Portland Cement

Alireza Baghchesaraei¹, Omid Reza Baghchesaraei²

Abstract—Portland cement is the most common type of cement in general usage in many parts of the world, as it is a basic ingredient of concrete, mortar, stucco and most non-specialty grout. There are different standards for classification of Portland cement. The two major standards are the ASTM C150 used primarily in the U.S. and European EN-197. EN 197 cement types CEM I, II, III, IV, and V do not correspond to the similarly-named cement types in ASTM C 150. Portland cement manufacture can cause environmental impacts at all stages of the process. When cement is mixed with water a highly alkaline solution (pH ~13) is produced by the dissolution of calcium, sodium and potassium hydroxides.

Keywords—New, Material, Portland Cement

I. INTRODUCTION

Portland cement is the most common type of cement in general usage in many parts of the world, as it is a basic ingredient of concrete, mortar, stucco and most non-specialty grout. It is a fine powder produced by grinding Portland cement clinker (more than 90%), a maximum of about 5% gypsum which controls the set time, and up to 5% minor constituents (as allowed by various standards). As defined by the European Standard EN197.1, Portland cement clinker is a hydraulic material which shall consist of at least two-thirds by mass of calcium silicates (3CaO·SiO₂ and 2CaO·SiO₂), the remainder consisting of aluminium- and iron-containing clinker phases and other compounds. The ratio of CaO to SiO₂ shall not be less than 2.0. The magnesium content (MgO) shall not exceed 5.0% by mass.¹ The last two requirements were already set out in the German Standard, issued in 1909). Portland cement clinker is made by heating, in a kiln, a homogeneous mixture of raw materials to a sintering temperature, which is about 1450 °C for modern cements. The aluminium oxide and iron oxide are present as a flux and contribute little to the strength. For special cements, such as Low Heat (LH) and Sulfate Resistant (SR) types, it is necessary to limit the amount of tricalcium aluminate (3CaO·Al₂O₃) formed. The major raw material for the clinker-making is usually limestone (CaCO₃). Normally, an impure limestone which contains SiO₂ is used - the CaCO₃ content can be as low as 80%. Secondary raw materials (materials in the rawmix other than limestone) depend on the purity of the limestone. Some of the secondary raw materials used are: clay, shale, sand, iron ore, bauxite, fly ash and slag. When a cement kiln is fired by coal, the ash of the coal acts as a secondary raw material.

Portland cement was developed from cements (or correctly hydraulic limes) made in Britain in the early part of the nineteenth century, and its name is derived from its similarity to Portland stone, a type of building stone that was quarried on the Isle of Portland in Dorset, England. Joseph Aspdin, a British bricklayer, in 1824 was granted a patent for a process of making a cement which he called Portland cement. His cement was an artificial hydraulic lime similar in properties to the material known as "Roman Cement" (patented in 1796 by James Parker and his process was similar to that patented in 1822 and used since 1811 by James Frost who called his cement "British Cement". The name "Portland cement" is also recorded in a directory published in 1823 being associated with a William Lockwood and possibly others. Aspdin’s son William in 1843 made an improved version of this cement and he initially called it "Patent Portland cement" although he had no patent. In 1848 William Aspdin further improved his cement and in 1853 moved to Germany where he was involved in cement making [1]. Many people have claimed to have made the first Portland cement in the modern sense, but it is generally accepted that it was first manufactured by William Aspdin at Northfleet, England in about 1842 [2]. The German Government issued a standard on Portland cement in 1878.

Today and because of economic problems, in my country and also other developing countries using cement is usuall and practical. It is one of the most important materials in these countries and I try to introduce all the kinds of portland cement and their usage. In addition, it is a new material in my country.

II. MATERIALS AND METHODS

Types of Portland cement

General

There are different standards for classification of Portland cement. The two major standards are the ASTM C150 used primarily in the U.S. and European EN-197. EN 197 cement types CEM I, II, III, IV, and V do not correspond to the similarly-named cement types in ASTM C 150.

Production

Schematic explanation of Portland cement production

There are three fundamental stages in the production of Portland cement:
1. Preparation of the raw mixture
2. Production of the clinker
3. Preparation of the cement
The chemistry of cement is very complex, so cement chemist notation was invented to simplify the formula of common oxides found in cement. This reflects the fact that most of the elements are present in their highest oxidation state, and chemical analyses of cement are expressed as mass percent of these notional oxides.

Rawmix preparation

A limestone prehomogenization pile being built by a boom stacker

A completed limestone prehomogenization pile

The raw materials for Portland cement production are a mixture (as fine powder in the 'Dry process' or in the form of a slurry in the 'Wet process') of minerals containing calcium oxide, silicon oxide, aluminium oxide, ferric oxide, and magnesium oxide. The raw materials are usually quarried from local rock, which in some places is already practically the desired composition and in other places requires the addition of clay and limestone, as well as iron ore, bauxite or recycled materials. The individual raw materials are first crushed, typically to below 50 mm. In many plants, some or all of the raw materials are then roughly blended in a "prehomogenization pile". The raw materials are next ground together in a rawmill. Silos of individual raw materials are arranged over the feed conveyor belt. Accurately controlled proportions of each material are delivered onto the belt by weigh-feeders. Passing into the rawmill, the mixture is ground to rawmix. The fineness of rawmix is specified in terms of the size of the largest particles, and is usually controlled so that there are less than 5-15% by mass of particles exceeding 90 μm in diameter. It is important that the rawmix contains no large particles in order to complete the chemical reactions in the kiln, and to ensure the mix is chemically homogenous. In the case of a dry process, the rawmill also dries the raw materials, usually by passing hot exhaust gases from the kiln through the mill, so that the rawmix emerges as a fine powder. This is conveyed to the blending system by conveyor belt or by a powder pump. In the case of wet process, water is added to the rawmill feed, and the mill product is a slurry with moisture content usually in the range 25-45% by mass. This slurry is conveyed to the blending system by conventional liquid pumps

Formation of clinker

The raw mixture is heated in a cement kiln, a slowly rotating and sloped cylinder, with temperatures increasing over the length of the cylinder up to a peak temperature of 1400-1450 °C. A complex succession of chemical reactions take place (see cement kiln) as the temperature rises. The peak temperature is regulated so that the product contains sintered but not fused lumps. Sintering consists of the melting of 25-30% of the mass of the material. The resulting liquid draws the remaining solid particles together by surface tension, and acts as a solvent for the final chemical reaction in which alite is formed. Too low a temperature causes insufficient sintering and incomplete reaction, but too high a temperature results in a molten mass or glass, destruction of the kiln lining, and waste of fuel. The resulting material is clinker. On cooling, it is conveyed to storage. Some effort is usually made to blend the clinker, because although the chemistry of the rawmix may have been tightly controlled, the kiln process potentially introduces new sources of chemical variability. The clinker can be stored for a number of years before use. Prolonged exposure to water decreases the reactivity of cement produced from weathered clinker.

The enthalpy of formation of clinker from calcium carbonate and clay minerals is ~1700 kJ/kg. However, because of heat loss during production, actual values can be much higher. The high energy requirements and the release of significant amounts of carbon dioxide makes cement production a concern for global warming. See "Environmental effects" below.

Cement grinding

A 10 MW cement mill, producing 270 tph

In order to achieve the desired setting qualities in the finished product, a quantity (2-8%, but typically 5%) of calcium sulfate (usually gypsum or anhydrite) is added to the clinker and the mixture is finely ground to form the finished cement powder. This is achieved in a cement mill. The grinding process is controlled to obtain a powder with a broad particle size range, in which typically 15% by mass consists of particles below 5 μm diameter, and 5% of particles above 45 μm. The measure of fineness usually used is the "specific surface", which is the total particle surface area of a unit mass of cement. The rate of initial reaction (up to 24 hours) of the cement on addition of water is directly proportional to the specific surface. Typical values are 320-380 m².kg⁻¹ for general purpose cements, and 450-650 m².kg⁻¹ for "rapid hardening" cements. The cement is conveyed by belt or powder pump to a silo for storage. Cement plants normally have sufficient silo space for 1-20 weeks production, depending upon local demand cycles. The cement is delivered to end-users either in bags or as bulk powder blown from a pressure vehicle into the customer's silo. In developed countries, 80% or more of cement is delivered in bulk, and many cement plants have no bag-packing facility. In developing countries, bags are the normal mode of delivery.

<table>
<thead>
<tr>
<th>Clinker</th>
<th>Mass%</th>
<th>Cement</th>
<th>Mass%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium silicate (CaO)₃</td>
<td>45-75%</td>
<td>Calcium oxide, CaO, C</td>
<td>61-67%</td>
</tr>
<tr>
<td>Dicalcium silicate (CaO)₂</td>
<td>18%</td>
<td>Silicon oxide, SiO₂, S</td>
<td>19-23%</td>
</tr>
<tr>
<td>Tricalcium aluminate</td>
<td>0-13%</td>
<td>Aluminium oxide, Al₂O₃, A</td>
<td>2.5-6%</td>
</tr>
<tr>
<td>Tetracalcium aluminoferrite</td>
<td>0-18%</td>
<td>Ferric oxide, Fe₂O₃, F</td>
<td>0-6%</td>
</tr>
<tr>
<td>Gypsum CaSO₄</td>
<td>12-10%</td>
<td>Sulfate</td>
<td></td>
</tr>
</tbody>
</table>

Setting and hardening

When water is mixed with Portland cement, the product sets in a few hours and hardens over a period of weeks. These processes can vary widely depending upon the mix used and
the conditions of curing of the product, but a typical concrete sets (i.e. becomes rigid) in about 6 hours, and develops a compressive strength of 8 MPa in 24 hours. The strength rises to 15 MPa at 3 days, 23 MPa at one week, 35 MPa at 4 weeks, and 41 MPa at three months. In principle, the strength continues to rise slowly as long as water is available for continued hydration, but concrete is usually allowed to dry out after a few weeks, and this causes strength growth to stop.

Setting and hardening of Portland cement is caused by the formation of water-containing compounds, forming as a result of reactions between cement components and water. Usually, cement reacts in a plastic mixture only at water/cement ratios between 0.25 and 0.75. The reaction and the reaction products are referred to as hydration and hydrates or hydrate phases, respectively. As a result of the reactions (which start immediately), a stiffening can be observed which is very small in the beginning, but which increases with time. The point in time at which it reaches a certain level is called the start of setting. The consecutive further consolidation is called setting, after which the phase of hardening begins.

Stiffening, setting and hardening are caused by the formation of a microstructure of hydration products of varying rigidity which fills the water-filled interstitial spaces between the solid particles of the cement paste, mortar or concrete. The behaviour with time of the stiffening, setting and hardening therefore depends to a very great extent on the size of the interstitial spaces, i.e. on the water/cement ratio. The hydration products primarily affecting the strength are calcium silicate hydrates ("C-S-H phases"). Further hydration products are calcium hydroxide, sulfatic hydrates (AFm and Aft phases), and related compounds, hydrogarnet, and gehlenite hydrate. Calcium silicates or silicate constituents make up over 70% by mass of silicate-based cements. The hydration of these compounds and the properties of the calcium silicate hydrates produced are therefore particularly important. Calcium silicate hydrates contain less CaO than the calcium silicates in cement clinker, so calcium hydroxide is formed during the hydration of Portland cement. This is available for reaction with supplementary cementitious materials such as ground granulated blast furnace slag and pozzolans. The simplified reaction of alite with water may be expressed as:

\[ 2Ca_3O_7SiO_4 + 6H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + 3Ca(OH)_2 \]

This is a relatively fast reaction, causing setting and strength development in the first few weeks. The reaction of belite is:

\[ 2Ca_3SiO_5 + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2 \]

This reaction is relatively slow, and is mainly responsible for strength growth after one week. Tricalcium aluminate hydration is controlled by the added calcium sulfate, which immediately goes into solution when water is added. Firstly, ettringite is rapidly formed, causing a slowing of the hydration (see tricalcium aluminate):

\[ Ca_3(AlO_2)_2 + 3CaSO_4 + 32H_2O \rightarrow Ca_6(AlO_2)_3(SO_4)_3 \cdot 32H_2O \]

The ettringite subsequently reacts slowly with further tricalcium aluminate to form "monosulfate" - an "AFm phase":

\[ Ca_6(AlO_2)_3(SO_4)_3 \cdot 32H_2O + CaC_2(AlO_2)_2(SO_4)_2 \cdot 12H_2O \rightarrow 3Ca_2AlFeO_5 + CaSO_4 + 16H_2O \]

This reaction is complete after 1-2 days. The calcium aluminoferrite reacts slowly due to precipitation of hydrated iron oxide:

\[ 2Ca_2AlFeO_5 + CaSO_4 + 16H_2O \rightarrow Ca_6(AlO_2)_3(SO_4)_3 \cdot 12H_2O + Ca(OH)_2 + 2Fe(OH)_3 \]

The pH-value of the pore solution reaches comparatively high values and is of importance for most of the hydration reactions.

Soon after Portland cement is mixed with water, a brief and intense hydration starts (pre-induction period). Calcium sulfates dissolve completely and alkali sulfates almost completely. Short, hexagonal needle-like ettringite crystals form at the surface of the clinker particles as a result of the reactions between calcium- and sulphate ions with tricalcium aluminate. Further, originating from tricalcium silicate, first calcium silicate hydrates (C-S-H) in colloidal shape can be observed. CaSO_4 + 16H_2O → Ca_6(AlO_2)_3(SO_4)_3 \cdot 12H_2O + Ca(OH)_2 + 2Fe(OH)_3

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costs about the same as Type I. Its typical compound composition is:

$$51\% (C_3S), 24\% (C_2S), 6\% (C_3A), 11\% (C_4AF), 2.9\% MgO, 2.5\% (SO_3), 0.8\% \text{ Ignition loss, and 1.0}\% \text{ free CaO.}$$

A limitation on the composition is that the $(C_3A)$ shall not exceed eight percent which reduces its vulnerability to sulfates. This type is for general construction that is exposed to moderate sulfate attack and is meant for use when concrete is in contact with soils and ground water especially in the western United States due to the high sulfur content of the soil. Because of similar price to that of Type I, Type II is much used as a general purpose cement, and the majority of Portland cement sold in North America meets this specification.

Note: Cement meeting (among others) the specifications for Type I and II has become commonly available on the world market.

Type III is has relatively high early strength. Its typical compound composition is:

$$57\% (C_3S), 19\% (C_2S), 10\% (C_3A), 7\% (C_4AF), 3.0\% MgO, 3.1\% (SO_3), 0.9\% \text{ Ignition loss, and 1.3}\% \text{ free CaO.}$$

This cement is similar to Type I, but ground finer. Some manufacturers make a separate clinker with higher $C_3S$ and/or $C_3A$ content, but this is increasingly rare, and the general purpose clinker is usually used, ground to a specific surface typically 50-80% higher. The gypsum level may also be increased a small amount. This gives the concrete using this type of cement a three day compressive strength equal to the seven day compressive strength of types I and II. Its seven day compressive strength is almost equal to types I and II 28 day compressive strengths. The only downside is that the six month strength of type III is the same or slightly less than that of types I and II. Therefore the long-term strength is sacrificed a little. It is usually used for precast concrete manufacture, where high 1-day strength allows fast turnover of molds. It may also be used in emergency construction and repairs and construction of machine bases and gate installations.

Type IV Portland cement is generally known for its low heat of hydration. Its typical compound composition is:

$$28\% (C_3S), 49\% (C_2S), 4\% (C_3A), 12\% (C_4AF), 1.8\% MgO, 1.9\% (SO_3), 0.9\% \text{ Ignition loss, and 0.8}\% \text{ free CaO.}$$

The percentages of $(C_2S)$ and $(C_4AF)$ are relatively high and $(C_3S)$ and $(C_3A)$ are relatively low. A limitation on this type is that the maximum percentage of $(C_3A)$ is seven, and the maximum percentage of $(C_3S)$ is thirty-five. This causes the heat given off by the hydration reaction to develop at a slower rate. However, as a consequence the strength of the concrete develops slowly. After one or two years the strength is higher than the other types after full curing. This cement is used for very large concrete structures, such as dams, which have a low surface to volume ratio. This type of cement is generally not stocked by manufacturers but some might consider a large special order. This type of cement has not been made for many years, because Portland-pozzolan cements and ground granulated blast furnace slag addition offer a cheaper and more reliable alternative.

Type V is used where sulfate resistance is important. Its typical compound composition is:

$$38\% (C_3S), 43\% (C_2S), 4\% (C_3A), 9\% (C_4AF), 1.9\% MgO, 1.8\% (SO_3), 0.9\% \text{ Ignition loss, and 0.8}\% \text{ free CaO.}$$

This cement has a very low $(C_3A)$ composition which accounts for its high sulfate resistance. The maximum content of $(C_3A)$ allowed is five percent for Type V Portland cement. Another limitation is that the $(C_4AF) + 2(C_3A)$ composition cannot exceed twenty percent. This type is used in concrete that is to be exposed to alkali soil and ground water sulfates which react with $(C_3A)$ causing disruptive expansion. It is unavailable in many places although its use is common in the western United States and Canada. As with Type IV, Type V Portland cement has mainly been supplanted by the use of ordinary cement with added ground granulated blast furnace slag or tertiary blended cements containing slag and fly ash.

Types Ia, IIa, and IIIa have the same composition as types I, II, and III. The only difference is that in Ia, IIa, and IIIa an air-entraining agent is ground into the mix. The air-entrainment must meet the minimum and maximum optional specification found in the ASTM manual. These types are only available in the eastern United States and Canada but can only be found on a limited basis. They are a poor approach to air-entrainment which improves resistance to freezing under low temperatures.

### EN 197

#### TABLE II

<table>
<thead>
<tr>
<th>Class</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Portland cement Comprising Portland cement and up to 5% of minor additional constituents</td>
</tr>
<tr>
<td>II</td>
<td>Portland-composite cement Portland cement and up to 35% of other single constituents</td>
</tr>
<tr>
<td>III</td>
<td>Blastfurnace cement Portland cement and higher percentages of blastfurnace slag</td>
</tr>
<tr>
<td>IV</td>
<td>Pozzolanic cement Portland cement and up to 55% of pozzolanic constituents</td>
</tr>
<tr>
<td>V</td>
<td>Composite cement Portland cement, blastfurnace slag and pozzolana or fly ash</td>
</tr>
</tbody>
</table>

Constituents that are permitted in Portland-composite cements are blastfurnace slag, silica fume, natural and industrial pozzolans, silicious and calcareous fly ash, burnt shale and limestone.

### White Portland cement

White Portland cement differs physically from the gray form only in its color, and as such can fall into many of the above categories (e.g. ASTM Type I, II and/or III). However, its manufacture is significantly different from that of the gray product, and is treated separately.

### Safety and environmental effects Safety

When cement is mixed with water a highly alkaline solution (pH ~13) is produced by the dissolution of calcium, sodium and potassium hydroxides. Gloves, goggles and a filter mask should be used for protection. Hands should be washed after
contact. Cement can cause serious burns if contact is prolonged or if skin is not washed promptly. Once the cement hydrates, the hardened mass can be safely touched without gloves.

In Scandinavia, France and the UK, the level of chromium(VI), which is thought to be toxic and a major skin irritant, may not exceed 2 ppm (parts per million).

Portland cement manufacture can cause environmental impacts at all stages of the process. These include emissions of airborne pollution in the form of dust, gases, noise and vibration when operating machinery and during blasting in quarries, consumption of large quantities of fuel during manufacture, release of CO$_2$ from the raw materials during manufacture, and damage to countryside from quarrying. Equipment to reduce dust emissions during quarrying and manufacture of cement is widely used, and equipment to trap and separate exhaust gases are coming into increased use. Environmental protection also includes the re-integration of quarries into the countryside after they have been closed down by returning them to nature or re-cultivating them.

Epidemiologic Notes and Reports Sulfur Dioxide Exposure in Portland Cement Plants, from the Centers for Disease Control states "Workers at Portland cement facilities, particularly those burning fuel containing sulfur, should be aware of the acute and chronic effects of exposure to SO$_2$ [sulfur dioxide], and peak and full-shift concentrations of SO$_2$ should be periodically measured." [4] "The Arizona Department of Environmental Quality was informed this week that the Arizona Portland Cement Co. failed a second round of testing for emissions of hazardous air pollutants at the company's Rillito plant near Tucson. The latest round of testing, performed in January 2003 by the company, is designed to ensure that the facility complies with federal standards governing the emissions of dioxins and furans, which are byproducts of the manufacturing process." [5] Cement Reviews' "Environmental News" web page details case after case of environmental problems with cement manufacturing. [6]

An independent research effort of AEA Technology to identify critical issues for the cement industry today concluded the most important environment, health and safety performance issues facing the cement industry are atmospheric releases (including greenhouse gas emissions, dioxin, NO$_x$, SO$_2$, and particulates), accidents and worker exposure to dust. [7]

The CO$_2$ associated with Portland cement manufacture falls into 3 categories:

1. CO$_2$ derived from decarbonation of limestone,
2. CO$_2$ from kiln fuel combustion,
3. CO$_2$ produced by vehicles in cement plants and distribution.

Source 1 is fairly constant: minimum around 0.47 kg CO$_2$ per kg of cement, maximum 0.54, typical value around 0.50 world-wide. Source 2 varies with plant efficiency: efficient precalciner plant 0.24 kg CO$_2$ per kg cement, low-efficiency wet process as high as 0.65, typical modern proactice (e.g UK) averaging around 0.30. Source 3 is almost insignificant at 0.002-0.005. So typical total CO$_2$ is around 0.80 kg CO$_2$ per kg finished cement. This leaves aside the CO$_2$ associated with electric power consumption, since this varies according to the local generation type and efficiency. Typical electrical energy consumption is of the order of 90-150 kWh per tonne cement, equivalent to 0.09-0.15 kg CO$_2$ per kg finished cement if the electricity is coal-generated.

Overall, with nuclear- or hydroelectric power and efficient manufacturing, CO$_2$ generation can be as little as 0.7 kg per kg cement, but can be as high as twice this amount. The thrust of innovation for the future is to reduce sources 1 and 2 by modification of the chemistry of cement, by the use of wastes, and by adopting more efficient processes. Although cement manufacturing is clearly a very large CO$_2$ emitter, concrete (of which cement makes up about 15%) compares quite favorably with other building systems in this regard. See also cement kiln emissions.

Cement plants as alternatives to conventional waste disposal or processing

Used tyres being fed to a pair of cement kilns

Due to the high temperatures inside cement kilns, combined with the oxidizing (oxygen-rich) atmosphere and long residence times, cement kilns have been used as a processing option for various types of waste streams. The waste streams often contain combustible material which allows the substitution of part of the fossil fuel normally used in the process.

Waste materials used in cement kilns as a fuel supplement:

1. Waste solvents and lubricants.
2. Hazardous waste; cement kilns completely destroy hazardous organic compounds
3. Bone meal; slaughter house waste due to bovine spongiform encephalopathy contamination concerns
4. Waste plastics
5. Sewage sludge
6. Rice shells
7. Sugar cane waste
8. Portland cement manufacture also has the potential to remove industrial byproducts from the waste-stream, effectively sequestering some environmentally damaging wastes. These include:
   1. Slag
   2. Fly ash (from power plants)
   3. Silica fume (from steel mills)
   4. Synthetic gypsum (from desulphurisation)

REFERENCES