

The Rise of Portland Cements

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ABSTRACT

This chapter tells the story of Portland cement, from its invention in the 19th century until its present-day hegemony as the number one manufactured mineral product. The success story of Portland cement is rooted in the unique combination of the abundance of its raw materials, the reactivity of the high-temperature clinker product toward water, and the properties of the calcium silicate and aluminate hydration products. Further development of Portland cements today mainly addresses the formidable challenge of reducing process CO₂ emissions. Options include partial replacement of clinker by low-carbon resources, material-efficient use of cement and concrete products, and end-of-pipe carbon capture and storage or use.

KEYWORDS: Portland cement; clinker; production; hydration products; CO₂

INTRODUCTION

Portland cement—usually simply referred to as cement—is one of the great inventions of mankind and has experienced stunning success since its first introduction in the early 19th century. Today, Portland cements are used in concrete, mortar, and many other applications. It is a “mineral” or inorganic powder that hardens when mixed with water and binds aggregates such as sand, gravel, or crushed rock together in a solid rock-like material. The use of Portland cements outstrips that of other mineral binders manifold. At present, the 4.2 billion tonnes of Portland

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cements produced worldwide every year cover more than 99% of the global cement market (U.S. Geological Survey (USGS) 2021). As an intermediate product, Portland cement is considered to be strategic a commodity essential to economic development and prosperity. Why and how a single mineral product has been able to assume such a dominant market position is the story of this chapter.

The stage of the story of Portland cements is our own planet Earth, in fact only the very top of it, namely, the uppermost part of the continental crust. For a construction material to be widely available and affordable, it must reflect the makeup of the Earth's crust and, as such, be made of abundant and, thus, inexpensive raw materials. When comparing the average composition of the Earth's crust with a typical composition of Portland cement in FIGURE 1, the much higher Ca content of Portland cement immediately catches the eye (Taylor 1997). Fortunately for Portland cement producers, Ca is concentrated through biological and chemical actions as CaCO_3 in limestone. Limestone is the quintessential raw material of Portland cement. It is a very common resource in areas where many humans live and thrive, close to the continental shelf or margin where most limestones form. Exceptions are the deep interiors of continents such as Africa or South America, which are often devoid of suitable limestone and, in the absence of alternatives, rely on costly cement imports to develop their housing and infrastructure (Schmidt et al. 2020).

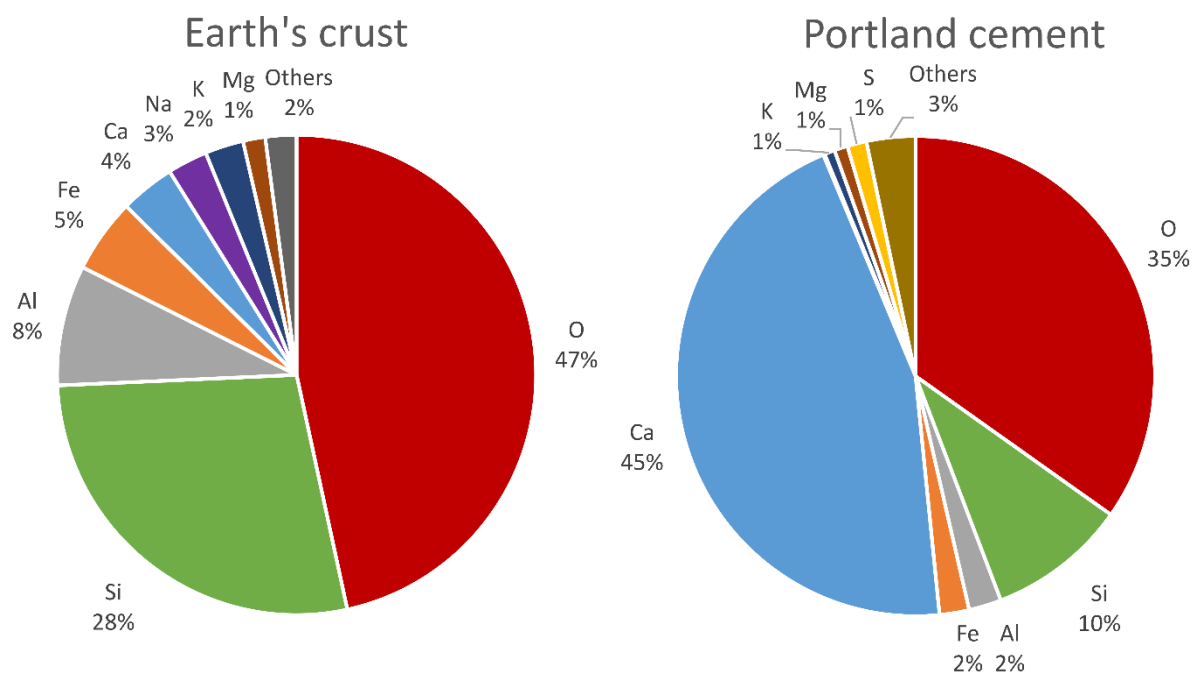


FIGURE 1. Average crustal composition (LEFT) versus Portland cement composition (RIGHT).

In the production of Portland cement, limestone is mixed with one or more sources of Si, Al, and Fe, to reach a well-defined raw meal composition. The limestone used is often impure and, therefore, already contributes part of the required Si, Al, and Fe. Clays or shale are conventionally added to fine-tune the raw meal composition, which is then fired at a temperature of 1450 °C to obtain the so-called clinker. The clinker is subsequently finely milled together with a small amount of Ca-sulfates (gypsum or anhydrite) to obtain the neat Portland cement product as a hydraulic binder (Bye 1999).

Before diving into the historical development and mineralogy of present-day Portland cements, it is of interest to describe what a hydraulic binder is and how it works. A hydraulic binder hardens via a reaction that requires water. It can also harden underwater, i.e., the water is a reagent and not a solvent that must be removed, as is often the case with organic glues. It is a common misconception that concrete needs to “dry” in order to harden. As a matter of fact, Portland cement as a hydraulic binder can be used for underwater concreting. The reaction of Portland cement with water produces stable solid hydrates. The hydration of Portland cement is a solution-mediated process, as illustrated in FIGURE 2 (Scrivener et al. 2019). The unstable high-temperature clinker minerals dissolve rapidly into the aqueous phase, and (meta-)stable cement hydrates readily start to precipitate from the supersaturated solution. These solid hydrates have a lower density than the clinker minerals and fill the space previously occupied by water. In doing so, large areas of solid–solid interfaces are created. The cohesion, or strength, of the binder is mainly understood to result from the weak surface adhesive forces, e.g., Van der Waals forces, acting across the solid–solid interfaces. In hydraulic binders, these attractive forces should be strong enough to resist redispersion by contact with water, as happens with clay particles in adobe, which are bricks made of compacted, dried earth with high clay contents and straw (Gartner and Macphee 2011).

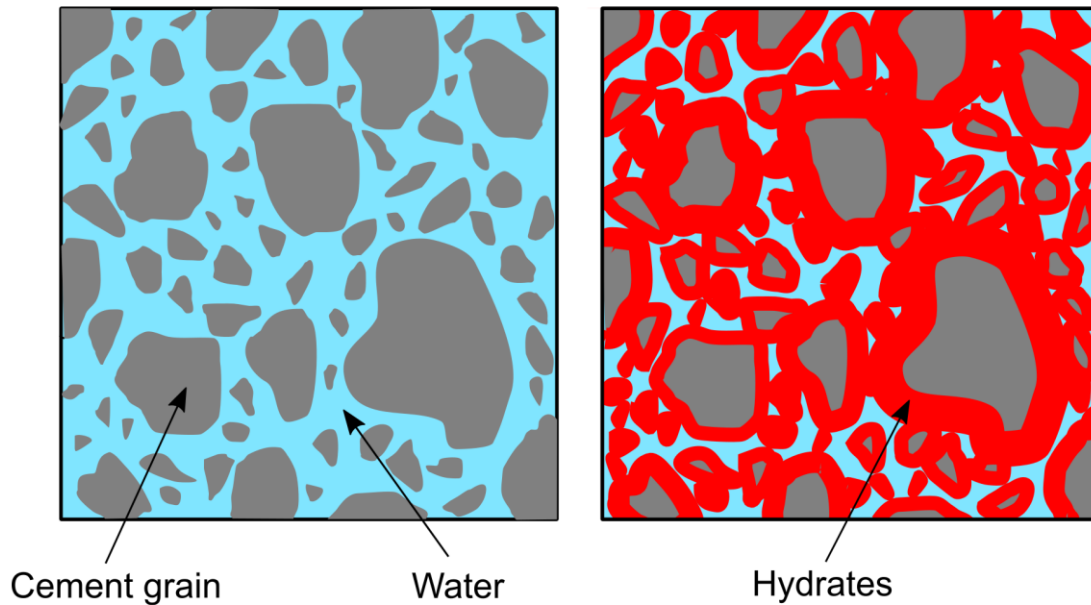


FIGURE 2. Schematic illustration of the microstructure of a hydraulic cement with water.

THE “INVENTION” OF PORTLAND CEMENT

As with many other important ideas, the invention of Portland cement came not as an out-of-the-blue “Eureka” moment, but sprouted from a long-standing tradition of the production of lime binders rooted in the antique world. Elsen et al. (2022 this issue) describe these binders in more detail. By the late 18th century, it was well known that limes produced in different locations had different properties. In some locations, so-called hydraulic limes were produced that were far more suitable for applications that required water resistance, such as marine infrastructure. In the United Kingdom, John Smeaton pioneered, or rather rediscovered, concrete as a mixture of hydraulic lime and aggregates to build the Eddystone lighthouse in 1759. Fifty years later, research by the French engineer Louis Vicat showed that the silica and alumina levels in the lime determined its hydraulic behavior. The underlying chemistry was, however, not well understood (Elsen et al. 2012). Neither Smeaton nor Vicat attempted to protect their findings, leaving the opportunity to Joseph Aspdin to claim his patent on what he branded “Portland cement” in 1824 (FIGURE 3).

Early or proto-Portland cements were quite different from the product we know today. At the time, the production was batch-wise using lime shaft or bottle kilns (furnaces or ovens for firing; see below). These kilns did not reach temperatures much above 1100–1200 °C, which is not sufficient to form Ca_3SiO_5 or alite, the main reactive phase of present-day Portland clinker.

Moreover, the type and proportions of raw materials varied significantly between competitors and were treated as trade secrets. This resulted in a wide variety of compositions and properties of early Portland cements. From 1840 onward, as new kiln types (the Hoffmann kiln and, eventually, the rotary kiln) were gradually introduced, a higher clinkering temperature of 1450 °C was used more consistently. This enabled the formation of alite and resulted in the product presently known as Portland cement (Trout 2019).

Box 3.1. Joseph Aspdin and his patent on Portland cement.

Joseph Aspdin was a resourceful bricklayer from Leeds (United Kingdom) that experimented with slaked lime and clay that were mixed in specific proportions and calcined to produce a hydraulic binder. In 1824, Aspdin obtained a patent on his method (FIGURE 3) that, in hindsight, is remarkably vague on crucial parameters such as mixture proportions and calcination temperature. He astutely branded his invention as “Portland cement” after Portland stone, a high-quality, white-grey limestone from the Portland peninsula (United Kingdom) and very popular at that time as building stone for major public buildings such as St. Paul’s Cathedral and Buckingham Palace in London.

PORTLAND CEMENT MINERALOGY

Clinker Minerals

Portland clinker is made up of four major hydraulic phases. Alite (Ca_3SiO_5 or C_3S) constitutes about 65 wt.% of a conventional Portland cement; belite (Ca_2SiO_4 or C_2S) is present at around 15 wt.%; and aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$ or C_3A) and ferrite ($\text{Ca}_2\text{AlFeO}_5$ or C_4AF) each represent about 10 wt.%. Calcium sulfates are added to the clinker to make Portland cement. The role of each consecutive reaction occurring in the kiln is illustrated by the clinker microstructure in FIGURE 4. Alite is recognized as large, blue-brownish, angular grains that have grown at the expense of

My method of making a cement or artificial stone for stuccoing buildings, waterworks, cisterns, or any other purpose to which it may be applicable (and which I call Portland cement) is as follows:—I take a specific quantity of limestone, such as that generally used for making or repairing roads, and I take it from the roads after it is reduced to a puddle or powder; but if I cannot procure a sufficient quantity of the above from the roads, I obtain the limestone itself, and I cause the puddle or powder, or the limestone, as the case may be, to be calcined. I then take a specific quantity of argillaceous earth or clay, and mix them with water to a state approaching impalpability, either by manual labour or machinery. After this proceeding I put the above mixture into a slip pan for evaporation, either by the heat of the sun or by submitting it to the action of fire or steam conveyed in flues or pipes under or near the pan till the water is entirely evaporated. Then I break the said mixture into suitable lumps, and calcine them in a furnace similar to a lime kiln till the carbonic acid is entirely expelled. The mixture so calcined is to be ground, beat, or rolled to a fine powder, and is then in a fit state for making cement or artificial stone. This powder is to be mixed with a sufficient quantity of water to bring it into the consistency of mortar, and thus applied to the purposes wanted.

In witness whereof, I, the said Joseph Aspdin, have hereunto set my hand and seal, this Fifteenth day of December, in the year of our Lord One thousand eight hundred and twenty-four.

JOSEPH (L.S.) ASPDIN.

FIGURE 3. Excerpt of patent BP 5022, disclosing Joseph Aspdin’s method of making “Portland cement”.

belite (rounded grains) and free lime (consumed) at the highest temperature section of the kiln (above 1350 °C) (Stutzman 2012). Both calcium silicates are embedded in a light-colored phase. This interstitial phase represents the melt that formed at temperatures above 1338 °C. This melt phase plays an important role in expediting the high-temperature formation of alite by facilitating contact between solids and enabling element diffusion through the melt phase. Upon cooling, the melt phase crystallizes into the C_3A and ferrite phases (Glasser et al. 2004).

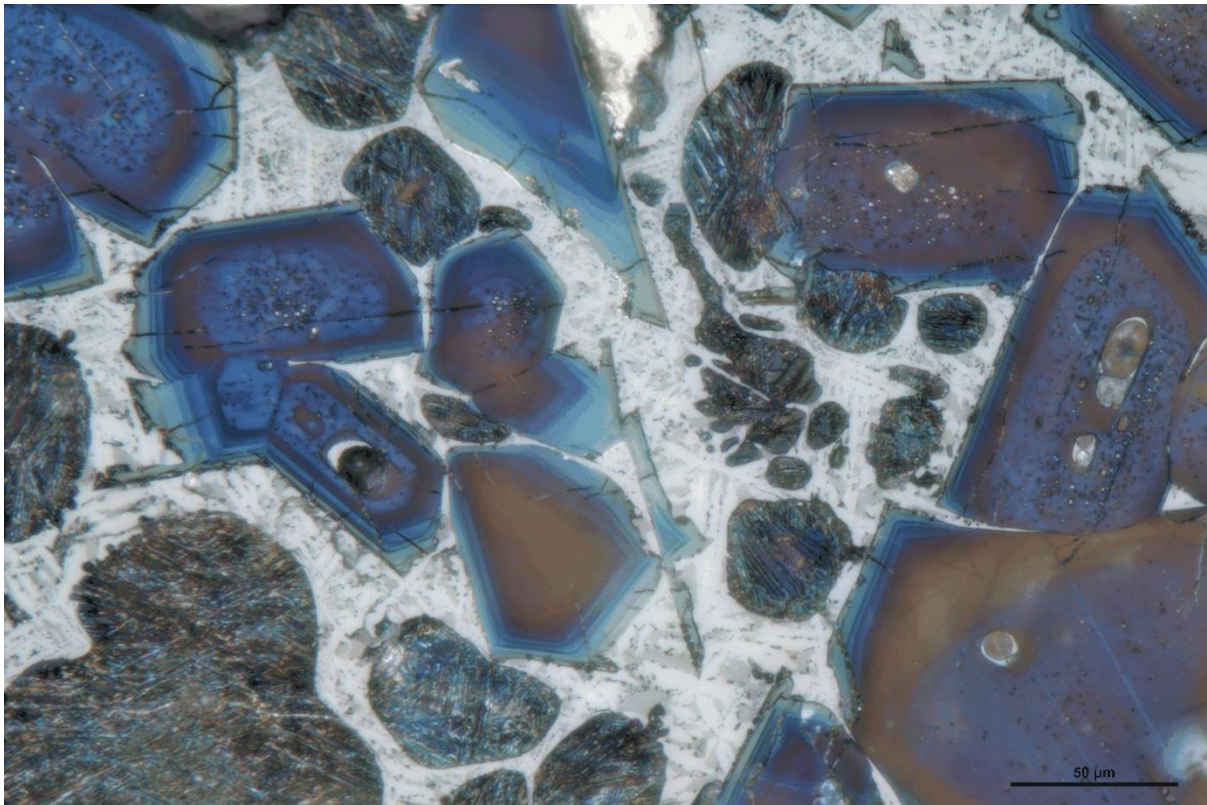


FIGURE 4. Portland clinker microstructure visualized by an optical micrograph of a nital-etched specimen (nital is a solution of nitric acid and alcohol). Alite grains are blue-brownish and generally angular showing growth zones, while belite grains are rounded and have a fine lamellar appearance. The light-colored interstitial phase represents an intergrowth of C_3A (darker zones) and ferrite (white elongated crystals). PHOTO COURTESY OF P. STUTZMAN.

The somewhat peculiar names for the main phases are not only used for convenience, but also intend to distinguish the impure phases present in Portland cement from the pure end-member stoichiometries. Impurities and solid solutions are important as they stabilize the crystal lattices of high-temperature polymorphs and prevent conversion into less-reactive polymorphs or phases when cooling to ambient conditions. The preservation of “metastable” high-temperature phases is key to the production of reactive cements that develop strength rapidly, within the course of a few hours after mixing. Understanding the crystal structures of the main clinker

phases provides insight into the differences in their reactivity. The high reactivity of C_3S is explained by the presence of O^{2-} ions in its structure. This is a rather unique feature among silicates and explains why C_3S is much more reactive than C_2S . In addition, the open structure and distorted coordination of the calcium atoms by oxygens contribute to the instability of C_3S (Taylor 1997), which is also polymorphic. At the high temperatures in the kiln, C_3S exhibits rhombohedral symmetry that converts into several monoclinic and eventually triclinic symmetries upon cooling. Rapidly cooled alite in Portland cement is usually monoclinic. Small amounts of Al and Mg substituted in the C_3S crystal lattice stabilize the higher-temperature monoclinic polymorphs (Maki et al. 1992). As the lowering of the symmetry during cooling involves only minor movements of atoms from the rhombohedral structure, the differences in reactivity between the polymorphs is not very significant (Bazzoni et al. 2014). This is in stark contrast to C_2S , where the polymorphs have very distinct atomic arrangements and reactivities. At room temperature, γ - C_2S , or calcium olivine, is the stable polymorph and has very low reactivity in Portland cement. High-temperature polymorphs (α , α'_H , α'_L , and β) have less ideal close packing and lower density. The lower monoclinic symmetry and more distorted coordination of the calcium atoms correlate with higher reactivity (Wang et al. 2015). Solid solutions with impurity ions (e.g., Al^{3+} , K^+ , SO_4^{2-} , PO_4^{3-}) are common and stabilize the higher-temperature polymorphs. Therefore, belite in Portland cement is usually the β - C_2S type but, in some cases, the more reactive α' -polymorph is also present. Nevertheless, even the most reactive belites will develop early strength more slowly than alite.

The high reactivity of alite comes at the expense of a higher CaO content and, consequently, a higher stoichiometric emission of CO_2 during its production from limestone and silica. TABLE 1 summarizes these characteristics for the main clinker phases in Portland cement and other types of cements that are used mainly in niche applications (Scrivener and Nonat 2011). It is clear that reducing the CaO content of cement is one of the main levers to reduce CO_2 emissions. Switching from mainly alitic to belitic cements would save about 10% in CO_2 emissions at the expense of a significantly slower strength gain. More effective would be the production of calcium (sulfo)aluminate cements that present significantly lower CO_2 emissions on a cement mass base, but also with respect to the volume of hydrates generated by the cement. As explained in more detail by Hanein et al. (2022 this issue), raw material cost (bauxite is the main concentrated source of alumina), dimensional stability, and durability are important challenges to tackle for these cements.

TABLE 1. CHARACTERISTICS OF MAIN CLINKER PHASES IN PORTLAND CEMENTS, CALCIUM ALUMINATE CEMENTS, AND CALCIUM SULFO-ALUMINATE CEMENTS—CAO CONTENT, FIRING

TEMPERATURE, CO₂ EMITTED PER CEMENT MASS, AND CO₂ EMITTED PER VOLUME OF HYDRATE. DATA FROM SCRIVENER AND NONAT (2011).

Phase	Raw materials	CaO (wt.%)	Temperature (°C)	CO₂ emitted on mass base (g CO₂/g binder)	CO₂ emitted per volume of hydrate (g CO₂/cm³ hydrate)
C₃S	Limestone + silica	74	1450	0.58	0.86
C₂S	Limestone + silica	65	1300	0.51	0.77
CA	Limestone + alumina	35	1500	0.28	0.48
C₄A₃S	Limestone + alumina + anhydrite	37	1300	0.22	0.39

Portland Cement Hydration Products

The hydration of Portland cement is a complex process that involves the simultaneous reactions of the four main clinker phases together with minor phases and calcium sulfates added during grinding. The hydration products are hydrates that all have much lower densities than the anhydrous clinker phases. Therefore, as FIGURE 5 shows, the total volume of solids is almost doubled as a result of hydration. However, it is interesting to note that there is a small decrease in the total volume (liquid + solid) because the initially free water has a higher effective density in the solid hydration products.

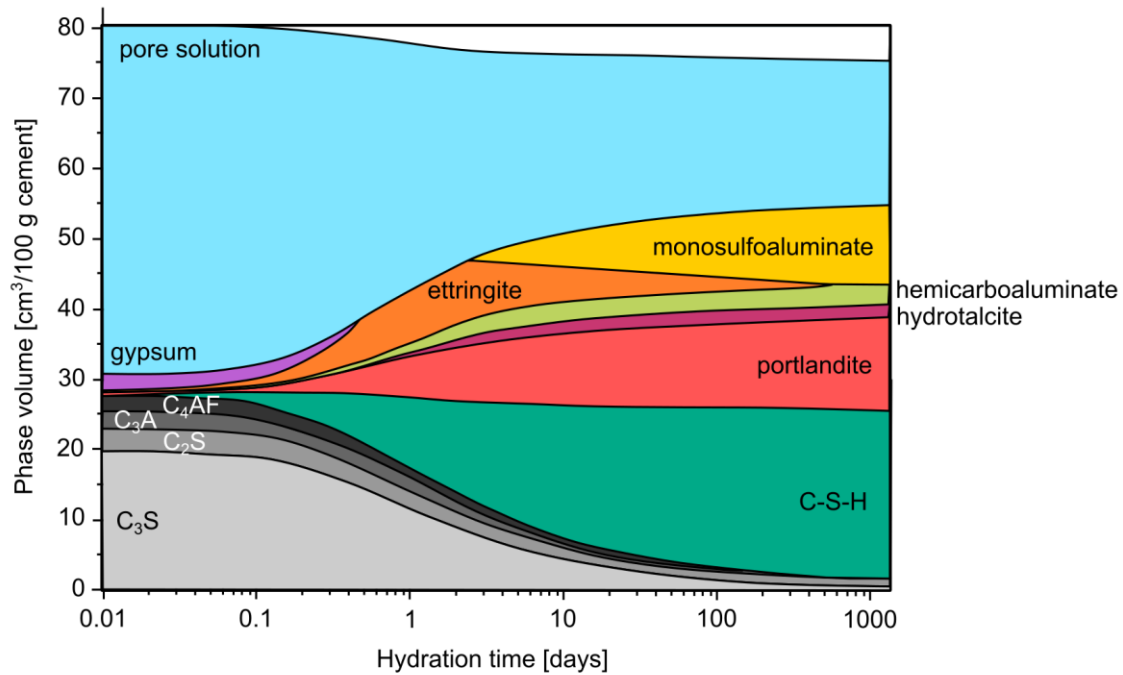


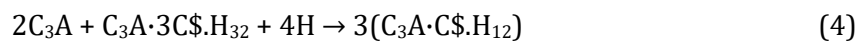
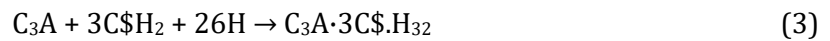
FIGURE 5. Hydration of Portland cement. ADAPTED FROM LOTHENBACH AND ZAJAC (2019).

Initially, the hydration reactions of alite and C_3A contribute most to the hardening of Portland cement, with belite and ferrite hydrate contributing more slowly. As shown in Eqs. (1) and (2), the hydration products of alite and belite are C-S-H (calcium silicate hydrate, with the hyphens denoting the variable stoichiometry) and CH ($Ca(OH)_2$ or portlandite).



Calcium silicate hydrate is the most important hydrate in Portland cement and has an average composition of $C_{1.7}SH_4$. It lacks the long-range order of a well-crystallized phase, yet is best described as a nanocrystalline material. Nowadays, there is consensus that C-S-H has a defect tobermorite structure. Tobermorite has a layered structure consisting of a distorted octahedral Ca-O sheet with, on either side, infinite chains of silicate tetrahedra that follow a dreierkette pattern, with a bridging tetrahedron protruding into the interlayer. The interlayer is populated with additional H_2O and Ca^{2+} ions to balance the negative charge of the layers (Bonaccorsi et al. 2005). The Ca/Si ratio of tobermorite is 0.83. The introduction of defects, such as the omission of silicate tetrahedra or chains and substitution of protons in the layer by Ca ions, enables a Ca/Si ratio of 1.7 to be reached (Richardson 2008).

The hydration of the C_3A and ferrite phases produces a series of crystalline calcium aluminate hydrates. The early hydration of C_3A in the presence of gypsum results in the formation of ettringite ($C_3A \cdot 3C\$.H_{32}$) (Eq. 3), a low-density hydrate that exhibits a needle-like habit (symmetry) reflecting its underlying columnar structure. Upon depletion of gypsum and the continued supply of aluminate, monosulfoaluminate ($C_3A \cdot C\$.H_{12}$) is formed at the expense of ettringite (Eq. 4).



When small amounts of carbonate are present, hemicarboaluminate ($C_3A \cdot 0.5Cc.H_{12}$) and monocarboaluminate ($C_3A \cdot Cc.H_{11}$) precipitate and ettringite is preserved (De Weerd et al. 2011). These phases are collectively called AFm phases. They are all “anionic clays,” or layered double hydroxide phases, and share a common structure of positively charged $Ca_2Al(OH)_6^+$ layers. Anion groups between the layers balance the charge. The number of additional water molecules in the layer and the crystal symmetry vary depending on the counteranion. The layered crystal structure is reflected in hexagonal sheet-like crystal habits (Matschei et al. 2007). Iron from ferrite is partially incorporated into the above-mentioned phases by solid solutions, but is also present as iron hydroxides and Fe-rich hydrogarnet (Dilnesa et al. 2011).

Recent progress in the determination of detailed and consistent hydrate solubility data has enabled thermodynamic models to make accurate predictions of the hydration product assemblage of Portland cement and a suite of other hydraulic cements (Lothenbach and Zajac 2019).

WHY IS PORTLAND CEMENT SO POPULAR?

The dominant position of Portland cement in the market is rooted in several causes. First of all, as discussed earlier, it is made of abundant and easily accessible raw materials that are readily available almost everywhere on Earth. Next, it can be produced at a large scale; one single production line can easily produce up to 1 million tonnes of clinker per year at surprisingly low cost (e.g., \$40–60 per ton). Portland cement, therefore, is very inexpensive—and concrete even more so—compared with many other construction materials (e.g., brick, steel, wood).

As a building material, Portland cement is also a robust product that is easy to use. As most people have experienced in their own backyard, it suffices to mix Portland cement with aggregates and

water to make mortar, concrete, or any other cementitious product. The fresh liquid mix can be cast in flexible forms, opening up options for creative architects. When hardened, it is watertight, and will not rot or corrode in continuous contact with water. Moreover, Portland cement protects steel from corrosion owing to its high internal pH (>13). This is crucial because steel reinforcement is used to improve the tensile and bending strength of concrete. The concrete covering the steel protects it from corrosion, but also enables the use of less steel for the same structure. At the same time, Portland cement concrete is a durable product that, when properly made, can have a service life of 100 years or more, even in chemically aggressive environments such as in contact with seawater.

Cement and concrete production is intimately linked to the development of a country's infrastructure and dwellings (FIGURE 6). The rapid economic development of China in the last decades was paralleled by a massive surge in Chinese cement production. In 2020, about 54% of the world's cement was made in China, and between 2019 and 2020, China produced as much cement as the USA did over the entire 20th century (USGS 2021). It would be very difficult to fulfill this global hunger for infrastructure with alternative materials such as steel, timber, or brick that are produced in much smaller amounts and often have very different properties, costs, and functionalities.



FIGURE 6. Critical infrastructure and buildings made of concrete (**LEFT TO RIGHT**): the Øresund Bridge connecting Denmark and Sweden; the Rio Madeira hydropower dam in Brazil under construction; and the Burj Khalifa skyscraper in Dubai.

EVOLUTION IN TECHNOLOGY SINCE 1824

The heterogeneity of early-day Portland cements was gradually solved by the progressive introduction of rotary kilns (from the 1880s onward) that enabled continuous production and better process control compared with the batch-by-batch firing in older lime kilns. A rotary kiln

is a long cylindrical steel tube lined internally with refractory bricks. The kiln is inclined by a few degrees toward its exit and slowly rotates to move the kiln charge toward the burner at its end. In older kilns, the raw material was mixed with water and fed as a slurry into a 150-m-long kiln. This so-called wet process requires large amounts of energy just to evaporate the water in the slurry, and has been gradually replaced by more energy-efficient dry-processing since the 1970s oil crisis (Bye 1999). Modern production lines (FIGURE 7) use preheaters and precalciners to dry, heat, and calcine the raw feed before it enters the rotary kiln. The suspension preheater intensifies the contact between the feed and the hot gases exiting the kiln, reducing the overall heat consumption. The precalciner increases the throughput of the kiln and allows the use of lower calorific fuels, for example, refuse-derived fuel (fuel from various types of waste). Today, the co-processing of waste as fuel for a kiln is common practice. In countries with advanced waste management systems, such as Germany or Belgium, waste or biomass-derived fuels can cover 80%–90% of the heat requirements of a kiln (Schneider 2015). State-of-the-art production lines today need 2.8–3.0 GJ per tonne of produced clinker, which is close to thermodynamic efficiency limits, and about half of that required by an old wet-process clinker kiln (Gartner 2004).

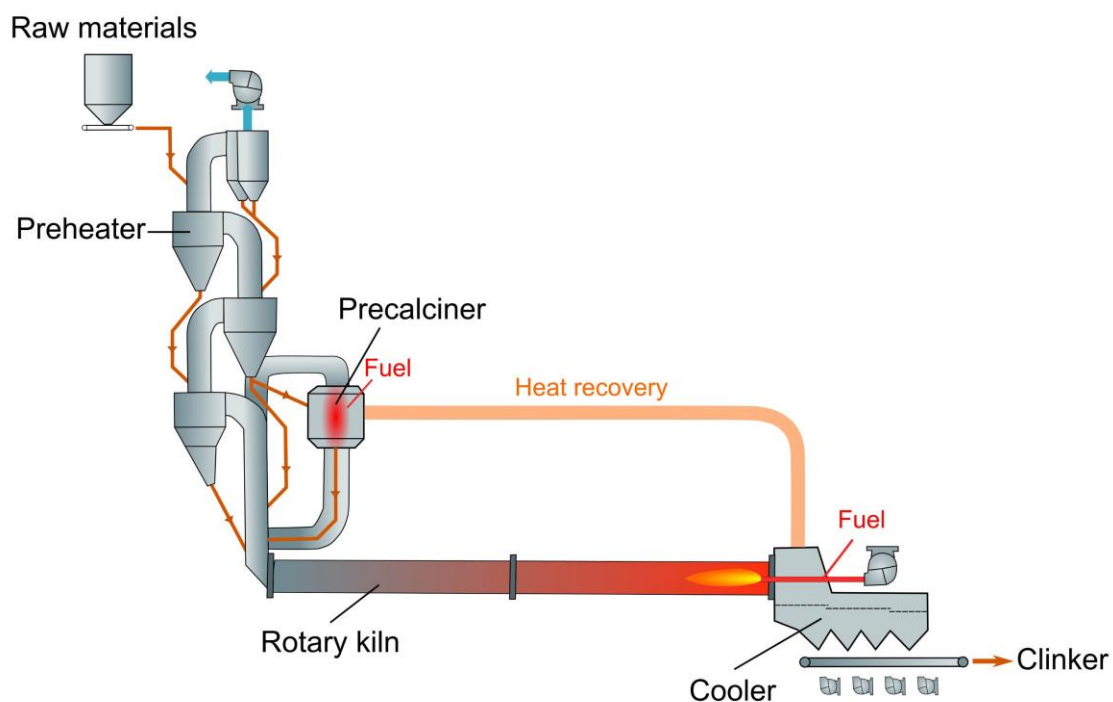


FIGURE 7. State-of-the-art Portland clinker manufacturing line with preheater, precalciner, rotary kiln, and clinker grate cooler.

WHERE NEXT?

Today, climate change mitigation is the main driver of change in the manufacture and use of Portland cement and concrete. It is estimated that Portland cement production is responsible for about 8%–10% of global CO₂ emissions (Scrivener et al. 2018). This large share mainly reflects the popularity and massive use of cement-based products (30 billion tonnes per year of concrete, mortar, etc.). As calcination of limestone is responsible for about 60% of the CO₂ emissions of the process, the production of Portland cement is one of the most difficult energy-intensive industrial processes to decarbonize. Switching to carbon-neutral fuels or energy will not help reduce these emissions. As modern kilns are near their thermodynamic energy-efficiency limits, cutting further back on CO₂ emissions will need to be achieved in other ways. Obviously, reducing the CaO content of the final product is key. A range of other cements, such as alkali-activated cements, calcium sulfo-aluminate cements, magnesia-based cements, and carbonation-hardening cements, is discussed elsewhere by Hanein et al. (2022 this issue). However, none of these cements have presently reached significant market shares. One approach that is widely practiced today is the partial replacement of Portland clinker by so-called supplementary cementitious materials (SCM), which can be mineral resources such as volcanic pumice or, more often, industrial by-products such as slags derived from the production of pig iron and fly ashes from coal-fired energy generation (Snellings et al. 2012). Without the use of SCM, CO₂ emissions would be 20%–25% higher. A major challenge for the near future will be shortages of tested and tried by-product SCM as a result of the gradual decarbonization of the steel and energy industries. Increasing or even sustaining the current use of SCM will require new resources. While other industrial residues may step in, abundant natural resources such as clays, limestone, pumice, or tuff have raised the most interest. For example, a combination of calcined kaolinitic clays and ground limestone can replace 50% of Portland clinker without compromising the strength or durability of the concrete end-product (Scrivener et al. 2018).

CONCLUSIONS

First introduced in the early 19th century, Portland cement has become a commodity produced at massive scale that satisfies the needs for construction of a rapidly growing urban population. Abundant raw materials, low cost, flexible and easy use, and good performance and durability are the main levers to its success. Unfortunately, there is no such thing as a free lunch. The release of fossil CO₂ from limestone during its production burdens Portland clinker with a significant and hard-to-abate carbon footprint. A broad range of measures, including resource and product

efficiency and electrification along the entire value chain from clinker, cement, and concrete production over construction to use and end-of-life stages, may reduce carbon footprints significantly, yet not fully. The balance, reportedly about 50%, will need to be captured and stored or used to reach carbon neutrality (Verein Deutscher Zementwerke (VDZ) 2020). Climate change mitigation presents a formidable challenge to cement and concrete producers and will, by necessity, incentivize rapid evolution in an otherwise conservative industry in the years to come. Here too, the energy transition materializes as a resource shift providing ample opportunity for Earth scientists to contribute.

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