Alternative non-Portland binders

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Abstract

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 binder 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 tons per annum global cement industry is carbon and energy intensive with most of the CO_2 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), the focus of this paper is specifically on materials of different chemistries, requiring less net calcined limestone and hence 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; harden chemically or mechanically by bonding fibers, 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 but are at the heart of the human built environment (Elsen et al. 2022).

Classification of alternative binders and chemistry of the reactants

The alternative non-Portland cementitious binders addressed in this paper, with the potential for a significant role in the future of the cement and concrete industry, include calcium sulfoaluminate-based cements, calcium aluminate cements, belite cements, alkali-activated materials, and magnesia-based cements. The mineralogy of these cements is described, along with phases present in the reacted/hardened materials. Finally, a brief sketch of carbonation hardening cements, which are those cured with CO_2, is also included.

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 Portland cement 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 also requires less energy than that of PC (Haha et al. 2019). Global production of CSA-based cements is three orders of magnitude less 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 ($Ca_4Al_3O_{12}SO_4$) is the main phase, ranging between 40 to 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 (Ca_2SiO_4), but which also contain 25-35 wt.% ye'elimite, are referred to as BCSA cements, some of which are covered by the European Technical Assessment (ETA-19/0458) as stand-alone rapid set binders, achieving >30 MPa compressive strength within a few hours. Figure 1 shows where these cements plot in a ternary diagram of CaO, Al_2O_3, and SiO_2. High-alumina clay (or industrial by-product) can be used to produce BCSA with diminished need of bauxite (Hanein et al. 2018).

The main hydration products of CSA and BCSA are crystalline ettringite and a disordered aluminium hydroxide gel, with stoichiometry close to 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 $Ca_4Al_2(OH)_{12}[SO_4]·6H_2O$ may precipitate. In BCSA pastes, the hydration of belite in the presence of high amounts of AH_3-gel yields strätlingite, $Ca_4Al_2(OH)_{12}[AlSi(OH)_8]_2·2H_2O$. In BCSA cements, C-S-H/C-A-S-H (calcium-silicate-hydrate/calcium-aluminum-silicate-hydrate) gel is formed at later ages, i.e., beyond 28 days, from the hydration of remaining belite; however, there is some debate over the extent of belite hydration.
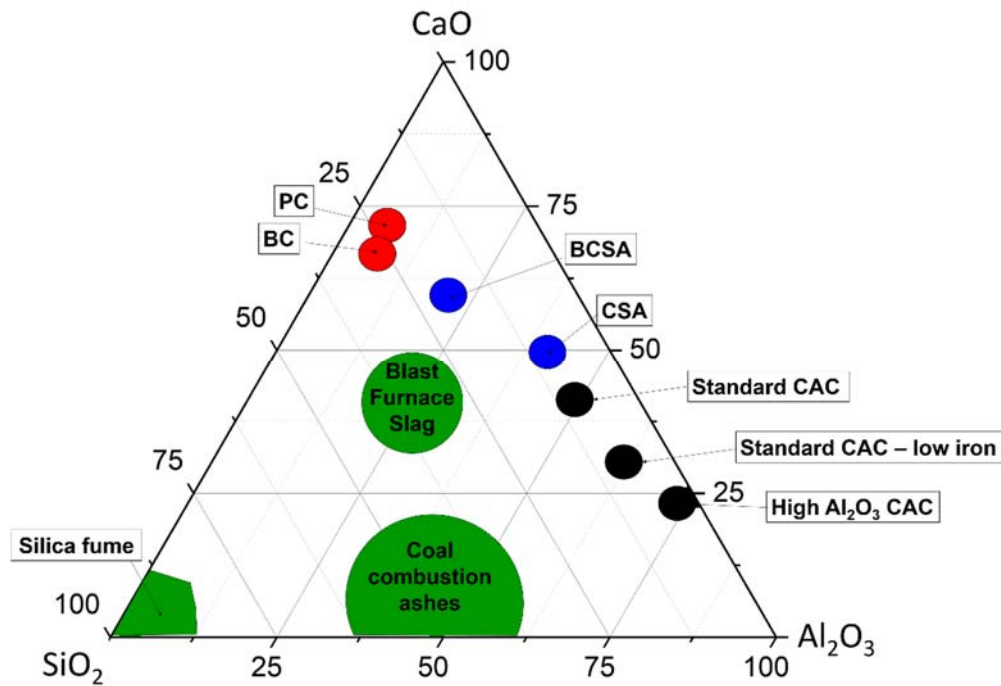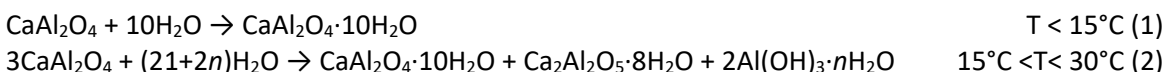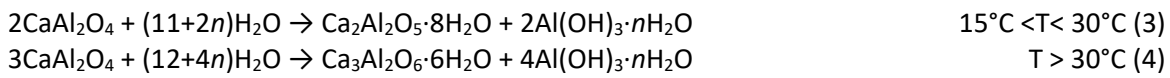
Figure 1. Pseudo-ternary CaO-SiO$_2$-Al$_2$O$_3$ diagram showing the composition of some alternative non-Portland cements, including precursors used in the production of alkali-activated materials. Compositions are normalised to the sum of SiO$_2$, Al$_2$O$_3$, and CaO contents.

Calcium aluminate cements

Calcium aluminate cements (CAC) 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 name *Fondu* ("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 SiO$_2$ contents and limestone. Calcium aluminate cements were historically used when rapid setting and hardening was needed and because of their high resistance to chemical attack. Nowadays, their main application is for castable refractories (non-metallic materials with chemical and physical properties utilized for creating heat-resistant structures that retain and insulate. Due to their high resistance to heat and thermal shock, castable refractory cements can be used to build kilns and furnaces) and in blends with PC for special applications.

Calcium aluminate cements are classified according to their aluminium content in three main groups (Figure 1): (i) standard CAC with 35-45 wt.% Al$_2$O$_3$ and 12-20 wt.% Fe$_2$O$_3$, for which limestone and ferruginous bauxites are used as raw materials; (ii) standard low-iron (medium) CAC with 45-60 wt.% Al$_2$O$_3$ and <3 wt.% Fe$_2$O$_3$, made with limestone and low-iron bauxite; and (iii) high-Al$_2$O$_3$ CAC with >70 wt.% Al$_2$O$_3$, made from limestone and metallurgical-grade alumina. All CAC contain as the main phase monocalcium aluminate, CaAl$_2$O$_4$. High-Al$_2$O$_3$ CAC may also contain CA$_2$, C$_{12}$A$_7$, and/or Al$_2$O$_3$, while medium/standard CAC may contain gehlenite and calcium titanate (perovskite) because bauxites sometimes contain TiO$_2$. The hydration mechanism of CaAl$_2$O$_4$ is complex and temperature-dependent but well known, and can be represented as:

CaAl$_2$O$_4$ + 10H$_2$O → CaAl$_2$O$_4$·10H$_2$O   T < 15°C (1)

3CaAl$_2$O$_4$ + (21+2n)H$_2$O → CaAl$_2$O$_4$·10H$_2$O + Ca$_2$Al$_2$O$_5$·8H$_2$O + 2Al(OH)$_3$·nH$_2$O   15°C <T< 30°C (2)

$$2CaAl_2O_4 + (11+2n)H_2O \rightarrow Ca_2Al_2O_5 \cdot 8H_2O + 2Al(OH)_3 \cdot nH_2O \qquad 15°C < T < 30°C \quad (3)$$
$$3CaAl_2O_4 + (12+4n)H_2O \rightarrow Ca_3Al_2O_6 \cdot 6H_2O + 4Al(OH)_3 \cdot nH_2O \qquad T > 30°C \quad (4)$$

The hexagonal calcium aluminate hydrates, $Ca_2Al_2O_5 \cdot 8H_2O$ and $CaAl_2O_4 \cdot 10H_2O$, are thermodynamically metastable with respect to hydrogarnet, $Ca_3Al_2O_6 \cdot 6H_2O$, and amorphous $Al(OH)_3 \cdot nH_2O$. Transformation from the 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 process of "conversion" can increase the porosity by more than 25% and therefore decrease mechanical strength (sometimes dramatically) and make the concrete vulnerable to chemical attack. In the 1970s, some buildings made with CAC concrete in UK and Spain collapsed due to this chemical process, which is complex and dependent on the water/cement ratio, temperature, the presence of SCM, and the nature of 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. It should be noted 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-levelling 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) Portland cements, which had a much lower alite content than modern PC, and can yield a CO_2 reduction of >30%, mainly due to 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 H_2O represents a C-S-H gel with a density of 2.0 gcm[-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 lower fraction of crystalline portlandite (compared to alite) and this can lead to more durable mortars/concretes (Cuesta et al. 2021).

$$Ca_2SiO_5 + (6-x)H_2O \rightarrow (CaO)_xSiO_2(H_2O)_{4.0} + (2-x)Ca(OH)_2 \quad 1.6 < x < 2.0 \qquad (5)$$
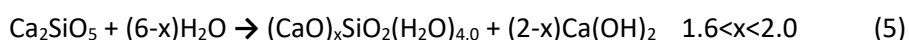
Belite cements have a main drawback: the slow reactivity of belite, which yields poor mechanical strengths at early age (<7 days). Consequently, the enhancement ("activation") of the early-age strengths of BC has been a research challenge (Cuesta et al. 2021). The strategies for activation are (i) chemical activation, which involves adding extra minor elements, such as boron, sodium, phosphorus, or sulfur, to the raw materials in the clinkering kilns with the objective of stabilising the high (more rapidly reactive) polymorphs of belite; and (ii) physical activation by reducing particle size and enhancing the particle defects by controlling the cooling rate. The increase of hydration temperature has been recently reported as an activation strategy; an increased curing temperature enhances BC (Shirani et al. 2021) and BCSA (ETA-19/0458) mechanical strengths, contrary to the well-known behavior of PC, due to increased belite reactivity and an almost negligible effect on pore coarsening (where pores get, on average, 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*", have been commercially produced and used for different purposes in construction and hazardous/radioactive waste management applications (Shi et al. 2003). 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.

Table 1. Constituents used in alkali-activated materials (Provis et al. 2015; Provis and van Deventer 2014; Shi et al. 2003). M denotes an alkali metal.

Examples of alkali activators		Precursors in approximate order of calcium content	
caustic alkalis	MOH	high calcium	blast furnace slag
non-silicate weak acid salts	M_2CO_3		granulated phosphorus slag
			steel slags
alkali silicates	$M_2O \cdot nSiO_2$		non-ferrous slags
alkali aluminates	$MAlO_2$		coal combustion ashes
non-silicate strong acid salts	M_2SO_4		mineral processing tailings
			incineration products of sludges
alkali earth oxides	CaO, MgO		volcanic glasses
			zeolites
			red mud/bauxite residue
			waste ceramics
			waste glass
			rice husk ash
			metakaolin
		low calcium	silica fume

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 SiO_2 and Al_2O_3 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). It should be noted that some waste materials containing Fe-rich glass can also be used in AAM but usually lead to slower strength development because of lower reactivity.

Since alkali activators account for most of the energy consumption, CO_2 emissions, and cost of an AAM, their doses should generally be kept as low as possible. In practice, to get desirable strength, an alkali dose of 3-7 g Na_2O_{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 (Walling and Provis 2016). The Mg is typically supplied as MgO or $Mg(OH)_2$, although with increasing interest in Mg recovery from industrial by-products or mine tailings due to restrictions in the supply of $MgCO_3$ 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 magnesia 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 control of particle reactivity by 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, properties that have led to their extensive commercial use as concrete repair materials and further have triggered growing interest as wasteform cements for the nuclear industry (Walling and Provis 2016).

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 reactivity of MgO decreases as burning temperature increases. The common acid phosphates used in MPC are $NH_4H_2PO_4$ and KH_2PO_4, forming NH_4-MPC and MKPC. A mixture of phosphoric acid and $Al(H_2PO4)_3$ or NaH_2PO_4 can also be used.

To further control the reaction rate of MPC, chemical additives (retarders) can be used, such as borax ($NaB_4O_7 \cdot 10H_2O$) and boric acid (H_3BO_3), which have been widely applied because of their effectiveness and the relatively low doses required (Wagh 2016). To save cost and/or reduce exothermic output, diluents/fillers are added; either sand as a diluent to produce a mortar for repair applications, or finer materials such as coal fly ash, blast-furnace slag, and wollastonite, which are slightly reactive and contribute to binder performance (Gardner et al. 2021).

Sorel cements

Magnesium oxychloride cements (MOC), also named Sorel cements for their inventor (Sorel 1867; Walling and Provis, 2016), are formed by reaction between MgO and $MgCl_2$. In this MgO-$MgCl_2$-H_2O 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 $MgCl_2$ solution of suitable concentration, to produce a cement that can generate excellent early-age strength ("3 – Air Hardening Binding Materials", 2011). Careful control of the ratios between MgO, $MgCl_2$, 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 of Sorel cement in practical application is probably its limited water resistance, which means that it is best suited to use indoors or under otherwise dry conditions. When it becomes moist, the main oxychloride binding phase $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ transforms to $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$, which finally dissolves to form $Mg(OH)_2$ and $MgCl_2$ solution. To improve the water resistance and stability, chemical additives with hydrophobic properties can be used. 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 oxysulfate (MOS) cement. MOS is produced by the combination of MgO with $MgSO_4$ 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 early stages of development.

Carbonation hardening cement

Carbonation hardening cement (CHC) refers to the hardening of poorly hydraulic minerals such as MgO and Mg silicates (Unluer and Al-Tabbaa 2013), γ-C_2S (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 CO_2 footprints than conventional cements; much of the emitted raw-material CO_2 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 as the water is not chemically bound, so is potentially recyclable.

Hardening mechanisms and reaction products

Despite the diverse chemistries of the non-Portland cements that have been described in the preceding sections, there are some important commonalities in mechanisms and binder structure between different classes of cements, which will be explored in this section. Fundamentally, the hardening of each of the classes of cement described in this paper – and similarly also for Portland cement – is a fluid-particle reaction process 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 hydration of CSA, CAC, BC, and Sorel cements); in other cases, it is an aqueous solution which may be alkaline (AAM) or acidic (MPC); and in yet other cases, the key agent which causes the chemical reactions that lead to hardening is CO_2 which dissolves into the interstitial fluid from the surrounding atmosphere. However, in all these scenarios, a sequence of dissolution-reprecipitation reactions results in the formation of the binding phase which 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

As a solid oxide particle, with sufficient solubility to be useful in cement formation, is reacting 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 also with species supplied in aqueous form, including the "activators" in AAM and the dissolved CO_2 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, Ca_3SiO_5, and the reasons for its very high reactivity with water become more evident when it is formulated as an oxysilicate $Ca_3O(SiO_4)$ (Plank 2020), where the highly reactive oxide anions, only bounded to calcium atoms, within this structure are highlighted. However, moderately-reactive oxides can be made much more amenable to 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 SiO_2 that forms a key precursor for magnesium silicate cements. Conversely, larger glassy silicate particles (for 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 Provis 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 thereby also 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 Portland cement – for which these admixtures have been primarily developed – have improved in flowability, and also in strength and durability, through the ability to reduce their water content via effective cementitious particle dispersion. However, comparatively less financial and intellectual investment have been dedicated to the development of corresponding admixtures tailored to the interfacial chemistry of alternative cements, and hence the admixtures which would enable lower-carbon concretes to compete on an equal footing with conventional Portland cement-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 process of hardening. 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, and N-A-S-H (alkali-aluminum-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 due to 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 direct formation of stable phases is calcium aluminate cement, as discussed above, and this brings important implications for the longer-term performance of the materials.

Nano- and micro- structure

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 which are 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 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, and this improvement over PC performance justifies their production, and even their higher cost, in isolation from any environmental considerations. The silicate-based alternative low-CO_2 binders, such as BC, usually develop lower mechanical strengths than PC at early ages, but comparable after 28 days (Figure 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 fineness and type of precursor material, curing conditions, type, amount, and ratio of binder to alkali activator (Figure 2). Moreover, the setting of AAM can be designed to vary between rather rapid and quite slow, 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 high compressive and flexural strengths after 28 days (Figure 2), which particularly contribute to good resistance to abrasion for industrial floors as an important application for these materials.
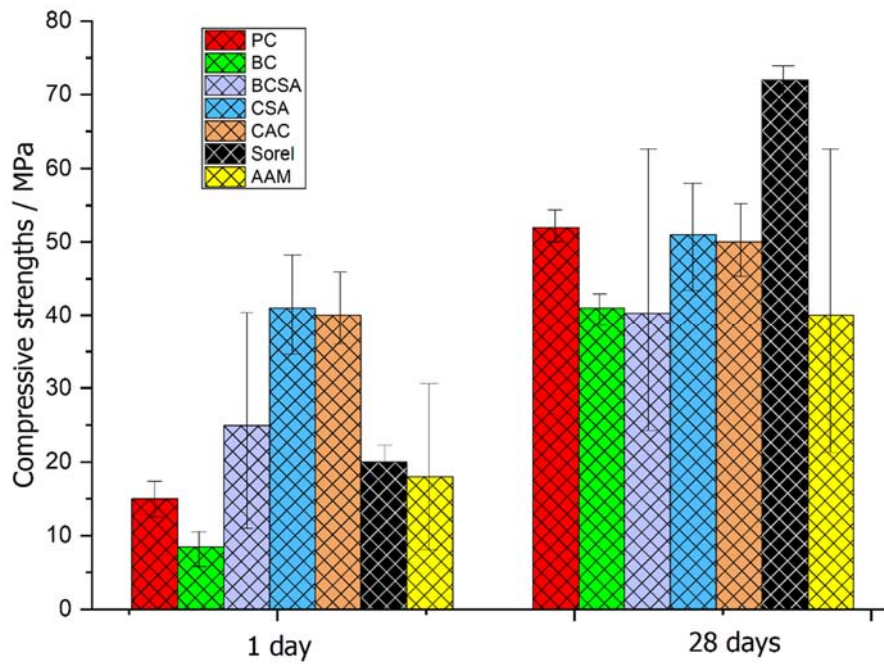
Figure 2. Compressive strengths of mortars made using different alternative non-Portland cements; the error bars indicate the range of mechanical properties reported in the literature depending on experimental conditions. An indicative result for standard PC mortars is included for comparison.

Summary and recommendations

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, is provided. Innovation in cements is a slow and incremental process due to the very high levels of confidence that are required in the final material; the performance needs to 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 materials 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.

Table 2. Toolkit of alternative non-Portland cements that can offer technical and/or environmental improvements in the cement sector.

	Major oxide constituents of hardened material	Typical raw materials	Primary applications	Main factors inhibiting wider usage
Calcium sulfoaluminate based cements	CaO; Al_2O_3; SO_3; SiO_2; Fe_2O_3	Limestone Bauxite Gypsum Clay/shale	Rapid set Self-levelling grouts Expansive/shrinkage-compensating agents	Availability of alumina source
Calcium aluminate cements	CaO; Al_2O_3; minor Fe_2O_3 and SiO_2	Bauxite Limestone	Refractories Specialty concrete Rapid set Acid resistance Sulfate resistant	Availability of alumina source Conversion resulting in strength regression
Belite cement	CaO; SiO_2; minor Al_2O_3 and SO_3	Limestone Clay/shale Sand	Oil well cement Low-heat construction for large pours	Setting time Low early strengths
Alkali activated materials	Al_2O_3; SiO_2; Na_2O; K_2O; sometimes CaO, MgO and Fe_2O_3	Varied; see Table 1	In-situ/general applications High-temperature resistant concretes Pre-cast applications Nuclear waste immobilisation (as "geopolymer" cements in particular)	Availability and sustainability of activators Consistency/variability of precursors
Lime-pozzolan cements (Elsen et al., 2022)	CaO; Al_2O_3; SiO_2; minor Fe_2O_3	Lime Pozzolana	Conservation work Potentially general concrete applications	Slow strength development Carbon footprint and energy requirements for lime production
Mg phosphates	MgO; P_2O_5; K_2O	Magnesite/Magnesia Potassium phosphate	Concrete repair materials Nuclear waste immobilisation	Availability of raw materials Very rapid setting
Mg silicates	MgO; SiO_2	Magnesite/Magnesia Silica fume Microsilica	Precast elements and blocks Potential use in nuclear waste immobilisation	Availability of raw materials Strength development Research gaps
Sorel cements	$MgCl_2$; MgO	Magnesite/Magnesia Magnesium chloride	Indoor concreting e.g. floors Wall panels Fire resistance Binder for wood composites	Dissolution of the binding phase in humid environment
Carbonation hardening cements	CaO; MgO; SiO_2; CO_2	Limestone Clay/shale Sand Magnesite/magnesia or magnesium silicates High-calcium metallurgical slags	Pre-cast blocks and elements	Limited to factory production

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