CHAPTER

13

CLAYS AND ASSOCIATED MINERALS IN CEMENT AND PLASTERS

13.1 THE EVOLUTION OF CEMENT

In the most general sense of the word, a cement is a binder, a substance that sets and hardens independently, and can bind other materials together. The word "cement" traces modern concrete that was made from crushed rock with burnt lime as binder. The volcanic ash and pulverized brick additives that were added to the burnt lime to obtain a hydraulic binder were later referred to as cementum, cimentum and cement. Cement used in construction is characterized as hydraulic cement and non-hydraulic cement. Hydraulic cements harden because of hydration and chemical reactions that occur independently of the mixture's water content, so they can harden even under water or when constantly exposed to wet weather; whereas non-hydraulic cements must be kept dry in order to retain their strength. Example of hydraulic cement is Portland cement and non-hydraulic cement is lime and gypsum plaster. Besides this the most important use of cement is the production of mortar and concrete. The term cement refers to the material used to bind the aggregate materials of concrete. Concrete is a strong building material that is durable in the face of normal environmental effects.

13.2 EARLY USES

It is uncertain where it was first discovered that a combination of hydrated non-hydraulic lime and a pozzolan produces a hydraulic mixture (see also: Pozzolanic reaction), but concrete made from such mixtures was first used by the Ancient Macedonians and three centuries later on a large scale by Roman engineers. They used both natural pozzolans (trass or pumice) and artificial pozzolans (ground brick or pottery) in these concretes. Many excellent examples of structures made from these concretes are still standing, notably the huge

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monolithic dome of the Pantheon in Rome and the massive Baths of Caracalla. The vast system of Roman aqueducts also made extensive use of hydraulic cement. Although any preservation of this knowledge in literary sources from the Middle Ages is unknown, medieval masons and some military engineers maintained an active tradition of using hydraulic cement in structures such as canals, fortresses, harbours and shipbuilding facilities.

13.3 MODERN CEMENT

Modern hydraulic cements began to be developed from the start of the Industrial Revolution (around 1800), driven by three main needs:

- Hydraulic cement render (stucco) for finishing brick buildings in wet climates.
- Hydraulic mortars for masonry construction of harbour works, etc.
- Development of strong concretes.

The most common type of cement used by concrete manufacturers is Portland cement, which is prepared by igniting a mixture of raw materials mainly composed of calcium carbonate or aluminium silicates. Portland cement can be defined as "hydraulic cement produced by pulverizing clinker consisting essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulphate as an interground addition". The phase compositions in Portland cement are denoted as tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF).

Table 13.1: Components of Portland cement

Name of component	*Phase*	*Formula*	*Composition in %*
Tricalcium silicate	(C_3S)	$3CaO\ SiO_2$	49
Dicalcium silicate	(C_2S)	$2CaO\ SiO_2$	25
Tricalcium aluminate	(C_3A)	$3CaO\ Al_2O_3$	12
Tetracalcium aluminoferrite	(C_4AF)	$4CaO\ Al_2O_3\ Fe_2O_3$	9

13.4 CHEMISTRY OF CEMENT

Hydration is the reaction that takes place between cement and water that leads to setting and hardening. All compounds present in Portland cement clinker are anhydrous, but when brought into contact with water, they are all attacked or decomposed, forming hydrated compounds. When the tri- or di-calcium silicates react with water a calcium-silicate-hydrate gel is formed. The chemical reactions that take place during hydration are summarized below:

- **Tricalcium silicate**

  $$2(3CaO{\cdot}SiO_2) + 6HO_2 \longrightarrow 3CaO{\cdot}2SiO_2{\cdot}3H_2O + 3Ca(OH)_2$$

- **Dicalcium silicate**

  $$2(2CaO{\cdot}SiO_2) + 4H_2O \longrightarrow 3CaO{\cdot}2SiO_2{\cdot}3H_2O + Ca(OH)_2$$

- **Tricalcium aluminate**

  $$3CaO{\cdot}Al_2O_3 + 6H_2O \longrightarrow 3CaO{\cdot}Al_2O_3{\cdot}6H_2O$$

- **Tetracalcium aluminoferrite**

  $$4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3 + 2Ca(OH)_2 + 10H_2O \longrightarrow 3CaO{\cdot}Al_2O_3{\cdot}6H_2O + 3CaO{\cdot}Fe_2O_3{\cdot}6H_2O$$

13.5 TYPES OF MODERN CEMENT

Masonry cements: These are used for preparing bricklaying mortars and stuccos, and must not be used in concrete. They are usually complex proprietary formulations containing Portland clinker and a number of other ingredients that may include limestone, hydrated lime, air entrainers, retarders, water proofers and colouring agents.

Expansive cements: Expansive cements, in addition, Portland clinker, expansive clinker and are designed to offset the effect of the constituent materials.

White blended cements: It is used to produce white clinker and white supplementary materials such as high-purity metakaolin.

Coloured cements: They are used to produce coloured Portland cement and it is used simultaneously in decorative purpose.

Very finely ground cements: They are made from mixtures with sand or slag. It is very dusty material.

13.6 CEMENT MANUFACTURING

Raw Materials

The main raw materials used in the cement manufacturing process are limestone, sand, shale, clay and iron ore. The main material, limestone, is usually mined on site while the other minor materials may be mined either on site or in nearby quarries. Another source of raw materials is industrial by-products. The use of by-product materials to replace natural raw materials is a key element in achieving sustainable development.

Raw Material Preparation

Mining of limestone requires the use of drilling and blasting techniques. The blasting techniques use the latest technology to ensure that vibration, dust and noise emissions are kept at a minimum. Blasting produces materials in a wide range of sizes from approximately 1.5 metres in diameter to small particles less than a few millimetres. Material is loaded at the blasting face into trucks for transportation to the crushing plant. Through a series of crushers and screens, the limestone is reduced to a size less than 100 mm and stored until required. Depending on size, the minor materials (sand, shale, clay and iron ore) may or may not be crushed before being stored in separate areas until required.

Raw Grinding

In the wet process, each raw material is proportioned to meet a desired chemical composition and fed to a rotating ball mill with water. The raw materials are ground to a size where the majority of the materials are less than 75 microns. Materials exiting the mill are called “slurry” and have flow ability characteristics. This slurry is pumped to blending tanks and homogenized to ensure that the chemical composition of the slurry is correct. Following the homogenization process, the slurry is stored in tanks until required. In the dry process, each raw material is proportioned to meet a desired chemical composition and fed to either a rotating ball mill or vertical roller mill. The raw materials are dried with waste process gases and ground to a size where the majority of the materials are less than 75 microns. The dry materials exiting either type of mill are called “kiln feed”. The kiln feed is pneumatically blended to ensure that the chemical composition of the kiln feed is well homogenized and then stored in silos until required.

Pyroprocessing

Whether the process is wet or dry, the same chemical reactions take place. Basic chemical reactions are: evaporating all moisture, calcining the limestone to produce free calcium oxide, and reacting the calcium oxide with the minor materials (sand, shale, clay and iron). This results in a final black, nodular product known as “clinker” which has the desired hydraulic properties. In the wet process, the slurry is fed to a rotary kiln, which can be from 3.0 m to 5.0 m in diameter and from 120.0 m to 165.0 m in length. The preheater tower and rotary kiln are made of steel and lined with special refractory materials to protect it from the high process temperatures. Process temperatures can reach as high as 1450°C during the clinker making process. Regardless of the process, the rotary kiln is fired with an intense flame, produced by burning coal, coke, oil, gas or waste fuels. Preheater towers can be equipped with firing as well. The rotary kiln discharges the red-hot clinker under the intense flame into a clinker cooler. The clinker cooler recovers heat from the clinker and returns the heat to the pyroprocessing system thus reducing fuel consumption and improving energy efficiency. Clinker leaving the clinker cooler is at a temperature conducive to being handled on standard conveying equipment.

Finish Grinding and Distribution

The black, nodular clinker is stored on site in silos or clinker domes until needed for cement production. Clinker, gypsum and other process additions are ground together in ball mills to form the final cement products. Fineness of the final products, amount of gypsum added, and the amount of process additions added are all varied to develop a desired performance in each of the final cement products. In the dry process, kiln feed is fed to a preheater tower, which can be as high as 150.0 metres. Material from the preheater tower is discharged to a rotary kiln which can have the same diameter as a wet process kiln but the length is much shorter at approximately 45.0 m. Each cement product is stored in an individual bulk silo until needed by the customer. Bulk cement can be distributed by truck, rail, or water depending on the customer's needs. Cement can also be packaged with or without colour addition and distributed by truck or rail.

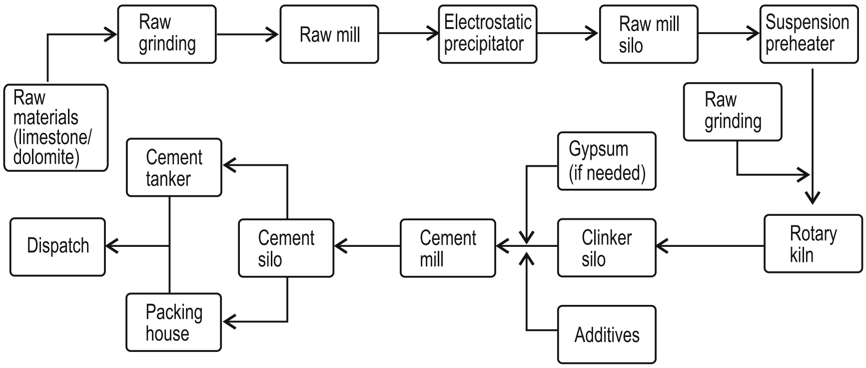

Fig. 13.1: Processing of cement

13.7 USE OF CEMENT

The most important use of cement is the production of mortar and concrete—the bonding of natural or artificial aggregates to form a strong building material that is durable in the face of normal environmental effects. The term cement refers to the material used to bind the aggregate materials of concrete. Concrete is a combination of cement and aggregate.

13.8 PORTLAND CEMENT

Cement is made by heating limestone (calcium carbonate) with small quantities of other materials (such as clay) to 1450°C in a kiln, in a process known as calcination, whereby a molecule of carbon dioxide is liberated from the calcium carbonate to form calcium oxide, or quicklime, which is then blended with the other materials that have been included in the mix. The resulting hard substance, called 'clinker', is then ground with a small amount of gypsum into a powder to make 'Ordinary Portland Cement', the most commonly used type of cement (often referred to as OPC).

Portland cement is a basic ingredient of concrete, mortar and most non-speciality grout. The most common use for Portland cement is in the production of concrete. Concrete is a composite material consisting of aggregate (gravel and sand), cement, and water. As a construction material, concrete can be cast in almost any shape desired, and once hardened, can become a structural (load bearing) element. Portland cement may be grey or white.

13.9 PORTLAND CEMENT BLENDS

Portland cement blends are often available as inter-ground mixtures from cement manufacturers, but similar formulations are often also mixed from the ground components at the concrete mixing plant.

Portland blast-furnace cement: It contains upto 70% ground granulated blast furnace slag, with the rest Portland clinker and a little gypsum. All compositions produce high ultimate strength, but as slag content is increased, early strength is reduced, while sulphate resistance increases and heat evolution diminishes. Used as an economic alternative to Portland sulphate-resisting and low-heat cements.

Portland fly-ash cement: It contains upto 30% fly ash. The fly ash is pozzolanic, so that ultimate strength is maintained. Because fly ash addition allows a lower concrete water content, early strength can also be maintained. Where good quality cheap fly ash is available, this can be an economic alternative to ordinary Portland cement.

Portland pozzolan cement: It includes fly ash cement, since fly ash is a pozzolan, but also includes cements made from other natural or artificial pozzolans. In countries where volcanic ashes are available (e.g. Italy, Chile, Mexico and the Philippines), these cements are often the most common form in use.

Portland silica fume cement: Addition of silica fume can yield exceptionally high strengths, and cements containing 5-20% silica fume are occasionally produced. However, silica fume is more usually added to Portland cement at the concrete mixer.

Masonry cements: These are used for preparing bricklaying mortars and stuccos, and must not be used in concrete. They are usually complex proprietary formulations containing Portland clinker and a number of other ingredients that may include limestone, hydrated lime, air entrainers, retarders, water-proofers and colouring agents. They are formulated to yield workable mortars that allow rapid and consistent masonry work. Subtle variations of masonry cement in the US are plastic cements and stucco cements. These are designed to produce controlled bond with masonry blocks.

Expansive cements: It contains, in addition to Portland clinker, expansive clinkers (usually sulphoaluminate clinkers), and are designed to offset the effects of drying shrinkage that is normally encountered with hydraulic cements. This allows large floor slabs (up to 60 m square) to be prepared without contraction joints.

White blended cements: It may be made using white clinker and white supplementary materials such as high-purity metakaolin.

Coloured cements: These are used for decorative purposes. In some standards, the addition of pigments to produce "coloured Portland cement" is allowed. In other standards (e.g. ASTM), pigments are not allowed constituents of Portland cement, and coloured cements are sold as "blended hydraulic cements".

Very finely ground cements: These are made from mixtures of cement with sand or with slag or other pozzolan type minerals that are extremely finely ground together. Such cements can have the same physical characteristics as normal cement but with 50% less cement particularly due to their increased surface area for the chemical reaction. Even with intensive grinding they can use upto 50% less energy to fabricate than ordinary Portland cements.

13.10 NON-PORTLAND HYDRAULIC CEMENTS

Pozzolan-lime cements: Mixtures of ground pozzolan and lime are the cements used by the Romans, and can be found in Roman structures still standing (e.g. the Pantheon in Rome). They develop strength slowly, but their ultimate strength can be very high. The hydration products that produce strength are essentially the same as those produced by Portland cement.

Slag-lime cements: Ground granulated blast furnace slag is not hydraulic on its own, but is "activated" by addition of alkalis, most economically using lime. They are similar to pozzolan lime cements in their properties. Only granulated slag (i.e. water-quenched, glassy slag) is effective as a cement component.

Supersulphated cements: These contain about 80% ground granulated blast furnace slag, 15% gypsum or anhydrite and a little Portland clinker or lime as an activator. They produce strength by formation of ettringite, with strength growth similar to a slow Portland cement. They exhibit good resistance to aggressive agents, including sulphate.

Calcium aluminate cements: These are hydraulic cements made primarily from limestone and bauxite. The active ingredients are monocalcium aluminate $CaAl_2O_4$ ($CaO \cdot Al_2O_3$ or CA in Cement chemist notation, CCN) and mayenite $Ca_{12}Al_{14}O_{33}$ ($12\,CaO \cdot 7\,Al_2O_3$, or C12A7 in CCN). Strength forms by hydration to calcium aluminate hydrates. They are well-adapted for use in refractory (high-temperature resistant) concretes, e.g. for furnace linings.

Calcium sulphoaluminate cements: These are made from clinkers that include ye'elimite ($Ca_4(AlO_2)_6SO_4$ or C4A3 in Cement chemist notation) as a primary phase. They are used in expansive cements, in ultra-high early strength cements, and in "low-energy" cements. Hydration produces ettringite, and specialized physical properties (such as expansion or rapid reaction) are obtained by adjustment of the availability of calcium and sulphate ions. Their use as a low-energy alternative to Portland cement has been pioneered in China, where several million tonnes per year are produced. Energy requirements are lower because of the lower kiln temperatures required for reaction, and the lower amount of limestone (which must be endothermically decarbonated) in the mix. In addition, the lower limestone content and lower fuel consumption leads to a CO_2 emission around half that associated with Portland clinker. However, SO_2 emissions are usually significantly higher.

13.11 THE SETTING OF CEMENT

Cement sets when mixed with water by way of a complex series of hydration chemical reactions still only partly understood. The different constituents slowly hydrate and crystallise while the interlocking of their crystals gives to cement its strength. After the initial setting, immersion in warm water will speed up setting. In Portland cement, gypsum is added as a compound preventing cement flash setting. The time it takes for cement to set varies and can take anywhere from twenty minutes for initial set, to twenty-four hours, or more, for final set.

13.12 TYPES OF PLASTERS

Plaster is an important building material used for various aspects such as coating walls, ceilings etc. Plaster starts as a dry powder similar to cement and like those materials it is mixed with water to form a paste which liberates heat and then hardens. Unlike cement, plaster remains quite soft after setting, and can be easily manipulated with metal tools. These characteristics make plaster suitable for a finishing, rather than a load-bearing material. In medical science it plays an important role as a binding material to do plasters because of its semi-liquid nature with presence of water. The term Plaster of Paris can refer to gypsum plaster; besides this another two types of plasters are well known: lime plaster and cement plaster.

Gypsum plaster: It is produced by mixing water with calcium sulphate hemihydrate, with the help of heat of about 300°F (150°C). When the dry plaster powder is mixed with water, it re-forms into gypsum. If plaster or gypsum is heated above 200°C, anhydrite is formed, which will also re-form as gypsum if mixed with water.

Gypsum plaster is often being used to simulate the appearance of surfaces of wood, stone, or metal.

Lime plaster: Lime plaster is a mixture of calcium hydroxide and sand. With the presence of carbon dioxide, calcium hydroxide change into calcium carbonate (limestone). To make lime plaster, limestone is heated to produce quicklime. Thus calcium carbonate change to calcium oxide, then water is added to produce slaked lime (calcium hydroxide). Additional water is added to form a paste and stored in air-tight containers as if it exposed to the atmosphere, the calcium hydroxide turns back into calcium carbonate.

Cement plaster: It 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. 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.

13.13 USES OF PLASTER

In Architecture

Plaster is used to create complex detailing for use in room interiors. These may be geometric (simulating wood or stone) or naturalistic (simulating leaves, vines and flowers). These are also often used to simulate wood or stone detailing found in more substantial buildings.

In Art

In the past the famous painters used thin layer of wet plaster to paint on it, known as intonaco. The pigments sink into this layer so that the plaster itself becomes the medium holding them, which accounts for the excellent durability.

Plaster may be cast directly into a damp clay mold. In creating this piece, molds or waste molds would be made of plaster. Some product of plaster when fired in a kiln become terra cotta building decorations, or these may be used to create cast concrete sculptures. If a plaster positive was desired this would be constructed or cast to form a durable image artwork. As a model for stonecutters this would be sufficient. If intended for producing a bronze casting the plaster positive could be further worked to produce smooth surfaces. An advantage of this plaster image is that it is relatively cheap; should a patron approve of the durable image and be willing to bear further expense, subsequent molds could be made for the creation of a wax image to be used in wax casting, a far more expensive process. In lieu of producing a bronze image suitable for outdoor use the plaster image may be painted to resemble a metal image; such sculptures are suitable only for presentation in a weather-protected environment. Plaster expands while hardening, and then contracts slightly just before hardening completely. This makes plaster excellent for use in molds, and it is often used as an artistic material for casting.

In Medicine

Plaster is widely used as a support for broken bones; a bandage impregnated with plaster is moistened and then wrapped around the damaged limb, setting into a close-fitting yet easily removed tube, known as an orthopaedic cast. Plaster is also used within radiotherapy when making immobilization cast for patients. Plaster bandages are used when constructing an impression of the patients head and neck, and liquid plaster is used to fill the impression and produce a plaster bust. Perspex is then vacuum formed over this bust creating an immobilization shell.

In Fire Protection

Plasters have been in use in passive fire protection, as fireproofing products, for many decades. The finished plaster releases water vapour when exposed to flame, acting to slow the spread of the fire, for as much as an hour or two depending on thickness. It also provides some insulation to retard heat flow into structural steel elements, which would otherwise lose their strength and collapse in a fire. Early versions of these plasters have used asbestos fibres, which have by now been outlawed in industrialized nations and have caused significant removal and re-coating work.

More modern plasters fall into the following categories:

- Fibrous (including mineral wool and glass fibre).
- Cement mixtures either with mineral wool or with vermiculite.
- Gypsum plasters, leavened with polystyrene beads, as well as chemical expansion agents to decrease the density of the finished product.

One differentiates between interior and exterior fireproofing. Interior products are typically less substantial, with lower densities and lower cost. Exterior products have to withstand more extreme fire and other environmental conditions. Exterior products are also more likely to be attractively tooled, whereas their interior cousins are usually merely sprayed in place.

13.14 SAFETY MEASURES IN PLASTERING

The chemical reaction that occurs when plaster is mixed with water is exothermic in nature and can therefore cause severe burns. Some variations of plaster that contains powdered silica or asbestos may present health hazards if inhaled. Asbestos is a known irritant; when inhaled in powder form can cause cancer, especially in people who smoke, and inhalation can also cause asbestosis. Inhaled silica can cause silicosis and (in very rare cases) can encourage the development of cancer. Persons working regularly with plaster containing these additives should take precautions to avoid inhaling powdered plaster, cured or uncured. Asbestos is rarely used in modern plaster formulations because of its carcinogenic effects.

QUESTIONS

1. Give the name of components with formula?
2. What is the role of modern cement?
3. Give a distinct idea on manufacture of cement with a clear flow chart diagram.
4. What are the types of Portland cement?
5. What is the setting of cement?
6. What are the types of plaster with its uses?

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