CHAPTER 2

THEORY

2.1. Flue-Gas Gypsum (FG)

FG is obtained from the desulfurization of combustion gases of fossil fuels, such as anthracite, bituminous coal, lignite and oil in large combustion plants, especially power stations. Numerous processes have been developed, and a few are used in industry. A brief description of more relevant technologies is as follows :

2.1.1. Desulfurization processes

(a.) Wet scrubbing

The technology employs an alkaline sorbent slurry which is predominantly lime or limestone based because it gives reasonably good SO_2 removal and rather good utilization (Chubu, 1985 and Stromberg and Jonsson, 1985). A scrubbing vessel or scrubber is located downstream of the boiler in which intimate contact between gas and sorbent is carried out, a process which readily removes over 90% of SO_2 from the flue gases. The resulting solid is predominantly calcium sulphite which can be further oxidized to calcium sulfate dihydrate which can be sold as a by-product to the building industry where it finds application as plaster board.

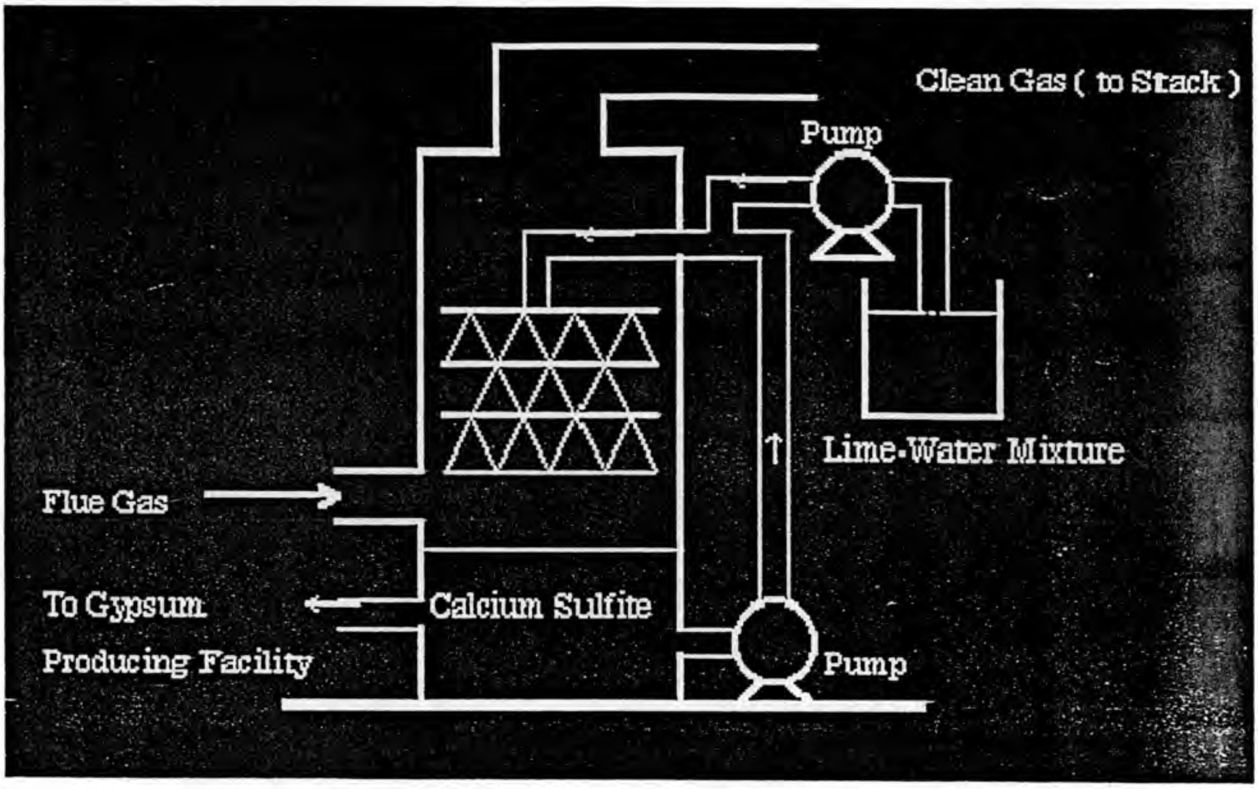

Fig. 2.1 Schematic diagram of the wet scrubbing (Chubu, 1985).

There are quite a number of developments in this technology to increase overall efficiency, for example, regenerative flue gas reheating and natural draft cooling tower. Holter and Gibhard (1989) had reported a process for making FG. The process comprised treating the flue gas in a wash tower with a wash water suspension containing calcium oxide, calcium hydroxide or calcium carbonate and converting the scrubbed SO_2 by oxidation with input atmospheric oxygen and by crystallization to calcium sulfate dihydrate crystals. After that the calcium sulfate dihydrate was separated by a cyclone separator and the crystal suspension was dewatered. By control of amount of the partial pressure of the suspension flow, the grain size of the calcium sulfate dihydrate crystal was precisely adjusted.

(b.) Spray dry scrubbing

This technology also employs a sorbent slurry or solution, however, the by product is dry and removal efficiency about 80 to 90% (Wirsching, Huller and Limmer, 1983). The slurry of sorbent, alkaline based, is sprayed into the scrubbing vessel in very fine droplets and dried (typically having a free water content of about 4 to 12% by weight) as it contacts the flue gas. At this point the sorbent reacts with the SO_2. The dry sorbent is picked up by the gas stream and carried into the dust collector for removal.

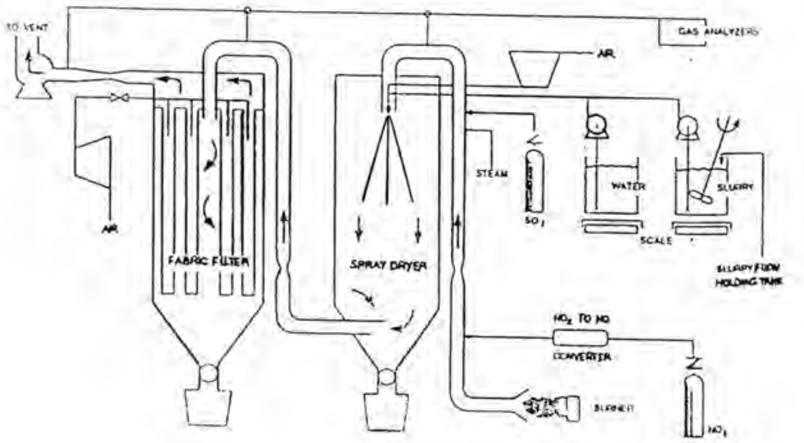

Fig. 2.2 Schematic diagram of the dry scrubbing (Stromberg and Hans, 1988).

Stromberg and Hans (1988) had reported the disadvantage with spray dry scrubbing in obtaining a high SO_2 removal. Because of the relative short residence time under wet condition in the spray dry scrubber and because of the low dissolution rate of limestone, a high SO_2 removal would not be reached in the spray dry scrubber, if nothing was done to enhance the dissolution of limestone. However, that limestone could be as efficient as slaked lime for SO_2 absorption during the dry reaction period. Bjerle, Klingspor and Karlsson (1984) had reported very good SO_2 removal with limestone as an absorbent in spray dry scrubbing, when operating at low approach temperatures.

(c.) Sorbent injection

The technology of calcium sorbent injection is a more recently developed technology and is the lowest in term of capital outlay of all the available SO_2 removal technologies. The sorbent can be added dry into one of three locations (Theodore and Buonicore, 1976).

- into the furnace (gas temperature 850 to 1250°C).
- into the economizer region (gas temperature 550 to 950°C).
- after air heaters (gas temperature close to saturation).

However, because of relatively poor contact between the sorbent and SO_2, efficiency is generally in the range 30 to 60% and hence, sorbent use is much higher. The residual sorbent and ash mixture is not a commercial product as with wet and spray dry scrubbing. Klingspor, Karlsson and Bjerle (1983) had reported that the research was underway with efficiencies expected to reach as high as 80% if techniques like humidification of the flue gas or other additive into the gas stream proved successful.

2.1.2 Reaction of desulfurization processes

Almost all of these processes are operated by the countercurrent washing the flue gas with aqueous suspensions of limestone or lime to remove the SO_2. The reaction takes place at pH 7-8 (Scholz, 1984) and produces an almost insoluble calcium sulfite ($CaSO_3.1/2H_2O$).

$$SO_{2(g)} + \underset{\text{(solid suspension)}}{CaCO_{3(s)}} + 1/2H_2O \text{ ------> } CaSO_3.1/2H_2O_{(s)} + CO_{2(g)} \quad \text{pH 7-8}$$

In the second step, the pH is allowed to fall below 5. So, the suspended calcium sulfite is converted to soluble calcium bisulfite ($Ca(HSO_3)_2$).

$2CaSO_3.1/2H_2O(s) + 2SO_2(g) + H_2O \text{ ------> } 2Ca(HSO_3)_2$ pH 5
(solid suspension) (solution)

This calcium bisulfite is easily oxidized by atmospheric oxygen to calcium sulfate dihydrate ($CaSO_4.2H_2O$) or gypsum so-called " Flue-gas gypsum".

$Ca(HSO_3)_2 + O_{2(g)} + 2H_2O \text{ ------> } CaSO_4.2H_2O(s) + H_2SO_4$ pH 5
(solution) (solid suspension)

The sulfuric acid (H_2SO_4) produced reacts with the remaining limestone to form additional gypsum.

$H_2SO_4 + CaCO_{3(s)} + H_2O \text{ ------> } CaSO_4.2H_2O(s) + CO_{2(g)}$

Gypsum crystals grow and are separated from the aqueous gypsum suspension in hydrocyclones and vacuum drum filters or centrifuges. The product is moist fine powder, fairly pure powder having high percentage of calcium sulfate that contains only minor quantities of impurities which are specific to process such as soluble salts (Na^+, Mg^{2+}, Cl^-) and calcium sulfite (Knauf, 1983 and Wirsching, Hamm and Huller, 1981) and is almost pure white color (Hamm and Huller, 1982). Chemical composition of FG is as shown in Table 2.1. About 5.4 tons of gypsum are produced per tonne of sulfur in the fuel.

The net reaction :

$SO_2(g) + CaCO_{3(s)} + 1/2O_{2(g)} + 2H_2O \text{ ------> } CaSO_4.2H_2O(s) + CO_{2(g)}$

Table 2.1 Chemical composition of some calcium sulfates (Wirsching, 1975).

	Natural gypsums		Natural anhydrites		Flue-gas gypsum	Phosphogypsums			Fluoro-anhydrite
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
Mineralogical analysis									
$CaSO_4 \cdot 2H_2O$	91.6	96.4	6.0	3.8	97.5	93.0	97.6	96.5	0.0
$CaSO_4$ II	6.4	0.9	88.8	83.7	0.0	0.0	0.0	0.0	94.7
$MgCO_3$	0.1	0.6	2.0	3.6	0.0	0.0	0.0	0.0	0.0
$CaCO_3$	1.9	1.3	3.1	5.3	0.0	0.0	0.0	0.0	0.0
Chemical analysis									
Combined water	19.1	20.1	1.3	0.8	20.6	19.5	19.2	19.2	0.0
SO_3	46.4	45.4	55.1	51.0	45.8	43.2	45.4	46.9	56.4
CaO	33.6	32.5	40.3	38.7	32.1	32.2	32.5	32.1	40.8
MgO	0.05	0.28	0.95	1.71	0.04	0.01	0.01	0.01	0.13
SrO	0.07	0.16	0.07	0.14	0.0	0.06	2.05	0.05	0.0
$Fe_2O_3 + Al_2O_3$	0.01	0.08	0.01	0.39	0.27	0.27	0.70	0.93	0.27
HCl-insoluble residue	0.10	0.47	0.10	2.49	0.32	1.51	1.00	0.68	0.69
Na_2O	0.02	0.01	0.04	0.11	0.01	0.47	0.14	0.02	0.03
Total P_2O_5	0.0	0.0	0.0	0.0	0.0	1.01	0.11	0.30	0.0
F	0.0	0.0	0.0	0.0	0.04	1.76	0.14	0.29	0.92
Others					0.20 SO_2 0.01 Cl				0.11 ZnO 0.69 K_2O
Organics	0.0	0.0	0.0	0.0	0.03	0.08	0.03	0.04	0.0
Ignition loss	0.54	0.71	2.08	4.45	0.4	1.38	0.34	0.43	0.14
Total	99.89	99.71	99.95	99.79	99.81	101.45	101.62	100.95	100.18
pH	6	6	6	6	6	3.1	9	4.2	10–12

1) Zechstein gypsum; 2) Keuper gypsum; 3) Zechstein anhydrite; 4) Keuper anhydrite; 5) Mitsubishi process; 6) From Moroccan raw phosphate, dihydrate process; 7) From Kola raw phosphate, dihydrate:hemihydrate process, after rehydration to dihydrate; 8) From Moroccan raw phosphate, hemihydrate/dihydrate process; 9) From hydrofluoric acid production. Zechstein is an Upper Permian deposit; Keuper, an Upper Triassic.

2.2 **Drying of FG** (Wirsching, 1984).

FG is obtained as finely divided crystals in an aqueous reaction medium. After filtration, the FG occurs as a moist finely divided powder with a free water content of approximately 10% in form of absorbed surface water. Furthermore, as compared with NG that contains about 20% chemically bonded water, water of crystallization or combined water, FG has no hygroscopic water.

2.2.1 Basics of drying.

Initially only the surface water is removed when the FG is heated and later heating will effect the removal of the combined water. These heating processes can be designed to follow one another but remain quite distinct from one another. In the first step, the absorbed surface water can be completely removed, referred as " drying process ". Second step, The combined water is removed, referred as " calcination ".

The energy levels of the two stages are quite distinct from each other, so the drying steps will produce a completely dry FG without removal of combined water.

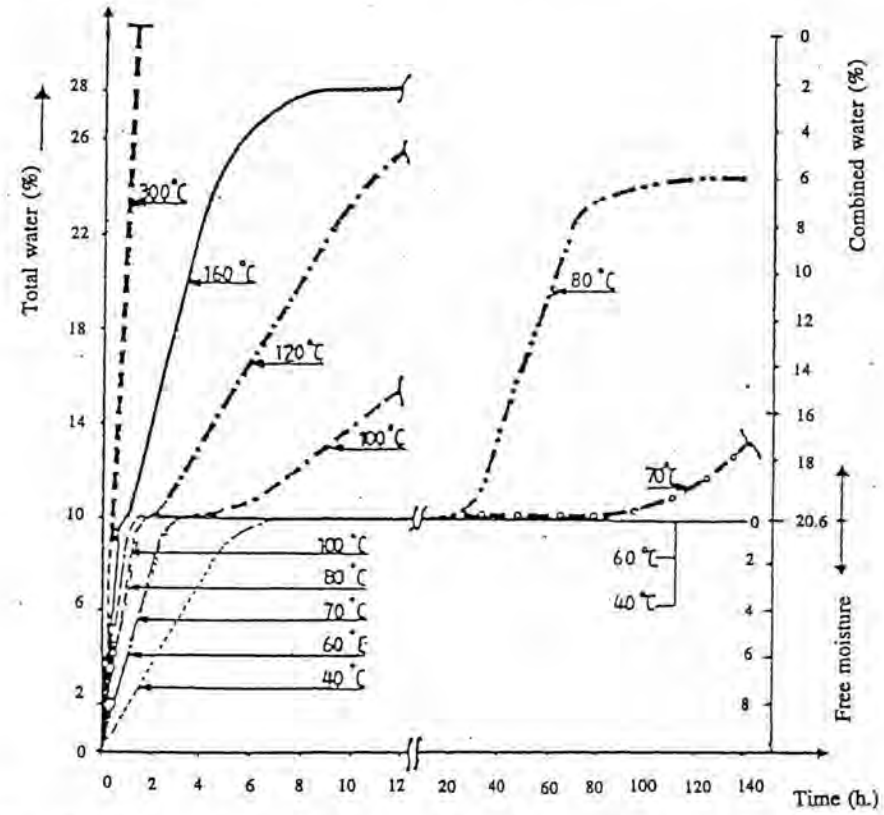

Fig. 2.3 Drying behavior curves of FG in relation of temperature and time (Wirsching, 1984).

The study at laboratory scale on drying and calcination of moist finely divided FG in relation to temperature and time has shown that the drying behavior curves of these two step are quite distinct from each other as shown in Fig. 2.3. From this it becomes apparent that the FG is only dried at temperature below 70 °C. At temperatue above 70 °C up to about 90 °C, the FG is first dried completely and subsequently calcination occurs.

2.2.2 The technique of drying

The process of calcination only starts at temperatures above 70°C and after a certain residence time, care should be taken that such conditions are not attained during the drying process.

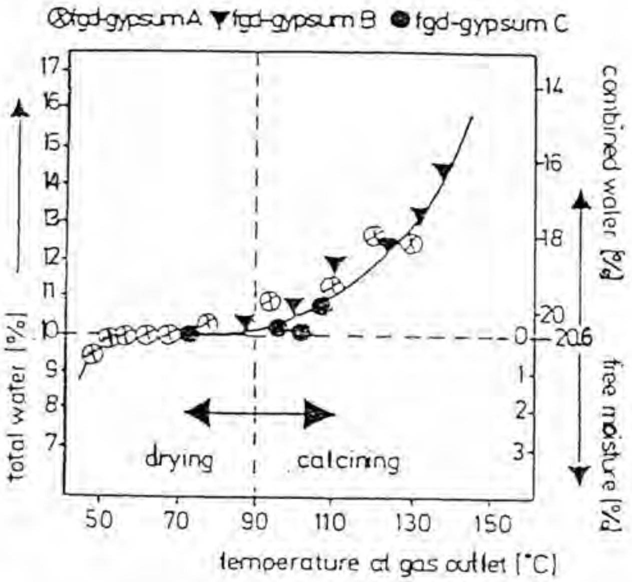

Fig. 2.4 Relationship between exhaust gas temperatures with drying and with calcination of the FG (Wirsching, 1984).

From Fig. 2.4, it follows that calcination of the FG can be avoided by limiting the outlet gas temperature to below 90 °C in order to carry out the drying process to its full. In the industrial drying of FG the aim is also to remove all of the surface water and preserve the combined water. It is moreover necessary to carry out drying with lowest possible energy consumption with in a short peroid of time and achieving high production.

In choosing the type of dryer for drying FG, the cocurrent drier available, in which the hot gases cocurrently come into direct contact with the moist FG, such as a rapid drier is recommended. Its design and mode of operation are described in Fig. 2.5.

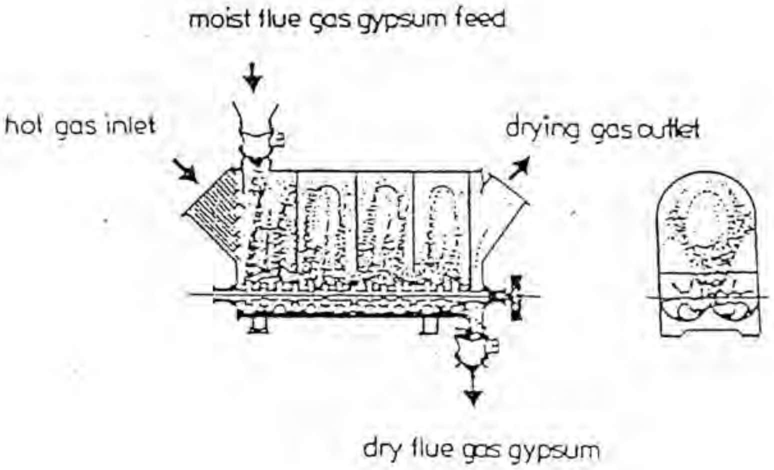

Fig. 2.5 Rapid dryer for drying FG (Wirsching, 1984).

The process in a rapid dryer is controlled by the exhaust gas temperature. The hot gas enters at a temperature of about 400 °C and exits at a temperature of about 90°C. The residence time of the FG in the drier being 8 to 13 seconds. Under these conditions all the surface water evaporates.

2.3 Agglomeration of FG

FG has size and shape of the crystals in various forms, depending on the desulfurization process. Its particle structures ranging from cubic (bulk density of 1.2 ton/m^3) to lath or rod shaped (bulk density of 0.5 ton/m^3), as well as small crystals (20–60 μm, maximum 200 μm), are shown in Fig. 2.6 a and b.

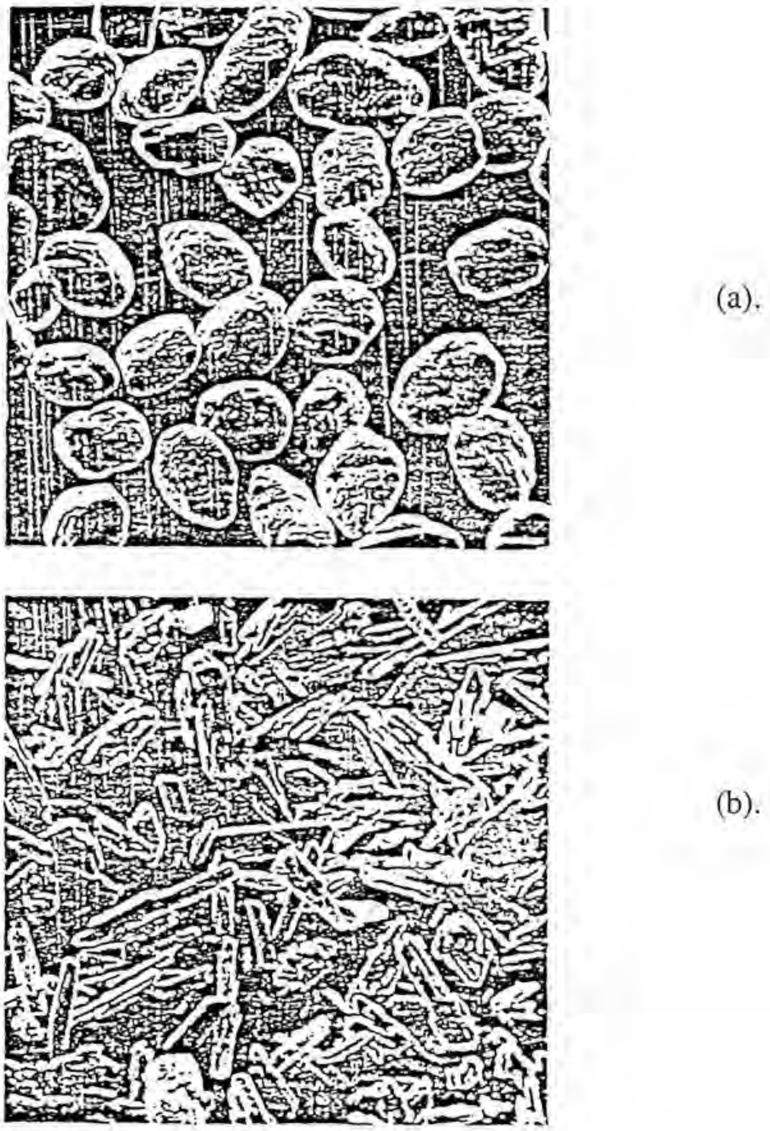

Fig. 2.6 SEM micrographs of particle structure. (a.) particle structure of FG : cubic shaped, bulk density of 1.2 ton/m^3 and (b.) particle structure of FG : rod shaped, bulk density of 0.5 ton/m^3 (Wirsching, 1984).

FG is an end product that can be used industrially. When used as a substitute for NG by the gypsum industry or cement industry, however, it must be treated further because its moist finely divided particle size and structure can often be disadvantageous. This causes problems with handling or with intermediate storage, or when NG is used alternately with FG, or even with the application of different types of FG. The thixotropic behavior of FG makes it unsuitable for the manufacture of multiphase plaster. In an effort to overcome this problem, the processes have been developed to modify the particle structure of FG and convert it into a lump product. These can be done by any one of the following processes.

1. agglomeration by means of pelletizers.
2. agglomeration by means of extrusion presses.
3. agglomeration by means of compacting presses.

2.3.1 Agglomeration by means of pelletizers

Pellets are produced when the FG is agglomerized in pelletizers (as shown in Fig. 2.7). This type of agglomeration requires bonding agents and the FG does not have to be dried first. For instance, when calcium sulfate hemihydrate is added to the moist FG, it requires at least 25% of hemihydrate and enough amount of water for hydration to ensure that the pellets will have the required strength. The pellets produced are 10 to 25 mm. in diameter, have 8 to 10% of free water content and an apparrent density of about 1.6 g/cm^3.

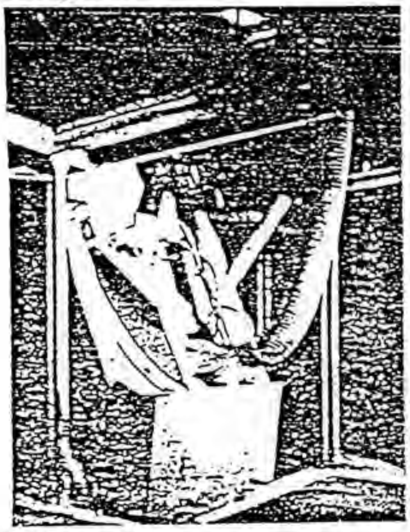

Fig. 2.7 Agglomeration of FG by means of Pelletizers producing pellets (Wirsching, 1984).

2.3.2. Agglomeration by means of extrusion presses

Granules are produced when the FG is agglomerized by means of an extrusion press (as shown in Fig. 2.8). The starting material is moist FG which has moisture content of 8 to 15% depending on its size distribution and the structure of the particles. The moist FG is squeezed through a flat die in form of cylindrical granules that have a diameter of 10 to 25 mm., moist and low strength. After that, the granules have to be dried immediately to achieve a higher strength. The dried granules have an apparent density of approximately 1.8 g/cm^3.

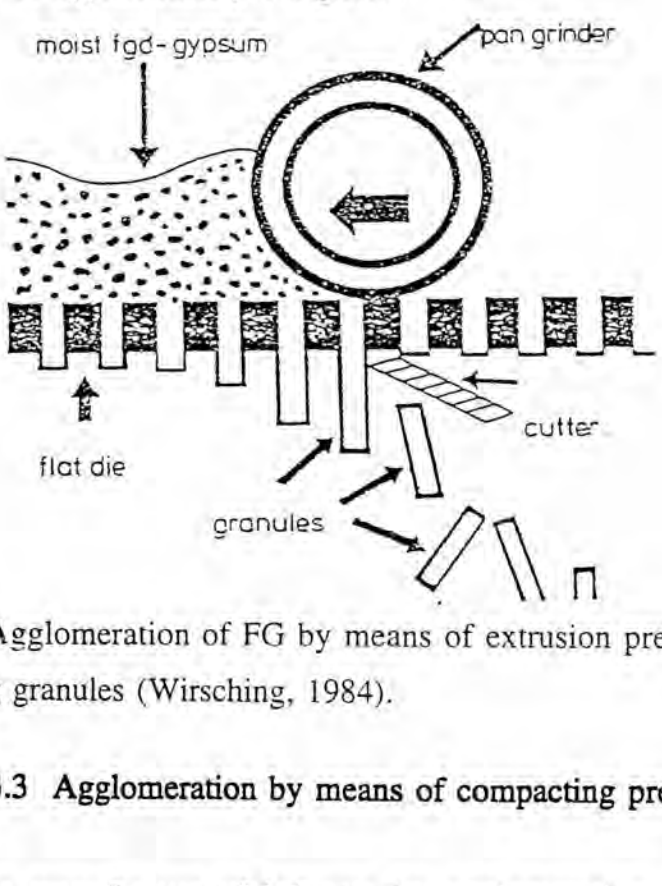

Fig. 2.8 Agglomeration of FG by means of extrusion press producing granules (Wirsching, 1984).

2.3.3 Agglomeration by means of compacting presses.

The manufacture of briquets by agglomeration the FG in dry state with a compacting press (Gebr, 1977). By using suitably designed press roller, such as cigar-shaped corrugated press roller (as shown in Fig. 2.9). Briquets can be produced to have a point strength over 500 N and apparent density of 2.15 g/cm^3 (Wirching, 1983). Natural gypsum has an apparent density of 2.3 g/cm^3. These briquets are very much like a product made from natural gypsum. Because of their high strength and high density the briquets are exceptionally abrasion resistant and can be stored in the open.

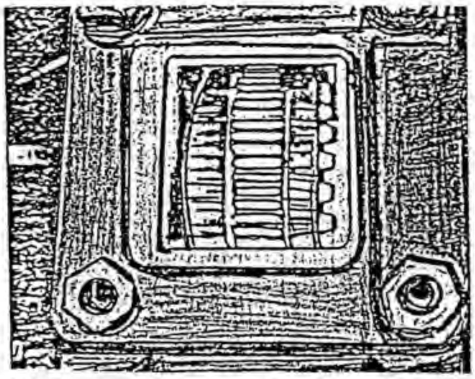

Fig. 2.9 Cigar shaped corrugated press roller of compacting press (Wirsching, 1984).

The advantage of this process is that no bonding agents or additives are needed to agglomerate the FG. Also it is found that the briquets easily detach from the mold without any leftover material sticking to the press and there are slightly wear and tear of the rollers because of the relative softness of gypsum grain (Mohs hardness 2). The process of compaction is as shown in Fig. 2.10

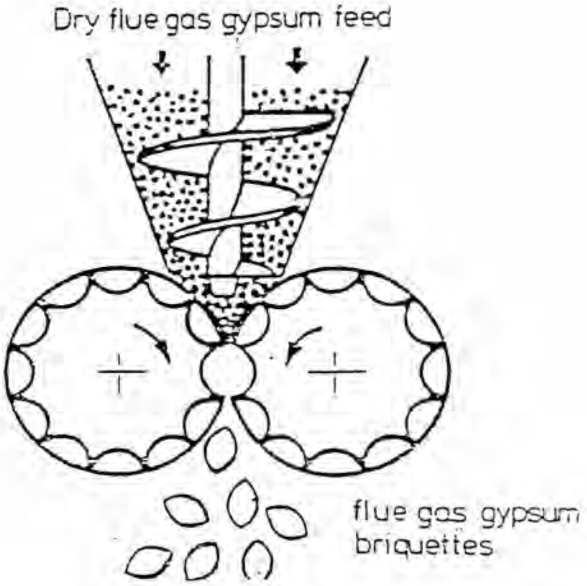

Fig. 2.10 Agglomeration of FG by means of a compacting press producing briquets (Wirsching, 1984).

2.3.4 Characterization of compacted FG

Test carried out on compacted FG shows that nothing is left of the gypsum particle, initial size and shape. Scanning electron micrographs reveal that the FG briquet is of a solid structure and the original FG crystals have intergrown into rocklike body, as shown in Fig. 2.11 The original structure of crystals can no longer be detected even after fine grinding of briquets.

Fig. 2.11 Scanning electron micrograph of the surface of a broken briquet (Wirsching, 1984).

The unfavorable particle size and shape of FG are successfully dealt with by compaction under high pressure and its thixotropic properties are completely eliminated. So, the FG can be used in the same way as NG.

2.4 Phase of calcium sulfate hydrate system ($CaSO_4.xH_2O$)

The $CaSO_4.xH_2O$ system is characterized by five solid phases as shown in Table 2.2.

- Calcium sulfate dihydrate, $CaSO_4.2H_2O$, (DH).
- Calcium sulfate hemihydrate, $CaSO_4.1/2H_2O$, (HH).
- Anhydrite III, $CaSO_4$, (AIII).
- Anhydrite II, $CaSO_4$, (AII).
- Anhydrite I, $CaSO_4$, (AI).

Table 2.2 Phases in $CaSO_4.xH_2O$ system (Wirsching, 1975).

Characteristic	Calcium sulfate dihydrate	Calcium sulfate hemihydrate	Anhydrite III	Anhydrite II	Anhydrite I
Formula	$CaSO_4 \cdot 2H_2O$	$CaSO_4 \cdot 1/2H_2O$	$CaSO_4$	$CaSO_4$	$CaSO_4$
Molecular mass M_r	172.17	145.15	136.14	136.14	136.14
Thermodynamic stability, °C	< 40	metastable*	metastable*	40 – 1180	> 1180
Forms or stages		two forms: α β	three stages: β-anhydrite III β-anhydrite III' α-anhydrite III	three stages: AII-s, slowly soluble anhydrite AII-u, insoluble anhydrite AII-E, *Estrichgips*	
Other names, often based on the application	gypsum raw gypsum synthetic gypsum chemical gypsum byproduct gypsum set gypsum hardened gypsum	*α-form:* α-hemihydrate autoclave plaster α-plaster *β-form:* β-hemihydrate stucco plaster β-plaster plaster of Paris *[26499-65-0]*	soluble anhydrite	raw anhydrite natural anhydrite anhydrite synthetic anhydrite chemical anhydrite byproduct anhydrite calcined anhydrite	high-temperature anhydrite
Synthesis conditions: temperature, °C, and atmosphere	< 40	α-form: > 45, from aqueous solution β-form: 45 – 200 in dry air	α- and β-AIII: 50 and vacuum or 100 in air β-AIII': 100 in dry air	200 – 1180	> 1180
Production temperature, °C	< 40	α-form: 80 – 180 β-form: 120 – 180	β-AIII and β-AIII': 290 α-AIII: 110	300 – 900, specifically AII-s: < 500 AIII-u: 500 – 700 AIII-E: > 700	not produced commercially

* Merastable in air saturated with water vapor

The first four phases exist at room temperature and are of interest to industry, but the fifth phase, AI, only exists above 1180°C (Gruver, 1951). So, it is not possible to produce a stable form of AI below that temperature.

2.5 Chemistry and Physics of calcium sulfate hydrate ($CaSO_4.xH_2O$)

2.5.1 Dehydration and rehydration

Gypsum ($CaSO_4.2H_2O$), both as NG and synthesized gypsum such as FG and phosphogypsum is useful as industrial material because

- it readily loses its water of hydration when heated, produces partially or totally dehydration calcined gypsum.
- when water is added to this calcined gypsum, it reverts to the original dihydrate, the set and harden product.

DH is both the starting material before the dehydration and the final product after rehydration.

Dehydration.

$$CaSO_4.2H_2O \xrightarrow{\text{heat}} CaSO_4.1/2H_2O + 3/2H_2O \uparrow$$

$$CaSO_4.2H_2O \xrightarrow{\text{heat}} CaSO_4 + 2H_2O \uparrow$$

Rehydration.

$$CaSO_4.1/2H_2O + 3/2H_2O \longrightarrow CaSO_4.2H_2O + \text{heat}$$

$$CaSO_4 + 2H_2O \longrightarrow CaSO_4.2H_2O + \text{heat}$$

Kelly et al. (1941) made a through study of the thermodynamic properties of the $CaSO_4.xH_2O$ system. Table 2.3 and Table 2.4 list the heat of hydration and dehydration of the various phase changes that are of industrial significance.

Table 2.3 Heats of hydration (Wirsching, 1975).

Phase change	Heats of hydration per mole (gram) of dihydrate at 25°C, J
$\beta\text{-}CaSO_4 \cdot 1/2\,H_2O + 3/2\,H_2O\,(l) — CaSO_4 \cdot 2\,H_2O$	$19\,300 \pm 85\ (111.9 \pm 0.50)$
$\alpha\text{-}CaSO_4 \cdot 1/2\,H_2O + 3/2\,H_2O\,(l) — CaSO_4 \cdot 2\,H_2O$	$17\,200 \pm 85\ (100.00 \pm 0.50)$
$\beta\text{-}CaSO_4\,III + 2\,H_2O\,(l) — CaSO_4 \cdot 2\,H_2O$	$30\,200 \pm 85\ (175.3 \pm 0.50)$
$\alpha\text{-}CaSO_4\,III + 2\,H_2O\,(l) — CaSO_4 \cdot 2\,H_2O$	$25\,700 \pm 85\ (149.6 \pm 0.50)$
$CaSO_4\,II + 2\,H_2O\,(l) — CaSO_4 \cdot 2\,H_2O$	$16\,900 \pm 85\ (98.0 \pm 0.50)$

Table 2.4 Heats of dehydration (Wirsching, 1975).

Phase change	Heat of dehydration per mole or tonne of dehydration products at 25°C	
	J/mol	kJ/t
$CaSO_4 \cdot 2H_2O \longrightarrow \beta\text{-}CaSO_4 \cdot 1/2H_2O + 3/2H_2O\ (g)$	86 700	597 200
$CaSO_4 \cdot 2H_2O \longrightarrow \alpha\text{-}CaSO_4 \cdot 1/2H_2O + 3/2H_2O\ (g)$	84 600	582 700
$CaSO_4 \cdot 2H_2O \longrightarrow \beta\text{-}CaSO_4III + 2H_2O\ (g)$	121 800	895 700
$CaSO_4 \cdot 2H_2O \longrightarrow \alpha\text{-}CaSO_4III + 2H_2O\ (g)$	117 400	863 100
$CaSO_4 \cdot 2H_2O \longrightarrow CaSO_4II + 2H_2O\ (g)$	108 600	798 000

2.5.2 Structure

The crystal structure of calcium sulfate consists of chains of alternate Ca^{2+} and tetrahedral SO_4^{2-} ions (as shown in Fig. 2.12), for the most part these $CaSO_4$ chains remain intact during phase changes.

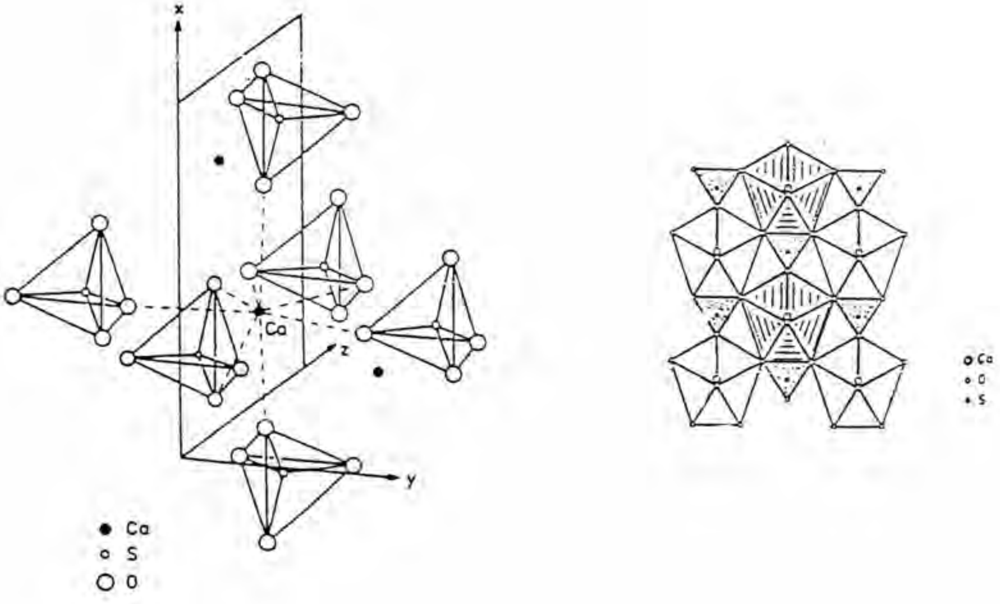

Fig. 2.12 Schematic drawing of the crystal structure of $CaSO_4$ octahedral coordination of Ca cation by $[SO_4^{2-}]$ anions (Kirfel and Will, 1980).

In DH, the water of crystallization is embedded in between the layers of sulfate radicals linked to the calcium ions, forming a layer lattice that linking between the layers by way of water molecules having weak bonds and thus allowing easy to clevage along this planes (as shown in Fig. 2.13). When calcium sulfate is dehydrated from DH to HH the volume decreases and wide channels that run parallel to the $CaSO_4$ chain are formed. It is in definite positions in these channels that the water of crystallization is loosely bound.

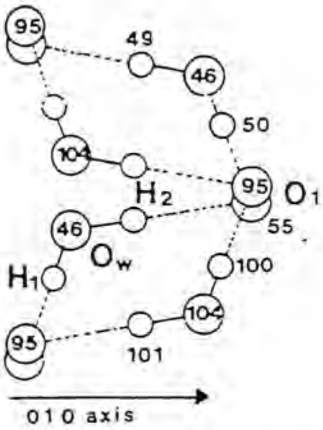

Fig. 2.13 The water molecule of gypsum projected on the (001) plane (Pedersen and Semmingsen, 1972).

This water is able to escape relatively easily, which explains the facile conversion to AIII. AII exhibits the closest packing of ions, which makes it the densest and strongest of the calcium sulfates. However, lacking empty channels, it reacts only very slowly with water. The most important physical properties of the calcium sulfate phases are shown in Table 2.5.

Table 2.5 Physical properties of the $CaSO_4.xH_2O$ (Wirsching, 1975).

Property	Calcium sulfate dihydrate	Calcium sulfate hemihydrate		Anhydrite III	Anhydrite II	Anhydrite I
		α-form	β-form			
Water of crystallization, wt%	20.92	6.21		0.00	0.00	0.00
Density ϱ, g/cm^3	2.31	2.757	2.619 – 2.637	2.580	2.93 – 2.97	undetermined
Hardness, Mohs	1.5	–		–	3 – 4	–
Solubility in water at 20 °C, g per 100 g of solution	0.21	0.67	0.88	hydrates to the hemihydrate	(0.27)	–
Refractive indices n_α	1.521	1.559*		1.501	1.570	undetermined
n_β	1.523	1.5595*		1.501	1.576	
n_γ	1.530	1.584		1.546	1.614	
Optical character	+			+	+	undetermined
Optical orientation	$n_\beta \| b$ $n_\gamma/c = 52°$	$c \| n_\gamma$		$c \| n_\gamma$	$n_\alpha \| c$ $n_\beta \| c$	undetermined
Axial angle $2V$	58 – 60°	14°		≈ 0°	42 – 44°	undetermined
Lattice symmetry	monoclinic	rhombohedral		hexagonal	rhombic	cubic
Space group	$C2/c = C_{2h}^6$	$C3_12 = D_3^6$		$C6_22 = D_6^4$	$Ccmm = D_{2h}^{17}$	undetermined
Lattice spacing, nm, a	1.047	0.683		0.699	0.696	undetermined
b	1.515	0.683		0.699	0.695	
c	0.628	1.270		0.634	0.621	

* Average

2.5.3 Solubility

Gypsum is slightly soluble in water (as shown in Table 2.5 and Fig. 2.14). The solubilities of the various forms of calcium sulfate are strongly affected by the presence of other solutes. Gemlin (1961) and Slack (1968) reported the study on the solubility of gypsum in acid, especially sulfuric acid, phosphoric acid and nitric acid. Gypsum is readily soluble in glycerol, sugar solutions and in aqueous solution of chelating agents, such as EDTA.

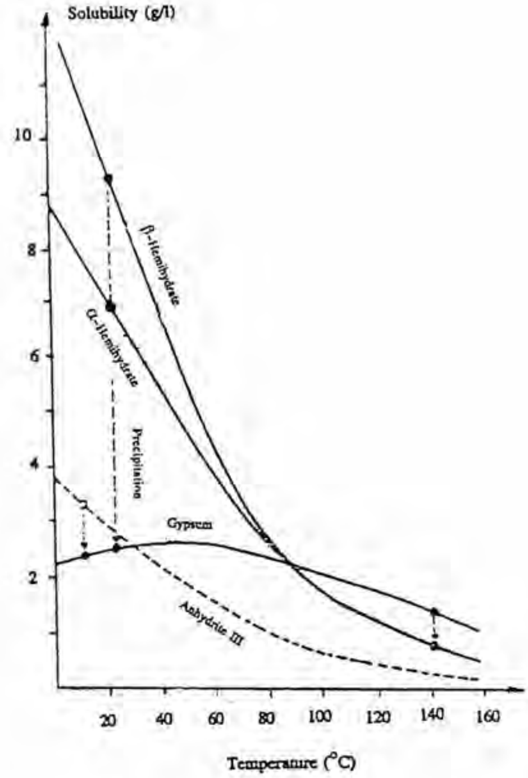

Fig. 2.14 Solubility curves for gypsum plasters (Lafarge, 1990).

2.6 Thermal behavior of gypsum

The thermochemical behavior of gypsum has been the subject of extensive studies. Elliott (1923) claimed that the first effect of heat on gypsum was to change its crystal form from monoclinic to orthorhombic without any loss of its water of crystallization and that weight loss leading to the formation of the HH and anhydrite followed.

Fleck et al. (1960) and Kuntze (1962) reported that DTA in air gave two large endothermic peaks at 180°C and 215°C. They were related to the evolution of 1.5 moles and 0.5 mole of water, respectively, after which γ-$CaSO_4$ (soluble anhydrite) was present which was confirmed by x-ray analysis. The γ-$CaSO_4$ formed changed to the β-form at 370°C and this transformation was exothermic (Khalil and Gad, 1972).

The endothermic peak at 1230°C was referred to the transformation of β-$CaSO_4$ to α-modification before decomposition to CaO and SO_3 (West and Sutton, 1954).

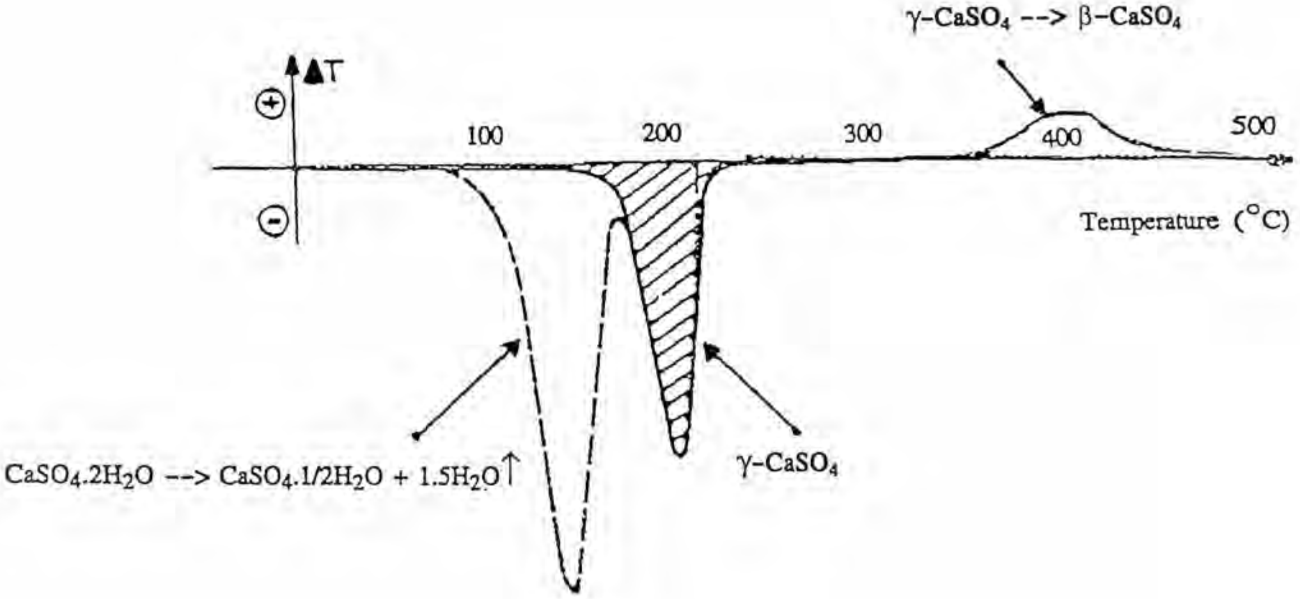

Fig. 2.15 Differential thermal analysis of gypsum (Lafarge, 1990).

2.7 Synthesis of different phases in $CaSO_4.xH_2O$ system

(Wirching, 1975).

The thermodynamic stability ranges for the calcium sulfate phases are shown in Table 2.2. Below 40°C, i.e., under atmospheric conditions, only DH is stable. The other phases are obtained at higher temperatures by progressive dehydration of the DH in the following order :

DH -----> HH -----> AIII -----> AII

Under normal atmospheric conditions HH and AIII are metastable and below 40°C in the presence of water or water vapor they undergo conversion to the DH , as AII does. However, between 40°C and 1180°C AII is stable.

2.7.1 Calcium sulfate hemihydrate (HH)

HH is occurred in two different forms α and β, representing two limiting states. They differ from each other in their methods of preparation, their morphology (as shown in Fig. 2.16 a and b), their application characteristic and their heat of hydration.

To synthesize pure phases in the laboratory, α-HH is obtained from the DH at high water-vapor partial pressure, e.g., above 45°C in acid or salt solution, or above 97.2°C in water under pressure. β-HH is made from the DH by heating at low water-vapor partial pressure, i.e., in dry air or vacuum between 45°C and 200°C.

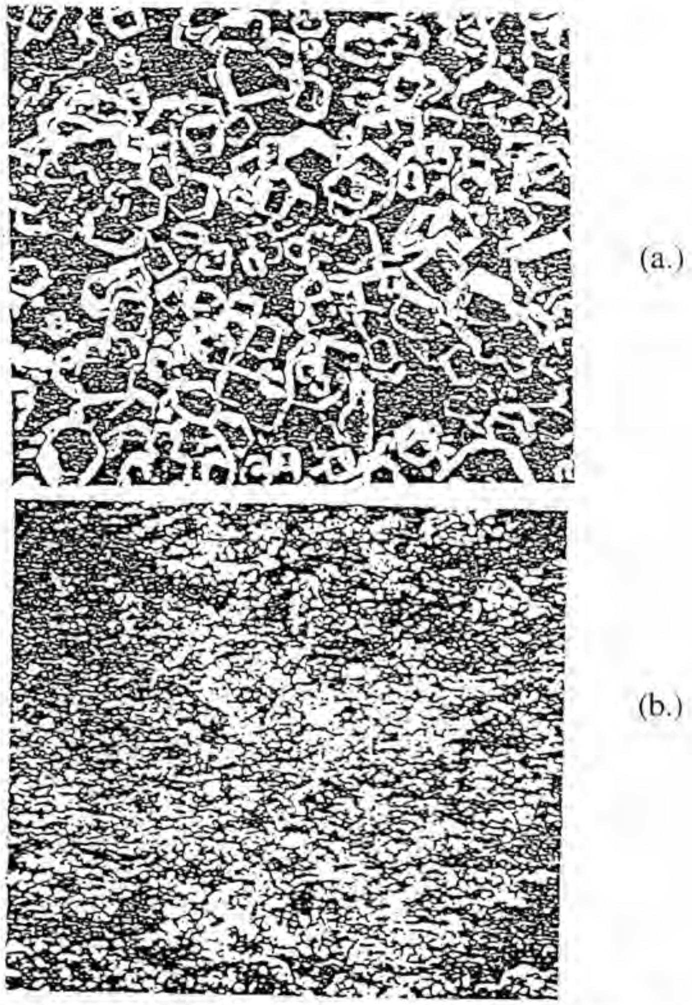

Fig. 2.16 SEM micrographs of HH a.) α-HH : compact, well-formed, blocky particles, b.) β-HH : flaky, irregular-shaped particles (Wirsching, 1975).

2.7.2 Calcium sulfate anhydrite III (AIII)

Lehmann and Rieke (1973) postulated three limiting stages for AIII, also known as soluble anhydrite : β–AIII, β–AIII$'$ and α–AIII. β–AIII is produced from the DH by careful heating at 50°C in a vacuum or up to about 200°C at atmospheric pressure. β–AIII$'$ is formed directly from the DH without formation of intermediate HH at very low water–vapor partial pressure, if water vapor is released rapidly and particle size is small. At high water–vapor partial pressure, if careful release of water at 50°C in a vacuum or at 100°C under atmosphere pressure yields α–AIII.

AIII is difficult to prepared pure because AII begins to form above 100°C and AIII reacts readily with water vapor to form HH.

2.7.2 Calcium sulfate anhydrite II and I (AII and AI)

AII is produced from calcining the DH, HH and AIII at elevated temperatures. AII is formed at temperature between 200°C and 1180°C. Above 1180°C, AI is formed. If temperature below 1180°C it reverts to AII.

2.7.3 Multiphase plaster (MP)

MP, anhydrous plaster and overburnt plaster are produced in dry calcining processes at temperatures between 300 and 900°C, for the most part they are calcined anhydrite (AII). There are three reaction stages :

a.) AII–s (slowly soluble anhydrite), produced between 300 and 500°C.

b.) AII–u (insoluble anhydrite), produced between 500 and 700°C.

c.) AII–E (partially dissociated anhydrite, Estrichgips), produced above ≈ 700°C.

In use, the difference among these products lies in rates of rehydration with water, which for AII-s fast, for AII-u slow and for AII-E in between, a little faster than AII-u. Transition between these different stages of reaction is possible. The properties and final phase composition of MP are shown in Tables 2.6 and 2.7.

Table 2.6 Properties of calcined gypsum (Wirsching, 1975).

Mode of production	Type of plaster	sieve residue >0.2mm,%	Combined water, %	Einstreu-menge E, g. plaster/ 100g. H_2O	Water to plaster ratio, 100/E	Setting time min		Strength of set and hardened gypsum			Density of dry gypsum	uses
						initial	final	flexural sterngth N/mm^2	com-pressive strength N/mm^2	hard-ness N/mm^2	kg/m^3	
Natural gypsum												
Rotary kiln	β-plaster (plaster of Paris)	1.0	4.1	137	0.73	13	28	4.8	11.2	19.1	1069	gypsum building component special building plasters
Kettle	β-plaster (plaster of Paris)	3.3	5.6	156	0.64	9	22	5.2	14.0	26.8	1133	gypsum building component special building plasters
Conveyor kiln	multiphase plaster (construction plaster)	36.6	0.8	167	0.60	6	35	5.1	15.5	25.9	1225	machine-applied plaster, multiphase plaster
Autoclave	α-plaster (molding plaster)	0	6.2	263	0.38	10	22	12.3	40.4	92.0	1602	molding plaster, industrial plaster, dental plaster
Flue-gas gypsum												
Rotary kiln (Knauf process)	β-plaster	3.1	3.4	135	0.74	9	21	4.7	11.0	21.5	1064	premixed plaster, bonding plaster, jointing plaster, gypsum building component
Kettle (Knauf process)	β-plaster	2.6	5.2	139	0.72	14	28	5.2	13.5	19.5	1070	premixed plaster, bonding plaster, jointing plaster, gypsum building component
Conveyor kiln (Knauf process)	multiphase plaster	26.2	2.0	177	0.56	6	20	6.7	20.8	34.1	1353	machine-applied plaster, multiphase plaster
Autoclave (Nitto Gypsum process)	α-plaster	0	6.0	270	0.37	13	26	12.0	45.0	90.2	1580	molding plaster, industrial plaster, dental plaster

*The test of the properties are carried out in accord with DIN 1168. The water to plaster ratio is calculated on the basis of quantity of gypsum plaster, g. in 100 g. of water. In German this is called the Einstreumenge and represented by E.

Table 2.7 Phase composition in% of overburnt plaster, plaster of paris and MP* (Wirsching, 1975).

	Plaster of Paris (rotary kiln)	Over-burnt plaster (con-veyor kiln)	Multiphase plaster, a mixture of plaster of Pa-ris and over-burnt plaster
Dihydrate, $CaSO_4 \cdot 2H_2O$	0-0.5	0-2	0-2
β-Hemihydrate, β-$CaSO_4 \cdot 1/2\,H_2O$	75	6	26
β-Anhydrite III, β-$CaSO_4$III	19	18	14
Anhydrite II, $CaSO_4$II**	5	74	58

* Impurities not considered. ** Consisting of reaction stages AII-s (slowly soluble A), AII-u (insoluble A), and AII-E (*Estrichgips*)

In MP, also in overburnt plaster and anhydrous plaster, these three stages of reaction have to have a definite ratio which is determined jointly by the raw material and the calcining process. In some of these processes (Schwiete and Knauf, 1969) the gypsum is calcined in such a way that the anhydrite phase is obtained along with the HH. In other processes the anhydrite phase is produced separately and mixed with β-HH afterwards. Plaster of various phase compositions are shown in Fig. 2.17.

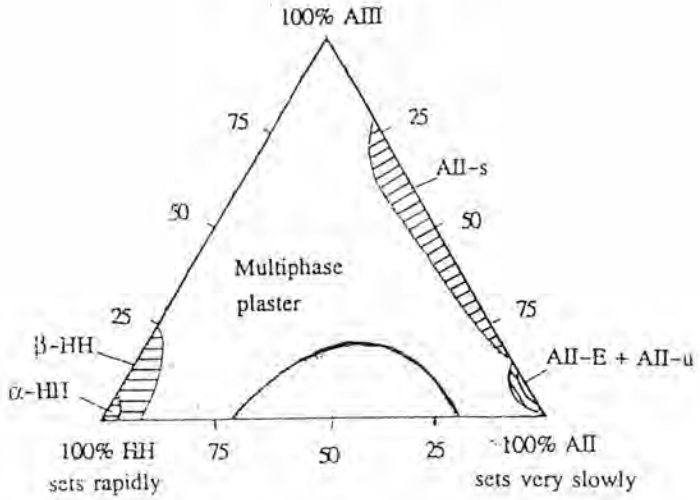

Fig. 2.17 Three-phase composition diagram of calcined gypsum, point P indicates the composition of MP consisting of 26% β-HH, 14% AIII and 58% AII (Wirsching, 1975).

2.8 Application and properties of gypsum plasters and products

2.8.1 Hydration, setting and hardening of gypsum plaster

HH, AIII and AII undergo hydration under ambient conditions, converting into DH. If hydration is carried out with just enough water to produce a homogeneous fluid, stable and nonsedimenting slurry, then this mixture sets and hardens because the crystal growth of DH forms interlocking needles.

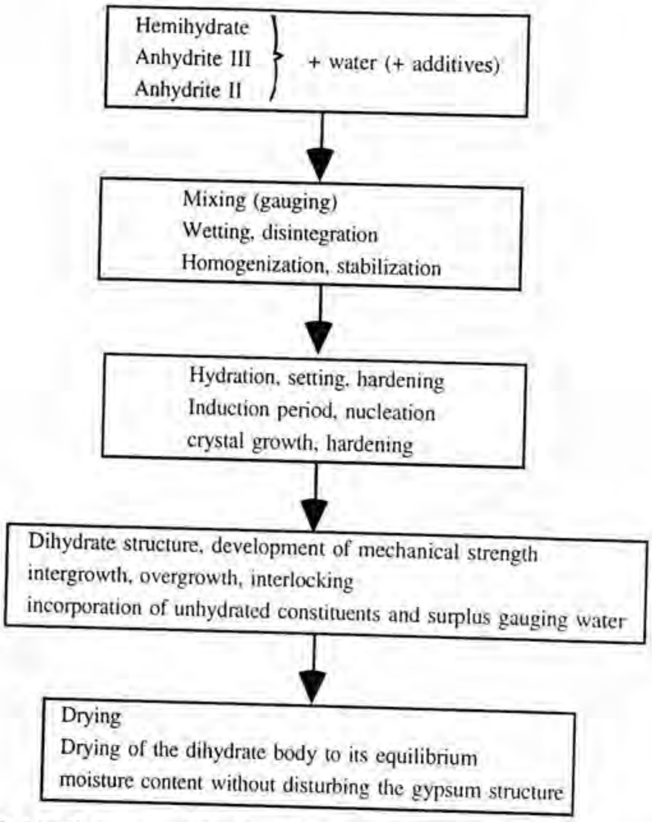

Fig. 2.18 Stages of hydration, setting and hardening of calcium sulfates (Wirsching, 1975).

Formation of DH crystals conforms to the law of nuclei formation and crystal growth. Mixing and wetting of the HH with water, it is converted directly into DH. There are no intermediate stages. AIII is converted via the HH and AII is converted directly into DH without AIII or HH intermediates.

After adding gypsum plasters to water which causes disintegration of the particles, it is followed by a short induction period, after which nuclei begin to form from the supersaturated solution, the accumulation of very small DH crystals with much excess water as clustering. Subsequently, after this nucleation, crystal growth begins which at least initially is accompanied by continuous recrystallization (described by Kronert and Haubert, 1972).

If the proportion of water is correct for setting and hardening, the slurry hardens by forming a DH structure, a final crystallization which according to Ludwig and Kuhlmann (1974) consists of intergrown, overgrown and interlocking of the long needle-like DH crystals and inclusion of unhydrated components. Excess water can be removed by drying.

Fig. 2.19 SEM micrograph of Structure of set and hardened gysum, the structure shows the needle-like particles that interlock and intergrow (Wirsching, 1975).

2.8.3 Aridization

Kuntze (1967) and Lehmann, Mathiak and Kurpiers (1973) reported that when calcined gypsums were stored, there was a change in their properties, called aging. This aging was caused by the uptake of water vapor from the air and formed dihydrate nuclei, accelerating the hydration process. To avoid this phenomenon, methods had been developed to bring about aging artificially. One method was called aridization, calcium chloride or similar salts were added in quantity up to about 0.2 wt% to the raw gypsum before the calcination.

2.8.3 Physicochemical properties of gypsum plaster

HH, AIII and AII can rehydrate in the presence of water, forming gypsum. Benze (1969) and Knauf, Kronert and Haubert (1972) proposed that the setting and hardening could be accelerated or retarded by numerous additives (as shown in Tables 2.8 and 2.9). The hydration of AII usually does not have to be retarded since it is slow enough and almost always requires acceleration. Many organic acids and their salts are useful as accelerators, especially sulfuric acid and its salts. DH is regarded as a special additive in this respect. Finely divided, it acts as a strong accelerator.

Worrall (1975) reported that the setting time and set strength could be modified considerably by the addition of suitable electrolytes. Among those that accelerate the setting is potassium sulfate, in addition to the majority of sulfate and chlorides of the alkaline metals. Retarders include borax, acetates and citrates, gelatin, starch.

Koslowski and Ludwig (1983) reported that retarders were usually organic acids and their salts and organic colloid that were the decomposition and hydrolysis product of biopolymers such as proteins as well as salts of phosphoric acid or boric acid.

Table 2.8 Effect of retarders on setting time of gypsum plasters (Jinawath, Sunalai and Mongkolkajit, 1996).

Additive [a]	Amount (g)	Induction period (min)	Final set (min)	Maximum ($^{\circ}$C/min) ▲T^{b}
none	-	37	76	1.6
$NaC_2H_3O_2$	1.7	60	110	-
$NH_4C_2H_3O_2$	0.8	70	118	1.1
$Na_2B_4O_7.10H_2O$	0.9	178	218	-
Succinic acid	0.2	213	271	0.5
Tartaric acid	0.2	61	106	1.0
Gelatin	0.1	-	240	-

[a] the retarder was dissolved in 60 ml of water and then mixed with 100 g of HH.

[b] maximum temperature rise in °C for a one minute interval.

Table 2.9 Effect of accelerators on setting time of gypsum plasters (Jinawath et al., 1996).

Additive [a]	Amount (g)	Induction period (min)	Final set (min)	Maximum (°C/min) ▲T[b]
none	–	37	76	1.6
Starch	1.0	29	68	1.4
$Al_2(SO_4)_3.18H_2O$	1.7	25	60	1.8
Na_2SO_4	0.4	10	33	3.2
$CuSO_4$	0.8	27	63	1.4
$CaSO_4.2H_2O$	2.0	N.I.[c]	39	1.8
K_2SO_4	1.0	N.I.[c]	28	5.1
$Ca(OH)_2$	1.0	23	58	1.8
NaCl	1.0	12	30	4.0

[a] the retarder was dissolved in 60 ml of water and then mixed with 100 g of HH.

[b] maximum temperature rise in °C for a one minute interval.

[c] no apparent induction period.

2.8.4 Factor affecting strength

The strength of set dried gypsum is directly proportional to its density, therefore dependent only on its porosity or on the water to plaster ratio and the size and structure of the pores (Satava, 1967). Albrecht (1953) reported that the strength was affected by moisture or additives without a change in density. The strength of gypsum products with a moisture content exceeding 5 % was only about one half that of air dried gypsum products (as shown in Fig. 2.20).

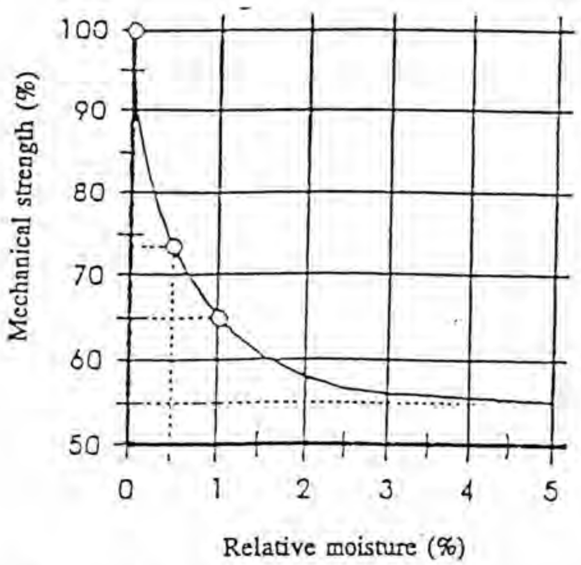

Fig. 2.20 Effect of relative moisture on mechanical strength of gypsum products (Lafarge, 1990).

Wandser (1962) reported that moist conditions reduced strength because of crystalline and textural changes, especially recrystallization which took place as a result of the solubility of gypsum in water. The deformation or creep of moist gypsum products under mechanical stress was likewise the result of structural change. Additive induced a change in structure by changing the crystal habit of the DH so that without a change in density, strength was changed even in dry state.

2.8.5 Characteristics of gypsum building materials for the construction

(a.) Plastering materials

Calcined gypsum is used for plastering. The best is MP because its phase composition results in quick initial setting and gradual final setting, smoothness, plasticity, high coverage, single-coat application, rapid drying of the finished plasterwork and high strength.

β-HH plaster without additives is not suitable for plastering because the initial setting occurs too late and the final setting too early and its particle size distribution is not suitable for plastering. However, additives, e.g., expanded perlite or vermiculite permit β–HH to be made into certain types of plastering material (Knauf, 1961).

Premixed gypsum plasters (projection plaster, bonding plaster and lightweight plaster), factory processed from MP or β–HH containing additives, are worked batchwise on site. The plaster is mixed with water and applied in one coat on all types of concrete and masonry. Premixed plasters already contain the necessary additives to ensure good workability. The application properties of these plasters are lists in Table 2.10.

<u>Table 2.10</u> Applicationsof projection plaster, bonding plaster and lightweight plaster (Wirsching, 1975).

Property	Projection plaster	Bonding plaster	Lightweight plaster
Water : plaster ratio	0.45–0.55	0.60–0.70	0.55–0.65
Initial setting, min	60–120	50–90	50–90
Final setting, min	170–220	80–200	100–170
Strength of set and hardened gypsum, N/mm^2			
Flexural strength	1–2	1–2	1–2
Compressive strength	4–6	3–5	3–7
Apparent density of dry gypsum, kg/m^3	1000–1200	850–1000	900–1100
Coverage, m^2 per 100 kg of plaster	9–10	13–14	12–13

* Tests conform to German (DIN) standard 1168 [48]

(b.) Gypsum plasterboards

Gypsum building components are manufactured in large quantities : plasterboards, partition panels, ceiling tiles and fiber–reinforced boards. These are light, porous, dry and nonbrittle products possessing excellent workability. β–HH is the starting material for all of these because it sets quickly and has certain properties for the finished product.

Many different types of gypsum plasterboards are manufactured, depending on their intended use. Distinctive features are size, edge configuration, weight, water resistant properties, structural behavior and strength. Gypsum plasterboard is used for both sheathing and finishing for interior walls and ceilings, it consists of set gypsum plaster. To produce them, β-HH is mixed with water (W/P 0.9-1.0) and the slurry, which sets quickly, is poured into molds. After 5-8 min they are taken out of the mold and dried. Then they are covered on each side with a kraft paper which has ivory color on the face side while the back is gray (Aeppli, 1972).

Table 2.11 Gypsum building materials and their properties (Wirsching, 1975).

	Plasterboard. 9.5 mm thick	Finished gypsum projection plaster
Apparent density and porosity		
Density, kg/m^3	900	1200
Pore voiume, %	60*	50
Pore radius, µm	≈ 99% > 0.05	≈ 99% > 0.05
Climatic properties		
Heat conductivity λ, WK^{-1}m^{-1} (DIN 4108)	0.21	0.35
Heat penetration coefficient b (equivalent)		
1/2-h test; J s$^{-1/2}$ m^{-2} K^{-1}	412	1172
2-h test	489	1410
Resistance to transmission of water vapor μ (DIN 4108)	8	10
Water vapor absorption coefficient a, m/h		
untreated surface	2.29	
rough fiber coated	2.98	2.5
wallpapered	2.66	
Heat expansion and equilibrium moisture content		
Linear coefficient of thermal expansion α_t, K^{-1}	13 × 10^{-6}	20 × 10^{-6}
Equilibrium moisture content at 20 °C and 65% relative humidity, wt%	0.5	0.3
Modulus of elasticity, N/mm^2	3000	2800

* Core