



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 ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$ ) and calcium sulfite<sup>(4,5)</sup> and is almost pure white color<sup>(6)</sup>. Chemical composition of FGD is as shown in Table 2.1. About 5.4 tons of gypsum are produced per ton of sulfur in fuel.

The net reaction :



Table 2.1 Chemical composition of some calcium sulfates.<sup>(2)</sup>

Characterization	Natural gypsum		Natural anhydrite		FGD gypsum		Phosphogypsum		Fluoroanhydrite
	1	2	3	4	5	6	7	8	9
Mineralogical analysis									
CaSO <sub>4</sub> ·2H <sub>2</sub> O	91.6	96.4	6.0	3.8	97.5	93.0	97.6	96.5	0.0
CaSO <sub>4</sub>	6.4	0.9	88.8	83.7	0.0	0.0	0.0	0.0	94.7
MgCO <sub>3</sub>	0.1	0.6	2.0	3.6	0.0	0.0	0.0	0.0	0.0
CaCO <sub>3</sub>	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
CO <sub>3</sub>	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 <sub>2</sub> O <sub>3</sub> + Al <sub>2</sub> O <sub>3</sub>	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 <sub>2</sub> O	0.02	0.01	0.04	0.11	0.01	0.47	0.14	0.02	0.03
Total P <sub>2</sub> O <sub>5</sub>	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
Other					0.20SO <sub>2</sub>				0.11ZnO
					0.01Cl				0.69K <sub>2</sub> O
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 Chemistry and Physics of calcium sulfate hydrate (CaSO<sub>4</sub>·xH<sub>2</sub>O)

### 2.2.1 Dehydration and rehydration

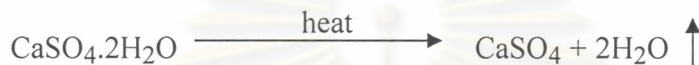
Gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), both as natural gypsum and synthesized gypsum such as FGD gypsum and phosphogypsum is useful as industrial material because

- it readily loses its water of hydration when heated, produces partially or totally dehydration calcined gypsum.

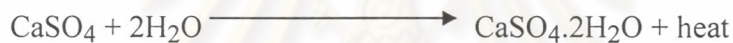
- when water is added to this calcined gypsum, it reverts to the original dihydrate, the set and harden product.

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

Dehydration.



Rehydration.



Kelly et al.<sup>(7)</sup> made a through study of the thermodynamic properties of the  $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$  system. Table 2.2 and Table 2.3 list the heat of hydration and dehydration of the various phase changes that are of industrial significance.

Table 2.2 Heats of hydration<sup>(2)</sup>.

Phase change	Heat of hydration per mole (gram) of dihydrate at 25°C.J
$\beta\text{-CaSO}_4 \cdot 1/2\text{H}_2\text{O} + 3/2\text{H}_2\text{O} (\text{l}) \longrightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	19300±85 (111.9±0.50)
$\alpha\text{-CaSO}_4 \cdot 1/2\text{H}_2\text{O} + 3/2\text{H}_2\text{O} (\text{l}) \longrightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	17200±85 (100.00±0.50)
$\beta\text{-CaSO}_4\text{III} + 2\text{H}_2\text{O} (\text{l}) \longrightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	30200±85 (175.3±0.50)
$\alpha\text{-CaSO}_4\text{III} + 2\text{H}_2\text{O} (\text{l}) \longrightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	25700±85 (149.6±0.50)
$\text{CaSO}_4\text{II} + 2\text{H}_2\text{O} (\text{l}) \longrightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	16900±85 (98.0±0.50)

Table 2.3 Heats of dehydration<sup>(2)</sup>.

Phase change	Heat of dehydration per mole or tonne Of dehydration products at 25°C	
	J/mol	KJ/mol
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \longrightarrow \beta\text{-CaSO}_4 \cdot 1/2\text{H}_2\text{O} + 3/2\text{H}_2\text{O} (\text{g})$	86700	597200
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \longrightarrow \alpha\text{-CaSO}_4 \cdot 1/2\text{H}_2\text{O} + 3/2\text{H}_2\text{O} (\text{g})$	84600	587200
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \longrightarrow \beta\text{-CaSO}_4\text{III} + 2\text{H}_2\text{O} (\text{g})$	121800	895700
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \longrightarrow \alpha\text{-CaSO}_4\text{III} + 2\text{H}_2\text{O} (\text{g})$	117400	863100
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \longrightarrow \text{CaSO}_4\text{II} + 2\text{H}_2\text{O} (\text{g})$	108600	79800

### 2.2.2 Phase of calcium sulfate hydrate system ( $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ )

The  $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$  system is characterized by five solid phases as shown in Table 2.4.

- Calcium sulfate dihydrate,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , (DH).
- Calcium sulfate hemihydrate,  $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$ , (HH).
- Anhydrite III,  $\text{CaSO}_4$ , (AIII).
- Anhydrite II,  $\text{CaSO}_4$ , (AII).
- Anhydrite I,  $\text{CaSO}_4$ , (AI).

Table 2.4 Phases in  $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$  system<sup>(2)</sup>.

Characteristic	DH	HH	AIII	AII	AI
Formula	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	$\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$	$\text{CaSO}_4$	$\text{CaSO}_4$	$\text{CaSO}_4$
Molecular mass	172.17	145.15	136.14	136.14	136.14
Thermodynamic Stability, °C	< 40	Metastable*	Metastable*	40-1180	> 1180
Forms or stages		Two forms : $\alpha$ $\beta$	Three stages : $\beta$ -anhydrite III $\beta$ -anhydrite III' $\alpha$ -anhydrite III Soluble anhydrite	Three stages : AII-s, slowly soluble AII-u, insoluble AII-E, Estrichgips	
Other name, often based on the application	Gypsum Raw gypsum Synthetic gypsum Chemical gypsum Byproduct gypsum Set gypsum Hardened gypsum	$\alpha$ -form : $\alpha$ -hemihydrate Autoclave plaster $\alpha$ -plaster $\beta$ -form : $\beta$ -hemihydrate Stucco plaster $\beta$ -plaster Plaster of paris		Raw anhydrite Natural anhydrite Anhydrite Synthetic anhydrite Chemical anhydrite Byproduct anhydrite Calcined anhydrite	High temperature anhydrite
Synthesis condition Temperature, °C and atmosphere	< 40	$\alpha$ -form : > 45 From aqueous solution $\beta$ -form : 45-200 In dry air	$\alpha$ - and $\beta$ -AIII : 50 and vacuum or 100 in air $\beta$ -AIII' : 100 In dry air	200-1180	> 1180
Production temperature, °C	< 40	$\alpha$ -form : 80-180 $\beta$ -form : 120-180	$\beta$ -AIII and $\beta$ -AIII' : 290 $\alpha$ -AIII : 110	300-900, specifically AII-s : < 500 AII-u : 500-700 AII-E : > 700	Not produced commercially

\* Metastable 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  $1180^\circ\text{C}$ <sup>(8)</sup>. So, it is not possible to produce a stable form of AI below that temperature.

### 2.2.3 Synthesis of different phases in $\text{CaSO}_4 \cdot x\text{H}_2\text{O}$ system<sup>(2)</sup>.

The thermodynamic stability ranges for the calcium sulfate phases are shown in Table 2.2. Below  $40^\circ\text{C}$ , 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 :



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

#### 2.2.3.1 Calcium sulfate hemihydrate (HH)

HH is occurred in two different forms  $\alpha$  and  $\beta$ , 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.

$\beta$ -HH is produced by simply heating under atmospheric condition at temperatures of about  $160^\circ\text{C}$  in a kettle or rotary kiln. If the heating is carried out under steam pressure in an autoclave, form of  $\alpha$ -HH can be obtained.  $\alpha$ -HH crystals (Fig. 2.1a) are prismatic and more regular in shape and have a smoother surface than  $\beta$ -HH (Fig. 2.1b).

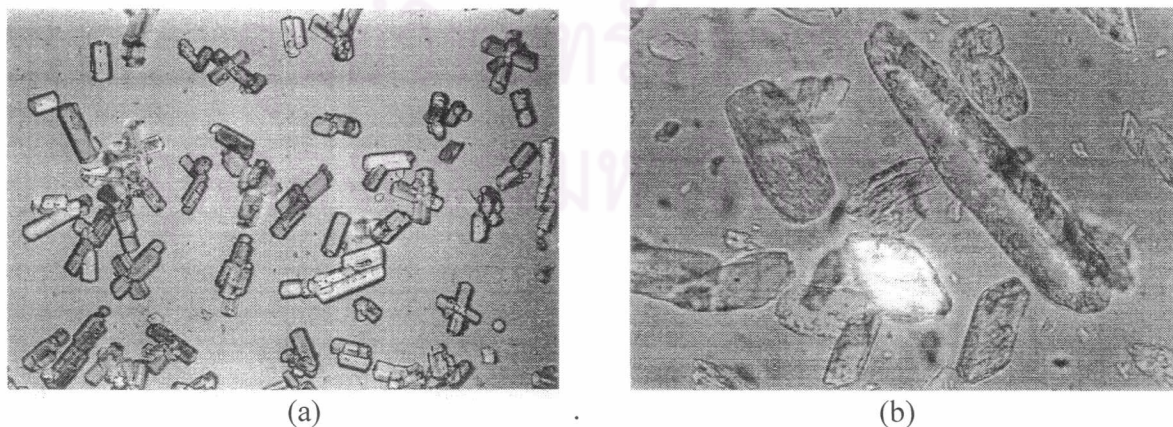


Fig. 2.1 Optical photographs of a.)  $\alpha$ -HH crystals and b.)  $\beta$ -HH crystals at polarized light<sup>(9)</sup>.

During the transformation to  $\alpha$ -HH by a controlled hydrothermal treatment, totally-new clearly-defined crystals form. Their size lies in the range of 1 to 1000  $\mu\text{m}$ , they are not porous and they do not disintegrate in contact with water. A plaster made of such a crystalline powder has a considerably lower water demand than  $\beta$ -HH. Thus, The product obtained from this plaster is much stronger and harder than that resulting from  $\beta$ -HH. Although particle size and the total surface area is one of the chief factors in determining the amount of gauging water required, the particle size distribution also plays an important role.

#### Production of $\alpha$ -HH<sup>(2,8)</sup>

##### a.) The classical vapor process (dry process)

Raw gypsum of appropriate quality in lump size is heated in an autoclave to temperatures between 110 and 150°C. The residence time can reach several hours, and depressurising, drying and grinding follow. Finally the material is heated again in order to eliminate residual dihydrate, when the process being carried out in batches. The method is robust and is therefore still used in most cases today.

##### b.) The classical suspension process (wet process)

In this case a suspension of fine particulate raw gypsum is heated in an autoclave. Generally, additives are used which control the crystal habits. The process can be carried out in batches, although the more economical continuous operation can also be used. Residence times are lower than those of the vapour process. The working temperature lies in the order of 135°C. Higher temperatures generate small crystals, and lower temperatures extend the necessary residence time. The process is able to use fine crystalline by-product gypsum (e.g. phospho-citro-titano-or FGD gypsum), which can be used wet off the filter. This process is more complex to control than vapor process.

##### c.) Pressureless process (Autoclave-free process)

These processes use the fact that the vapor pressure is reduced in solution of an electrolyte. Since the vapor pressure of dihydrate is close to that of water, the dehydration can take place at atmospheric pressure, and therefore

an autoclave is not needed. Many different salts, acids and even organic compounds have been proposed as appropriate electrolytes.

#### Action mechanism of crystallization modifiers<sup>(10)</sup>

A preliminary study indicated that the addition of crystallization modifiers during dynamic slurry hydrothermal dehydration increases grain size and decreases aspect ratio of  $\alpha$ -HH, which results in a decrease in water requirement and an improvement of strength. The mechanism is briefly described as follows :

$\alpha$ -HH belongs to the hexagonal crystal system and its crystal faces have different properties. In the absence of crystallization modifiers,  $\alpha$ -HH grows in the C-axis direction more rapidly than in other directions and ends in the form of a fine needle crystal. The crystallization modifiers are selectively adsorbed on C-axis crystal faces and restrain growth of crystal in this direction. Thus, short prisms or even hexagonal plates are obtained.

Common organic crystal habit modifiers used in gypsum based systems are organic acids, amines and their derivatives; common inorganic crystal habit modifiers are divalent metal ions and divalent anions based on metallic elements (such as  $\text{HPO}_4^{2-}$ ,  $\text{AlF}_5^{2-}$  and  $\text{SiF}_6^{2-}$ ). The organic modifiers affect crystal growth by selective adsorption onto the growing C-axis crystal faces and restrain growth of crystal in this direction. Thus, short prisms or even hexagonal plates are obtained. The inorganic modifiers affect crystal growth by substitution in the growing lattice for either  $\text{Ca}^{2+}$  or  $\text{SO}_4^{2-}$ . The latter result in a gypsum crystal with co-crystalline impurities that is essentially a solid solution of a dilute second phase in the gypsum crystal.

#### 2.2.3.2 Calcium sulfate anhydrite III (AIII)

Lehmann and Rieke<sup>(11)</sup> postulated three limiting stages for AIII, also known as soluble anhydrite :  $\beta$ -AIII,  $\beta$ -AIII' and  $\alpha$ -AIII.  $\beta$ -AIII is produced from the DH by careful heating at 50°C in a vacuum or up to about 200°C at atmospheric pressure.  $\beta$ -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  $\alpha$ -AIII.

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

### 2.2.3.3 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.

### 2.2.3.4 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 2.5.



Table 2.5 Properties of calcined gypsum<sup>(2)</sup>.

Mode of production	Type of plaster	Sieve residue >0.2mm,%	Combined water,%	Einstreumenge E, g plaster/ 100g H <sub>2</sub> O	Water to plaster ratio, 100/E	Setting time (min)		Strength of set and hardened gypsum			Density of dry gypsum	Uses
						Initial	Final	Flexural strength N/mm <sup>2</sup>	Compressive strength N/mm <sup>2</sup>	Hardness N/mm <sup>2</sup>	kg m <sup>3</sup>	
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 plaster
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 plaster
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 calculate on the basis of quality of gypsum plaster, g. in 100 g. of water. In Germany, this is called the Einstreumenge and represented by E

### 2.3 Pozzolanas

The term 'pozzolana' has two distinct meaning. The first one indicates the pyroclastic rocks, especially glassy and sometimes zeolitised, which occur either in the neighborhood of Pozzouli (the ancient Puteoli of the Roman times) or around Rome<sup>(12)</sup>. The second meaning includes all those inorganic materials either natural or artificial, which harden in water when mixed with calcium hydroxide (lime) or with materials that can release calcium hydroxide (Portland cement clinker). Nowadays the term 'pozzolana' will be referring to the latter meaning, definitely wider than the former, and will therefore embrace a large number of very different materials in terms of origin, composition, and structure.

The more commonly accepted classification concerns the origin of pozzolanas and therefore the first subdivision is between natural and artificial materials. Natural materials do not require any further treatment apart from grinding ; artificial pozzolanas result from chemical and/or structural modification of materials originally having no or only weak pozzolanic properties. The later can be residues of certain production methods or products manufactured from selected raw materials.

The classification of pozzolanas shown in Fig. 2.2<sup>(13)</sup> is basically identical to that proposed at the 6<sup>th</sup> International Congress on the Chemistry of Cement held in Moscow in 1974.

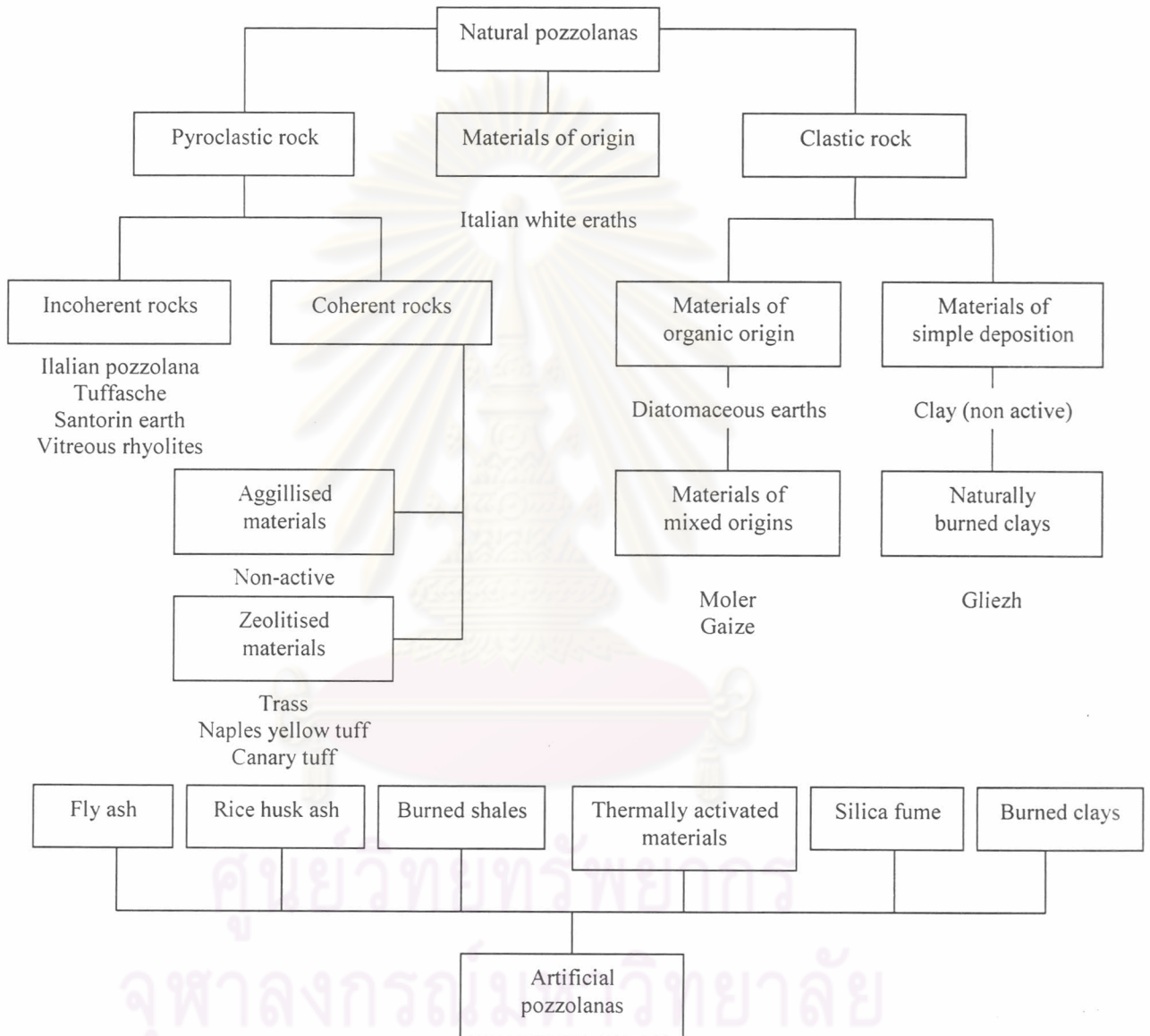


Fig. 2.2 Classification of pozzolanas<sup>(13)</sup>.

### 2.3.1 Natural pozzolanas

#### 2.3.1.1 Materials of volcanic origin (pyroclastic rocks)

Pyroclastic rocks are resulted from explosive volcanic eruptions which project minute particles of melted magma into the atmosphere. The rapid pressure decrease occurring during the eruption causes the gases originally dissolved in the liquid magma to be released. As a consequence, each particle will contain a number of microscopic bubbles and ducts forming microporous structure<sup>(14)</sup>. Simultaneously, the particles are subject to a quenching process which is responsible for their glassy state. The materials can be deposited either on the ground or water. Generally, the ground deposits, which are loose and heterogeneous are composed of ashes mixed with fragments coming from the volcanic duct walls or the base of the volcano.

#### 2.3.1.2 Materials of sedimentary origin

Clays and the so-called diatomaceous earths are sedimentary rocks which are capable of combining with lime. The former originates from the alteration of igneous rocks whereas the latter form from the siliceous skeletons of microorganisms (diatoms) deposited in the fresh or sea waters. Since both materials are resulted from deposition in water in spite of their different origin, it is not surprising that diatoms and clay minerals occur mixed together.

Clay minerals<sup>(15-18)</sup>, especially those belonging to the montmorillonite group, can react with lime giving calcium silicate and aluminate hydrate but they can not replace pozzolana as they increase the water demand and lower the strength of mortar and concrete.

Diatomaceous earths are highly reactive towards lime owing to their high content of amorphous silica and high specific surface area. In spite of the strongly pozzolanic behavior, the use of diatoms in pozzolanic cements is hampered by their huge specific surface area which causes the water demand of cement to increase. Small additions of diatomites to concrete improve plasticity and reduce bleeding.

Gaize is a sedimentary rock which contains 30-35% of active silica, which is easily soluble in potassium hydroxide solutions and confers a certain pozzolanic

activity to the rock<sup>(19)</sup>. Gaize contains up to 50% quartz and substantial amount of clay minerals. Since these minerals can reduce the workability of mortars, gaize is used after burning at about 900°C<sup>(19,20)</sup>.

### 2.3.1.3 Materials of mixed origin (hybrid rocks)

The stratified deposits of a crumbly rock composed of materials of different origin (volcanic, sedimentary, and organic). The upper layers show a silica content up to 90%, considerable loss on ignition and small amount of other oxides. As far as the innermost deeper layers are concerned, the silica content is appreciably less ; alumina can reach about 20%, but other oxides are present only in very small amount<sup>(21)</sup>. The low iron content explains the light color of these materials, generally known as white earth. For the layers that are richer in silica, FTIR analysis shows a band at 0.405 nm that is typical of dried silica gel, which is attributed to the groundmass. In the patterns of the high-alumina layers, this band fails to occur and peaks of montmorillonite-type clays attacked by acid solution appear<sup>(22)</sup>. The crystalline minerals, sometimes clear but often altered, consist of feldspar, biotite, quartz, zeolite, and diatomite skeletons<sup>(23)</sup>.

## 2.3.2 Artificial pozzolans

### 2.3.2.1 Fly ash

Fly ashes are consisted of finely divided ashes produced by burning pulverized coal in power stations. They are removed from the combustion gases and collected by special mechanical devices and electrostatic precipitators. Owing to the high temperature reached during the instantaneous burning of coal, most of the mineral component contained in the coal melts and forms small fused drops. The subsequent sudden cooling transforms them partly or entirely into spherical glass particles.

Fly ashes are considered to be composed to relatively few mineral phases, since the coal mineral matter dose not contain more than five or six components ; clay minerals, pyrite, quartz, and one or two calcium, iron, magnesium carbonate<sup>(24)</sup>. Moreover, considering the mineral distribution in the coal and burning conditions in the

boilers, every particle is probably produced by coal fragments containing only one or two mineral species<sup>(25)</sup>.

Fly ashes particles are typically spherical and glassy, but they also show other typologies. An ash particle classification, based on criteria such as shape, color, crystallinity and texture, is given in Table 2.6<sup>(25)</sup>. The finest glassy particles are generally thick but many are hollow. Sometimes the biggest ones look like empty spheres filled with other smaller spherical particles. Other types of particles are irregular and sometimes contain a variable amount of bubbles, which makes them take on a spongy aspect, or a high content of crystalline minerals. The morphology and behavior of fly ashes depended on the burning process<sup>(26)</sup>. The particle diameters of fly ash range from  $< 1$  to  $> 150 \mu\text{m}$ . Specific surface area is extremely variable ranging from  $< 2000$  to  $> 8000 \text{ cm}^2/\text{g}$  (Blaine), but sometimes lower and higher values occur<sup>(25)</sup>.

**Table 2.6** Types of fly ash particles characterized by microscopic examination<sup>(25)</sup>.

Type	Shape	Color	Crystalline and texture	Characteristic size ( $\mu\text{m}$ )	Comment
1	Spherical and rounded	Colorless	a.) Glassy, clear, solid b.) Glassy, containing small bubbles c.) Glassy, with crystal traces d.) Predominantly crystalline, solid	0-20  10-50	Deepening color suggests
2	Spherical and rounded	Light brown to black	Lighter colored ones, glassy ; all solid	5-30	increasing iron content
3	Rounded	White in reflected light	Glassy, spongy	10-200	Small and large bubbles, giving a range from foam to cenospheres
4	Irregular	Light brown	Partially crystalline, solid	10-100	Irregularity of profile and surface very marked
5	Irregular	Varicolored in reflected light	Partially crystalline, solid	50-500	Agglomerated particles, apparently sintered ; generally containing red particles and areas
6	Irregular	Black	Solid or porous	20-200	Partially burnt coal particles, sometime containing mineral matter
7	Angular	Colorless	Crystalline, solid	10-100	Probably quartz
8	Angular	Red	Crystalline, solid	5-50	Probably hematite

### 2.3.2.2 Burned clays and shale

Clay mineral gains a distinct pozzolanic activity when burned at temperatures between 600 and 900°C. The loss of combined water due to the thermal

treatment causes the crystalline network on the clay minerals to be destroyed. While silica and alumina remain in a messy, unstable, amorphous state. Heating does not affect anhydrous minerals such as quartz or plagioclase, so that pozzolanic activity depends only on the clay mineral content as well as on the thermal treatment conditions<sup>(27-29)</sup>.

The burning or retorting of certain oil shales produce ashes which harden when mixed with water. Their chemical composition varies largely according to their origin. The silica content can vary between 22% and 42%<sup>(30)</sup> and conversely lime can vary between 55% and 22%<sup>(31)</sup>. Burned shales have a more complicated mineralogical composition than burned clays depending on their composition, temperature and duration of burning. As an example, shale burned at temperature ranging between 750 and 840°C contains  $\beta$ -quartz,  $\beta$ -cristobalite, calcite,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, and muscovite, which are already present in shale, and gehlenite, anorthite, wollastonite, orthoclase, anhydrite, and CaO formed during the burning process<sup>(31)</sup>.

### 2.3.2.3 Microsilica

The manufacturing processes of silicon metal and ferrosilicon alloys in an electric arc furnace at temperatures up to 2000°C generate a fume containing spherical microparticles of amorphous silicon dioxide. This is the reason why the product is called 'silica fume' or, owing to its form and chemical composition, 'microsilica', 'condensed silica fume', volatilized silica<sup>(32)</sup>. The reduction of quartz to silicon releases gaseous SiO. This is transported by combustion gases to lower-temperature zones where it is oxidized by air and condenses in the form of tiny particles of silicon dioxide.

The main features of microsilica are high silica content, high specific surface area and amorphous structure. These characteristics account for the substantial pozzolanic activity of microsilica, in terms of both its capacity of binding lime and rate of reaction. Microsilica particles are spherical and have an average diameter of 0.1  $\mu\text{m}$ . The BET specific surface area ranges from 15 to 25  $\text{m}^2/\text{g}$ , with typical values of 20  $\text{m}^2/\text{g}$ <sup>(33)</sup>.

### 2.3.2.3 Other materials

Ash exhibiting a marked pozzolanic character can be obtained by burning rice husk within certain temperature ranges. Rice husk ash contains > 80% silica<sup>(34)</sup> and its BET specific surface area is as high as 50-60 m<sup>2</sup>/g or over 152 m<sup>2</sup>/g<sup>(35)</sup>. Crystalline silica, such as quartz and cristobalite, can be present in large amounts depending on the burning conditions.

The pozzolanic activity of rice husk ash depends on the firing temperature and the retention period. The sensitivity to burning conditions is the primary reason which prevents the using of this material as pozzolana<sup>(36)</sup>. The amorphous fraction of rice husk contains silica in polymeric form only<sup>(37)</sup>.

## 2.4 Lime-pozzolana mixes

Until the 19<sup>th</sup> century, lime-pozzolana mixes were the only hydraulic mortars capable of hardening in water and, at the same time, of resisting the attack of aggressive waters, including sea water. Due to their slow rate of hardening, lime-pozzolana-water system is in any help to formulate a correct interpretation of both the behavior and properties of pozzolana-containing cements.

### 2.4.1 Pozzolanic reaction

The terms 'pozzolanic activity' covers all reactions occurring among the active constituents of pozzolans : lime and water. Nevertheless the difficulty in following the evolution of pozzolan's active phases throughout the hydration process, the progress of pozzolanic reaction is commonly evaluated in terms of diminution of the free lime in the system or increase in the silica and alumina soluble in acid<sup>(38)</sup> by using the Florentin attack method.

Pozzolanic activity includes two parameters, namely the maximum amount of lime that a pozzolan can combine and the rate at which such combination occurs. Both factors depend on the nature of pozzolans and, more precisely, on the quality and quantity of the active phases. The heterogeneity of the pozzolana family, as well as the complex phenomena occurring during hydration, do not allow a model of pozzolanic 'activity' to be defined and only enable general trends to be identified.

There is a general agreement that the overall amount of combined lime essentially depends on the following :

1. The nature of the active paste.
2. Their content in pozzolana.
3. Their  $\text{SiO}_2$  content.
4. The lime/pozzolana ratio of the mix.
5. Length of curing.

Whereas the combination rate also depends on :

6. The specific surface area (BET) of pozzolana.
7. Water/solid mix ratio.
8. Temperature.

The amount of combined lime is related to the  $\text{SiO}_2$  content in the active pastes, which ranges in between 45 and 75% in volcanic glass and in fly ash<sup>(39)</sup>, but reaches and sometimes exceeds 95% in very active amorphous microsilica, such as natural silica gels or silica fume<sup>(40)</sup>. This means that in addition to the silica content, other chemical and structural factors play an important role in determining pozzolanic activity. Also, the glasses of fly ashes can have a different composition and structure and this can cause different reactivity levels<sup>(41)</sup>. Combined lime also depends on the curing time (Fig. 2.3), but the rate of combination varies widely between one pozzolana and another. Fig. 2.3 shows that after 90-day curing, the reaction of fly ashes is far from being complete<sup>(42)</sup>.

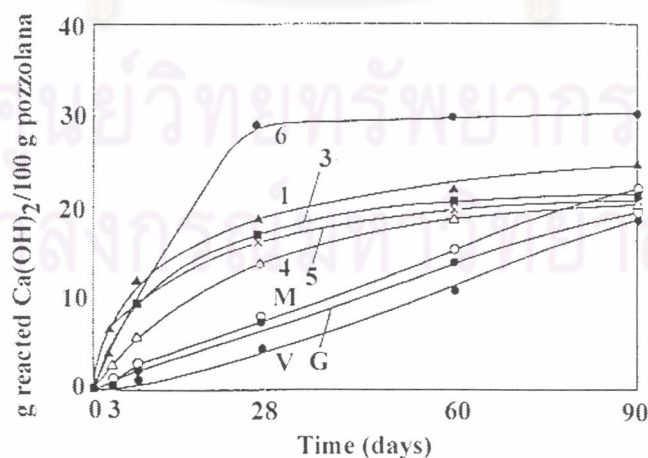


Fig. 2.3  $\text{Ca(OH)}_2$  combined by pozzolana/hydrated lime = 70:30 (1-6 are natural pozzolan, M, G, and V are fly ashes)<sup>(47)</sup>.



The rate of pozzolanic reaction increases with temperature<sup>(43, 44)</sup> (Fig. 2.4). Between 50 and 90°C, 1:3 lime/natural pozzolana mixes, compacted with 10% water under a compressive load of 130 MPa, react quickly, so that most lime is already fixed after 1 day of reaction<sup>(45)</sup>. Above 70°C, however, combined lime tends to stop increasing or to decrease<sup>(45)</sup>. As shown in Fig. 2.5, evidence of this inversion is also found in fly ashes at 60°C and is likely to be due to the variation in the composition of the hydrated phases.

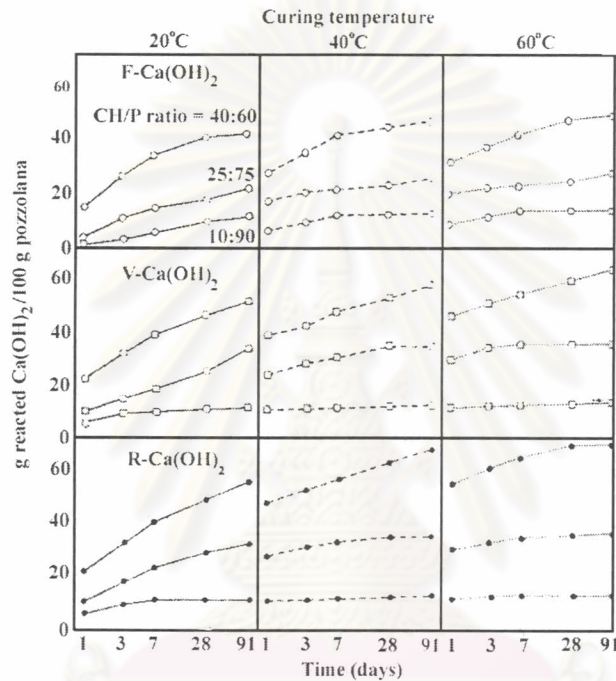


Fig. 2.4  $\text{Ca(OH)}_2$  reacted with pozzolanas F, V, and R estimated by X-ray diffraction analysis varying the mixing ratio and curing temperature, water/binder = 0.56<sup>(44)</sup>.

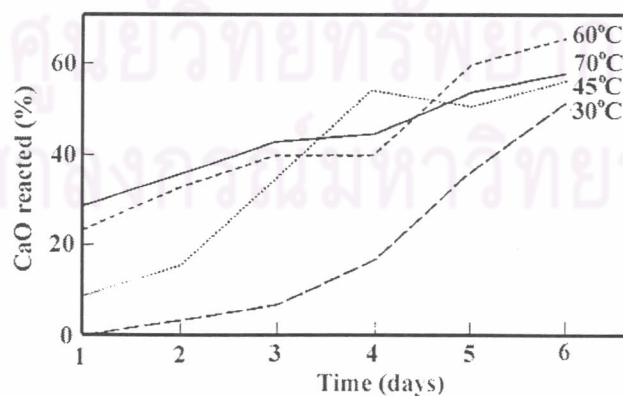


Fig. 2.5 Lime reacted at various time and temperature ( $\text{CaO}/\text{fly ash} = 1.4$ , water/binder = 0.5)<sup>(45)</sup>.

Temperature substantially increases microsilica reactivity : depending on the lime/silica ratio, after 2.5 hours of treatment at 55°C, combined lime is as high as 22-25% of the added CaO and at 90°C it attains 68-90%. After 24 hours of hydration, unreacted lime stabilizes at 3-8% independently of both temperature and CaO/SiO<sub>2</sub> ratio of the mix<sup>(46)</sup>. Conversely, the amount of combined pozzolana, expressed in terms of silica which becomes soluble in acid, always increases with the temperature of hydration.

The pozzolanic reaction is also influenced by other parameters. The addition of gypsum to pozzolana-lime-water (in excess) system<sup>(47, 48)</sup> improves the rate of lime combination. The larger the water content of the mix<sup>(49)</sup>, the higher the rate of lime combination. Thus, the pozzolanic reaction is slower in paste than in dispersion and it is still incomplete after many years.

#### 2.4.2 Reaction products

The reaction of pozzolana-lime mixes produces the same compounds as those which are found upon hydration of Portland cement since the overall chemical composition of the two mixes falls in the same field. Pozzolanas, dispersed in saturated or almost saturated lime water react with lime and form calcium silicate hydrate (C-S-H) and hexagonal aluminates, 4CaO.Al<sub>2</sub>O<sub>3</sub>.13H<sub>2</sub>O (C<sub>4</sub>AH<sub>13</sub>)<sup>(50, 51)</sup>. With excess water, the combination of lime accelerated by the addition of gypsum. When gypsum occurs in pozzolana-lime pastes, ettringite also forms<sup>(52)</sup>. Whenever, the content of calcium sulfate exceeds specific values, the formation of ettringite causes pastes to crumble<sup>(53)</sup>. The rate of ettringite formation depends on the rate of dissolution of alumina<sup>(54)</sup>.

The CaO/SiO<sub>2</sub> ratio of C-S-H is variable and seem to depend on the type of pozzolana, the time and the temperature of curing. Low-lime fly ashes mixed with lime and water form C-S-H, C<sub>4</sub>AH<sub>13</sub>, 2CaO.SiO<sub>2</sub>.Al<sub>2</sub>O<sub>3</sub>.8H<sub>2</sub>O (C<sub>2</sub>SAH<sub>8</sub>), and sometimes carboaluminate as well<sup>(54)</sup>. If fly ash contain sulfates, ettringite also appears<sup>(55, 56)</sup>. C<sub>4</sub>AH<sub>13</sub> decreases with time whereas the 4CaO.Al<sub>2</sub>O<sub>3</sub>.CO<sub>3</sub>.11H<sub>2</sub>O (C<sub>4</sub>A $\bar{C}$ H<sub>11</sub>) content increases<sup>(56)</sup>. High-lime fly ashes may contain variable amounts of free lime which, upon mixing, are transform into Ca(OH)<sub>2</sub> and can thus harden without any further addition of lime<sup>(57)</sup>. If fly ash releases lime and sulfate, the formation of ettringite occurs without external additions<sup>(58)</sup>. If fly ashes contain high percentages of sulfate fly ash-lime paste will swell. At temperature

between 50 and 90°C, the main product of pozzolanic reaction is amorphous C-S-H, similar to that obtained upon hydration of the Portland cement, and poorly crystallized tobermorite<sup>(45)</sup>.

### 2.4.3 Strength of lime-pozzolana mixes

The strength of lime-pozzolana pastes increases with decreasing the lime/pozzolana ratio but, beyond certain value<sup>(59-60)</sup>, it is also found to decrease (Fig. 2.6). The addition of gypsum does not change this behavior<sup>(48)</sup>. Hardening of pozzolana-lime mortar is slow but long-lasting and thus compressive strength at 2 years can be as high as three times the 28-day strength<sup>(60)</sup>. The addition of gypsum increases strength (Table 2.7)<sup>(52)</sup>, it should not exceed certain levels if disintegration of specimens<sup>(53)</sup>, due to the formation of large quantities of ettringite, is to be avoided.

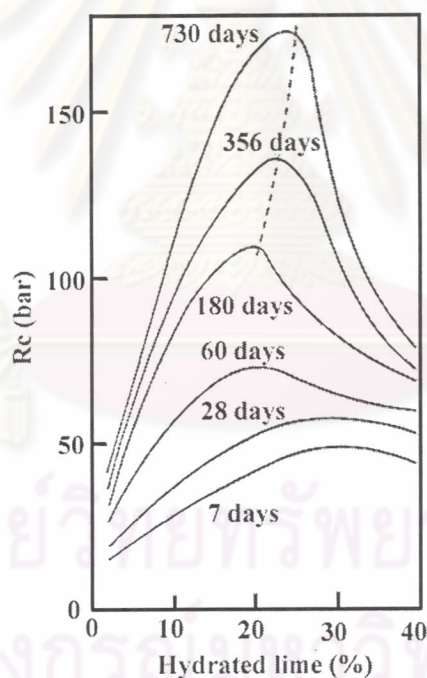


Fig. 2.6 Influence of lime content on the compressive strength of hydrated lime-pozzolana mixes (water/binder = 0.08)<sup>(48)</sup>.

**Table 2.7** Compressive strength (MPa) of lime-pozzolana mixes of different content<sup>(52)</sup>.

Curing time	CaSO <sub>4</sub> (%)				
	0	2.5	5	7.5	10
			Ca(OH) <sub>2</sub> = 15%		
7 days	16	31	28	56	65
14 days	24	47	66	102	118
28 days	51	85	108	120	140
3 months	87	120	170	163	160
6 months	122	138	175	170	180
1 year	135	156	180	181	163
2 year	150	165	187	176	148
			Ca(OH) <sub>2</sub> = 25%		
7 days	8	22	30	28	51
14 days	20	35	58	62	68
28 days	49	55	125	144	150
3 months	110	105	198	208	181
6 months	168	175	233	239	215
1 year	190	208	266	268	202
2 year	212	230	280	275	187

Early strength and 180-day strength of lime-pozzolana mixes are improved by adding KOH or NaOH, as well as Na<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>CO<sub>3</sub>, or CaCl<sub>2</sub><sup>(61, 62)</sup>. The 28-day paste strength can be as high as 30 MPa, but rapid setting can occur<sup>(63)</sup>. Similar results have been obtained with lime-fly ash mixture. Paste strength attains the highest level for 10-15% lime content and increases with increasing fineness of fly ash<sup>(60)</sup>.

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