The Rise of Portland Cements

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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 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 CaCO₃ 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).

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).

**Figure 1** Average crustal composition (left) versus Portland cement composition (right).

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

Photo: Ruben Snellings.
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).

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 (Fig. 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 ºC, which is not sufficient to form Ca3SiO5 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 ºC was used more consistently. This enabled the formation of alite and resulted in the product presently known as Portland cement (Trout 2019).

PORTLAND CEMENT MINERALOGY

Clinker Minerals

Portland cement is made up of four major hydraulic phases. Alite (Ca3SiO5 or C3S) constitutes about 65 wt.% of a conventional Portland cement; belite (Ca3SiO5 or C3S) is present at around 15 wt.%; and aluminate (Ca4Al2O6 or C4A) and ferrite (Ca2AlFeO5 or C3AF) each represent about 10 wt.%. Calcium sulfates are added to the clinker to make Portland cement. The consecutive reactions occurring in the kiln are illustrated by the clinker microstructure in Figure 4. Alite is recognized as large, blue-brownish, angular grains that have grown at the expense of belite (rounded grains) and free lime (consumed) at the highest temperature section of the kiln (above 1350 ºC) (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 C3A and ferrite phases (Glasser et al. 2004).

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 C3S is explained by the presence of O2− ions in its structure. This is a rather unique feature among silicates and explains why C3S is much more reactive than C2S. In addition, the open structure and distorted coordination of the calcium atoms by oxygens contribute to the instability of C2S (Taylor 1997), which is also polymorphic. At the high temperatures in the kiln, C3S 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 C3S crystal lattice stabilize the high-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 C2S, where the polymorphs have very distinct atomic arrangements and reactivities. At room temperature, γ-C2S, or calcium olivine, is the stable polymorph and has very low reactivity in Portland cement. High-temperature polymorphs (α, β, α′, γ-C2S, 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., Al3+, K+, SO42−, PO43−) are common and stabilize the high-temperature polymorphs. Therefore, belite in Portland cement is usually the β-C2S 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 CO2 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 CO2 emissions. Switching from mainly alitic to belitic cements would save about 10% in CO2 emissions at the expense of a significantly lower strength gain. More effective would be the production of calcium (sulfo)aluminates cements that present significantly lower CO2 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.

### 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.

Initially, the hydration reactions of alite and C2S contribute most to the hardening of Portland cement, with belite and

<table>
<thead>
<tr>
<th>Phase</th>
<th>Raw materials</th>
<th>CaO (wt.%)</th>
<th>Temperature (°C)</th>
<th>CO2 emitted on mass base (g CO2/g binder)</th>
<th>CO2 emitted per volume of hydrate (g CO2/cm³ hydrate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3S</td>
<td>Limestone + silica</td>
<td>74</td>
<td>1450</td>
<td>0.58</td>
<td>0.86</td>
</tr>
<tr>
<td>C2S</td>
<td>Limestone + silica</td>
<td>65</td>
<td>1300</td>
<td>0.51</td>
<td>0.77</td>
</tr>
<tr>
<td>CA</td>
<td>Limestone + alumina</td>
<td>35</td>
<td>1500</td>
<td>0.28</td>
<td>0.48</td>
</tr>
<tr>
<td>C4A3S</td>
<td>Limestone + alumina + anhydrite</td>
<td>37</td>
<td>1300</td>
<td>0.22</td>
<td>0.39</td>
</tr>
</tbody>
</table>
The hydration of Portland cement. Adapted from Lothenbach and Zajac (2019).
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 (Fig. 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 precalcer 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).

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 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 36%, will need to be captured and stored or used to reach carbon neutrality (Global Cement and Concrete Association 2021). 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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