part of the technology includes thorough cleaning of the raw material by flotation and counter-current washing, this method which includes in the second stage recrystallization in an autoclave, provides a very pure semi-hydrate free from dangerous material that may lead to the formation of efflorescence. The resultant product is either α-semi-hydrate gypsum plaster (in this case the semi-hydrate is, after leaving the autoclave, separated in a centrifuge, washed with hot water of 80 - 90 °C and dried) or the centrifuged α-semi-hydrate is mixed with cold water to form a slip of the required consistency which is directly poured into moulds for the production of partition elements.

With regard to the fact that the autoclave dehydration takes place in the presence of active additives that influence the dehydration process, it is possible to obtain by this method a product with controlled qualities, i.e. with a controlled size and shape of the crystals.

The production flow sheet for this technology is shown in Fig..10.

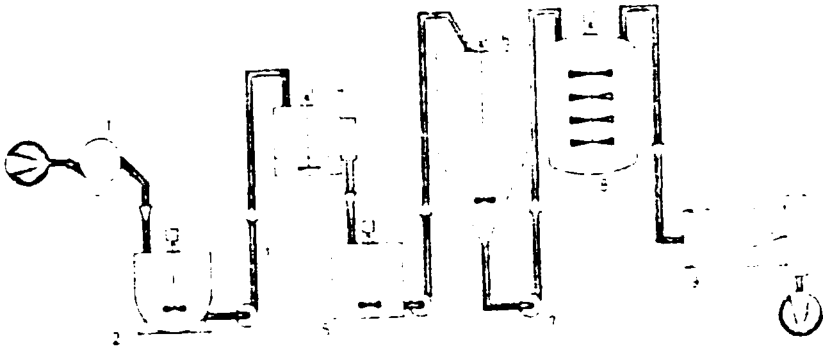

Fig.10. Gebrüder Giulini technological line for the production of α -hemihydrate by-product gypsum plaster. 1-Filter; 2- blunger; 3- pipeline; 4- flotation; 5- storage tank and pump; 6- water cyclon; 7- pump; 8- autoclave; 9- centrifuge.

An analogical method has also been worked out by a group of authors at VNIISTROM in the USSR.

From literature are known references also about the firing of by-product gypusm at temperatures around 1000 °C; the product obtained approaches with its properties flooring gypsum plaster or Keon cement.

As follows from an analysis of by-product gypsum materials, they contain a certain quantity of water soluble salts which can form under certain conditions efflorescences on ~~concrete~~ building elements. For the formation of efflorescence there must be simultaneously present in the product a certain quantity of water and the temperature and humidity of the outer environment must cause and aid, respectively, the internal movement of the liquid phase in a direction towards the surface of the product, where then evaporation occurs; a consequence of those physical and chemical processes is then the formation of efflorescences.

The most effective way of preventing these unpleasant phenomena is to thoroughly free the raw material, i.e. the dihydrate crystals, from both rests of salts (mother liquor after the separation of phosphoric acid) on their surface and also inside the crystals. In this respect the Giulini Process has shown itself to be highly effective and reliable. This is documented by the following listing of the chemical composition of the original raw material, the washed raw material before entry into the autoclave and the final product (semi-hydrate) after centrifuging.

	Starting dihydrate	Washed dihydrate	Semi-hydrate after centrifuge
SiO_2	1.25	0.74	0.7
F	2.12	0.4	0.34
P_2O_5 total	0.78	0.74	0.5
P_2O_5 water soluble	0.28	0.05	0.03
Na_2O total	1.22	0.2	0.03
Na_2O water soluble	1.06	0.05	0.015
Al_2O_3	0.08	0.07	0.05
Fe_2O_3	0.02	0.015	0.15
C	0.15	0.05	0.03

Note: The values are given in weight per cent.

It was ascertained through a closer study of the efflorescence problem that efflorescences can be formed by sodium salts (sulphate, phosphate, fluoride, fluorosilicate, carbonate, hydroxide and tripolyphosphate), as well as by magnesium sulphate. The intensity of the efflorescences is influenced by the character of the anion. The most intensive efflorescences are formed in the presence of Na_2HPO_4, Na_2CO_3 and Na_2SO_4, the least intensive ones in the presence of sodium fluorosilicate Na_2SiF_6.

Efflorescences are either not formed at all or only to a very limited extent in the presence of NaCl, $CaCl_2$, $MgCl_2$, Na_2SO_4, NaH_2PO_4 and primary calcium phosphate $Ca(H_2PO_4)_2$, if the concentration does not exceed 0.4 %, referred to cation-oxides. Efflorescences are also not formed during the simultaneous presence of Na_2SO_4 and $CaCl_2$.

If we list the individual salts in accordance with their degree of danger of efflorescence formation, we obtain the following series:

Na_2CO_3, $Na_2HPO_4 > Na_2SO_4$, $MgSO_4$, NaH_2PO_4, NaF, NaOH, $Na_5P_3O_{10} \gg Na_2SiF_6 > K_2SO_4$, $NaHSO_4 >$ KCl, NaCl, $MgCl_2$, $CaCl_2$, $Ca(H_2PO_4)_2$.

To determine bindingly valid limits of the maximum permissible contents of the individual efflorescence forming materials is an extremely complicated problem, the solution of which is naturally influenced by external conditions. On the basis of laboratory results it can be stated approximately that the total contents of water soluble Na_2O + MgO (including the salt contents in the crystals) should not exceed in the raw material or in the fired semi-hydrate the value of 0.1 %. Below this limiting value, and especially below the limit of 0.05 %, there occurs practically no formation of efflorescences. In the region of 0.1 - 0.2 % the formation of efflorescences is already probable, depending on the character of the present sodium and magnesium salts, and with their contents above 0.2 % it is absolutely certain.

Messrs. Giulini state that the overall Na_2O content must be reduced below 0.04 % in order to definitely (with guarantees) prevent the formation of efflorescences.

To round off the overall characteristics of problems that are associated with the utilization of by-products, it should still be stated that for the production of semi-hydrate gypsum plaster can also be utilized by-products formed in the production of certain organic acids (citric acid, tartaric acid), but also during the conversion of ammonium sulphate with milk of lime which is utilized in the desulphurization of flue gases, especially from thermal power stations. The last method is gaining increased importance especially in recent years when more and more attention is being paid to the cleanness and protection of the environment.

In the concluding part of this chaper should also be mentioned one grave problem that occurred in connection with the production of phospho-gypsum plaster. This is the question of its radioactivity.

The executed measurements have proved increased contents of Ra and U in phosphorites in contrast to natural gypsum rocks.

Phosphates from Morocco, by-product gypsum formed by processing the latter as well as gypsum plasters manufactured from them, have a one to two orders higher content of Ra and U than current rocks and building materials. The Kola-apatite concentrate forms an exception among the phosphate rocks. The Ra und U contents in the kola-apatite concentrate, in the by-product gypsum formed from it and in the phospho-gypsum plaster manufactured from this by-product gypsum, are of the same order as have been found in other building materials or rocks employed for their manufacture. Of interest is, however, the higher Th content which, however, no longer appears in the by-product gypsum which implies that the major part of the Th present is transferred into the produced phosphoric acid.

In comparison with natural gypsum plaster which is classified by a number of authors as a building material with the lowest contents of radionuclides, the radionuclides contents in by-product gypsum and phosphate-gypsum plaster from the kola-apatite concentrate are approximately 2 - 3 times higher. For a comparison with modern building materials (e.g. on the basis of slag and fly ash), in which higher radionuclide contents can be expected, we are still lacking data about the contents of radionuclides in these products or raw materials.

On the basis of executed measurements and the contemporary state of the art it can be stated that the contents of radionuclides in phospho-gypsum plaster from the kola-apatite concentrate are not higher than in other currently used building materials; there can thus be no objections to phosphate-gypsum plaster from the point of view of ionizing radiation. As regards African phosphates, the level of radionuclides contents is higher. Since, however, at present exist no specifications or standards limiting the maximum permissible contents of radionuclides in building materials or raw materials for the production of the latter, no final conclusions can be drawn from the above findings. In this respect technical workers still have a lot of work before them.

We believe that the entire matter of radioactivity of not only phospho-gypsum plaster, but also of building materials generally, should be brought to certain conclusions. Measurements should be carried out of the contents of radionuclides in building materials and raw materials used for their production. These measurements should then be supplemented with exposure rates at selected building sites. And on the basis of all these findings should then in cooperation with hygienists be worked out a general specification or recommendation about the maximum permissible contents of radionuclides in building materials.

6. Setting of gypsum plaster

The discovery that a gypsum plaster suspension spontaneously sets into a solid mass is several thousand years old, but the first explanation of the entire process was ~~first~~ given only by Lavoisier. He showed that during the setting process there occurs a conversion of semi-hydrate to dihydrate. This is the chemical basis of the entire process which does not, however, explain the actual reason for the gain in strength.

The explanation of the strength gaining process was found by Le Chatelier. He pointed out that the semi-hydrate is under normal temperature conditions a material that is in water approximately five times more soluble than the dihydrate. After mixing the semi-hydrate with water, there occurs a dissolution of the semi-hydrate up to the state of saturation and the following conversion to dihydrate. Since the solubility of the semi-hydrate, converted to $CaSO_4$, is approx. 8 g/l and the solubility of the dihydrate is only approx. 2 g/l, the solution becomes gradually supersaturated. Such a solution is naturally unstable and separates the dihydrate in the form of a large number of small needle-shaped crystals which grow together into a continuous solid mass, naturally interwoven with a continuous network of pores. Only today has it been possible with the aid of the scanning electron microscope to confirm the correctness of Le Chatelier's idea.

By the separation of the dihydrate from the solution is decreased the concentration of the latter, thus conditions are created for a further dissolution of the semi-hydrate, and the process continues.

The crystallization process can be divided into two stages. The first stage is characterized by the formation of crystallization nuclei, the second by the growth of the crystals. For the first stage holds true - the greater the supersaturation of the semi-hydrate solution, the quicker are formed the crystallization nuclei. If the supersaturation is low, there need not occur the formation of microcrystals.

If the crystallization nuclei are formed too quickly, they are very small, not stable and in due course disintegrate again. The crystallization nuclei must therefore have a certain so called critical size, so that they are stable under the given solution supersaturation conditions and can become real nuclei for the new phase.

The second crystallization state is characterized by the crystal growth rate. The latter is dependent on the degree of supersaturation, i.e. on the difference between the concentration of the material in the solution and the solubility of the newly formed structure, and on the dimensions of the crystal itself, on which are successively deposited further mono-layers.

The energy liberated in the growth of crystals is always greater than the energy liberated in the formation of crystallization nuclei. It follows from the above that the crystallization nuclei can be formed only at the beginning of the entire crystallization process - approximately up to the beginning of setting. After the formation of a certain quantity of these nuclei can already occur their growth. During this growth is first of all formed a rigid structural framework. If during this stage there accurs the action of mechanical forces, then this leads to a reduction of the strength of the hardening gypsum plaster. Only through a further growth of the crystals their contact faces are increased, the crystals grow together, and the strength values of the mass are increased.

A further increase of the strength of gypsum plaster products can still be attained by their drying. This can be explained by a further hydration and evaporation of the water which is always present in the suspension - for rheological reasons in greater quantities than required for the mere hydration process. Through drying is formed from the excess water containing sulphate solution which is stored between the crystals, further gypsum rock which further links the individual, already existing crystals among each other. Apart from that, after the evaporation of the water there does not occur so readily the mutual shift of the crystals as in the presence of water.

A significant role in the setting of gypsum plaster play the additives that are added either already during the grinding operation or only during the preparation of the paste - the so called setting regulators. In accordance with the character of their action, they can be divided into five groups.

To the first group belong strong and weak electrolytes and such non-electrolytes that change the solubility of the semi-hydrate and dihydrate, but do not form on their particles badly soluble films.

Certain additives, such as NaCl, KCl, Na_2SO_4, and others, increase the solubility of the semi-hydrate in water and speed up the setting of the gypsum plaster. Other additives, such as NH_4OH, C_2H_5OH, and others, act in exactly the opposite way. The effectiveness of certain salts is concentration dependent; at a certain concentration they act as an accelerator, at another as a retarder.

The second group includes substances that form crystallization nuclei. e.g. gypsum rock, $CaHPO_4 \cdot 2H_2O$, and others. They can be classed as setting accelerators.

To the third group belong surfactants (surface active substances) that are capable of absorption both on the semi-hydrate and on the gypsum rock and which retard the formation of crystallization nuclei. This group includes e.g. lime-glue retarders, sulphite lyes, keratine retarders and carboxy-methyl cellulose.

The fourth group contains substances that form through a mutual reaction on the surface of the semi-hydrate particles protective, sparingly soluble films. These are e.g. phosphate, oxalates and borates of alkalic metals, boric acid, etc; these substance retard the setting process.

In the fifth group are then included mixed products which contain e.g. a mixture of electrolytes and surfactants, etc.

In certain countries is the addition of setting regulators a normal procedure and is generally carried out during the grinding operation.

7. Types, properties and utilization of gypsum plaster

In the technical standard specifications of the individual countries, gypsum plaster is first of all divided in accordance with the type of application. With regard to the favourable technical properties of the gypsum plaster, it is employed in many fields. The greatest consumer is the building industry, followed by the ceramic and metallurgical industries; the health services are consumers of special gypsum plaster types.

If we do not take into consideration the relevant modification (α, β), it is generally possible to divide semi-hydrate gypsum plaster in accordance with the basic fields of utilization into the following groups:

- gypsum plaster for the building industry (stucco, plaster),
- technical gypsum plaster (modelling, moulding),
- gypsum plaster for the health services (surgical, dental).

In accordance with the main properties, semi-hydrate gypsum plaster can then be divided as follows:

- according to the attained strength,
- according to the speed of setting,
- according to the fineness of grinding.

The national standard specifications of the individual countries generally contain certain specificities in the classification which are dependent on the traditions of the relevant country, the raw materials, production facilities, etc.

The basic groups of gypsum plasters are then further divided into classes of quality.

The national standard specifications include in a number of cases also special gypsum plaster types with improved properties that are destined for special purposes.

Gypsum for the building industry is generally used for the production of structural elements and for stucco and plastering work. Here we are as a rule concerned with the β-modification.

Technical gypsum plasters are employed in the first place for modelling and moulding purposes. In case of models exposed to only moderate stresses we are as a rule concerned with β-gypsum plaster, in case of higher mechanical requirements is used an addition of α-gypsum plaster which prevails for special hard gypsum plasters for moulding purposes.

Gypsum plasters for the health services are employed primarily in surgery and furthermore in dental surgery for the taking of dental prints.

For the sake of completeness should also be mentioned various types of special and mixed binders, generally on the base of anhydrite (anhydrite binders), products of the flooring gypsum plaster type and products of the Keen cement type. A large separate group of binders that have been developed in the USSR form gypsum plaster-cement-puzzolana binders which have especially in the USSR found a broad field of application in prefabrication.

The specific density of the usual quick setting semi-hydrate gypsum plaster is 2.60 - 2.75 g/cm^3. The density in the bulk state is 800 - 1100 kg/m^3, in the lightly compacted state 1250 - 1450 kg/m^3.

The main technological properties of gypsum plaster are:

- fineness of grind,
- quantity of water required for preparation,of a paste with a
- normal density (consistence),
- beginning and end of setting,
- mechanical strength in the hardened state.

The fineness of grind of the gypsum plaster characterizes the relative representation of particles of the individual sizes and is expressed as a rule in the form of a rest on standard sieves. The fineness of grind influences the water-gypsum ratio, the mechanical strength and the rate of setting. It is one of the very important properties of gypsum plaster.

The second very important property of gypsum plaster is the quantity of water that is required for the preparation of a paste of normal consistence (i.e. as given by the standard specification). The normal consistence depends on the composition and properties of the raw materials, on the methods and conditions of dehydration and on the fineness of grind; it influences in turn the moulding properties of the suspension and the resultant mechanical strength of the product. The theoretical water consumption for the rehydration of semi-hydrate to dihydrate is 18.6 %. In practice, however, for the attainment of a normal consistence of β-gypsums for the building industry 50 - 70 % water are required, for high strength α-gypsum plasters the corresponding figure is 30 - 40 %. Thus for this reason the hardened and dried gypsum plaster product exhibits a high porosity which reaches values of 40 - 60 % and even higher.

The quantity of water contained in the fresh product does not, however, influence only its resultant mechanical properties, but also the heat consumption for the drying of the product in the final phase of the technological process.

A pronounced property of gypsum plaster is its rapid setting. Because of this very property it has found broad applications in building prefabrication and other fields (modelling, preparation of moulds, castings, etc.). The entire setting process is generally divided into two phases - the beginning of setting which in quick-setting gypsum plasters occurs as a rule within 3 - 6 minutes, and the end of setting which is usually in the range of 8 - 25 minutes.

The mechanical strength of the hardened gypsum plaster is undoubtedly its most significant property. Since gypsum plaster products are as a rule cast from a gypsum plaster paste which contains essentially a larger quantity of water than the theoretical water consumption for hydration (the water-gypsum plaster ratio is generally 0.6 - 1.0), the make-up water quantity exerts a considerable influence on the final strength of the gypsum plaster after processing. Onto one gram of semi-hydrate are bound in the solid phase 0.18 grams of water, i.e. conversion onto gypsum rock. If there will be more water in the suspension, it will remain unreacted in the spaces between the dihydrate crystals. After hardening the water evaporates and leaves behind a continuous network of pores. Since the volume of the system does not change during the process of hardening, it is possible to illustrate the volume ratios by the diagram which is shown in Fig. 11.

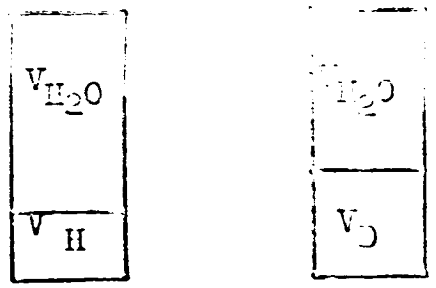

Fig. 11. Scheme of gypsum plaster hardening water-gypsum plaster ratio 0,5; V_{H_2O} volume of water
V_H -volume of semihydrate;
V_D -volume of dihydrate;

The resultant porosity p is thus unambiguously determined by the water-gypsum plaster ratio w (quantity of water per gram of gypsum plaster). From the specific volumes of the participating substances it can then be derived that porosity

$$p = \frac{w - 0.15}{w + 0.36}$$

The strength which is generally for the application of the gypsum plaster the most important property, can be relatively simply related to porosity. It holds true that

$$\sigma = \sigma_0 \cdot \log \frac{p_{kr}}{p} ,$$

where σ and p_{kr} are constants.

Since porosity is determined by the water-gypsum plaster ratio, the dependence of the strength can be expressed by an analogical relation

$$\sigma = \sigma_0 \left[\log \frac{w + 0.36}{w - 0.15} + \log p_{kr} \right] .$$

Thus to attain high strength means to reduce the water-gypsum plaster ratio. The latter can not, however, be reduced arbitrarily since for the processing and application of gypsum plaster a certain measure of workability of the starting suspension (paste) is required, i.e. viscosity, plasticity, general rheological properties which make it possible to give the suspension [illegible] [illegible] the [illegible]

[illegible]

[illegible] gypsum plaster ratio, but [illegible] the same time also on the nature of the solid phase. With a given water-gypsum plaster ratio, these properties are dependent on the shape, size and size distribution of the semi-hydrate particles, and also on their porosity. The apparent viscosity of the suspension will be the higher, the more non-spherical the shape of the particles will be, i.e.

corpuscules → platelets → needles.

This, of course, concerns non-porous semi-hydrate particles. If the particles of the latter will be porous, also the water-gypsum plaster ratio will be increased by the proportion of the water that entered the pores. The water in the particle pores does not participate in the fluidity of the suspension and to attain the required workability it is necessary to add another dose of water which will then coat the outer surface of the particles.

The third factor is the distribution and representation of the individual particle sizes. Monodispersion systems require more water that polydispersion systems.

The way towards the attainment of a high strength, which implies the reduction of the water-gypsum plaster ratio, is represented by the preparation of the semi-hydrate in the form of corpuscular, non-porous particles with a suitable size distribution. Conversely, if a high porosity of the hardened mass is required (e.g. in the production of casting moulds in the ceramic industry), it will be most advantageous to prepare a semi-hydrate with porous particles, as far as possible of a small size, so that before setting no sedimentation occurs in the suspension. The required properties of the gypsum plaster can thus be attained by the method of preparation of the semi-hydrate and by changing the distritution of its particle size.

The dependence of the strength of the hardened masses after drying on porosity for three types of gypsum plasters is shown in the diagram in Fig. 12. Straight line A corresponds to α-gypsum plaster with corpuscular particles, line B to β-gypsum plaster with needle shaped particles and

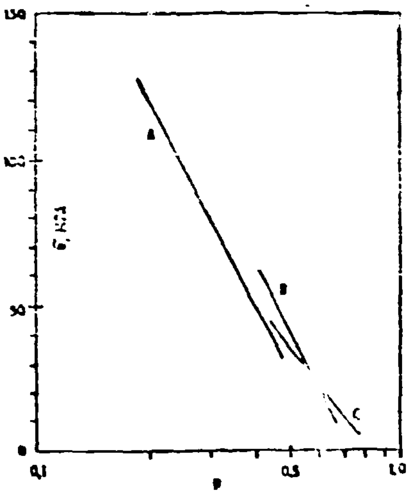

Fig. 12. Dependence of hardened gypsum plaster suspensions on the porosity (after drying).
A – α gypsum plaster with corpuscular particles;
B – α gypsum plaster with needle particles;-
C – β gypsum plaster

8. Gypsum plaster products

The building industry is undoubtedly the largest consumer of gypsum plaster due to its good workability and the good properties of the final product. Quick setting predestines gypsum plaster for processing in an industrial manner to prefabs.

The development of the industrial processing of gypsum plaster took place especially after the Second World War. Developments were orientated especially to those countries which have sufficient home resources of natural gypsum rock (USA, Canada, Great Britain, France, the Federal Republic of Germany, the German Democratic Republic, the USSR, Poland, and others). In the sixties then occurred a rapid development of the gypsum plaster industry in Japan which, of course, started to expand on the basis of utilization of by-product gypsum.

In the postwar years began in a number of countries the production of a wide range of gypsum plaster products for the building industry. In the course of the years there occurred, however, on the basis of technical and economic experience of leading world companies (US Gypsum, Gebrüder Kauf, Kaiser Gypsum, British Gypsum, National Gypsum, and others), a narrowing down of the range of gypsum plaster products for the building industry which is at present to a large part limited to the following:

- partition elements from cast gypsum plaster,
- large-area thin gypsum plaster board (gypsum-carton board and gypsum-fibre board),
- decorative and sound insulation panels,
- gypsum plasters for mechanical applications (as a rule lightweight with light fillers),
- auxiliary gypsum plaster masses which make possible a trouble-free erection of the products.

Wall panels from cast gypsum plaster and/or gypsum plaster concrete, often also lightweight in the form of cellular gypsum plaster, have for both technical and economic reasons found no general application in the mass building industry. An exception forms here, however, the USSR where gypsum plaster prefabrication has reached a high stage of development, but mainly using gypsum-plaster-cement-puzzolana binders.

In the field of cast gypsum plaster elements are today under Europen conditions being utilized almost exclusively elements with a size of 666 x 500 mm and a thickness of usually 6, 8 and 10 cm; the thickness tolerance is ± 0.1 mm. On the elements periphery are formed tongues and grooves which makes erection much easier and more accurate. The dimensions are selected in such a way that 3 elements correspond to an area of 1 m^2.

For the production are employed almost exclusively compartment moulds which are not dismantled; the finished products are pushed out hydraulically from these compartments. Since the walls of the individual mould chambers are made from a very hard material and are polished, also the products exhibit an absolutely smooth surface.

The moulds are supplied with a differing number of chambers (8, 16, 24, 32); the operating cycle depends on the setting time of the gypsum plaster. As a rule, 4 to 5 cycles per hour are attained. This means that e.g. a 24 compartment mould will produce with a 5 cycles per hour rate in 8 hours

$$24 \times 5 \times 8 = 960 \text{ pieces} = 320 \text{ m}^2.$$

In this case the actual moulding plant is operated by one worker.

In some countries have previously also been manufactured partition elements, the length of which corresponded to the height of one floor, the width was usually 60 cm (Messrs. Samieux, France). The elements were made either from pure cast gypsum plaster or from lightweight gypsum plaster with longitudinal cavities and with the addition of light fillers (Hungary), respectively.

With regard to the great risk of damaging these elements both during transportation and erection, for which with regard to their weight erection equipment was required, in recent years was observed a decrease in the interest for this type of elements.

To the group of large-area thin board materials belong in the first place gypsum plaster carton-board, consisting of a gypsum plaster core provided with a shell from a special carton in the function of an outer reinforcement, and furthermore gypsum plaster fibreboard, reinforced in the mass, as a rule with cellulose fibres.

Gypsum plaster carton-board is undoubtedly the most progressive gypsum plaster product. The simple production technology makes today possible the building of highly mechanized lines with a yearly capacity of 15 - 20 million m^2, related to a thickness of 9.5 (10) mm.

The production of board of this type has today in a number of countries (USA, Great Britain, France, the Federal Republic of Germany, Sweden, Finland, Japan, Australia) already a relatively old tradition; other countries are gradually introducing this production.

For the manufacture of gypsum plaster carton-board is generally used stucco gypsum plaster; during the last period also gypsum plaster obtained from by-product gypsum is being introduced.

The second basic raw material is a special carton with a square weight of 350 - 400 g/m^2 and a thickness of 0.6 mm ; apart from that, further stringent requirements are placed on this carton, e.g. rigidity, vapour permeability, maintenance of flatness, sufficient strength in the moist state, and others.

Additional raw materials can be setting retarders and accelerators, respectively and furthermore fibrous additives - e.g. a pulp suspension obtained the pulping of waste paper or an addition of glass fibres (USA, Federal Republic of Germany, German Democratic Republic), employed especially in the production of board with an increased flame resistance.

The machinery equipment is generally manufactured in several capacity versions:

m^2/hour	thousands m^2/day	millions m^2/year
250	6	1.5
500	12	3
1,000	24	6
1,200	28.2	8
1,800	43	12
2,400	57.6	14

Lately information has also been published about a line with a capacity of 20 million m^2/year.

The basic technological data about the consumption of raw materials and power are as follows:

semi-hydrate gypsum plaster, kg/m^2	7
water, litres/m^2	6
carton, m^2/m^2	2.06
heat consumption, kcal/m^2	4,500
electric power consumption, kWh/m^2	0.3
required number of workers per shift	8

The production range includes boards with differently shaped edges; also various types of cut sizes (base for plasters) or perforated board for acoustic as well as decorative lining of walls and ceilings are supplied. The board thickness is as a rule 9.5 - 18 mm, the width usually 125 cm, the length (depending on thickness) is 200 - 400 cm.

In great detail have been worked out erection systems for all methods of utilization (wall and ceiling linings, dome shaped lower ceilings, partition walls, acoustic linings, fire protection linings, etc.) and generally together with the deliveries of board for a certain purpose are simultaneously supplied also all erection aids, including cements, bandages, etc. Large companies (Knauf - FRG, British Gypsum Limited - Great Britain, and others) have training centres where they instruct erection crews of the customers how to correctly handle the board. All this contributes very considerably to the good name and to the very broad utilization of gypsum plaster carton-board in the building industry.

To this should still be added that many foreign companies have also introduced the production of elements from gypsum plaster carton-board which consists of a core (as a rule a paper honeycomb, expanded polysterene, etc.) coated on both sides with gypsum plaster carton-board.

With regard to the fact that for the production of gypsum plaster carton-board high quality special carton in quantities of approximately 1.5 kg/m^2 is required, endeavours have been made all over the world for a number of years to replace the carton with a cheaper raw material, less exacting as regards quality. Essentially this means a transition to a homogeneous dispersion of fibres into the gypsum plaster mass. Here we may be concerned with inorganic fibres (glass, mineral fibres) and organic fibres (of plant and animal origin and synthetic fibres).

The application of glass fibres requires an entirely different technology (Elagit - CIR). The experience gained with both mineral fibres and synthetic fibres has not been too favourable. Animal fibres are really of no practical significance; thus remain only plant origin fibres which can be limited to pulp fibres. For reasons of cost it is attractive to utilize above all waste paper.

As regards the contemporary state of the production technology for gypsum plaster carton-board abroad, the first factory was built by the former company ISELEA in Briare (France), later Poliot and Chausson on the basis of a patent of Messrs. Knauf (FRG) in the years 1968 - 69. Here was applied a wet suspension technology together with the Hatschek moulding machine with a capacity of 1.5 million m^2/year. The commissioning of the line was accompanied by great difficulties; no detailed reports have been received recently whether this plant produces or not.

A Japanese trade journal reports favourably about the utilization of this technology in 1976.

With regard to the [illegible] during work with the gypsum plaster [illegible] on the Hatschek machine (blinding of screens, clogging of felts, partial hardening of gypsum plaster in the dead zones of the water circulation, [illegible] clogging of suction boxes, etc.), no expansion of this technology has occurred within the last 6 - 7 years.

Towards the end of the sixties took place a realization of a dry technology in the Federal Republic of Germany by Messrs. FEMA Ettlingen (FRG); in this case we are concerned with a continuous technology with a capacity of 1.[illegible] million m^2/year. The product is Fe[illegible]platten board with a size of 100 x 150 cm and a thickness of 10 mm. In accordance with information received from the company, the production cost in 1970 have been 30 % lower in comparison with gypsum plaster carton-board.

According to latest reports from the Federal Republic of Germany, a further elaboration of this technology was taken up by Messrs. G. Siempelkamp and Co. - Krefeld who are offering as part of their [illegible] production lines with capacities of [illegible], [illegible] and [illegible] m^2/hour; the width of the board is 120 and 125 cm, respectively, length [illegible] - [illegible] cm, thickness 10 mm.

Two production lines have been in operation in the Federal Republic of Germany since 19[illegible]; in 19[illegible] was built a line for the production of board with a width of 12[illegible] cm, length up to 500 cm and thickness 10 mm. In the Middle East was built in 1975 a production line with a capacity of 500 m^2/h; the board width is 120 cm, thickness 10 mm and length 300 cm.

It follows from the above information that the dry technology for the production of gypsum plaster fibreboard is gradually gaining - even face-to-face with the strong competition of gypsum plaster carton-board - its merited position; the production capacities of the lines are, however, still lagging considerably behind.

The dry production of gypsum plaster fibreboard is basically a simple matter; it has, however, its difficulties and problems that are given by the basic raw material - gypsum plaster.

Waste paper which is employed as reinforcement, is first of all separated in a hammer crusher; the separated [illegible] is placed into an intermediate storage bin and shredded in a dry state. The fibres obtained are pneumatically conveyed into a bin with the simultaneous separation of insufficiently shredded fractions which are returned into the first intermediate storage bin. The conveyers feeding the two grinding mills are provided with magnetic guards.

The gypsum plaster is stored in silos that are filled either pneumatically or via an elevator. During the extraction of the gypsum plaster for the preparation of the dry mix with the fibres is added from a separate bin ground gypsum rock to accelerate setting. All the three components (gypsum plaster, gypsum rock, fibres) are thoroughly mixed to give a homogenous mixture which is conveyed via a screw into the working bin of the feed equipment which spreads the mixture onto the moulding conveyer belt. After the required layer has been applied, it is moistened with the necessary quantity of water and continuously pressed to the required thickness. After setting, the strip is trimmed on both sides and laterally cut to the required lengths; the obtained board is then rapidly fed onto a travelling platform and inserted into the individual stages of the dryer.

If required, thickness calibration is carried out after drying; the ground off material is returned into the gypsum rock bin.

Out of the most important technical and economic indices can be given the following:

<u>Consumption of raw materials, water and energies for 1 m^2, thickness 10 mm</u>:

- consumption of gypsum plaster	8.[illegible] kg
- consumption of waste paper	1.7 kg
- water consumption	5.5 litre
- fuel oil consumption	0.5 litre
- electric power consumption	1.35 kWh

A very important technological operation in the manufacture of gypsum plaster elements and board is their drying, i.e. the removal of the excess make-up water which does not enter into the reaction with the binder. At present, drying in the factories is carried out in artificial drying plants, usually with hot air.

The entire process of drying gypsum plaster products can essentially be divided into individual sections which differ from one another in the character of the change of the moisture contents of the mass, in the rate of drying and in the temperature distribution with regard to the cross section of the dried product.

The drying process is shown diagrammatically in Fig. 13.

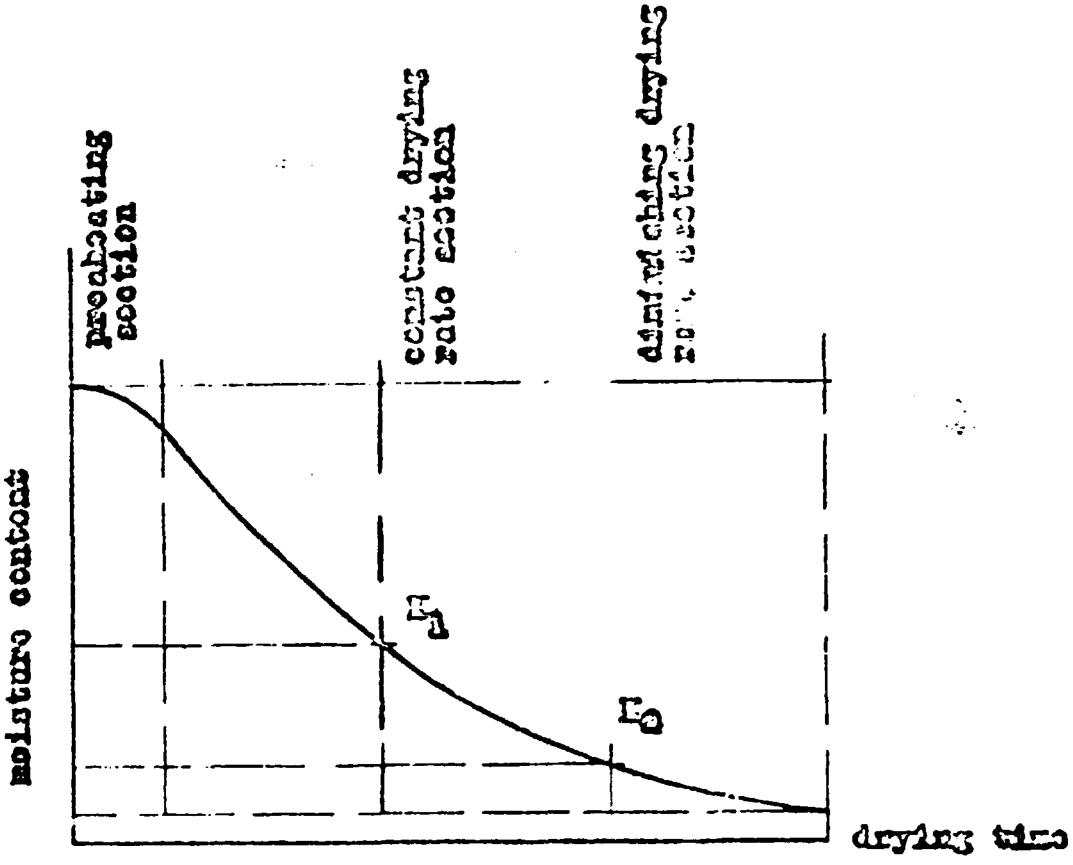

Fig.13. Drying-rate curve of gypsum plaster products

Preheating corresponds to the time section when moisture removal is taking place simultaneously with the warming through of the material. In this section the temperature of both the surface and inside layers of the material is increased up to the preset value which is close to the temperature of the wet and dry bulb thermometer - psychrometer. The subsequent change to the moisture of the point K 1 which is called the first critical point, proceeds in a linear manner; this is the so called section with a constant drying rate. Beyond the point K 1, the linear change of the moisture content of the material is converted into a curve which approaches asymptotically the equilibrium moisture; this is the so called section of the diminishing drying rate. From the critical point K 2 the temperature of the material then begins to rise rapidly and approaches the temperature of the ambient environment.

The evaporation of moisture from the surface of the product depends on the moisture difference between the surface and inside layers; this difference causes a shift of moisture towards the surface from the bottom layers and an overall reduction of the moisture of the material. In the course of the period of the constant drying rate, this transfer of moisture to the surface via a system of capillaries proceeds continuously and the layer bordering on the heat tranfer medium (air) has sufficient capabilities for providing a constant rate of moisture removal.

After the first critical point has been attained, the rate of drying is reduced due to a lower supply of moisture into the outer layers. Then there occurs the second critical point when the moisture evaporation zone is transferred into the depth of the material.

During the period of drying with a constant rate, the main part of the moisture is removed from the gypsum plaster products. With regard to the intensification of the drying process, this period can proceed at higher temperatures of the drying medium, since the temperature of the material itself is increased only slightly during this period and does not attain a height, at which there could occur dehydration of the dihydrate.

Greatest attention should be given to the transition into the period of the decreasing rate of drying, especially after the attainment of the second critical moisture. A rapid increase in the temperature of the material, caused by a shift of the evaporation zone into the depth of the pores and capillaries, can easily lead to dehydration of the gypsum plaster on the surface and especially on the corners and edges of the products. The effectiveness of drying is thus given by the temperature, moisture content and the rate of movement of the drying medium.

The drying of board products is generally carried out in multi-stage dryers which are divided into three zones with regulated moisture and temperature conditions.

For the drying of thick-walled gypsum plaster elements tunnel dryers are employed, with a combined intake of the heating medium. In this case up to a distance of two thirds of the tunnel length (taken from the entrance of the material to be dried) the hot gases are introduced counter-currently and in the last third co-currently. Intensified drying plants operate on the co-current principle and in this case the incoming temperature of the drying medium can be increased up to 250 °C with a simultaneous increase of its moisture content to 100 - 140 g/kg of the dry medium.

Of extraordinary importance is the correct determination of the limits of the possible action of higher temperatures onto the gypsum plaster and the degree of moisture of the products during the individual drying periods, especially in the vicinity of the critical points. The final moisture of the board and elements should as a rule not exceed 6 %.

An important part of the schedule of gypsum plaster products form in certain countries decorative facing board and acoustic insulation board.

In the case of decorative board, we are generally concerned with squares 60 x 60 cm, thickness 5.8 cm, of a tub type which are provided on two sides with a lug and on two sides with a groove to facilitate erection. The board surface is diversely profiled and/or perforated.

As regards sound insulation board, the inner space of the reverse side of the board is generally filled with a glass or mineral wool mat which is generally enclosed in a thin textile fabric.

Board of this type has found considerable applications in the German Democratic Republic, Poland and in the USSR where, however, board of larger dimensions is manufactured.

For mounting onto both walls and ceilings a detailed erection procedure has been worked out, including the relevant erection aids.

In many countries gypsum plaster is also being used for plasters which are characterized not only by high strength and a high aesthetic effect, but also by a great durability, insulation properties and fire resistance. Here we are usually concerned with a mixture of gypsum plaster and lime, sometimes only with pure gypsum plaster.

The development of gypsum plasters has in recent years been characterized by an increase in the production of plaster mixes with a lightweight filler (expanded perlite and vermiculite) which are generally prepared industrially in a separate production plant and brought to the building site already in the form of mixes. Plaster mixes with lightweight fillers have sufficient strength, a good workability and are characterized by much more favourable thermal insulating properties. In a number of cases they are also employed for fire prevention purposes; in this case they are applied onto wire nettings. The most advanced countries in this respect are above all the USA, Great Britain and the Federal Republic of Germany.

In connection with these gypsum plasters it is necessary to mention also their machine application; various spraying equipments have been developed that make possible the transport of the plaster mix through a pipeline up a height of several floors; this simplifies the work and in connection with the simple application by spraying (spray gun) speeds up considerably and enhances the quality of finishing operations on the building site.

To auxiliary gypsum plaster masses - cements - is devoted the following chapter.

9. Gypsum plaster cements

For the joining of gypsum plaster elements from cast gypsum plaster, for work with gypsum plaster carton-board or for joining gypsum plaster products with other building materials are most suitable gypsum plaster cements.

It is recommended to carry out surface finishing operations on gypsum plaster elements, possibly also on elements from other building materials, with the aid of gypsum plaster spatula masses.

These gypsum plaster joining and spatula materials are generally made by the manufacturers of gypsum plaster or gypsum plaster products under various trade names and for diverse specific applications. Their production is a precondition for the successful assembly and erection of elements.

The basic starting component for their production is usually semi-hydrate gypsum plaster, the properties of which are, however, modified by various additives; especially the following are involved:

- rheological properties,
- water retention in relation to base,
- adhesion to base,
- period of workability,
- volume changes on setting and hardening,
- mechanical strength,
- resistance to mildew,
- anticorrosion properties.

The rheological properties are generally improved with the aid of:

- cellulose ethers (alkyl-, hydroxyalkyl- or carboxyalkyl-),
- ethylene based polymers (polyvinyl alcohol, polyacryl amide),
- natural macromolecular substances (glue, starch, gum, glutine, alginate) or materials obtained by the treatment of natural macromolecular substances, e.g. starch (ethers, esters, dextrine),
- surfactants, i.e. non-ionogenous or anion-active tensides (alkyl- or aryl-sulphonates, addition products of alkenoxides with fatty acids, alkohols and amines or phenols),
- various mineral additives, such as e.g. ground limestone, dolomite, kaolin or even gypsum rock.

Water retention is the capability of the water suspension (paste) applied to a suction base to hold back in itself the water. This capability is one of the most important properties of these materials, since it makes possible the maintenance of the paste workability right up to the moment, when the gypsum plaster begins to set. As the most effective substances for this purpose have proven themselves practically only cellulose ethers, and out of them above all methylcellulose. It is also recommended to employ for this purpose a urea-formaldehyde preconcentrate.

An improvement of adhesion to the base can be obtained by the addition of cellulose ethers and polymers on the basis of ethylene and its derivatives.

The period of workability depends on the water retention and on the beginning of setting of the gypsum plaster present. Mostly we are concerned with a prolongation of the setting period; the employed retarder must not reduce the strength of the hardened gypsum plaster, must not form efflorescences and must be effective in small concentrations (0.01 - 0.1 %). As setting retarders are for this purpose as a rule recommended hydrolyzed proteins, sodium tripolyphosphate and furthermore cellulose ethers containing alkyl and carboxyalkyl groups which at the same time increase the water retention.

At the same time, the employed additives must not endanger the soundness (stability of volume) of the gypsum plaster during setting in the form of a cement, nor the mechanical strengths.

In certain cases the gypsum plaster based cement materials have to be resistant to mildew; this can generally be achieved through the addition of organic tin compounds.

Since gypsum plaster cement materials often come into contact with the metal supporting construction and with metal door frames, respectively, it is necessary to increase the pH of the paste prepared by making up the cement material with water. This is usually achieved by the addition of a small quantity of $Ca(OH)_2$ which at the same time influences favourably the solubility of the employed cellulose derivatives.

Gypsum plaster cement materials with satisfactory properties can generally be obtained by the addition of 1 % methyl cellulose, 1 % $Ca(OH)_2$ and 0.2 % keratine retarder of the setting process to the β-semi-hydrate gypsum plaster.

The composition of these materials is as a rule the subject of commercial interests of the individual companies and is not quoted in the references.

10. Utilization of gypsum rock in the cement industry

Portland cement clinker, ground to the relevant fineness without a setting regulator, sets mostly in contact with water rapidly. In order to attain the current values specified by the standards for the beginning and end of setting, it is necessary to add during grinding a certain small quantity of a regulator - setting retarder.

The reaction kinetics of the action of setting regulators has already in the past been investigated by various authors. Candlot, who was among the first researchers in this field, postulated that calcium sulphate or calcium hydroxide retard in the solution the hydration of C_3A and thus cause a slowing down of the setting process.

Forsén was the first to present an overall general review of the action of setting retarders. Based on studies of the concentration of the individual ions in the solution, he arrived at the conclusion that the setting regulators influence the solubility of the aluminates. Forsén divided the setting regulators into four groups in accordance with the type of curves (see Fig. 14) obtained in the system beginning of setting - quantity of additive, as given below:

I. $CaSO_4.2H_2O$, $Ca(ClO_3)_2$, CaJ_2,
II. $CaCl_2$, $Ca(NO_3)_2$, $CaBr_2$, $CaSO_4.1/2\ H_2O$,
III. Na_2CO_3, Na_2SiO_3,
IV. Na_3PO_4, $Na_2B_4O_7$, Na_3AsO_4, $Ca(CH_3COO)_2$.

In the presence of Group I regulators the solubility of the aluminates is low, even with a higher content of the latter. The solubility of the aluminates in the presence of Group II regulators is low, but ~~also~~ only in case of a low content of the latter. With a higher content, however, the solubility of the aluminates again rises and the retarding effect vanishes. The Group III regulators act in a similar manner as the Group II regulators. With a low concentration, the aluminates remain insoluble, whereas with an increased concentration of e.g. Na_2CO_3 there occurs in the presence of $Ca(OH)_2$ their dissolution. The Group IV regulators then practically prevent altogether the setting and hardening of the cement.

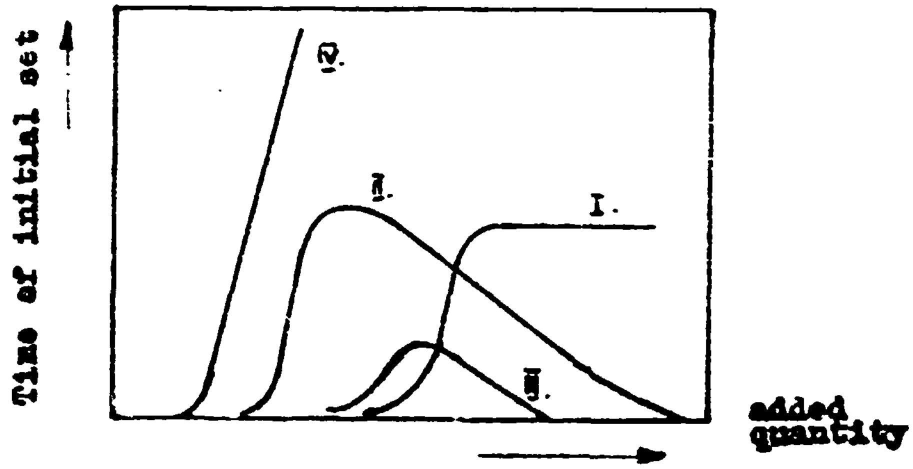

Fig.14. Influence of setting regulaters on the initial setting

In present day industrial processes there is only one significant cement setting regulator, i.e. calcium sulphate, above all in the form of the dihydrate $CaSO_4.2H_2O$.

As far as the mechanism of action of gypsum rock in the setting of cement is concerned, there practically still holds true the theory formulated for the first time by Michaelis and confirmed by KÜhl. According to this theory there occurs during the contact of cement with water an immediate hydration of C_3A with the formation of hexagonal C_4AH_{13} which is unstable and is transformed into the stable cubic form C_3AH_6, in the form of colloids with a very high water content that cause setting. In the presence of gypsum rock, however, is formed first of all metastable aluminate-hydrate $3\ CaO.Al_2O_3.3\ CaSO_4.32\ H_2O$ - trisulphate, Ettringite, Candlot´s salt which crystallizes from the solution in the form of needle-shaped crystals, thus retarding the beginning of the setting process, until either all the SO_3'' ions are consumed or until the actual setting covers up this reaction. But already Michaelis found out also the destructive effect of this trisulphate and called it therefore the "cement bacillus".

During the hydration of C_4AF are formed according to American and Soviet authors aluminate-hydrates; in the presence of gypsum rock also calcium-aluminate-sulphates, i.e. beside trisulphate, identified by Lerch, Ashton and Bogue, also monosulphate $3CaO.Al_2O_3.CaSO_4.12H_2O$.

Out of numerous investigations carried out for the purpose of clarifying the action of gypsum rock, should be mentioned especially the work of Lerch, according to the results of which the necessary SO_3 content influences as a setting regulator not only the C_3A content, but also the fineness of grind and the alkali contents, especially the Na_2O content. For these factors determined O.F. de la Barona, with a SO_3 content of 2.5 - 4.0 %, the following values: 0.8 % alkalis, 8 % C_3A and a specific surface according to Blaine of 3,250 cm^2/g.

As regards the mechanism and formation of aluminate-sulphate hydrates, J.D. Ans and H. Eick have found that with an increasing gypsum rock content is decreased the monosulphate content, for the benefit of trisulphate, until the former almost vanishes, and with a sufficiently high SO_3 content only trisulphate is formed. The SO_3 concentration in the solution is markedly increased only when all the monosulphate has been converted into trisulphate.

For interest´s sake it can be stated that some authors believe that trisulphate is not stable and is decomposed after a certain period of time with the formation of solid solutions with aluminium hydrate and $Ca(OH)_2$ that correspond in composition to monosulphate. But other authors state conversely that monosulphate is a metastable form which in contact with water that contains dissolved calcium sulphate, is gradually transformed into stable trisulphate.

But generally prevails the view that the final product of the reaction between C_3A and calcium sulphate in an alkaline environment is always trisulphate.

It follows from the above brief summary that the calcium sulphate content plays, with regard to the C_3A content, a primary role in the setting of the cement, mainly during the first initial period, and thus influences to a considerable extent also the strength of the cement, beside other equally important factors which are the alkali contents, the fineness of grind and the storage temperature.

The task of calcium sulphate is directly linked with the solubility of its individual hydrates. If the cement contains the more soluble semi-hydrate, there occurs an instantaneous supersaturation of the solution with calcium sulphate which manifests itself by a so called false setting.

From the point of view of cement manufacture is of great significance the fact, to what extent can gypsum rock which is present in the cement, be dehydrated without a harmful influence onto setting. The Polish authors Sulikowski and Piechowicz have found experimentally that the furthest limit of gypsum stone dehydration to semi-hydrate is 60 %.

With regard to the genesis of the gypsum rock resources is for the utilization also of importance the anhydrite content. Laboratory tests have shown that any quantity of anhydrite in the gypsum rock itself influences neither setting nor soundness. It causes, however, an increase of the water quantity for a normal consistence which in its consequences negatively influences the strength of the cement. This circumstance led to the conclusion that the anhydrite content in the gypsum rock should not exceed the limit of 30 %.

As regards the optimum SO_3 content in the cement, this value lies in the region of 2.5 - 3.5 %; this is also specified in the standards for cements in most countries. But since the optimum SO_3 content is dependent on the C_3A content, there manifests itself in recent years in certain national standards a tendency to introduce a standard limit for the SO_3 content in accordance with the C_3A content.

A number of authors have dealt in recent years with the problem of possibilities of utilizing by-product calcium sulphates in the function of cement setting regulators. At the same time was naturally investigated also the influence of the contents of the present potentially dangerous substances (water soluble P_2O_5, fluorides).

It was proved quite definitely that by-product gypsum of the usual quality can be employed in the function of a cement setting regulator; but the quantity of this additive is generally reduced from the usual 5 - 6 % of gypsum rock to 2 - 3 % of by-product gypsum. This fact is due to a different crystalline structure, from which follows a higher solubility.

For your general information it is possible to present a classification of gypsum rocks for the production of gypsum plaster binders and cement according to the International Standard ISO 1587 (1975). This standard specification divides natural gypsum rock into 4 classes according to the dihydrate contents Tg :

Class 1	$Tg \geq 90\,\%$
Class 2	$80 < Tg < 90\,\%$
Class 3	$70 \leq Tg < 80\,\%$
Class 4	$55 \leq Tg < 70\,\%$.

The higher quality classes are as a rule utilized for the production of gypsum plaster, the lower grades as cement setting regulators.

For the sake of completeness should be mentioned that in 1966 was published a tentative draft of the Document ISO/TC 74/SC2 (U.K.-3) 63 Draft Proposal for an ISO Recommendation "By-product Gypsum", put together by A.C. Tallentire from ICI Ltd. This material lists the following criteria for the chemical composition of by-product gypsum:

Combined water	- This shall not be less than 17.5 % of the weight of gypsum.
Total loss on ignition	- This shall not be greater than 20 % of the weight of gypsum.
Sulphur trioxide content	- Shall not be less than 42 % of the dry gypsum.
Calcium oxide content	- Shall not be less than 2/3 of the sulphur trioxide content.
Total phosphate content	- Expressed as P_2O_5. The total P_2O_5 content shall not be greater than 1.25 % based upon the weight of gypsum.
Acidity	- As a partial measure of the soluble P_2O_5 content (phosphoric acid:monocalcium phosphate), the acidity when determined by the method given, shall not exceed 50 mls of N/10 sodium hydroxide.
Fluorine content (F)	- Shall not exceed 1.8 % by weight, based upon the weight of dry gypsum.

Iron and aluminium content - Expressed as $Fe_2O_3.Al_2O_3$: the combined iron and aluminium content as expressed as R_2O_3 shall not exceed 1.1 % by weight when based upon the weight of dry gypsum.

Organic content - Expressed as carbon (C). The carbon content shall not exceed 0.1 % by weight of the dry gypsum.

In accordance with currently available information, no further work has been done by the relevant ISO Commission on this draft.

11. Testing

The testing of gypsum plaster serves to prove its quality in the sense of the technical requirements of the quality standard; in production it then serves for the control of the technological process.

Out of the fundamental properties of gypsum plaster which are as a rule stipulated in the national standard specifications, the following can be listed:

- fineness of grind,
- quantity of water necessary for the preparation of the gypsum plaster paste,
- beginning and end of setting,
- linear changes,
- hardness,
- tensile bending strength and compressive strength,
- chemical composition.

The fineness of grind is generally determined as the rest on a sieve with an appropriate mesh size. The mesh sizes are in accordance with the standard specifications of various countries usually 0.09; 0.2; 0.5; 0.8; 1.0; 1.25 mm. Screening is generally carried out in the dry state; since the gypsum plaster clogs on screening especially the fine sieves, sometimes screening in isopropyl-alcohol is chosen. Before the test, the sample to be tested must be dried; the drying temperature should not exceed 50 ± 2 °C. The fineness of grind is expressed as the rest on the relevant sieve in weight per cent.

The quantity of water required for the preparation of a standard gypsum plaster paste is determined in accordance with the standard specifications of various countries as a rule as

- the water-gypsum plaster ratio,
- bulk quantity,
- standard consistence.

The water-gypsum plaster ratio expresses the weight relationship between water and gypsum plaster.

The bulk quantity is a quantity of gypsum plaster which is thoroughly wetted with 100 g of water. The procedure is as follows: into a metered quantity of water is poured at a determined rate gypsum plaster up to the moment when the gloss of the water level disappears. The result is the average value out of three determinations which do not differ from one another by more than 5 grams.

The standard consistence is determined by pouring out the cake, the penetration of a steel ball through the paste or the penetration of test cylinder of the Vicat apparatus through the gypsum plaster under test.

The pouring out of the cake is tested either with the aid of the Southard cylinder or the conical test mould of the Vicat apparatus. The test is repeated with a different water quantity, until the diameter of the gypsum plaster cake, stipulated by the standard specification, is obtained.

Analogical is the procedure during the testing of the penetration of a steel ball (diameter 25.4 mm, weight 66.7 g, height of fall 254 mm) through the gypsum plaster paste, as well as during the determination of the gypsum plaster paste density with the aid of the Vicat density determination cylinder with a diameter of 19 ± 0.1 mm and a total weight of the moving parts of the apparatus of 50 ± 0.5 g.

The beginning and end of setting is generally determined on a gypsum plaster paste of standard consistency. For practical purposes is often employed the test on cakes. The beginning of setting is characterized by the time from mixing the gypsum plaster with water up to the moment when a cut with a knife into the cake no longer closes itself. The end of setting is then the moment when thumb pressure applied to the cake surface no longer causes an imprint.

Exact is, however, the Vicat method which utilizes the Vicat needle with a diameter of 1 ± 0.05 mm, with a total weight of the moving parts of the apparatus of 300 ± 0.5 g.

The beginning of setting is given by the moment when with a free penetration through the gypsum plaster paste the needle no longer reaches the watch glass, on which rests the conical mould. The end of setting is determined by the instant when the needle does not penetrate into the test specimen surface deeper than 0.5 mm.

Linear changes are generally tested with the aid of the Graf-Kaufmann instrument with a dial indicator. The tests are carried out on specimens 40 x 40 x 160 mm, provided with metal measuring contacts; the specimens are prepared from a standard consistency paste. The tests are generally carried out in accordance with a preset programme, in which are specified the storage conditions (time, humidity, temperature).

Hardness is usually determined from the diameter or depth of the imprint of a steel ball with a diameter of 10 mm, caused either by free fall or by a pressure of a stipulated value, measured with a dynamometer.

The tensile bending strength is determined in most cases on prisms with the dimensions 40 x 40 x 160 mm. After the rupturing of the latter, on the fragments is then determined the compressive strength on a compression area of 25 cm^2. The specimens are prepared from a standard consistence paste. The testing time is usually selected after two hours and after drying to a constant weight. If we are dealing with slowly setting gypsum plasters, the beginning of the test period is usually shifted (e.g. 6 - 8 hours). The strength is expressed in MPa. During both the bending strength test and the compressive strength test must be maintained the permissible rate of loading of the test specimen.

During the chemical analysis are generally determined the contents of

- moisture,
- water of crystallization,
- SiO_2,
- CaO,
- SO_3,
- R_2O_3 .

Moisture is determined by drying to a constant weight at a temperature of 50 ± 2 °C.

The water of crystallization is determined by drying to a constant weight at a temperature of 230 ± 5 °C.

SiO_2 is determined after the decomposition with hydrochloric acid, drying and subsequent filtration by the usual gravimetric method.

In the filtrate is determined R_2O_3 by precipitation with ammonia and in the next filtrate then CaO in the form of oxalate. Additionally it is also possible to determine the MgO content as pyro-phosphate.

SO_3 is determined in a separately weighed specimen after the decomposition by hydrochloric acid as $BaSO_4$.

In a number of cases are, however, applied also modern titration methods, as well as physical and chemical methods.

12. Conclusion

The material presented is a brief cross-sectional information about the problems of gypsum plaster and gypsum plaster products manufacture and about problems that are associated with the utilization of this material. Briefly are also discussed new technical solutions which are related to the utilization of by-product calcium sulphates.

In conclusion is presented a brief summary of the chemism of gypsum rock application as a setting regulator, and the last chapter is devoted to the testing of the gypsum plaster properties.

We are here concerned with a very extensive complex of problems where every chapter could be elaborated further into an extensive survey paper. This, however, is not made possible by the available scope and time.

Perhaps even in this brief summary the material will fulfill its purpose and contribute to the development of the gypsum plaster industry. The broad potential applications of gypsum plaster products in industry, and above all in the building industry, fully deserve this.