



SHREE H. N. SHUKLACOLLEGE OF SCIENCE

(AFFILIATED TO SAURASHTRA UNIVERSITY)

Shree H.N. Shukla College Campus Nr. Lalpari lake, Behind old Marketing Yard
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UNIT-4

Cement

❖ Introduction

A cement is a binder, a chemical substance used for construction that sets, hardens, and adheres to other materials to bind them together. Cement is seldom used on its own, but rather to bind sand and gravel (aggregate) together. Cement mixed with fine aggregate produces mortar for masonry, or with sand and gravel, produces concrete. Concrete is the most widely used material in existence and is behind only water as the planet's most-consumed resource.

Cements used in construction are usually inorganic, often lime or calcium silicate based, which can be characterized as hydraulic or the less common non-hydraulic, depending on the ability of the cement to set in the presence of water (see hydraulic and non-hydraulic lime plaster).

✚ **Hydraulic cements** (e.g., Portland cement) set and become adhesive through a chemical reaction between the dry ingredients and water. The chemical reaction results in mineral hydrates that are not very water-soluble and so are quite durable in water and safe from chemical attack. This allows setting in wet conditions or under water and further protects the hardened material from chemical attack. The chemical process for hydraulic cement was found by ancient Romans who used volcanic ash (pozzolana) with added lime (calcium oxide).

✚ **Non-hydraulic** cement (*less common*) does not set in wet conditions or under water. Rather, it sets as it dries and reacts with carbon dioxide in the air. It is resistant to attack by chemicals after setting.

The word "cement" can be traced back to the Ancient Roman term opus caementicium, used to describe masonry resembling modern concrete that was made from crushed rock with burnt lime as binder. The volcanic ash and pulverized brick supplements that were added to the burnt lime, to obtain a hydraulic binder, were later referred to as cementum, cimentum, cäment, and cement. In modern times, organic polymers are sometimes used as cements in concrete.

✚ **World production is about four billion tonnes per year**, of which about half is made in China. If the cement industry were a country, it would be the third largest carbon dioxide emitter in the world with up to 2.8 billion tonnes, surpassed only by China and the United States. The initial calcination reaction in the production of cement is



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responsible for about 4% of global CO₂ emissions. The overall process is responsible for about 8% of global CO₂ emissions, as the cement kiln in which the reaction occurs is typically fired by coal or petroleum coke because a luminous flame is required to heat the kiln by radiant heat transfer. As a result, the production of cement is a major contributor to climate change.

Chemistry

Cement materials can be classified into two distinct categories: hydraulic cements and non-hydraulic cements according to their respective setting and hardening mechanisms. Hydraulic cement setting and hardening involves hydration reactions and therefore requires water, while non-hydraulic cements only react with a gas and can directly set under air.

Hydraulic cement



10 cm

Clinker nodules produced by sintering at 1450 °C.

By far the most common type of cement is hydraulic cement, which hardens by hydration of the clinker minerals when water is added. Hydraulic cements (such as Portland cement) are made of a mixture of silicates and oxides, the four main mineral phases of the clinker, abbreviated in the cement chemist notation, being:

C3S: alite ($3\text{CaO}\cdot\text{SiO}_2$);

C2S: belite ($2\text{CaO}\cdot\text{SiO}_2$);

C3A: tricalcium aluminate ($3\text{CaO}\cdot\text{Al}_2\text{O}_3$) (historically, and still occasionally, called celite);

C4AF: brownmillerite ($4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Fe}_2\text{O}_3$).

The silicates are responsible for the cement's mechanical properties — the tricalcium aluminate and brownmillerite are essential for the formation of the liquid phase during the sintering (firing) process of clinker at high temperature in the kiln. The chemistry of these reactions is not completely clear and is still the object of research.

First, the limestone (calcium carbonate) is burned to remove its carbon, producing lime (calcium oxide) in what is known as a calcination reaction. This single chemical reaction is a major emitter of global carbon dioxide emissions.



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The lime reacts with silicon dioxide to produce dicalcium silicate and tricalcium silicate.

The lime also reacts with aluminium oxide to form tricalcium aluminate.

In the last step, calcium oxide, aluminium oxide, and ferric oxide react together to form cement.

 *Non-hydraulic cement*[\[edit\]](#)



Calcium oxide obtained by thermal decomposition of calcium carbonate at high temperature (above 825 °C).

A less common form of cement is non-hydraulic cement, such as slaked lime (calcium oxide mixed with water), which hardens by carbonation in contact with carbon dioxide, which is present in the air (~ 412 vol. ppm \approx 0.04 vol. %). First calcium oxide (lime) is produced from calcium carbonate (limestone or chalk) by calcination at temperatures above 825 °C (1,517 °F) for about 10 hours at atmospheric pressure:

The calcium oxide is then spent (slaked) by mixing it with water to make slaked lime (calcium hydroxide):

Once the excess water is completely evaporated (this process is technically called setting), the carbonation starts:

This reaction is slow, because the partial pressure of carbon dioxide in the air is low (~ 0.4 millibar). The carbonation reaction requires that the dry cement be exposed to air, so the slaked lime is a non-hydraulic cement and cannot be used under water. This process is called the lime cycle.

History[\[edit\]](#)

Perhaps the earliest known occurrence of cement is from twelve million years ago. A deposit of cement was formed after an occurrence of oil shale located adjacent to a



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bed of limestone burned by natural causes. These ancient deposits were investigated in the 1960s and 1970s.

Alternatives to cement used in antiquity

Cement, chemically speaking, is a product that includes lime as the primary binding ingredient, but is far from the first material used for cementation. The Babylonians and Assyrians used bitumen to bind together burnt brick or alabaster slabs. In Ancient Egypt, stone blocks were cemented together with a mortar made of sand and roughly burnt gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), which often contained calcium carbonate (CaCO_3).[12]

Ancient Greece and Rome

Lime (calcium oxide) was used on Crete and by the Ancient Greeks. There is evidence that the Minoans of Crete used crushed potsherds as an artificial pozzolan for hydraulic cement. Nobody knows who first discovered that a combination of hydrated non-hydraulic lime and a pozzolan produces a hydraulic mixture (see also: Pozzolanic reaction), but such concrete was used by the Ancient Macedonians, and three centuries later on a large scale by Roman engineers.

There is... a kind of powder which from natural causes produces astonishing results. It is found in the neighborhood of Baiiae and in the country belonging to the towns round about Mount Vesuvius. This substance when mixed with lime and rubble not only lends strength to buildings of other kinds but even when piers of it are constructed in the sea, they set hard underwater.

—Marcus Vitruvius Pollio, Liber II, De Architectura, Chapter VI "Pozzolana" Sec. 1
The Greeks used volcanic tuff from the island of Thera as their pozzolan and the Romans used crushed volcanic ash (activated aluminium silicates) with lime. This mixture could set under water, increasing its resistance to corrosion like rust. The material was called pozzolana from the town of Pozzuoli, west of Naples where volcanic ash was extracted. In the absence of pozzolanic ash, the Romans used powdered brick or pottery as a substitute and they may have used crushed tiles for this purpose before discovering natural sources near Rome. The huge dome of the Pantheon in Rome and the massive Baths of Caracalla are examples of ancient structures made from these concretes, many of which still stand. The vast system of Roman aqueducts also made extensive use of hydraulic cement. Roman concrete was rarely used on the outside of buildings. The normal technique was to use brick facing material as the formwork for an infill of mortar mixed with an aggregate of broken



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Thank you

