

综合评述

有替代硅酸盐水泥熟料的生产的选项吗?

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摘 要: 人们一直在寻找 CO₂ 排放量低的水硬性胶凝材料, 用它替代传统的以硅酸盐水泥熟料(Portland clinker, PC)为主的水泥。介绍了几种处于不同发展时期的新型非 PC 基的胶凝材料体系。目前大多数水泥生产商都尽可能多地用辅助性胶凝材料替代硅酸盐水泥熟料。火山灰材料具有低的水硬性, 它可使用高浓度碱金属溶液来激发, 得到介于“地聚合物”和石灰激发火山灰胶凝材料间的复合胶凝材料。较远期可以期待基于贝利特、硫铝酸钙和铁铝酸钙矿物组成的水泥熟料, 如拉法基公司的 Aether™ 已投入生产。更远的将来, 不产生 CO₂ 的原材料, 如硅酸镁等, 可能使得水泥生产中实现 CO₂ 零排放, 然而, 这些胶凝材料的耐久性有待验证, 用其配制的混凝土中钢筋锈蚀的防护是实际应用中的关键问题。

关键词: 非 PC 基的胶凝材料; 水泥生产; 能源消耗; 二氧化碳排放

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Are There Any Practical Alternatives to the Manufacture of Portland Cement Clinker?

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Abstract: There is a continuing need to look for alternative hydraulic binders with lower associated CO₂ emissions than conventional Portland clinker (PC) based cements. Several novel non-PC-based binder systems that are at various different stages of development are reviewed. Currently, most cement makers are trying to replace PC to as great an extent as possible with supplementary cementitious materials (SCMs) in order to reduce the carbon footprint of cements, but are reaching limits due to the low hydraulic reactivity of pozzolans. In favorable cases this may be compensated by activation with concentrated basic alkali metal solutions, *e.g.* in complex formulations lying in between “geopolymers” and lime-activated pozzolanic binders. But an alternative approach, using clinkers based on belite, calcium sulfoaluminate and calcium aluminoferrite, such as Lafarge’s Aether™, also shows promise, as such clinkers can be made in conventional cement kilns. In the longer term, binders based on raw materials with no fossil CO₂ content, such as magnesium silicates, might allow cements to be manufactured with zero carbon footprints. However, proof of durability in service seems likely to be the rate-limiting step for the acceptance of all such alternative binders, and the binder’s ability to protect reinforcing steel from corrosion remains the most critical issue for many applications.

Key words: non-Portland clinker-based binder system; cement manufacture; energy consumption; carbon dioxide emissions

1 Introduction

Concrete is by far the most widely used of man-made materials. Concrete is a low energy-consuming material, with both “embodied energy” and “embodied carbon” values generally lower than all other construction materials except uncured softwood, stone, air-dried clay or rammed-earth blocks.

The modern world cannot exist without concrete, and it is extremely unlikely that any alternative construction

material will ever replace concrete in most of its current applications. The basic raw materials required for making conventional Portland clinker (PC) based cements, *i.e.* limestone, silica, clay minerals and coal, as well as aggregates and water of the quality needed to make ordinary concrete, are globally available in vast quantities. Thus, one can consider concrete to be highly “sustainable” in terms of raw materials supply. However, the enormous volumes of concrete produced worldwide, coupled with a new appreciation of CO₂’s role in climate

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change and ocean acidification, have recently led to public concerns about total cement industry-generated CO₂ emissions, which are estimated to constitute at least 5% of total anthropogenic CO₂ emissions.

There is still plenty of room for improvement in the way we make cement and concrete, and even apparently small improvements in the technology can mean quite large energy savings and CO₂ emissions reductions at the scale of the planet. So the question that is currently of most interest to the cement industry in this respect is: how can we continue to make high-quality hydraulic binders, and use them to make cost-competitive concretes, while reducing the total specific CO₂ emissions (often referred to as the “carbon footprint” of the binder) to the minimal values theoretically feasible?

The following five binder systems will be discussed in detail, based on a thorough review of published information.^[1] For all of these systems the raw materials are sufficiently abundant for the binder to be of global interest as a Portland clinker substitute; but the practical performance and manufacturing costs are not yet known with much confidence.

1) Pozzolans activated by lime and/or alkalis, *e.g.* high-volume fly ash cements and “geopolymers”;

2) Reactive calcium silicates produced by “non-Portland” processes, *e.g.* “Celitement™” (KIT, Germany);

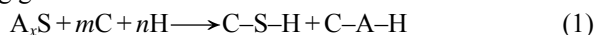
3) Systems based on MgO hydration and carbonation, *e.g.* binders proposed by Tec-Eco (AU) and Novacem (UK);

4) Systems based on precipitation of calcium carbonates, *e.g.* binders recently proposed by Calera Corp. (USA);

5) Systems based on combinations of calcium aluminates, silicates and sulfates with higher alumina/silica ratios than PC, *e.g.* Lafarge’s “Aether™”.

2 Pozzolans activated by lime and/or alkalis

We define “pozzolans” as reactive aluminosilicates, (A_xS), or in some cases relatively pure silica ($x \rightarrow 0$), which can be either glassy (such as natural volcanic glasses or man-made glasses such as fly ash or silica fume) or poorly crystalline (such as metakaolin). The best known and best-understood class of pozzolan-based cements is that based on lime (C) activation, which includes activation by Portland cement. This involves the following generalized reaction:



where, A_xS—pozzolan; water—H; calcium silicate hydrates—C-S-H; calcium aluminate hydrates—C-A-H.

The precise compositions of the C-S-H and C-A-H phases formed vary greatly with the reaction conditions and the presence of other anionic components such as sulfates and carbonates, which preferentially enter the

C-A-H phases. Mixed C-A-S-H phases can also form, especially in the absence of sulfates.

The pozzolanic reaction consumes lime, pozzolans and water to make new hydrated phases that occupy more volume than the original solid phases. Traditional pozzolanic cements, as developed by the Romans, used lime as the activator, but this reaction is too slow at room temperature to be of use for most modern concrete applications. The advantage of using alite as the activator is that its hydration is sufficiently rapid to give reasonable early concrete strengths, while the slower pozzolanic reaction can then be used to consume the excess free lime produced. In many pozzolanic cements, the ultimate C-S-H may have a lower C/S ratio than the average value of about 1.7 typical of pure Portland cements, which allows for even more C-S-H to form.

In addition to lime activation, certain pozzolans can also be activated by reaction with other bases. A particularly interesting case is the reaction between alumina-rich pozzolans (such as metakaolins or coal fly ashes) and basic alkali metal silicate solutions [RS_z (aq.)], where *z* can also be zero (*i.e.* for pure alkali hydroxide solutions):



This reaction is referred to by many people as “geopolymerization”, following the terminology of Davidovits,^[2] but the product is no more or less a “polymer” than is C-S-H, and it is considered by most authors to be a poorly crystalline zeolite precursor “gel”.^[3] Since (for cost reasons) R is almost always N (sodium oxide), such products are commonly referred to as “N-A-S-H gels.” For comparison, the main amorphous products formed during the hydration of Portland-pozzolan cements are often referred to as “C-A-S-H gels,” rather than C-S-H gels, because of their significant alumina contents. The main difference is that C-A-S-H has a generally two-dimensional (lamellar) nanostructure based on calcium hydroxide sheets, related to tobermorite or jennite, whereas N-A-S-H has nanostructure related to zeolites, based on a three-dimensional aluminosilicate network. Thus, if one likes to think in terms of polymerization networks, C-A-S-H can be considered to be essentially a 2-D calcium hydroxide polymer stabilized by silica and some alumina, and N-A-S-H can be considered to be a 3-D silica framework polymer stabilized by alumina and alkali metal cations. The most important quantitative aspect of this structural difference lies in the base/acid ratio, *e.g.* (C+R)/(S+A), which is much higher for C-A-S-H gels than for N-A-S-H gels. This means that more basic elements (mostly calcium oxide) are required for C-A-S-H-based binders than for N-A-S-H-based binders. Since the two basic components needed, *i.e.* either CaO or Na₂O, cannot easily be obtained without very significant CO₂ emissions, (of the order of 1 000 kg CO₂ per tonne of metal oxide in both cases), it can be seen that binders based on N-A-S-H gels tend to have an in-

herent advantage as low- CO_2 binders, provided that the reactive aluminosilicates required come from a low-energy and low- CO_2 source.

Another important difference between “geopolymerization” (reaction (2)) and “pozzolanic hydration” (reaction (1)) lies in the role of water. Reaction (1) is a true hydration reaction, in which anhydrous oxide phases are converted to hydrated phases incorporating significant amounts of chemically bound water; whereas reaction (2) is essentially a coupled dissolution/condensation process in which the final product incorporates the alkali metal oxide into its structure but in principle contains very little chemically bound water—in fact, the theoretical value of n in reaction (2) may well be zero. In terms of kinetics there is also an important difference between the two reactions. In normal pozzolanic hydration the basic oxide, CaO , even if present initially, converts almost immediately to its hydrated form, portlandite ($\text{Ca}(\text{OH})_2$), in contact with water, and so for most purposes one can consider the reaction to be between portlandite, which is sparingly soluble in water, and the pozzolan, which is extremely poorly soluble in water. Thus, the concentrations of the principal reactants present in the aqueous phase remains relatively small but also relatively constant throughout the reaction; and the reaction rate is mainly controlled by phase boundary reactions (dissolution and precipitation) which depend mainly on the surface areas of the solids involved. This means that changes in dilution (*i.e.* the water-binder ratio) have little effect on the overall kinetics, and mainly affect the properties of the final product as a result of the changes in porosity resulting from the presence of excess water beyond that needed for the stoichiometry of the hydration reaction. On the other hand, geopolymerization involves the presence of a concentrated alkali solution because essentially all of the alkali metal required is initially present in a water-soluble form (as alkali hydroxide or silicate). Moreover, the kinetics of geopolymerization are strongly dependent both on the alkali concentration and on the temperature, *i.e.* highly concentrated alkali solutions coupled with elevated curing temperatures are preferable for rapid hardening.^[1–3] This sensitivity to dilution with excess water makes geopolymerization difficult to use in normal concrete applications, since concrete aggregates are often wet. On the other hand, the inherently low bound water content of fully-reacted geopolymer pastes gives them excellent fire resistance and relatively low drying shrinkage (after initial dry curing). Thus, “pure” geopolymers appear better suited for “low-temperature ceramics” applications than as an alternative to Portland clinker-based cements for ordinary construction applications.

However, in order to benefit from the relatively low basic oxide content of these alkali-activated pozzolanic systems in terms of reduced net CO_2 emissions, while nevertheless being able to produce binders suitable for

use in ordinary concretes cured at ambient temperatures, researchers are currently in the process of developing optimized combinations of alkali- and lime-activated binders.^[4] Unfortunately, as the number of ingredients increases, so does the complexity of the system. Thus, quality control may well become the overriding problem in practice. Moreover, due to the need for significant amounts of basic calcium in order to obtain quick setting and hardening at ambient temperatures, many of these formulations may not end up being much better than conventional PC-pozzolan cements in terms of their overall CO_2 emissions.

3 Reactive calcium silicates produced by “non-Portland” processes, *e.g.* “Celitement™”

It is generally accepted that C–S–H is the most important binding phase in hydrated Portland cement pastes. Researchers at the Karlsruhe Institute of Technology (Germany) have recently developed a new class of binder, called “Celitement™,” that reportedly makes use of these binding properties in a more energy-efficient way, avoiding the need to produce Portland clinkers, and resulting in significantly lower CO_2 emissions for equivalent concrete performance.^[5] Their approach is to produce a coating of a C–S–H precursor phase on the surface of particles of a relatively unreactive hard filler such as quartz. The precursor phase is typically formed from $\alpha\text{-C}_2\text{SH}$, a calcium silicate hydrate produced by reaction of lime and silica in an autoclave. Crystalline $\alpha\text{-C}_2\text{SH}$ is not hydraulically reactive, but it can apparently be activated by intergrinding it with the hard mineral filler. Reportedly, the $\alpha\text{-C}_2\text{SH}$ becomes amorphous (and probably also dehydrates to some extent) as it is ground, and thus forms a reactive coating on the filler particles that can hydrate in water at ambient temperatures, leading to C–S–H-mediated bonding between the coated particles. The manufacture of Celitement thus typically requires three fundamental steps: 1) the calcination of limestone to make quicklime; 2) reaction of lime, silica and water at about 200 °C and 1.5 MPa pressure to produce $\alpha\text{-C}_2\text{SH}$, and 3) drying and intergrinding of $\alpha\text{-C}_2\text{SH}$ with the hard filler (by means of a special process). The net CO_2 emissions may reportedly, in favorable cases, be as low as 50% of those of CEM I OPCs. This is mainly because the binder contains a high content of a hard filler with low embodied energy. It is reported that certain Celitement compositions can give mortar compressive strengths of up to 80 MPa after 28 d of humid curing, and also can give a low permeability matrix which might be helpful in retarding steel corrosion. On the other hand, the high filler content of most Celitement binders implies that they will probably require significant dosages of dispersants (superplasticizers) in order to achieve such performance.^[5]

4 Systems based on MgO hydration and carbonation

MgO-based cements are not new. Sorel cements, invented over 140 years ago,^[6] are based on the hydration of MgO in concentrated solutions of either magnesium chloride or magnesium sulfate, forming hydrated magnesium hydroxy-chlorides or hydroxy-sulfates, respectively.^[7] The performance of Sorel cements is strongly dependent on the ratios of the main ingredients as well as the reactivity of the MgO used.^[8] However, they generally set and harden very rapidly, can give considerably higher mechanical strengths than gypsum plasters, and also have good fire resistance. So, despite their relatively high cost, they have some good specialty applications, mainly for use in dry environments. Despite their high basicity, Sorel cements usually carbonate only very slowly in use, probably due in part to the formation of complex hydroxy-carbonate hydrates at the surface. It is also reported that the water-resistance of hardened Sorel cement products can be improved significantly by treating them with soluble phosphate salts.^[7]

Another important class of MgO cements is based on magnesium phosphates.^[7,9] Magnesium forms relatively insoluble hexahydrated binary orthophosphates (struvites) with either ammonium or potassium. The hydration reaction is usually accomplished by adding solid MgO to a concentrated aqueous solution of the di-hydrogen phosphate salt of the monovalent cation, (*e.g.* a solution of KH_2PO_4). This type of cement can set and harden very quickly, and can also give very high strengths. Due to the low solubility of struvite, the water-resistance of such binders is generally good.

Despite the fact that magnesium is one of the most common elements on the surface of the earth, the two classes of MgO-based cements described above are restricted to specialty applications in part because of the relatively high cost of pure MgO, usually obtained by calcination of (relatively scarce) magnesite. It is often stated that magnesium is abundant in the oceans. Average seawater contains about $1\,290 \times 10^{-6}$ of Mg^{2+} , which is equivalent to about 2.2 g/L of MgO. But this Mg is present in a fully-neutralized form. Thus, MgO can only be separated from seawater by the addition of a strong base, *e.g.* lime (CaO or $\text{Ca}(\text{OH})_2$) or “hard-burned dolime” (an intimate mixture of CaO and MgO), to precipitate brucite, which is then dried and calcined to give periclase. So this is, overall, a more energy-intensive and expensive process than the calcination of magnesite. Note also that magnesium phosphate cements suffer from an even more severe sustainability problem due to the global scarcity of phosphate ores and their priority application in fertilizers.

However, the average content of MgO in surface rocks is very great. Thus, over the last decade, several fresh

attempts have been made to try and develop more sustainable cement technologies based on magnesium oxide. An Australian company called “Tec-Eco” developed and patented a series of binders incorporating various amounts of reactive MgO produced by calcining magnesite at low temperatures.^[10] The inventor, John Harrison, claimed that the low-temperature calcination of magnesite required less energy and emitted less CO_2 than the manufacture of Portland cements, and that adding reactive MgO to Portland-pozzolan cements could improve their performance and also increase their capacity to absorb atmospheric CO_2 .^[11] Other researchers have since investigated the details of such systems but have not observed any remarkable benefits due to the incorporation of MgO.^[12] In any case, Harrison’s proposition that MgO-based cements were inherently more sustainable than CaO-based cements was not supported by the evidence, because a) MgO derived from natural magnesite or from seawater releases more fossil CO_2 per unit mass than calcination of limestone to make lime (or OPC clinker), and must also accomplish this highly endothermic reaction by the combustion of fossil fuels; and, b) brucite-rich pastes carbonate even less rapidly than hydrated Portland cement pastes under most exposure conditions. The possibility also exists that one could make prefabricated articles by deliberately carbonating wet MgO under an elevated partial pressure of CO_2 , and that this might allow one to develop a strong microstructure based on metastable hydrated magnesium carbonates such as “nesquehonite” ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), as suggested in Ref. [11] But it is already known that one can produce strong precast products by the carbonation of Portland cement concretes, and some conventional concrete block makers already do this, so it is still not clear why carbonated precast products made from MgO that itself is derived from MgCO_3 should be any more sustainable than those made from lime or OPC.

However, the above situation has changed significantly over the last three years, due to the research of Vlasopoulos and Cheeseman at Imperial College, London. They developed and patented a new class of MgO-based hydraulic binders which also include significant amounts of crystalline magnesium hydroxy-carbonate hydrates such as hydromagnesite ($\text{Mg}(\text{OH})_2 \cdot 4\text{MgCO}_3 \cdot 4\text{H}_2\text{O}$).^[13] But, more importantly, they also noted that it should in theory be possible to extract reactive MgO from common magnesium silicate rocks with acceptably low energy requirements and CO_2 emissions. This approach is the basis of a start-up company called “Novacem” which is currently conducting the R & D needed in order to determine how to make such cements in industrial quantities. Evidently, much of this work is still confidential, but the summary given here is based mainly on a recent public presentation.^[14]

The important difference between the Novacem ap-

proach and previous approaches is the idea that MgO might be extracted from common basic magnesium silicate rocks, such as peridotites or serpentinites, with overall CO₂ emissions low enough to render the overall process sustainable. The advantages of using basic magnesium silicates as raw materials are twofold: firstly, they are very abundant on a global basis, despite the fact that they are not as well-distributed over the Earth's surface as limestone or clays; and, secondly, they contain essentially no fossil CO₂. The Earth's mantle is roughly 70% magnesium orthosilicate (Mg₂SiO₄), and this occurs as surface deposits in the form of olivine. Partial hydration of such rocks near the Earth's surface usually leads to the formation of serpentine (Mg₃Si₂O₅(OH)₄). Since neither of these minerals contains fossil CO₂, the main industrial problem is how to efficiently extract reasonably pure MgO from them with acceptably low costs and CO₂ emissions associated with the energy used. Novacem's approach is to make use of supercritical carbonation in a high-pressure reactor. This decomposes magnesium silicate into magnesite and amorphous silica, which can, if necessary, be separated. The magnesite can be calcined in the usual way to give a reactive periclase, and the resulting CO₂ gas can be recaptured and returned to the pressure reactor, so it essentially serves only as a "catalyst" in the process.

A second important feature of Novacem's approach is the deliberate inclusion of certain types of magnesium carbonate in the cement formulation itself, in order to control the setting and hardening properties.^[13] If these magnesium carbonates are obtained by consumption of CO₂ from the atmosphere or from other industrial processes during the manufacture of the Novacem cement, and are included in sufficient amounts in the cement composition, the manufacture and use of such cements could in theory even be net CO₂-negative. Thus, the Novacem approach does not specifically require that the binder absorb atmospheric CO₂ during its working life (e.g. in hardened concrete structures) in order for it to be considered a "low-CO₂" cement. However, any such absorption would be an additional bonus.

Recent results suggest that Novacem binders are capable of giving good-enough compressive strength development for a wide range of potential concrete applications.^[14] However, it is currently too early to determine whether or not the manufacture of Novacem will be industrially feasible at an acceptable cost and whether or not the desirable theoretically-predicted CO₂ balance can be achieved in practice. Moreover, even if the approach is ultimately successful in the above terms, there will also still be much work to be done to establish the quality and reliability of such cements for major construction applications. One important issue will presumably be that of reinforced concretes, as magnesium hydroxides are far less basic than calcium hydroxides, implying that MgO-

based cementitious matrixes will probably only be capable of buffering the pH of their pore solutions at values close to 10, which is too low for the conventional passivation of steel. However, this problem is not unique to Novacem. Many of the low-CaO binder systems discussed in this paper are likely to have difficulty in maintaining a high-enough pH for the passivation of steel over long periods of exposure to the atmosphere, because of their tendency to carbonate rapidly. In this respect, the high CaO content of Portland cements is still a major durability advantage in most structural applications unless the permeability of the paste matrix of low-CaO binders can be made so low as to limit steel corrosion rates to acceptable levels by restricting transport of ions and/or oxygen.

5 Systems based on precipitation of calcium carbonates

Calcium carbonate, in the form of limestone, is one of the most globally-abundant raw materials for the manufacture of hydraulic binders. Clearly, it would be of great interest to be able to use it as a major binder ingredient without the need to decarbonate it first, thus avoiding the release of its fossil CO₂ into the atmosphere. Currently, limestone powders are used in various classes of Portland cement concretes, and it is known that calcite can actually react chemically with the aluminates in cement, to form calcium carboaluminate hydrates which are classed as "AFm" phases, and may also contain some Fe³⁺ ions substituting for Al³⁺.^[15] The more reactive alumina available, the more carboaluminate hydrates can form, and some of this reactive alumina can come from SCMs such as slags or fly ashes.^[16-17] However, the amount of calcium carbonate that can react in this way in conventional PC-based cements is generally less than about 10%. So it is interesting to note that "pure" calcium carbonate-based cements have been shown to be feasible on a laboratory scale. Such binders were initially developed primarily for use in the field of biomaterials, i.e. as potential bone-repair cements.^[18-19] The approach used was to precipitate reactive amorphous calcium carbonate (ACC) powders by mixing solutions of calcium chloride with solutions of sodium bicarbonate, followed by rapid drying. In order to stabilize amorphous forms of CaCO₃, magnesium or strontium ions were included in the chloride solution. It was shown that mixtures of ACC and vaterite powders would then react in water to precipitate calcite or aragonite, and that this reaction gave a hardened product. In one case, a paste compressive strength of 13 MPa was obtained at a water-solid ratio of 0.4.

The importance of the above work is that it shows clearly that hydraulic binders can be made from calcium carbonates without any decarbonation. It is especially interesting to note that the "hydration" reaction essen-

tially involves no binding of water, since both the initial binder phase (ACC+vaterite) and the final “hydration” products (aragonite or calcite) are ostensibly anhydrous forms of CaCO_3 . This appears to confirm the mechanism proposed by Shchukin and Amelina^[20] for the development of strength in crystalline binders, *i.e.* the formation of “bridging” contacts when crystals growing from a supersaturated solution come into contact with one another.

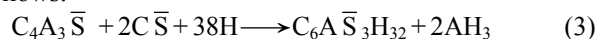
The work of Combes *et al.*^[18–19] was aimed at biological applications, rather than binders that might be more suitable for construction applications. However, Brent Constantz of the Calera Corporation of California has recently suggested that carbonate-based binders or aggregates might potentially be produced in large quantities and at an acceptable cost by the carbonation of sea water or various brines in the presence of suitable sources of alkalinity.^[21] Apparently, the alkalinity could potentially be produced at an acceptably low energy cost by a proprietary new low-voltage “electrodialysis” process in which salt water can be separated into two separate solutions rich in NaOH and HCl, respectively, without producing significant amounts of unwanted gaseous products such as hydrogen or chlorine as occurs in the conventional “Chlor-Alkali” process widely used in the industrial production of NaOH and chlorine. The excess HCl produced by this new process could presumably be neutralized by dissolving basic minerals, as suggested by House *et al.*^[22] This could constitute a novel approach to the sustainable capture of anthropogenic CO_2 emissions and their conversion into industrially useful products, although little detailed technical information on such products or the manufacturing processes involved has yet been published.

6 Belite-calcium sulfoaluminate-ferrite (BCSAF) cements: Lafarge’s “Aether™” technology

Many types of calcium sulfoaluminate-based cement have been developed over the past few decades for a wide range of possible applications, especially in China, although relatively few are actually produced industrially.^[23] There have also been many attempts to develop reactive belite cements in order to reduce the temperature and energy costs of clinkering in Portland cement kilns.^[24–26] One approach being investigated by Lafarge is to combine the two above approaches to make intermediate clinker compositions containing belite, calcium sulfoaluminate (ye’elimite) and calcium aluminoferrite solid solution as the three principal phases, (given in decreasing order of content), and also including certain combinations of minor elements in order to stabilize the belite in the more reactive α form.^[27] Such “BCSAF” clinkers can produce cements with similar performance

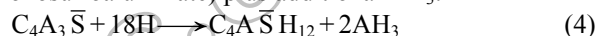
to Portland cements (OPCs) and can be manufactured in conventional Portland cement plants with the emission of 20%–30% less CO_2 than the equivalent OPCs.^[28] More recently, Lafarge has adopted the name “Aether™” for cements produced using this technology, which is now the subject of a European Community “Life+” development project.

The hydration path of Aether cements is very different to that of OPCs. It is the hydration of ye’elimite together with added calcium sulfate, (*e.g.* as anhydrite) to give ettringite plus an amorphous aluminum hydroxide gel (AH_3) that accounts for most of the strength development during the first day.^[28] This reaction can be represented as follows:



Even on these short timescales, the importance of reactive species availability is highlighted in the study by Sahu, *et al.*^[29] which shows that the rate of ettringite formation and its subsequent impact on the reaction kinetics is dependent on the rate of solubility of the calcium sulfate phase used.

Once the readily soluble sulfate has been exhausted, ye’elimite can continue to hydrate to give an AFm phase (monosulfoaluminate) plus additional AH_3 :



After the first day, most of the additional strength development is due to hydration of the belite and ferrite phases, although their initial hydration products are different from those produced by essentially the same phases in OPC, which is not surprising given the ions available for precipitation. The latest evidence suggests that belite initially hydrates mainly together with the consumption of AH_3 , as shown below, to give crystalline strätlingite (C_2ASH_8) rather than C–S–H as usually formed in OPCs.



The ferrite phase also apparently hydrates with consumption of some belite to produce katoites (siliceous hydrogarnets) covered by the general formula $[\text{C}_3(\text{A},\text{F})\cdot\text{S}_x\text{H}_{6-2x}]$ where the A/F ratio is unknown but x is probably not greater than 1.^[30] Thus, by 14 d the main hydrates all appear to be crystalline. This implies that it is not necessary to rely on amorphous phases such as C–S–H or AH_3 for strength generation in such cements. However, C–S–H does begin to form later on, as belite continues to hydrate after all of the AH_3 has been consumed, (at which point strätlingite also begins to be consumed by reaction with lime produced by belite hydration, giving more katoite).^[31–32] It is interesting to note that the compressive strengths of moist-cured concrete specimens made from BCSAF cements in 2006 continued to increase steadily over at least several months, and did not exhibit major bulk volume changes, despite the major changes in the hydrate phase assemblage that we may now assume to have taken place.^[33]

7 Concluding remarks

In developing new hydraulic binders for large scale use, a number of key objectives must be met:

1) CO₂ emissions and energy consumption from manufacture should be as low as possible. Of course, ordinary pollutant emissions (*e.g.* NO_x, SO_x, Hg, *etc.*) must also be at least within regulatory limits defined for PC manufacture.

2) The binder must be fit for the purposes for which it will be used (concretes, mortars, *etc.*) The issue of durability (or service life) is critical, and it is expected to be the issue which will cause the greatest delay in the implementation of new cement technologies. This is because it is so difficult to assure durability in any given application by means of short term testing. The best approach is begin as early as possible to evaluate all conceivable types of chemical and physical deterioration mechanism for the hardened binder in typical proposed applications. But it is also necessary to consider the components or structures in which the binder may be used, to determine whether problems might arise from interactions with other components. The most obvious example of this is the ability of the binder to protect steel reinforcing elements from corrosion. This is something that Portland cement concretes do very well because they can buffer the pH at a high enough value to keep steel in a passive state, and they have the ability to maintain this pH for a long time not only due to buffering by portlandite but also by forming a fairly good barrier to carbonation from atmospheric CO₂. All of the alternative binder systems discussed here seem likely to be less effective in this respect, and, unless the binder is not going to be proposed for use in reinforced concretes, this perceived risk must be addressed by careful research.

3) The properties of the freshly-mixed binder must be well understood and amenable to control by additives or admixtures in order to assure that concretes or mortars can be mixed and placed effectively and that they will then set and harden in a reasonable time under the desired conditions of use. In addition, the need for special curing procedures after placing and even after demoulding must be assessed. Some alternative binder systems, (for example, many pozzolan-rich systems), gain strength and reduce their porosity only very slowly, so their performance, (especially surface durability), can be seriously impaired if they are not properly cured for long enough. In this respect, it is also important to remember that actual curing of concrete in the field is often far less than is desirable or recommended. Thus, it is necessary to provide a significant safety margin to allow for the risk of poor on-site placing and curing practices.

4) Raw materials must be cheap and readily available locally. Ideally, wastes and by-product materials from other sectors, or recycled construction materials, should

be consumed in making such binders.

5) Other processing costs also need to be acceptable, such that the final cost of such binders is low enough to be competitive as a means of reducing cement-related industrial CO₂ emissions, as opposed, for example, to the proposed separation of CO₂ from cement plant exhaust gases followed by pressurization for transport and underground storage.

It will be difficult to change global cement manufacturing so as to greatly reduce CO₂ emissions in a short time frame. Even if suitable raw materials and production processes are available globally, transportation costs (and their associated CO₂ emissions) may be high, which suggests that no single solution to the problem is likely, and thus that a wide variety of local solutions are likely to co-exist. This will require a good supply of well-trained engineers.

In looking at the alternative systems currently known, it appears that those closest to industrialization are high-substitution pozzolanic binders, which includes not only PC-activated pozzolans but also alkali-activated pozzolans, or combinations of both. Next in line are binders based on alternative clinkers rich in belite and calcium sulfoaluminate, which can be made in existing cement plants. Finally, in the very long term, other very different binders, such as binders based on magnesium silicate raw materials, appear to hold promise for extremely low CO₂ emissions.

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