Chemical composition of building raw materials, chemistry of inorganic bonding compounds I.

Ing. Milena Pavlíková, Ph.D.
K123, D1045
224 354 688, milena.pavlikova@fsv.cvut.cz

tpm.fsv.cvut.cz
Overview

Fundamental concepts

**Building raw materials:** primary and secondary

**Fillers, additives and admixtures**

**Inorganic binding materials:**

- Air (non-hydraulic) binders
  - Mortars
  - Plasters
**Fundamental concepts**

**Material:** substance or substances mixture in the solid state with specific physical function

*Characterisations:*
- solid state
- shape and size
- physical function
- stable at standard conditions

**Building binders:** substance which sets and hardens independently, and can bind other materials together

**Binding property**

*Division:*
- cements
- pastes
- sealing compounds
Cement:

- technical term for inorganic building binders
- active component
- binder makes plasticity possible

Cement division according to the hydraulicity:

1. **air** (non-hydraulic) – clay, soil, gypsum, lime
2. mixed with hydraulic admixtures – lime-pucolana cements
3. latent hydraulic – blast-furnace slag
4. hydraulic – hydraulic lime, roman cement, cement
Building raw materials

- Primary raw materials:
  - clays
  - siliceous materials
  - carbonates
  - sulfates
  - others
- Secondary raw materials:
  - fly ash
  - slags
  - silica fume
  - waste gypsum and others
Rocks

**Rock:** naturally occurring aggregate of minerals and/or mineraloids, need not have a specific chemical composition.

The Earth's **lithosphere** is made of rock.

**Petrology** is the scientific study of rocks.

**Mineral** is a naturally occurring substance formed through geological processes that has a characteristic chemical composition, a highly ordered atomic structure and specific physical properties. Minerals range in composition from pure elements and simple salts to very complex silicates with thousands of known forms.

The study of minerals is called **mineralogy**.

In general rocks are of three types: igneous, sedimentary, and metamorphic.
Igneous (etymology from Latin ignis, fire) rock

formed by **solidification of cooled magma**
(molten rock), with or without crystallization, either below the surface as **intrusive** (plutonic) rocks or on the surface as **extrusive** (volcanic) rocks

**melting** is caused by one or more of the following processes:

- an increase in temperature
- a decrease in pressure
- change in composition

Over 700 types of igneous rocks have been described, most of them formed beneath the surface of the Earth's crust.

**Examples:**

Basalt       Tuff
Sedimentary rock

covers 75-80% of the Earth's land area, and includes common types such as chalk, limestone, dolomite, sandstone, conglomerate and shale

Sedimentary rocks are classified by the source of their sediments, and are produced by one or more of:

• weathering in situ or erosion
• biogenic activity
• precipitation from solution

The sediments are then compacted and converted to rock by the process of lithification - process in which sediments compact under pressure, and gradually become solid rock.

Essentially, lithification is a process of porosity destruction through compaction and cementation.

Sedimentary rocks contain important information about the history of Earth. They contain fossils, the preserved remains of ancient plants and animals.

Coal is considered a type of sedimentary rock.
Clastic rock

- **formed** from fragments broken off from parent rock, by weathering in situ or erosion by water, ice or wind, followed by transportation of sediments, often in suspension, to the place of deposition

- **composed** of discrete fragments or clasts of materials derived from other rocks, largely of quartz with other common minerals including feldspar, amphiboles, clay minerals, and sometimes more exotic igneous and metamorphic minerals

- **classification according to the particle size:**
  - Shales - consist mostly of clay minerals, classified on the basis of composition and bedding, finest with particles less than 0.002 mm.
  - Siltstone - particles between 0.002 to 0.063 mm
  - Sandstone - grains 0.063 to 2 mm
  - Breccia - grains 2 to 263 mm

- **classification according to the composition of the particles, the cement, and the matrix:**
  - Orthoquartzite - a very pure quartz sandstone
  - Arkose - a sandstone with quartz and abundant feldspar
  - Greywacke - a sandstone with quartz, clay, feldspar, and metamorphic rock fragments
Biochemical and precipitated sedimentary rocks

- contain materials **generated by living organisms**, and include carbonate minerals created by organisms, such as corals, molluscs, and foraminifera, which cover the ocean floor with layers of calcite which can later form limestone.

- Other examples include **stromatolites**, the flint nodules found in chalk (which is itself a biochemical sedimentary rock, a form of limestone), and coal and oil shale (derived from the remains of tropical plants and subjected to pressure).

- **Precipitate sedimentary** rocks form when mineral solutions, such as sea water, evaporate.

  - **Examples:**
    - Halite (NaCl)
    - Gypsum (CaSO₄·2H₂O)
Metamorphic rock

• result of the transformation of a pre-existing rock type, the protolith (sedimentary rock, igneous rock or another older metamorphic rock)
• metamorphism is a process, which means "change in form".
• protolith is subjected to heat and pressure (temperatures greater than 150 to 200 °C and pressures of 1500 bars) causing profound physical and/or chemical change
• metamorphic rocks make up a large part of the Earth's crust and are classified by texture and by chemical and mineral assemblage (metamorphic facies)

Their formation:
- by being deep beneath the Earth's surface, subjected to high temperatures and the great pressure of the rock layers above
- by tectonic processes such as continental collisions which cause horizontal pressure, friction and distortion
- when rock is heated up by the intrusion of hot molten rock called magma from the Earth's interior

• The study of metamorphic rocks provides us with very valuable information about the temperatures and pressures that occur at great depths within the Earth's crust.
• Some examples of metamorphic rocks are:

  Gneiss

  Slate

  Marble

  Schist
Weathering

**Mechanical weathering:**
- the breakdown of rock into particles without producing changes in the chemical composition of the minerals in the rock
- **Important agents:** ice, water and wind.
- **Important processes:** abrasion, thermal expansion, freeze, hydraulic action, heating and cooling of the rock, and salt-crystal growth

**Chemical weathering:**
- the breakdown of rock by chemical reaction.
- the minerals within the rock are changed into particles that can be easily carried away
- Air and water are both involved in many complex chemical reactions.
- The minerals in igneous rocks may be unstable under normal atmospheric conditions, those formed at higher temperatures being more readily attacked than those which formed at lower temperatures.
- **Processes:**
  - Dissolution
  - Hydration
  - Hydrolysis
  - Oxidation
• Rock particles in the form of clay, silt, sand, and gravel, are transported by the agents of erosion (usually water, and less frequently by ice and wind) to new locations and redeposited in layers.
• These agents reduce the size of the particles, sort them by size, and then deposit them in new locations.
• The sediments dropped by streams and rivers form alluvial fans, flood plains, deltas, and on the bottom of lakes and the sea floor.
• The wind may move large amounts of sand and other smaller particles.
• Glaciers transport and deposit great quantities of usually unsorted rock material as till.
• These deposited particles eventually become compacted and cemented together, forming clastic sedimentary rocks. Such rocks contain inert minerals which are resistant to mechanical and chemical breakdown such as quartz, zircon, rutile, and magnetite.
• Quartz is one of the most mechanically and chemically resistant minerals.
Clays

- Hydrous aluminium phyllosilicates (form parallel sheets of silicate tetrahedra with $Si_2O_5$)
- Common weathering products and low temperature hydrothermal alteration products
- Very common in fine grained sedimentary rocks such as shale, and siltstone and in fine grained metamorphic slate

Clay minerals include the following groups:

- **Kaolin group** - kaolinite, dickite, halloysite and nacrite
- **Smectite group** - dioctahedral smectites such as montmorillonite and saponite (soapstone)
- **Illite group** - clay-micas, illite

- **Chlorite group** - variety of similar minerals with considerable chemical variation
• Clays exhibit plasticity when mixed with water in certain proportions.
• When dry, clay becomes firm and when fired in a kiln, permanent physical and chemical reactions occur which, amongst other changes, causes the clay to be converted into a ceramic material.
• **Usage:**
  • production of earthenware, stoneware and porcelain
  • bricks, cooking pots, art objects, dishware and even musical instruments such as the ocarina
  • in many industrial processes, such as paper making, cement production and chemical filtering
  • used in the manufacture of pipes for smoking tobacco
  • depending on the content of the soil, clay can appear in various colors, from a dull gray to a deep orange-red.
  • where natural seals are needed, such as in the cores of dams, or as a barrier in landfills against toxic seepage
  • adsorption capacities in various applications, such as the removal of heavy metals from waste water and air purification
Silica minerals

• Approximately 30% of all minerals are silicates.
• The basic chemical unit of silicates is the \((\text{SiO}_4)\) tetrahedron.
• The silicates are divided into the following subclasses by their structures:
  • Nesosilicates (single tetrahedrons) – olivine, topaz, zircon
  • Sorosilicates (double tetrahedrons) – leucit (\(\text{KA}_2\text{Si}_2\text{O}_6\))
  • Inosilicates (single and double chains) – wollastonite (\(\text{CaSiO}_3\))
  • Cyclosilicates (rings) – beryl (\(\text{Be}_3\text{Al}_2 (\text{SiO}_3)_6\))
  • Phyllosilicates (sheets) – kaolinite (\(\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\))
  • Tectosilicates (frameworks) – feldspathoids, quartz, and zeolites
Quartz

- found in a **variety of forms**, as quartz crystals, massive forming hills, quartz sand (silica sand), sandstone, quartzite, tripoli, diatomite, flint, opal, chalcedonic forms like agate, onyx etc., and in with numerous **other forms** depending upon **colour** such as purple quartz (amethyst), smoky quartz, yellow quartz or false topaz (citrine), rose quartz and milky quartz.
- Only pure quartz crystal or rock crystal, clear, free from any inclusion, has an important property: it expands (mechanically) under the influence of electric current and conversely pressure induces a measurable electric current - **piezoelectricity**.
- common constituent of granite, sandstone, limestone, and many other igneous, sedimentary, and metamorphic rocks
Feldspar

• make up as much as 60% of the Earth's crust
• This group of minerals consists of framework or tectosilicates.
• Compositions of major elements can be expressed in terms of three endmembers:
  • K-feldspar $\text{KAlSi}_3\text{O}_8$
  • Albite $\text{NaAlSi}_3\text{O}_8$
  • Anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$
• Uses:
  • common raw material in the production of ceramics
  • used for thermoluminescence dating and optical dating in earth sciences and archaeology
  • ingredients in household cleaners
  • anti-caking agent used in powdered forms of non-dairy creamer
**Clinkstone** - member of a group of extrusive igneous rocks (lavas) that are rich in nepheline and potash feldspar. The typical phonolite is a fine-grained, compact igneous rock that splits into thin, tough plates which make a ringing sound when struck by a hammer, hence the rock's name

**Uses**: production of colour glass, ceramic, electroporcelane, fertilizers

**Basalt** (composed from MgO and CaO and low in SiO$_2$ and Na$_2$O plus K$_2$O)

gray to black extrusive volcanic rock, usually fine-grained, high strength, durability against acids

**Uses**: ceramic and insulation materials (mineral wools)

**Mica** (X$_2$Y$_4$-6Z$_8$O$_{20}$(OH,F)$_4$ in which X is K, Na, or Ca or less commonly Ba, Rb, or Cs, Y is Al, Mg or Fe or less commonly Mn, Cr, Ti, Li, etc., Z is chiefly Si or Al but also may include Fe$^{3+}$ or Ti)

sheet silicate minerals, highly perfect cleavage, which is the most prominent characteristic of mica, is explained by the hexagonal sheet-like arrangement of its atoms, has a lamellar form with a shiny luster,

**Uses**: high dielectric strength and excellent chemical stability → capacitors for radio frequency applications, insulator in high voltage electrical equipment, is resistant to heat → instead of glass in windows for stoves and kerosene heaters, to separate electrical conductors in cables, emergency lighting, pressed mica sheets are often used in place of glass in greenhouses, muscovite mica is the most common substrate for sample preparation for the atomic force microscope, toothpaste includes powdered white mica, heating wire (like Kanthal, Nichrome, etc..) in heating elements and can withstand up to 900 °C
**Asbestos** (Fe7Si8O22(OH)2)

- long, thin fibrous crystals, soft and pliant, resistance to heat, electricity and chemical damage, sound absorption and tensile strength
- inhalation of asbestos fibers can cause serious illnesses, including mesothelioma and asbestosis

**Vermiculite** ((MgFe,Al)3(Al,Si)4O10(OH)2·4H2O)

expands with the application of heat

**Uses:**
- moulded shapes, bonded with sodium silicate for use in high-temperature and refractory insulation, fireproofing of structural steel and pipes
- soil conditioner, growing medium for hydroponics, packing material, suitable as a substrate for various animals and/or incubation of eggs
- lightweight aggregate for plaster, proprietary concrete compounds, firestop mortar and cementitious spray fireproofing
- means to permit slow cooling of hot pieces in glassblowing, lampwork, steelwork, and glass beadmaking
- used in in-ground swimming pools to provide a smooth pool base, used in commercial handwarmers
Carbonates

Calcit (CaCO₃)
transparent to opaque, colour is white or none, (shades due to impurities), very reactive to acid solutions, making acid rain insoluble in cold water, acidity can cause dissolution of calcite and release of carbon dioxide gas
primary constituent of the shells of marine organisms (plankton, the hard parts of red algae, some sponges)
common constituent of sedimentary rocks (limestone), much of which is formed from the shells of dead marine organisms.
primary mineral in metamorphic marble, it also occurs as a vein mineral in deposits from hot springs, and it occurs in caverns as stalactites and stalagmites
in volcanic or mantle-derived rocks such as carbonatites

Limestone
Pure limestone is almost white, because of impurities, such as clay, sand, organic remains, iron oxide and other materials, many limestones exhibit different colors, especially on weathered surfaces
may be crystalline, clastic, granular, or massive, depending on the method of formation.
Crystals of calcite, quartz, dolomite or barite may line small cavities in the rock.
Uses: used on all types of buildings and sculptures. Limestone is readily available and relatively easy to cut into blocks or more elaborate carving. It is also long-lasting and stands up well to exposure. However, it is a very heavy material, making it impractical for tall buildings, and relatively expensive as a building material.
 manufacture of quicklime (calcium oxide) and slaked lime (calcium hydroxide); Cement and mortar; Pulverized limestone is used as a soil conditioner to neutralize acidic soil conditions;
Crushed for use as aggregate—the solid base for many roads; as a reagent in desulfurizations; glass making;
Toothpaste; added to bread as a source of calcium
**Travertine**

Banded, compact variety of limestone formed along streams, particularly where there are waterfalls and around hot or cold springs. Calcium carbonate is deposited where evaporation of the water leaves a solution that is supersaturated with chemical constituents of calcite.

**Tufa**

Porous or cellular variety of travertine, is found near waterfalls.

**Coquina**

Poorly consolidated limestone composed of pieces of coral or shells.

**Dolomite (CaMg\((\text{CO}_3)\)_2)**

Name of a sedimentary carbonate rock and a mineral, both composed of calcium magnesium carbonate found in crystals.

Uses: Ornamental stone, a concrete aggregate and as a source of magnesium oxide. It is an important petroleum reservoir rock, and serves as the host rock for large strata-bound Mississippi Valley-Type (MVT) ore deposits of base metals (that is, readily oxidized metals) such as lead, zinc, and copper. Where calcite limestone is uncommon or too costly, dolomite is sometimes used in its place as a flux (impurity remover) for the smelting of iron and steel. In horticulture, dolomite and dolomitic limestone are added to soils and soilless potting mixes to lower their acidity ("sweeten" them). Home and container gardening are common examples of this use.

**Magnesite (MgCO_3)**

Uses: A slag former in steelmaking furnaces, in conjunction with lime, in order to protect the magnesium oxide lining a catalyst and filler in the production of synthetic rubber and in the preparation of magnesium chemicals and fertilizers to the production of lime, important product in refractory materials.

**Marble**
Soapstone (steatite or soaprock, $3\text{MgO}.4\text{SiO}_2.\text{H}_2\text{O}$)

metamorphic rock, a talc-schist, largely composed of the mineral talc and is rich in magnesium
very similar to talc, commonly used as a carving material, soft (because of the high talc content, talc being 1 on Mohs hardness scale), and may feel soapy when touched, hence the name

Uses: for inlaid designs, sculpture, coasters, and kitchen countertops and sinks
insulator or housing for electrical components, due to its durability and electrical characteristic
for beads and seals in ancient civilizations
Refractory material (1320-1380°C)

Sulfates

Gypsum ($\text{CaSO}_4.2\text{H}_2\text{O}$)

Is deposited in lake and sea water, as well as in hot springs, from volcanic vapors, and sulfate solutions in veins. Hydrothermal anhydrite in veins is commonly hydrated to gypsum by groundwater in near surface exposures. It is often associated with the minerals halite and sulfur.

Uses: gypsum boards, plaster ingredient, fertilizer and soil conditioner, plaster of Paris (surgical splints; casting moulds; modeling); blackboard chalk, component of Portland cement used to prevent flash setting of concrete, medicinal agent

alabaster - very fine-grained white or lightly-tinted variety of gypsum
Secondary raw materials

Why we recycle?
1. Shortage of primary raw materials
2. Lower energy – intensive in building materials production

Wastes in civil engineering:
• from building industry and demolition
• from building materials production
• from power, mining, metallurgical, chemical etc. industry
  • Fly ash
  • Slags
  • Silica fume
  • Waste gypsum
  • Others – clinker, calcium carbide

Uses: for the creation of roads, bridges, golf courses, noise barriers and for filling in waterways
Fly ash

one of the residues generated in the combustion of coal
captured from the chimneys of power generation facilities

Components - depends upon the source and makeup of the coal being burned,
   includes substantial amounts of silica (silicon dioxide, SiO₂) (both
   amorphous and crystalline) and lime (calcium oxide, CaO).

Uses: as a supplement Portland cement in concrete production, where it can
   bring both technological and economic benefits, as pozzolan greatly
   improves the strength and durability of concrete, the use of ash is a key
   factor in their preservation

in synthesis of geopolymers and zeolites

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contains trace concentrations of many heavy metals that are known to be
detrimental to health in sufficient quantities
Silica fume (microsilica)

• byproduct of the reduction of high-purity quartz (87-99%) with coke in electric arc furnaces in the production of silicon and ferrosilicon alloys
• consists of very fine vitreous particles with a surface area on the order of 20 000 m²/kg with particles approximately 100 times smaller than the average cement particle
• extreme fineness and high silica content → highly effective pozzolanic material
• used as an addition in Portland cement concretes to improve properties - compressive strength, bond strength, and abrasion resistance, reduces the permeability of concrete to chloride ions, which protects concrete's reinforcing steel from corrosion
High Reactivity Metakaolin (HRM)

- Highly processed reactive aluminosilicate pozzolan, a finely-divided material that reacts with slaked lime at ordinary temperature and in the presence of moisture to form a strong slow-hardening cement.
- Between 100-200°C, clay minerals lose most of their adsorbed water, between 500-800°C kaolinite becomes calcined by losing water through dehydroxilization.
- Particle size of metakaolin is smaller than cement particles, but not as fine as silica fume.

**Advantages:**
- Increased compressive and flexural strengths.
- Reduced permeability (including chloride permeability), increased resistance to chemical attack, increased durability.
- Reduced effects of alkali-silica reactivity (ASR).
- Enhanced workability and finishing of concrete.
- Reduced shrinkage, due to "particle packing" making concrete denser.
- Improved color by lightening the color of concrete making it possible to tint lighter integral color.

**Uses:**
- High performance, high strength, and lightweight concrete.
- Precast and poured-mold concrete.
- Fibercement and ferrocement products.
- Glass fiber reinforced concrete.
- Countertops, art sculptures.
- Mortar and stucco.
Fillers

- particles added to a matrix material, usually to improve its properties
- to lower the consumption of more expensive binder material or to better some properties of the mixed material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Binder</th>
<th>Filler</th>
<th>Importance of filler</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concrete</td>
<td>cement</td>
<td>gravel, stone, sand</td>
<td>cheaper</td>
</tr>
<tr>
<td>Drywall</td>
<td>gypsum</td>
<td>cardboard</td>
<td>tenacity, volume, main part</td>
</tr>
<tr>
<td>Particle board</td>
<td>Synthetic Resin, glue</td>
<td>sawdust</td>
<td>tenacity, volume, main part</td>
</tr>
<tr>
<td>Plastic explosive</td>
<td>Plasticizer, oil</td>
<td>explosive</td>
<td>explosiveness</td>
</tr>
<tr>
<td>Tyre rubber</td>
<td>rubber</td>
<td>Soot</td>
<td>Volume, better mechanic properties</td>
</tr>
<tr>
<td>Resin epoxy</td>
<td>epoxy</td>
<td>Microspheres</td>
<td>Improve viscosity of resin</td>
</tr>
</tbody>
</table>
Chemical admixtures

- materials in the form of powder or fluids that are added to the concrete to give it certain characteristics not obtainable with plain concrete mixes. In normal use, admixture dosages are less than 5% by mass of cement, and are added to the concrete at the time of batching/mixing.

- The most common types of admixtures are:
  - Accelerators speed up the hydration (hardening) of the concrete.
  - Retarders slow the hydration of concrete, and are used in large or difficult pours where partial setting before the pour is complete is undesirable.
  - Air-entrainers add and distribute tiny air bubbles in the concrete, which will reduce damage during freeze-thaw cycles thereby increasing the concrete's durability. However, entrained air is a trade-off with strength, as each 1% of air may result in 5% decrease in compressive strength.
  - Plasticizers (water-reducing admixtures) increase the workability of plastic or "fresh" concrete, allowing it to be placed more easily, with less consolidating effort. Superplasticizers (high-range water-reducing admixtures) are a class of plasticizers which have fewer deleterious effects when used to significantly increase workability. Alternatively, plasticizers can be used to reduce the water content of a concrete (and have been called water reducers due to this application) while maintaining workability. This improves its strength and durability characteristics.
  - Pigments can be used to change the color of concrete, for aesthetics.
  - Corrosion inhibitors are used to minimize the corrosion of steel and steel bars in concrete.
  - Bonding agents are used to create a bond between old and new concrete.
  - Pumping aids improve pumpability, thicken the paste, and reduce dewatering – the tendency for the water to separate out of the paste.
Mineral admixtures and blended cements

- inorganic materials with pozzolanic or latent hydraulic properties. These very fine-grained materials are added to the concrete mix to improve the properties of concrete or as a replacement for Portland cement (blended cements).
- **Pozzolana**, also known as pozzolanic ash, is a fine, sandy volcanic ash, originally discovered and dug in Italy at Pozzuoli in the region around Vesuvius, but later at a number of other sites. Vitruvius speaks of four types of pozzolana. It is found in all the volcanic areas of Italy in various colours: black, white, grey and red.
  - Finely ground and mixed with lime it creates a hydraulic cement and can be used to make a strong mortar that will also set under water.
  - Pozzolana is a siliceous and aluminous material which reacts with calcium hydroxide in the presence of water to form compounds possessing cementitious properties at room temperature.
Inorganic binding materials

- Air binders
- Mortars
- Plasters
Calcium carbonate is a natural product that can be found as marl, chalk, limestone or marble.

- **extraled** from quarries or mines.

Gathered by mechanical loaders or buckets, the rocks are then transported and unloaded in crushers where they are washed, screened, crushed, ground and stored according to their use.

The very pure limestone that to make lime is light to dark grey in colour with a CaCO₃ content of about 98% to produce calcium or dolomitic quicklime (CaO or CaO.MgO respectively).

- Part of the extracted stone, **selected** according to its chemical composition and granulometry, is **calcinated** at about 1000°C in different types of kiln, fired by such fuels as natural gas, coal, fuel oil, lignite, etc..

quicklime is produced.

The pebble-lime thus produced is screened, crushed or ground and stored according to the characteristics demanded by the customers.
Calcination up to 1050°C – *burnt lime* – high porosity, low bulk density and high specific surface, quick and complete hydration

Clacination over 1050°C – *overburnt lime* – higher bulk density, lower porosity and specific surface

Quicklime can be **hydrated**, i.e. combined with water. Depending on the quantity of water added and the intended use, hydrated lime (\(\text{Ca(OH)2} = \text{calcium hydroxide}\)) is obtained either in the form of very fine dry powder, or as a "putty lime" very much appreciated for quality ceiling works, or a "lime milk" in different concentrations, which is easy to pump and practical to use in different industrial processes.
Calcium carbonate (CaCO₃) is burned in a kiln at 900°C < T < 1000°C, producing carbon dioxide (CO₂) as a gas.

Carbon dioxide combines with water (H₂O) to form calcium hydroxide (Ca(OH)₂), also known as hydrated lime or powdered cement, which is packaged in large paper bags.

Calcium hydroxide is used to create lime mortar, which can form a protective alkaline skin of calcium carbonate.

Sand (SiO₂) is mixed with lime mortar to create lime putty (is produced by adding water to hydrated lime powder).

Lime mortar is used in construction, often mixed with water to form lime putty.
Gypsum

- common laboratory and industrial chemical
- In the form of $\gamma$-anhydrite (the nearly anhydrous form), it is used as a desiccant.
- The hemihydrate ($\text{CaSO}_4\cdot \sim 0.5\text{H}_2\text{O}$) is better known as plaster of Paris, while the dihydrate ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$) occurs naturally as gypsum.
- The anhydrous form occurs naturally as $\beta$-anhydrite ($\text{CaSO}_4$).
- Depending on the method of calcination of calcium sulfate dihydrate, specific hemihydrates are sometimes distinguished:
  - **alpha-hemihydrate** - crystals are more prismatic and when mixed with water form a much stronger and harder superstructure than
  - **beta-hemihydrate**
Dehydration reactions

The dehydration (specifically known as calcination) begins at approximately 80 °C, although in dry air, some dehydration will take place already at 50 °C. The heat energy delivered to the gypsum at this time (the heat of hydration) tends to go into driving off water (as water vapour) rather than increasing the temperature of the mineral.

Heating gypsum to between **100 °C and 150 °C** partially dehydrates the mineral by driving off approximately 75% of the water contained in its chemical structure. The temperature and time needed depend on ambient partial pressure of H₂O. Temperatures as high as 170 °C are used in industrial calcination, but at these temperatures **γ-anhydrite** begins to form. The reaction for the partial dehydration is:

\[
\text{CaSO}_4\cdot2\text{H}_2\text{O} + \text{heat} \rightarrow \text{CaSO}_4\cdot\frac{1}{2}\text{H}_2\text{O} + \frac{1}{2}\text{H}_2\text{O} \text{ (steam)}
\]

The partially dehydrated mineral is called **calcium sulfate hemihydrate** or calcined gypsum (commonly known as plaster of Paris) (CaSO₄·nH₂O), where n is in the range 0.5 to 0.8.
On heating to 180 °C, the nearly water-free form, called γ-anhydrite (CaSO4.nH2O where n=0 to 0.05) is produced. γ-Anhydrite reacts slowly with water to return to the dihydrate state, a property exploited in some commercial desiccants.

On heating above 250 °C, the completely anhydrous form called β-anhydrite or "natural" anhydrite is formed. Natural anhydrite does not react with water, even over geological timescales, unless very finely ground.

In contrast to most minerals, when mixed with water at normal (ambient) temperatures, it quickly reverts chemically to the preferred dihydrate form, while physically "setting" to form a rigid and relatively strong gypsum crystal lattice:

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

This reaction is **exothermic** and is responsible for the ease with which gypsum can be cast into various shapes including sheets (for drywall), sticks (for blackboard chalk), and molds (to immobilize broken bones, or for metal casting).

The **endothermic property** of this reaction is exploited by drywall to confer fire resistance to residential and other structures. In a fire, the structure behind a sheet of drywall will remain relatively cool as water is lost from the gypsum, thus preventing (or substantially retarding) damage to the framing (through combustion of wood members or loss of strength of steel at high temperatures) and consequent structural collapse.

Mixed with polymers, it has been used as a bone repair cement.

Small amounts of calcined gypsum are added to earth to create strong structures directly from cast earth, an alternative to adobe (which loses its strength when wet).
Mortars

- material used in masonry to bind construction blocks (stone, brick, breeze blocks (cinder blocks), etc.) together and fill the gaps between them.
- Mortar is a mixture of sand, a binder such as cement or lime, and water and is applied as a paste which then sets hard.
- Mortar can also be used to fix, or point masonry when the original mortar has washed away.
Portland cement mortar

- is created by mixing Portland cement with sand and water.
- It was invented in the mid-nineteenth century, as part of scientific efforts to develop stronger mortars than existed at the time.
- It was popularized during the late nineteenth century, and by 1930 it had superseded lime mortar for new construction. The main reason for this was that it sets hard and quickly, allowing a faster pace of construction. However, as a general rule, it should not be used for the repair of older buildings constructed in lime mortar, which require the flexibility, softness and breathability of lime if they are to function correctly.
Lime mortar

- is created by mixing sand, slaked lime and water.
- The earliest known use of lime mortar dates to about 4000 BC in Ancient Egypt. Lime mortars have been used throughout the world, notably in Roman Empire buildings throughout Europe and Africa. The vast majority of pre-1900 masonry buildings in Europe and Asia are built from lime mortar.
- The process of making lime mortar is simple. Limestone is burnt in a kiln to form quicklime. The quicklime is then slaked (mixed with water) to form slaked lime, either in the form of lime putty or of hydrated lime powder. This is then mixed with sand and water to form mortar.
- This kind of lime mortar, known as non-hydraulic, sets very slowly through reaction with the carbon dioxide in air. A very thick wall made of lime mortar may take centuries to completely set and harden. This is normal and not problematic.
- The speed of set can be increased by using impure limestones in the kiln, to form a hydraulic lime that will set on contact with water. Such a lime must be stored as a dry powder. Alternatively, a pozzolanic material such as calcined clay or brick dust may be added to the mortar mix. This will have a similar effect of making the mortar set reasonably quickly by reaction with the water in the mortar.
- Lime mortar is considered breathable in that it will allow moisture to freely move through it and evaporate from its surface. In old buildings with walls that shift over time, there are often cracks which allow rain water into the structure. The lime mortar allows this moisture to escape through evaporation and keeps the wall dry. Repointing or rendering an old wall with cement mortar stops this evaporation and can cause problems associated with moisture behind the cement.
Plasters

- Plaster is used as a building material similar to mortar or cement. Like those materials plaster starts as a dry powder that is mixed with water to form a paste which liberates heat and then hardens. Unlike mortar and cement, plaster remains quite soft after drying, and can be easily manipulated with metal tools or even sandpaper. These characteristics make plaster suitable for a finishing, rather than a load-bearing material.

- Plaster was a common building material for wall surfaces in a process known as lath and plaster, whereby a series of wooden strips are covered with a semi-dry plaster and then hardened into surface. The plaster used in most lath-and-plaster construction was mainly lime plaster.

- Lime plaster cure time is about a month. To stabilize the lime plaster during curing, small amounts of Plaster of Paris were mixed into the putty. Because Plaster of Paris sets quickly, "retardants" were used to slow setting time enough to allow workers to mix large working quantities of lime putty plaster.

- A modern form of this method uses expanded metal mesh over wood or metal structures, which allows a great freedom of design as it is adaptable to both simple and compound curves. Today this building method has been partly replaced with drywall, also composed mostly of gypsum plaster.

- In both these methods a primary advantage of the material is that it is resistant to a fire within a room and so can assist in reducing or eliminating structural damage or destruction provided the fire is promptly extinguished.
Lime plaster

- is a mixture of calcium hydroxide and sand (or other inert fillers).
- Carbonation: carbon dioxide in the atmosphere causes the plaster to set by transforming the calcium hydroxide into calcium carbonate (limestone).
- To make lime plaster - limestone (calcium carbonate) is heated to produce quicklime (calcium oxide), water is then added to produce slaked lime (calcium hydroxide), which is sold as a white powder.
- Additional water is added to form a paste prior to use. The paste may be stored in air-tight containers. Once exposed to the atmosphere, the calcium hydroxide turns back into limestone, causing the plaster to set.
- Lime plaster is used for true frescoes. Pigments, diluted in water, are applied to the still wet plaster.
Cement plaster

- is a mixture of suitable plaster sand, portland cement and water which is normally applied to masonry interiors and exteriors to achieve a smooth surface.
- Interior surfaces sometimes receive a final layer of gypsum plaster.
- Walls constructed with stock bricks are normally plastered while face brick walls are not plastered.
- Various cement-based plasters are also used as proprietary spray fireproofing products. These usually use vermiculite as lightweight aggregate. Heavy versions of such plasters are also in use for exterior fireproofing, to protect LPG vessels, pipe bridges and vessel skirts.
Literture

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