Alternative Non-Portland Binders

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A background on non-Portland cementitious binders is presented, followed by a review of the key alternative binders that are currently of interest. The mineralogy of these cements is described, along with phases present in the reacted/hardened materials. The similarities and differences between the setting processes, as controlled by reactions at the solid–liquid interface, provide insight into the ways in which different classes of binders develop their performance and thus offer value to society.

Keywords: alternative cements; low-carbon binders; cement toolkit; hardening mechanisms; performance

BACKGROUND ON NON-PORTLAND BINDERS

The 4.2 billion tonnes per annum global cement industry is carbon and energy intensive with most of the CO₂ evolution (raw-material and fuel-derived) originating from the calcination of limestone. While Portland cement (PC) dominates the cement sector at present (Scrivener and Snellings 2022 this issue), the focus of this paper is specifically on materials of different chemistries, requiring less net calcined limestone, that may be able to act as eco-efficient alternatives to PC for certain applications. The development of cement binders (used to transform materials into a cohesive whole as a means of providing structural stability; hardening chemically or mechanically by bonding fibres, filler powder, and other substances together) began several thousand years ago and was driven by infrastructure and shelter requirements and local raw material availability, rather than, as now, planetary health indicators. However, binders including alkali-activated and carbonation-hardening systems are not particularly new cement technologies and are at the heart of the human-built environment (Elsen et al. 2022 this issue).

THE REACTANTS

Calcium Sulfoaluminate–based Cements

Calcium sulfoaluminate (CSA)-based cements have been commercialised for over 60 years, most notably in China and the USA where they have been used in both structural and non-structural applications. The production process of CSA-based clinkers is similar to that of PC but at a lower temperature, usually 1250–1300 °C. Calcium sulfoaluminate–based cement is potentially a lower-carbon alternative to PC (Hanein et al. 2018), and its manufacture requires less energy than that of PC (Ben Haha et al. 2019). Global production of CSA-based cements is three orders of magnitude lower than that of PC and is limited by the availability and economics of the alumina source (normally bauxite). In traditional CSA-based cements, ye’elimite (Ca₄Al₆O₁₂SO₄) is the main phase, ranging between 40 wt.% and 80 wt.%. Calcium sulfoaluminate–based cements also contain other phases such as belite, gehlenite, or other calcium aluminates and, depending on the desired application, gypsum/anhydrite in higher quantities than PC (Bescher et al. 2019). The performance of these cements is influenced by many factors, such as the clinker mineralogy (major and minor phases), fineness, and water-to-cement ratio. Calcium sulfoaluminate–based cements (high ye’elimite) are commonly used as active components for blended cements with niche applications, e.g., shrinkage compensation. Calcium sulfoaluminate–based cements in which the main (>40 wt.%) phase is belite (Ca₂SiO₄), but which also contain 25–35 wt.% ye’elimite, are referred to as BCSA cements, some of which are described by the European Technical Assessment (ETA-19/0458) as stand-alone rapid set binders, achieving compressive strengths of >30 MPa within a few hours. Figure 1 shows where these cements plot in a ternary diagram of CaO, Al₂O₃, and SiO₂. High-alumina clay (or industrial by-products) can be used to produce BCSA with a diminished need for bauxite (Hanein et al. 2018).

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ặp Photo: Christiane Rößler.
The main hydration products of CSA and BCSA are crystalline ettringite and a disordered aluminium hydroxide gel, with stoichiometry close to that of hydrated gibbsite, originating from the reaction of ye’elimite, calcium sulfate, and water. If not enough calcium sulfate is available for full ettringite formation, AFm-type phases with compositions close to Ca₄Al₂(OH)₁₂(SO₄)⋅6H₂O may precipitate. In BCSA pastes, the hydration of belite in the presence of high amounts of A-H₂O gel yields strätlingite, Ca₃Al₂(Al₂O₆)(OH)₁₅⋅2.₂5H₂O. In CSA cements, calcium silicate-hydrate/calcium-aluminium-silicate-hydrate (C-S-H/C-A-S-H) gel is formed at later ages (i.e., beyond 28 days) from the hydration of the remaining belite; however, there is some debate over the extent of belite hydration.

**Calcium Aluminate Cements**

Calcium aluminate cements (CACs) have been produced commercially since the early 20th century and are used in niche applications today. They were initially developed as “Ciment Fondu,” a high-sulfate resistance material (Pöllmann 2012). The term *fondue* (“molten” in French) was derived from the molten state of the material that is manufactured at ~1550°C by firing a mix of bauxite or other aluminium-bearing rocks with low SiO₂ contents and limestone. Calcium aluminate cements were historically used when rapid setting and hardening were needed and because of their high resistance to chemical attack. Nowadays, their main application is for castable refractories, for special applications.

Calcium aluminate cements are classified into three main groups according to their aluminium content (Fig. 1): (i) standard CAC with 35–45 wt.% Al₂O₃ and 12–20 wt.% Fe₂O₃, for which limestone and ferruginous bauxites are used as raw materials; (ii) standard low-iron (medium) CAC with 45–60 wt.% Al₂O₃ and <3 wt.% Fe₂O₃, made with limestone and low-iron bauxite; and (iii) high-Al₂O₃ CAC with >70 wt.% Al₂O₃, made from limestone and metallurgical-grade alumina. All CACs contain monocalcium aluminate, CaAl₂O₄, as the main phase. High-Al₂O₃ CAC may also contain Ca₂Al₂O₆ and/or Al₂O₃, while medium-standard CAC may contain gehlenite and calcium titanate (perovskite) because bauxites sometimes contain TiO₂. The hydration mechanism of Ca₂Al₂O₄ is complex and temperature-dependent but well known, and can be represented as follows.

\[
\begin{align*}
\text{CaAl}_2\text{O}_4 + 10\text{H}_2\text{O} & \rightarrow \text{Ca}_2\text{Al}_2\text{O}_4\cdot10\text{H}_2\text{O} & T < 15 \, ^\circ\text{C} (1) \\
3\text{CaAl}_2\text{O}_4 + (21 + 2n)\text{H}_2\text{O} & \rightarrow \text{Ca}_2\text{Al}_2\text{O}_4\cdot10\text{H}_2\text{O} + \\
\quad & \text{Ca}_2\text{Al}_2\text{O}_5\cdot8\text{H}_2\text{O} + 2[\text{Al(OH)}_3\cdot\text{nH}_2\text{O}] & 15 \, ^\circ\text{C} < T < 30 \, ^\circ\text{C} (2) \\
2\text{CaAl}_2\text{O}_4 + (11 + 2n)\text{H}_2\text{O} & \rightarrow \text{Ca}_2\text{Al}_2\text{O}_5\cdot8\text{H}_2\text{O} + \\
\quad & 2[\text{Al(OH)}_3\cdot\text{nH}_2\text{O}] & 15 \, ^\circ\text{C} < T < 30 \, ^\circ\text{C} (3) \\
3\text{CaAl}_2\text{O}_4 + (12 + 4n)\text{H}_2\text{O} & \rightarrow \text{Ca}_3\text{Al}_2\text{O}_6\cdot6\text{H}_2\text{O} + \\
\quad & 4[\text{Al(OH)}_3\cdot\text{nH}_2\text{O}] & T > 30 \, ^\circ\text{C} (4)
\end{align*}
\]

The hexagonal calcium aluminate hydrates, Ca₂Al₂O₅·8H₂O and CaAl₂O₄·10H₂O, are thermodynamically metastable with respect to hydrogarnet, Ca₄Al₂O₆·6H₂O, and amorphous Al(OH)₃·nH₂O. Transformation from less dense metastable hydrates to more stable denser hydrates occurs on a timescale of days to years when the material is held above 20 °C. This “conversion” process can increase the porosity by more than 25%, thereby reducing the mechanical strength (sometimes dramatically) and making the concrete vulnerable to chemical attack. In the 1970s, some buildings made with CAC concrete in the UK and Spain collapsed as a result of this chemical process, which is complex and dependent on the water/cement ratio, temperature, presence of supplementary cementitious materials, and nature of the aggregates. The main method of mitigating conversion is to ensure that the CAC is formulated at a low water/cement ratio, so that water released by conversion processes triggers further hydration of residual anhydrous CAC clinker grains to fill the generated pore space. Note that CAC can also be used in combination, blended with calcium sulfates, to produce ettringite and aluminium hydroxide gel, for example, as binders in self-leveling mortars.

**Belite Cement**

Belite cements (BC) are based on the total or partial substitution of alite by belite in a PC clinker (Chatterjee 1996), while the remaining (ferro)aluminates are in the same proportion as in PC. Belite cements resemble historical (19th- and early 20th-century) PC, which had a much lower alite content than modern PC, and can yield a CO₂ reduction of ~30%, mainly as a result of the lower calcium demand of belite than alite and the lower clinkering temperature, i.e., 100 °C less than PC (Cuesta et al. 2021); however, BC is slightly more difficult to grind. The main hydration products of BC are, like PC, portlandite and C-S-H gel (reaction (5), where the amount of water may vary with time and experimental conditions; 4 mol of H₂O represents a C-S-H gel with a density of 2.0 g·cm⁻³), as well as ettringite from the aluminate–sulfate reaction as in conventional PC (Shirani et al. 2021). The reaction of belite yields a relatively larger fraction of C-S-H gel per unit volume of binder and a lower fraction of crystalline portlandite (compared with alite), which can lead to more durable mortars/concretes (Cuesta et al. 2021).

\[
\begin{align*}
\text{Ca}_2\text{SiO}_3 + (6 - x)\text{H}_2\text{O} & \rightarrow (\text{CaO})_x\text{SiO}_2(\text{H}_2\text{O})_{4.x} + (2 - x) \\
\text{Ca(OH)}_2 & 1.6 < x < 2.0 \tag{5}
\end{align*}
\]
Belite cements have a major drawback: the slow reactivity of belite, which yields poor mechanical strengths at early ages (<7 days). Consequently, the enhancement (“activation”) of the early-age strengths of BC has been a research challenge (Cuesta et al. 2021). The strategies for activation are (i) chemical activation, which involves adding extra minor elements, such as boron, sodium, phosphorus, or sulfur, to the raw materials in the clinker production kilns with the objective of stabilising the high (more rapidly reactive) polymorphs of belite; and (ii) physical activation by reducing the particle size and enhancing the particle defects by controlling the cooling rate. Increasing the hydration temperature has recently been reported as an activation strategy; an increased curing temperature enhances the BC (Shirani et al. 2021) and BCSA (ETA-19/0458) mechanical strengths, contrary to the well-known behaviour of PC, because of the increased belite reactivity and almost negligible effect on the pore coarsening (where pores, on average, get larger). Hydration activation by admixtures, such as C-S-H seeding or different alkaline salts, may also be considered.

**Alkali-activated Materials**

The first use of alkali-activated material (AAM) as a component of cementing material dates back to 1895, when Whiting patented cements based on ground slag powder and caustic additives. Work on the topic was sporadic and scattered after that, until industrial-scale production began in the 1950s in Belgium and the former Soviet Union. Since then, AAM, sometimes also called “geopolymers,” has been commercially produced and used for different purposes in construction and hazardous/radioactive waste management applications (Shi et al. 2006). Today, AAM represents a wide category of binders that use alkalis (usually in aqueous form) mixed with powdered aluminosilicate reactants/precursors. Alkali-earth oxides are sometimes used as a component of an activator in conjunction with an alkali metal–based component, or used alone in Roman-type “lime–pozzolan cements.” In addition to the most widely used precursors such as blast furnace slag, calcined clays, and coal combustion ashes, a range of other materials that contain reactive aluminosilicate components can be used. **Table 1** lists the main reactants for AAM.

The solid precursors listed in **Table 1** are mostly industrial by-products or wastes resulting from thermal processes—which yield glassy or otherwise reactive silicate constituents—rich in SiO₂ and Al₂O₃ and with varying amounts of CaO. The aluminosilicates dissolve under alkaline conditions, and then precipitate new aluminosilicate gels as the binding products. Curing at elevated temperature is sometimes beneficial to enhance reactivity (Zhang et al. 2016). Note that some waste materials containing Fe-rich glass can also be used in AAM, but usually lead to slower strength development because of their lower reactivity.

Because alkali activators account for most of the energy consumption, CO₂ emissions, and cost of an AAM, their doses should generally be kept as low as possible. In practice, to obtain a desirable strength, an alkali dose of 3–7 g Na₂O eq/100 g precursor is usually sufficient for slag-based AAM, whereas this is doubled or tripled for AAM based on fly ashes or other low-calcium materials.

**Magnesia Silicate Cements**

A magnesia-based cement uses magnesium compounds as the main building blocks of the binding phases, generally via precipitation of low-solubility hydrous Mg-rich mineral phases (Wall and Provis 2016). The Mg is typically supplied as MgO or Mg(OH)₂, although there is increasing interest in Mg recovery from industrial by-products or mine tailings as a result of restrictions in the supply of MgCO₃ from which MgO is usually produced. By analogy with the calcium silicates comprising PC, the concept of developing a magnesium–silicate bond to form a cement has existed for over 100 years, but the use of this material as a cement-forming system remained relatively unresearched for more than 50 years and is still not fully understood. Modern magnesia silicate cements are generally formed by mixing the magnesium source with a highly reactive silica powder (e.g., silica fume or microsilica) and water to form a magnesium-silicate-hydrate (M-S-H) binder. The reaction between MgO and reactive silica can be slow at ambient temperature, leading to a lower rate of strength development than for PC; however, recent developments have enabled the acceleration of M-S-H formation through the control of particle reactivity via chemical activation (Zhao et al. 2019).

**Magnesia Phosphate Cements**

Magnesia phosphate cements/ceramics (MPC) are formed through an acid–base reaction between MgO and soluble acid phosphate. Because of the nature of this reaction, when a highly reactive MgO and acid phosphate solution are used, the mixture usually has a high reaction rate and rapid strength development. These properties have led to their extensive commercial use as concrete repair materials and have further triggered growing interest as wasteform cements for the nuclear industry (Wall and Provis 2016).

**Table 1**

<table>
<thead>
<tr>
<th>Examples of alkali activators</th>
<th>Precursors in approximate order of calcium content</th>
</tr>
</thead>
<tbody>
<tr>
<td>caustic alkalis</td>
<td>MOH</td>
</tr>
<tr>
<td>non-silicate weak acid salts</td>
<td>M₂CO₃</td>
</tr>
<tr>
<td>alkali silicates</td>
<td>M₂O·nSiO₂</td>
</tr>
<tr>
<td>alkali aluminates</td>
<td>MAI₂O₃</td>
</tr>
<tr>
<td>non-silicate strong acid salts</td>
<td>M₂SO₄</td>
</tr>
<tr>
<td>alkali-earth oxides</td>
<td>CaO, MgO</td>
</tr>
</tbody>
</table>

**Notes:**
- **CaO**: The aluminosilicates dissolve under alkaline conditions, and then precipitate new aluminosilicate gels as the binding products.
- **MgO**: Magnesium compounds as the main building blocks of the binding phases, generally via precipitation of low-solubility hydrous Mg-rich mineral phases.
- **M₂CO₃**: Magnesia silicate cements.
- **M₂SO₄**: Magnesia phosphate cements/ceramics (MPC).
- **M₂O·nSiO₂**: Alkali silicates.
- **MAI₂O₃**: Alkali aluminates.
- **CaO, MgO**: Alkali-earth oxides.

**Constituents Used in Alkali-Activated Materials** (Shi et al. 2006; Provis and van Deventer 2014; Provis et al. 2015). Here, M denotes an alkali metal.
Unlike many of the cements described in this paper, one of the main challenges in the use of MPC is to prevent an overly rapid reaction. Therefore, hard- and dead-burned MgO, calcined at 1000–1500 °C and 1500–2000 °C, respectively, are used in preference to the more reactive light-burned magnesia because the reactivity of MgO decreases with increasing burning temperature. The common acid phosphates used in MPC are NH₄H₂PO₄ and KH₂PO₄, forming NH₄·MPC and MKPC. A mixture of phosphoric acid and Al(H₂PO₄)₃ or NaH₂PO₄ can also be used.

To further control the reaction rate of MPC, chemical additives (retarders) can be used, such as borax (Na₂B₄O₇·10H₂O) and boric acid (H₃BO₃), which have been applied because of their effectiveness in the relatively low doses required (Wagih 2016). To save cost and/or reduce exothermic output, diluents/fillers are added, either as sand to be a diluent to produce a mortar for repair applications, or finer materials such as coal fly ash, blast-furnace slag, or wollastonite, which are slightly reactive and contribute to the binder performance (Gardner et al. 2021).

**Sorel Cements**

Magnesium oxychloride cements (MOC), also called Sorel cements for their inventor (Sorel 1867; Walling and Proviss 2016), are formed via reaction between MgO and MgCl₂. In this MgO–MgCl₂–H₂O ternary system, the reactivity of MgO is very important because it affects the total reaction heat, setting time, and strength development. Therefore, usually higher-reactivity (light-burned) magnesia and small particle size are essential, in combination with a MgCl₂ solution of suitable concentration, to produce a cement that can generate excellent early strength (Zhang 2011). Careful control of the ratios between MgO, MgCl₂, and water is necessary for a stable cement with high strength, but without too much residual MgO, which can potentially cause expansion in the longer term via its slow hydration to brucite (Mg(OH)₂). The most challenging issue for Sorel cement in practical application is probably its limited water resistance, which means that it is best suited for use indoors or under otherwise dry conditions. When it becomes moist, the main oxychloride binding phase 5Mg(OH)₂·MgCl₂·8H₂O transforms to 3Mg(OH)₂·MgCl₂·8H₂O, which finally dissolves to form a Mg(OH)₂ and MgCl₂ solution. Chemical additives with hydrophobic properties can be used to improve the water resistance and stability. These cements are not suitable for making mild-steel reinforced concrete, as the steel will be susceptible to corrosion in the presence of chloride, but are valuable in unreinforced applications under conditions where they can be protected from moisture. It is worth noting that there is an analogue to MOC, which is magnesium oxy sulfamate (MOS) cement. Magnesium oxy sulfamate cement is produced by the combination of MgO with MgSO₄ solution and can have attractive engineering properties in many applications, but is considered inferior to MOC; nonetheless, there is room for improvement as MOS is still in its early stages of development.

**Carbonation-hardening Cement**

Carbonation-hardening cement refers to the hardening of poorly hydraulic minerals such as MgO and Mg silicates (Unluer and Al-Tabbaa 2013), γ-C₂S (Guan et al. 2016), rankinite (Smigelskyte et al. 2020), and wollastonite (Daval et al. 2009)—which can either be produced directly or sourced from industrial wastes—in the presence of water. Such systems can offer lower CO₂ footprints than conventional cements; much of the emitted raw-material CO₂ can be re-absorbed during hardening, and the production temperatures of the precursors, even if not derived from wastes, are lower than those of PC clinker. Carbonation-hardening cement can also be useful in regions where water is scarce because the water is not chemically bound and is potentially recyclable.

**HARDENING MECHANISMS AND REACTION PRODUCTS**

Despite the diverse chemistries of the non-PCs that have been described in the preceding sections, there are some important commonalities in the mechanisms and binder structures between the different classes of cements, which will be explored in this section. Fundamentally, the hardening of each cement class described in this paper—for example, of fly ash, with particles mainly in the 1–50 μm range—will be explored in this section. Fundamentally, the hardening of each cement class described in this paper—for example, of fly ash, with particles mainly in the 1–50 μm range—that leads to the dissolution of a (partially) soluble particulate solid oxide, evolution of an interstitial fluid toward saturation with respect to one or more new mineral phases, and precipitation of those phases to form a space-filling, mechanically strong binder. In some cases, the fluid is water (e.g., in the hydration of CSA, CAC, BC, and Sorel cements); in other cases, it is an aqueous solution that may be alkaline (AAM) or acidic (MPC); and in yet other cases, the key agent that causes the chemical reactions that lead to hardening is CO₂, which dissolves into the interstitial fluid from the surrounding atmosphere. However, in all of these scenarios, a sequence of dissolution–reprecipitation reactions results in the formation of a binding phase that, in turn, enables the cement to perform as intended, giving strength and impermeability through the formation of solid phases with lower solubility than that of the original particulate precursor.

**Hydrolysis, Dispersion, and Role of the Solid–Liquid Interface**

When a solid oxide particle, with sufficient solubility to be useful in cement formation, reacts with an aqueous fluid—which is the first step in the setting process of each of the cements described in this paper—its surface is partially hydrolysed and its constituent ions are released into the aqueous environment. These constituent ions then react with each other and potentially with species supplied in aqueous form, including the “activators” in AAM and the dissolved CO₂ in carbonation-hardening cements, through chemical reaction processes that are mediated by the aqueous environment.

The fact that the successful formation of a hardened cement depends so strongly on the hydrolysis of surface species from solid oxides also means that the control of the reactive surface area of the precursor oxide is essential. The main reactive phase in PC is tricalcium silicate, Ca₃SiO₅, and the reasons for its very high reactivity with water become more evident when it is formulated as an oxysilicate Ca₃O(SiO₄) (Plank 2020), where the highly reactive oxide anions, only bound to calcium atoms, within this structure are highlighted. However, moderately reactive oxides can be made more amenable for use in cements when they are present in extremely fine particles. A key example of this is silica fume, which is a nanoscopic (<50 nm) form of amorphous SiO₂ that is a key precursor for magnesium silicate cements. Conversely, larger glassy silicate particles (e.g., example coal fly ash, with particles mainly in the 1–50 μm range) require a very elevated pH to react at a comparable rate to form a cementing binder; alkali-activated fly ash cements use a pH in excess of 14 to accelerate the dissolution of the silicate glass from the fly ash grains (Duxson and Proviss 2008).

Additionally, for this set of chemical processes to proceed effectively, the particles need to be dispersed so that their surface area is fully available for reaction. In cements, this
is often achieved through the addition of a surface-active admixture, known in the context of concrete technology as a "(super-) plasticiser" or "(high-range) water reducer." These molecules act at the solid–liquid interface to provide control of the surface chemistry and, consequently, of the flow characteristics of the concrete. The ability to effectively disperse cementitious powders when a concrete is in the fluid state has been central to many important advances in concrete formulation and processing technology over the past decades. Concretes based on PC—for which these admixtures have been primarily developed—have improved in flowability, and in strength and durability, through the ability to reduce their water content via effective cementitious particle dispersion. However, comparatively less financial and intellectual investments have been dedicated to the development of corresponding admixtures tailored to the interfacial chemistry of alternative cements. Hence, admixtures that would enable lower-carbon concretes to compete on an equal footing with conventional PC-based materials do not yet exist. Important steps have been made toward this development for some types of cements, most notably AAM, but this remains a critical area requiring further development in the future.

Precipitation Pathways
Once dissolution of a cementitious precursor particle has progressed to a sufficient extent, the interstitial fluid reaches saturation (or supersaturation) with respect to one or more hydrous minerals. These will then start to precipitate, in general via a nucleation-growth pathway, and fill in the interstitial space to initiate the hardening process. The newly formed mineral phases may be crystalline (e.g., struvite-group minerals in MPC, ettringite in sulfoaluminate cements, or the various hydrated calcium aluminates in CAC) or crystallographically disordered (e.g., C-(A)-S-H, M-S-H, N-A-S-H (alkali-aluminium-silicate-hydrate)). The newly formed phases, particularly when they are disordered, are often loosely described as "gel" phases, and the result of their hardening as a "hardened gel." The process of precipitation in most cements can usually be described relatively accurately by geochemical-style models that assume instantaneous equilibrium between the interstitial fluid and the newly formed hydrate phases (Lothenbach 2010). Even though the overall reaction process is clearly under kinetic control because of the supply of hydrolysed species via precursor dissolution, the precipitation process in the majority of cements discussed in this paper tends to yield stable (rather than metastable) phases. A clear exception to this trend toward the direct formation of stable phases is CAC, as discussed above, and this brings important implications for the longer-term performance of the materials.

Nanostructure and Microstructure
As the chemistry of the interstitial fluid within a cement evolves over time, and as it eventually becomes the pore fluid of the hardened cement, the nature of the phases in equilibrium with the fluid will naturally also change. This means that some of the initially formed solids end up being transient in the hardening process, and thus redissolve or otherwise convert to the final stable phase assemblage of the cement. The fact that both the initial precipitation and later redissolution–reprecipitation processes take place non-homogeneously in space leads to the formation of complex microstructures of binding hydrate phases containing embedded remnant precursor particles.

MECHANICAL PERFORMANCE
Arguably, the most important engineering characteristic of concrete is its compressive strength, which is the ability of a mortar/concrete specimen to resist failure under compressive load. The alternative non-Portland binders described here have quite different applications, and the development of their mechanical properties are directly related to these. For example, many applications of CSA- and CAC-based mortars require high mechanical strengths at early ages (i.e., 1 day of hydration). This improvement over the PC performance justifies their production, and even their higher cost, in isolation from any environmental considerations. The silicate-based alternative low-CO₂ binders, such as BC, usually develop lower mechanical strengths than PC at early ages, but are comparable after 28 days (Fig. 2). There are ongoing debates about whether construction methodologies could be adapted to work with lower early strength materials in the drive for lower emissions across the industry, but pragmatically, this does not appear to be a preferred option for the construction sector, and hence alternative cements probably need to be designed to match or exceed the strength development profile of PC in most engineering applications.

The mechanical strength development profiles of AAM cements depend on the fineness and type of precursor material, curing conditions, type, amount, and ratio of binder to alkali activator (Fig. 2). Moreover, the setting of AAM can be designed to vary between rather rapid and quite slow, thereby opening up a range of production routes including precasting and on-site concreting. Sorel cements are used in panels for good fire resistance, but are also distinguished by their high compressive and flexural strengths after 28 days (Fig. 2), which particularly contribute to good resistance to abrasion for industrial floors as an important application for these materials.

![Figure 2](image_url) Compressive strengths of mortars made using different alternative non-Portland cements. The error bars indicate the range of mechanical properties reported in the literature depending on the experimental conditions. An indicative result for standard Portland cement (PC) mortars is included for comparison. BC indicates belite cement, CAC indicates calcium aluminate cements, CSA indicates calcium sulfoaluminate, BCSA indicates CSA-based cements in which the main phase is belite, and AAM is alkali-activated material.
SUMMARY AND RECOMMENDATIONS

This chapter provides a discussion of alternative non-Portland cements, with a view toward their increased global usage and potential attractive techno-economic and environmental profiles depending on situation and location. Innovation in cements is a slow and incremental process because of the very high levels of confidence that are required in the final material; namely, the performance must be proven and tested to obtain agreement between all participants in the value chain. The materials discussed can be application-specific and the calculations of the relative environmental and economic benefits compared to Portland cement vary between regions and applications. The pathway to sustainability in the cement industry requires a validated toolkit of options, assessed locally for material availability, technical performance, and economic and environmental viability. This level of detailed assessment is more laborious than the use of prescriptive standards, but is necessary to achieve climate goals. A non-exhaustive summary of this toolkit is provided in Table 2.

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<th>Table 2</th>
<th>TOOLKIT OF ALTERNATIVE NON-PORTLAND CEMENTS THAT CAN OFFER TECHNICAL AND/OR ENVIRONMENTAL IMPROVEMENTS IN THE CEMENT SECTOR.</th>
</tr>
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<tbody>
<tr>
<td><strong>Calcium sulfoaluminate–based cements</strong></td>
<td><strong>Major oxide constituents of hardened material</strong></td>
</tr>
<tr>
<td></td>
<td>CaO; Al₂O₃; SO₃; SiO₂; Fe₂O₃</td>
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<tr>
<td><strong>Calcium aluminate cements</strong></td>
<td>CaO; Al₂O₃; minor Fe₂O₃ and SiO₂</td>
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<tr>
<td><strong>Belite cement</strong></td>
<td>CaO; SiO₂; minor Al₂O₃ and SO₃</td>
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<td><strong>Alkali-activated materials</strong></td>
<td>Al₂O₃; SiO₂; Na₂O; K₂O; sometimes CaO, MgO, and Fe₂O₃</td>
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<td><strong>Lime–pozzolan cements</strong></td>
<td>CaO; Al₂O₃; SiO₂; minor Fe₂O₃</td>
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<td>(Elsen et al. 2022 this issue)</td>
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<td><strong>Mg phosphates</strong></td>
<td>MgO; P₂O₅; K₂O</td>
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<tr>
<td><strong>Mg silicates</strong></td>
<td>MgO; SiO₂</td>
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<tr>
<td><strong>Sorel cements</strong></td>
<td>MgCl₂; MgO</td>
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<tr>
<td><strong>Carbonation-hardening cements</strong></td>
<td>CaO; MgO; SiO₂; CO₂</td>
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REFERENCES


