GYPSUM
Gypsum

Gypsum is a binding material obtained by heating and thus driving off some or all of the crystallization water in the structure of gypsum rock.

- Pure gypsum rock: CaSO\(_4\).2H\(_2\)O
- Impurities: MgO, Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), SiO\(_2\), CaCO\(_3\), MgCO\(_3\)...
CALCINATION

Gypsum rock when heated to 100-190°C loses ¾ of its H₂O

\[ \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + \frac{3}{2} \text{H}_2\text{O} \]

Plaster of Paris

This low burning process is INCOMPLETE CALCINATION.

When calcination is carried out at temperatures above 190°C all water is removed.

\[ \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 + 2\text{H}_2\text{O} \]

gypsum anhydrite

This high-burning process is COMPLETE CALCINATION.
Production of Gypsum

- Excavating
- Crushing (~25 mm diameter)
- Grinding
- Heating (calcining)
- Cooling and Pulverizing
- Marketing in Bags
The gypsum rock is calcined either in **kettle kilns** or in **rotary kilns**.

If the temperature inside the kiln is about 160°C → **Plaster of Paris**

If the temperature inside the kiln is about 200-205°C → **anhydrite**
Setting and Hardening of Gypsum

When gypsum is mixed with water, the resultant paste is plastic (shapeable) which sets and subsequently hardens as time passes.

**Setting**: the loss of the initial plasticity or the gaining of rigidity.

**Hardening**: the gain in strength and the ability of the material to resist indentation or abrasion.

\[
\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + \frac{3}{2}\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}
\]

\[
\text{CaSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}
\]

If the amount of water used in the preparation of the paste is more than that required for the chemical reactions, the extra water is lost eventually through evaporation.
Plaster? Stucco? Mortar?

Plaster is a material used in a plastic state, which can be troweled, to form a hard covering for the interior surfaces. The plaster to form a hard covering for exterior surfaces is called stucco.

Mortar is a material used in a plastic state, which can be troweled, and becomes hard in place, to bond units of masonry structures.

Mortars and plasters are made of a mixture of sand, water and a binding material (such as gypsum, lime, or portland cement).
Why sand is added to gypsum pastes?

Gypsum paste is too sticky to be troweled. Besides, it shows excessive shrinkage upon drying. The use of sand:

• eliminates stickiness of the gypsum paste
• reduces the shrinkage
• provides economy
Properties of Gypsum Pastes and Mortars

- Setting Time
- Plasticity
- Strength
Setting Time

The time from first mixing the gypsum and water until the attainment of rigidity is called **setting time**.

Important for shaping the material.

Pure gypsum paste $\rightarrow \sim 30$ min.

Anhydrous gypsum pastes or pastes containing some impurities $\rightarrow >30$ min.
Plasticity

Plasticity is the ease with which the plaster or mortar can be shaped and spreaded. It should not be too sticky or too stiff.

The plasticity of the gypsum mortar is largely affected by the amount of water in the mix. The plasticity is also affected by the sand content. Inclusion of sand reduces the stickiness of the paste. However, too much sand decreases workability. Approximately 2/3 by weight of the mixture is constituted of sand in gypsum mortars.
Strength

Compressive strength of gypsum plasters and mortars is \( \sim 3 \) or more times greater than their tensile strength.

Plaster of Paris shows typically linear \( \sigma-\varepsilon \) diagram up to fracture.
Factors Affecting Strength of Gypsum

The water/gypsum ratio:

Gypsum upon hydration reacts with a definite amount of water to reform $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. If the water/gypsum ratio is high, then the amount of water leaving the mixture by evaporation will be high. Thus, there will be more voids left behind leading to lower strength.

A water/gypsum ratio of 0.6 (by weight) is approximately the lowest ratio at which the material is plastic enough to be shaped.
Factors Affecting Strength of Gypsum

The sand content of the mortar:

The higher the amount of sand in a mortar, the lower the amount of paste (in unit volume of the mix). Therefore, addition of higher amounts of sand decreases the strength. A mortar containing two parts of sand to one part of paste has about 60% of the ultimate strength of a mix made without sand.

On the other hand, if no or very little sand is added, the material may show a lot of shrinkage upon drying, leading to cracks. Thus very low strength may be obtained.
Fireproofing

Gypsum products have high fireproofing properties.

Although the surface is decomposed at temperatures exceeding 100°C, it forms a powder. This powder, covering the surface, acts as an effective insulator.
Admixtures for Gypsum

Set Retarders: Borax, tartaric acid, some organic materials, glue, sawdust and blood are used as retarders (max. 0.2%).

Set Accelerators: Alum, sodium sulfate, zinc sulfate and potassium sulfate are used as accelerators.
Admixtures for Gypsum

Materials Imparting Greater Plasticity: Sand and hydrated lime (15%) are the common materials used to increase plasticity.

Materials Imparting Greater Cohesion and Higher Tensile Strength: Inclusion of a small amount of organic fiber (hair and wood fibers) or asbestos fiber results in better cohesion and higher tensile strength.
Uses of Gypsum

Plaster of Paris; sculpturing and making architectural adornments mold

Gypsum; molds for the ceramic industry. The molds made from gypsum are porous, thus, absorb water from the plastic clay and make it more rigid.
Uses of Gypsum

Gypsum plasters; used as wall covering. Wall covering plasters consist of about 70-75% sand, 15-25% gypsum and some admixtures to control the working qualities, setting time, etc.

Plaster is also cast into building blocks for the construction of partition walls or for covering metal elements in a structure and thus providing protection for them against fire.

*Do not use gypsum products in exterior work or in moist interior work (Gypsum disintegrates in these conditions)*
By-Product Gypsum

- **Phosphogypsum** – Major by-product of phosphoric acid production
- **Desulfogypsum** – Obtained from the desulfurization of combustion gases in coal burning power plants (Harmful sulfur dioxide $\text{SO}_2$ gas is turned into $\text{CaSO}_4\cdot2\text{H}_2\text{O}$)
Example

How much Plaster of Paris can be obtained by calcination of 1 ton of pure gypsum rock?

Ca: 40, O: 16, S:32, H:1

\[
\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \quad \text{172 (100 °C - 190 °C)} \quad \rightarrow \quad \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + \frac{3}{2}\text{H}_2\text{O} \quad \text{145}
\]

\[
1000 \quad \rightarrow \quad x \quad \text{kg}
\]

\[
x / x = 843 \text{ kg}
\]
500 kg of a gypsum rock sample is calcined and 320 kg of pure plaster of Paris is obtained. Determine whether the gypsum rock is suitable for commercial use?

\[
\begin{align*}
\text{CaSO}_4 \cdot 2\text{H}_2\text{O} & \xrightarrow{100 ^\circ \text{C} - 190 ^\circ \text{C}} \text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + \frac{3}{2}\text{H}_2\text{O} \\
172 & \quad 145 \\
x & \quad 320 \quad x=379.6 \text{ kg}
\end{align*}
\]

\[
\frac{379.6}{500} \times 100 = 75.9\% > 70\%
\]

It can be used commercially.
Production of Quicklime

Lime is produced from limestone by heating the stone and driving off the CO\textsubscript{2} from its composition at approximately 900°C.

\[ \text{CaCO}_3 \xrightarrow{\sim 900^\circ C} \text{CaO} + \text{CO}_2 \]

Quicklime

- Pure limestone $\rightarrow \text{CaCO}_3$
- Impurities $\rightarrow \text{MgCO}_3$, Al\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}

When dolomitic limestone ($\text{CaCO}_3.\text{MgCO}_3$) is heated to high temperatures resultant quicklime contains a lot of CaO and some MgO.
Types of Quicklime

- High-calcium quicklimes (containing 90% or more CaO).
- Calcium quicklimes (>75% CaO).
- Magnesian quicklimes (>20% MgO).
- Dolomitic (high-magnesian) quicklimes (>25% MgO).

The quicklime becomes a binding material when mixed with water (slaked or hydrated) and brought to the form of slaked lime \( \text{Ca(OH)}_2 \) or \( \text{Ca(OH)}_2 \cdot \text{Mg(OH)}_2 \).
Manufacture of Quicklime

- Crushing (or pulverization) of the limestone
- Calcination of the crushed (or pulverized) limestone
- Grinding of the quicklime, although some quicklimes are marketed in lumps.

There are various types of kilns used for calcination:

- intermittent kiln,
- rotary kiln, and
- reactor kiln.
Slaking of Quicklime

Quicklime intended to use in construction must first be slaked to form a lime paste (slaked lime).

\[ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \ (\text{+heat}) \]

The amount of water required for hydration of pure quicklime is 32.1% by weight. In the presence of impurities this value decreases.

During slaking, volume expands about 2.5 to 3 times.
**Slaking of Quicklime**

\[ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{Heat} \]

CaO is mixed with enough water in a slaking box until a putty has been formed.

The putty is then covered with sand to protect it from the action of the air & left for seasoning for 2-3 weeks.

If CaO is not slaked well, it will absorb moisture from air & since the volume expands upto 2.5-3 times popouts will occur.

The slaked lime can also be bought from a factory.
Setting & Hardening of Lime

When hydrated lime is mixed with water, a plastic mixture is obtained. This mixture sets and hardens with time. Setting and hardening occur upon the reaction of Ca(OH)$_2$ with CO$_2$ from air.

\[ \text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \]
Air Slaked Lime

When the quicklime is exposed to air, the exposed surfaces absorb moisture from the air and slake.

The expansion accompanying slaking causes the lumps to fall into a more or less fine powder.

Immediately, the slaked lime is attacked by CO$_2$ of the air to form powdered CaCO$_3$ which has no binding value. However, it forms a film which protects the inner portions of the bulk of the material.
Properties of Lime Mortars

Hydrated lime is generally used in making mortars. The properties of the lime mortar depend on:

• the amount of CaO present in the lime
• the proportions of the materials that constitute the mortar.
Setting and Hardening

Lime is a slow setting material; it takes a considerable time to gain rigidity. Setting time of lime is affected by:

- the humidity and CO$_2$ content of the air (Setting time of lime is longer when the amount of moisture in the air is high and when the amount of carbon dioxide is low).

- the amount of CaO present in lime.

High-calcium limes set more quickly than magnesian or dolomitic limes.
Plasticity

If the lime mortar spreads easily and smoothly, it is plastic; if it sticks to the trowel or cracks, it is non-plastic.

Lime paste is a sticky material. Addition of sand reduces the stickiness of the paste. However, too much sand causes non-plastic mortar.

Addition of sand to lime paste
- adjusts its plasticity
- reduces the shrinkage of the mass upon drying.
- provides economy.

High-calcium limes have greater sand-carrying capacity than magnesian and dolomitic limes.
Strength of Lime Mortars

Tensile strength << Compressive strength
Drying shrinkage and cracking may be reduced by adding sand.

Factors affecting strength:
- Chemical composition of lime
  Magnesian Limes > Calcium Limes
- Sand amount & properties
  Adding sand decreases strength
- Amount of water
  Voids are formed after evaporation
- Setting conditions
  Lower humidity & higher CO₂ higher strength
Durability

**Lime is not resistant to the action of running water**; lime mortars show some solubility when exposed to such a condition. The solubility of lime decreases if it is subjected to hot water (reason for clogging hot water pipes).

Since lime shows some solubility in water, and since hydrated lime is quite porous, lime mortars do not show sufficient durability when they are exposed to a humid climate.

Therefore, lime mortars to be used on the exterior work are usually mixed with some amount of portland cement in order to achieve greater durability.
Uses

Lime mortars: plastering and masonry construction. The disadvantage of lime plasters over gypsum is its longer setting time.

Used in the production of calcium silicate and autoclaved aerated concrete masonry units.

Lime is also used as a whitewash material for painting the inner walls of buildings (hydrated lime + water)
Hydraulic Lime

Hydraulicity is the ability of a material to set and harden under water.

When the clayey limestone is heated to ~1000°C the CO₂ of the limestone is driven off.

The calcined product contain appreciable amounts of lime silicates and a sufficient amount of free CaO.

When mixed with water, the CaO in them will combine with some water and turn to Ca(OH)₂. Approximately 1/4 to 1/3 of the slaked hydraulic lime consists of Ca(OH)₂. On the other hand, the calcium silicates will react with water and form some calcium-silicate-hydrate (C-S-H) that is similar to the hydration product in portland cements. Thus, the formation of some C-S-H provides the hydraulic binding capacity of these limes.
Example

How much water is necessary to slake the quicklime obtained from 10 tons of pure limestone?
(Ca: 40, O: 16, C:12, H:1)

\[
\begin{align*}
\text{CaCO}_3 & \rightarrow \text{CaO} + \text{CO}_2 \\
\text{CaO} + \text{H}_2\text{O} & \rightarrow \text{Ca(OH)}_2
\end{align*}
\]

\[
\begin{align*}
\frac{\text{CaCO}_3}{100} & \quad \frac{\text{CaO}}{18} \\
10,000 & \quad x / x = 1800 \text{ kg}
\end{align*}
\]