

Alternative Cement Clinkers

Ellis Gartner¹, Tongbo Sui²

¹ Imperial College, London; <e.gartner@imperial.ac.uk>

² Sinoma Research Institute, Beijing, China; <suitongbo@sinoma.com.cn>

Abstract

This article reviews proposed technical approaches for the manufacture and use of alternatives to Portland Cement Clinker as the main reactive binder component for ordinary concrete construction in non-specialty applications, while giving lower net global CO₂ emissions in use. A critical analysis, taking into account a wide range of technical considerations, suggests that, with the exception of alkali-activated systems, (treated in a separate paper in this issue,) there are only four classes of alternative clinker system that deserve serious attention with respect to global reductions in concrete-related CO₂ emissions:

- (A) Reactive Belite-rich Portland cement (RBPC) clinkers
- (B) Belite-Ye'elite-Ferrite (BYF) clinkers
- (C) Carbonatable Calcium Silicate clinkers (CCSC)
- (D) Magnesium oxides derived from magnesium silicates (MOMS)

A and B are “hydraulic” clinkers, (i.e. clinkers which harden by reaction with water,) C is a “carbonatable” clinker, (i.e. one which hardens by reaction with CO₂ gas) and D can fall into both categories.

1 Introduction

The term “alternative cement clinker” as used here refers to a man-made mineral material that, when ground to a fine powder, is capable of reacting sufficiently rapidly with water and/or CO₂ in such a way as to produce a hardened mass which can be used as the binder in a concrete or mortar and which will harden rapidly enough to be adaptable to modern construction practices that currently make use of conventional Portland Cement Clinker (PCC) based binders. The objective of the critical analysis of alternative clinker technologies presented in this paper was to determine their interest as a means of obtaining net GHG emissions reduction with respect to conventional PCC- and lime-based technologies applied to large scale construction applications, i.e. construction concretes and mortars, or equivalent (including soil stabilization applications). The authors wish to state clearly that, since much of the information available to them during the writing of this paper was not available in the form of citable scientific references, they have tried their best to present a realistic view of the current state of the art based primarily on their own detailed personal knowledge and experience of the subject matter. The paper thus includes many of their personal opinions on the subject, not always supported by published data, and they take full responsibility for that.

Due to increasing concerns over global CO₂ emissions, many different types of alternative binder have been proposed in recent decades; but we cannot treat all of them in detail this paper. Those that we will not treat in more detail in this paper are briefly summarized below, together with the reasons why:

1. **Alkali-activated binders:** These are important and complex enough to justify a separate paper.[1]
2. **Binders based on reactive calcium silicates produced by hydrothermal processing:** At least two research groups are currently trying to develop CO₂-efficient approaches to the manufacture of

hydraulic binders by hydrothermal processing.[2][3] At the heart of these approaches is the observation that a di-calcium silicate hydrate, α -C₂SH, can easily be made by low-temperature autoclaving of lime-silica mixtures. The α -C₂SH can then be activated by intergrinding with hard fillers (“mechanochemical activation”) and/or heating at low temperatures (“thermal activation”) to give a “clinker” which is apparently very close to ordinary belite (C₂S) in composition, but far more reactive and presumably still at least somewhat hydrated. Intergrinding supposedly also produces an intimate bond with the hard filler particles. In the case of intergrinding the resulting reactive material is equivalent to a filled activated belite cement; and the thermally-activated product can also be blended with various low-CO₂ fillers to make an equivalent binder. The overall manufacturing process is complex due to the need for more processing steps than required for OPC production: (preparation of lime, grinding of silica sources, blending, autoclaving, low-temperature drying, blending/grinding with fillers). Because these approaches are still under development at the laboratory level, no reliable estimate of their overall energy- and CO₂-efficiencies in an industrial context can yet be made. However, simple thermodynamic arguments show that the manufacture of the reactive calcium silicate component itself is unlikely to be significantly more energy- or CO₂-efficient than simple production of the equivalent amount of belite in a high-belite Portland Cement clinker. This is because the calcium source is “quicklime” (CaO) which is itself produced by calcination of limestone; and the enthalpy of manufacture of quicklime is significantly higher per unit CaO content than that of belite (see Appendix). Thus, the main interest of this type of binder appears to lie in the very significant increase in reactivity relative to what is possible with equivalent binders made from belite-rich Portland cement clinkers, and the resultant increased level of dilution with low-CO₂ fillers which may be made possible by such increased reactivity.

3. **Binders based on MgO derived from magnesite or seawater:** Well-known technologies already exist for using MgO to make binders suitable for construction applications. “Sorel” cements, based on mixtures of powdered MgO with concentrated solutions of magnesium chloride or sulfate, have been known for well over a century and have some applications in construction, but are only suitable for use in dry environments. Magnesium phosphate cements, based on mixtures of powdered MgO with concentrated solutions of ammonium- or potassium-dihydrogen phosphate, have also been used in specialty construction applications for many decades. They have good water-resistance, rapid strength gains and high ultimate strengths. However, neither of these MgO-based binder technologies is currently suitable for general construction applications, mainly due to the scarcity of the raw materials compared to those required for PCC, but also because the manufacture of the main “clinker” component for both of these technologies, MgO, involves a very energy- and CO₂-intensive production process. Currently, the main source of MgO is calcination of natural magnesite, (MgCO₃, a very scarce mineral compared to limestone) which results in total CO₂ emissions of the order of 1.55 tons of CO₂ per tonne of MgO produced (see detailed calculation in the appendix). Some MgO is also produced from brines or seawater, but with an even higher carbon footprint. Because the carbon footprint of MgO produced in these ways is almost a factor of two higher than for PCC, we discount the use of conventionally-sourced MgO-based hydraulic binders in concrete as a route to improved carbon-efficiency in construction. In order to circumvent this problem, certain groups have proposed the use of carbonation hardening instead of hydration hardening as a way of reducing the carbon footprint of MgO based-binders,[4] and this is indeed possible; but at the moment it seems to us that such binders offer no special advantages relative to the calcium-based carbonatable binders discussed in detail in section (C) of this paper, and still suffer from the relative scarcity of the main raw material.[5]

However, due to its long-term interest, we have decided to include, in section (D) of this paper a detailed discussion of the long-term potential for producing large reductions in net CO₂ emissions relative to PCC-based binders if an energy-efficient method can be developed for making MgO-based binders from basic magnesium silicate rocks. Such rocks are extremely abundant and rich sources of magnesium which, unlike magnesites, contain essentially no chemically combined (“fossil”) CO₂ and thus have the potential to make very carbon-efficient MgO-based products if suitably energy-efficient extraction technologies can be invented to separate the MgO in a reasonably pure and reactive form.

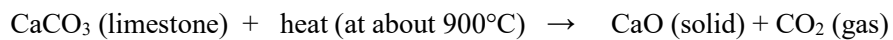
4. **Binders based primarily on precipitated calcium carbonates:** In or around 2009 an apparently novel approach to the production of low-CO₂ hydraulic binders was proposed and heavily promoted by a well-funded start-up company in California, the Calera Corporation. Unfortunately, little published scientific data is available on this process, but a brief description can be found in [6]. The basic concept apparently was to capture CO₂ from industrial flue gases and use it to precipitate calcium (or magnesium) carbonates, the Ca (or Mg) source being seawater or brines. The precipitated calcium or magnesium carbonates could then be used as construction materials; and it was suggested that, for some applications, the calcium carbonates could be used as hydraulic binders via an approach previously proposed by French researchers for the manufacture of bio-compatible binders for use in bone replacement, etc.[7] This initially sounded promising, but simple elemental and energy balance calculations soon showed it to be unworkable because Ca and Mg ions occur in relatively dilute solution in seawater or brines, and mainly as chlorides, so any process which precipitates them in large amounts must pump huge volumes of water and also dispose of the equivalent quantities of chlorides. Calera proposed two possible approaches for the chlorides: convert them to sodium chloride (in which case the process consumes an equivalent quantity of sodium hydroxide, an energy-intensive commodity chemical,) or else use a specially-developed electrolytic process to convert the chlorides to (relatively dilute) hydrochloric acid. However, global demand for hydrochloric acid is very small compared to that for cement, so, if the process were ever operated on a large scale, most of this dilute hydrochloric acid would end up as a hazardous waste stream. Moreover, both of these approaches have high primary energy footprints, making them far less sustainable than had appeared at first sight. In addition, calcium carbonate cements themselves give a highly porous and water-sensitive product not suited to most ordinary concrete applications. Given all of the above issues, the Calera process is not considered to be a serious approach for reducing the global carbon footprint of concrete construction.

5. **Binders based on phosphates:** Both magnesium phosphates (see (3.) above) and calcium phosphates have well-known applications in hydraulic binders, some of which are in widespread use for specialty applications; but they cannot be considered suitable for general construction applications given the global scarcity of phosphate resources and the clear need to reserve them primarily for agricultural uses.

In addition to the above pre-selection process, there is another important fundamental issue that must be clarified before entering into the details of the selected binder systems, and that is the question of hydration curing versus carbonation curing. Almost all conventional concrete is produced using hydraulic binders based on PCC, i.e. binders that harden by a reaction between the clinker and water. The hardening of such concretes requires moist curing to ensure that sufficient water remains available for the hydration reaction over the minimum period of time necessary for the concrete to gain the required strength, a time that typically ranges from one day to several weeks depending on the curing temperature and the reactivity of the binder. Since all conventional hydraulic binders are based on strongly basic calcium

compounds, they all can all also slowly react with CO₂ (either from the atmosphere, or else deliberately added to the curing chamber in some precast products plants) to produce calcium carbonate. Thus, conventional concretes do slowly absorb CO₂ throughout their working life, although in most structural applications it is desirable to minimize the rate of this carbonation reaction because it limits the ability of the concrete matrix to protect embedded steel reinforcement against corrosion. For this reason, the industry does not generally claim any “CO₂ credit” for the CO₂ absorbed by concrete over its lifetime, or even at the end of its working life, even though the amounts of CO₂ absorbed in this way can be very significant.[8]

It is important to note that all CaO-based binders are manufactured using calcium carbonate in the readily available mineral form of limestone as essentially the only source of CaO. In all such industrial processes the CaCO₃ must be decarbonated by heating to about 900°C, releasing an equivalent amount of CO₂ in the flue gases which are exhausted into the atmosphere:



(Note: in the above equation, the solid product is assumed to be free lime, but in practice the presence of aluminosilicate solids will lead to some formation of calcium silicates or aluminates directly.)

It is the above reaction which accounts for more than half of the CO₂ emitted in the manufacture both of PCC and also of lime (traditionally used in many construction applications for many millennia). The total emissions can be divided into two types: the CO₂ originally bound in the limestone, which we refer to as “fossil” or “raw-materials” (RM) CO₂, and the CO₂ released by the combustion of the fuel required to provide the heat to drive the reaction, which we refer to as “fuel-derived” (FD) CO₂. Some values are given in the appendix for specific cement compounds. But the important point to note here is that essentially all of the RM-CO₂ emitted during limestone decarbonation reaction can, in theory, be reabsorbed by the hardened concrete if exposed to air for long enough. The main problem is that the process is very slow: for large concrete objects, it may even take thousands of years. This is a major reason why the industry does not seriously attempt to take any credit for it at the moment. But the process can be greatly accelerated if the concretes are deliberately cured under a concentrated CO₂ atmosphere, using, for example, the CO₂-rich flue gases from fossil-fuel-burning industrial plants such as cement plants or power plants. This is not new and has been practiced to a small extent for many decades, but its use is very limited because it is mainly suitable for making non-steel-reinforced precast concrete products such as blocks or bricks, and because the rate of the process has traditionally been quite slow, limiting the efficiency of the industrial facilities. The recent development of improved CO₂-curing techniques by Solidia, which will be discussed in detail later in this paper, may allow a significant increase in the use of this approach, but it is still likely to be limited primarily to factory-produced, non-steel reinforced products. Moreover, the maximum possible level of CO₂ reabsorption is limited by the amount of reactive CaO (and also to some extent the reactive MgO) in the binder. The FD-CO₂ can never be recaptured in this way.

Now, if reactive anhydrous calcium silicate and aluminate compounds were abundantly available in nature, instead of calcium carbonates, it would be possible to make binders that could absorb more CO₂ by carbonation during use than emitted by the fuel required for the manufacturing process. One would thus be able to make “carbon-negative” PCC-based binders which could be used in construction while serving to reduce net global CO₂ emissions. But such raw materials are not available to us to any significant extent because they are so reactive with water and the atmosphere that they do not survive very long at the Earth’s surface. The main sources of such raw materials that are readily available to us are industrial waste products such as metallurgical slags, which are usually rich in calcium silicates; or

else old concretes. Such materials still have some potential to absorb CO_2 , and this process could be accelerated artificially if it could be made economically viable. Various processes have been proposed for making carbonation-hardened products from such calcium-silicate rich wastes, but few are efficient enough to justify the investment. However, the good news is that a very efficient industrial process already exists for using such wastes to reduce global CO_2 emissions - the conventional PCC manufacturing process itself! If calcium-silicate-rich industrial wastes, such as slags, and even the fine fraction of crushed recycled concrete, can be returned to a PCC manufacturing plant, they can be used to replace some of the limestone needed in the raw materials for manufacturing PCC. This is a very CO_2 -efficient way to use such materials. The main limiting factor is usually simply the cost of transport, although the presence of undesirable impurities can also limit the maximum degree of substitution in any one plant. Since the costs of transport are usually high in relation to their CO_2 emissions, this type of recycling should become more economically viable as the cost of emitting CO_2 increases due to taxes or other imposed policies designed to reduce such emissions.

In the preceding paragraphs, we only considered CaO-based binders, but it is also possible to make MgO-based binders, as noted in (3.) above, which can also carbonate in use or be deliberately hardened by carbonation. However, in the case of MgO, we do have potentially enormous natural resources of CO_2 -free raw materials in the form of basic magnesium silicate rocks, which in theory could permit the manufacture of MgO without any release of RM- CO_2 . This is why only approach D in this paper, "MOMS," has a significant theoretical potential to produce truly carbon-negative concretes.

Based on the above analyses, the remainder of this paper examines in considerable detail only the four alternative cement clinker technologies currently under development by industry and/or the academic community which, in our opinion, deserve serious attention with respect to construction in the current global industrial-environmental-economic context. All four approaches are intended to reduce the CO_2 emissions associated with the manufacture clinker as well as the carbon footprints of the resultant concretes or mortars in a wide range of construction applications. However, the large-scale implementation of any such approach will ultimately depend on its economic value with respect to conventional OPC-based concrete technologies, assuming that the relevant environmental and sustainability issues can be effectively integrated into the economic evaluation process. The four selected approaches are listed below:

- (A) Reactive Belite-rich Portland cement (RBPC) clinkers
- (B) Belite-Ye'elimite-Ferrite (BYF) clinkers
- (C) Carbonatable Calcium Silicate clinkers (CCSC)
- (D) Magnesium oxides derived from magnesium silicates (MOMS)

The concept of belite-rich Portland cement is not new, but it takes advantage of the fact that modern OPCs have very high alite (C_3S) contents compared to the type of Portland clinkers manufactured a century or more ago. Market demand for rapid concrete hardening has driven cement manufacturers towards higher and higher alite contents, at the expense of higher CO_2 emissions. Since the 1990s the development in China of new approaches to manufacturing reactive belite-rich Portland clinkers (RBPC) in which belite with increased reactivity is the major component holds some hope of reversing the trend, especially for mass concrete applications where low heats of hydration are required. Conveniently, RBPC cements can be manufactured in conventional cement plants, and they are still defined as Portland cements. They are thus covered by most existing Portland cement and concrete norms, so their use is currently only limited by market demand.

The other three approaches are not yet commercialized to any significant extent. In terms of their level of scientific and technical development, BYF and CCSC are both fairly advanced in the sense that the basic technology builds on knowledge that has existed for several decades. BYF clinker technology can be considered to be an extension of the calcium sulfoaluminate (CSA) cement technology which has been developed and commercialized primarily in China since the early 1970s, but with a recent re-orientation intended to make it more competitive with PCC for mass applications. The CCSC concept has also been around for a similar length of time in academic circles, but has only recently begun to be developed in an industrial context by a US-based “start-up” company, Solidia. It is now in early-stage commercialization in close association with a global cement manufacturer, LafargeHolcim. The MOMS approach remains purely academic at the moment, but, in view of its theoretical potential to reduce CO₂ emissions greatly if a sufficiently energy-efficient manufacturing process could be developed, it will also be treated here.

2 Technology presentation

2.1 Description

2.1.1 *Reactive Belite-rich Portland Clinkers (RBPC)*

RBPC belong to the same family as OPC in terms of clinker mineralogy, i.e. they are in the C₂S-C₃S-C₃A-C₄AF system. They are also commonly known as high belite cements (HBC). The difference in clinker composition between RBPC and OPC lies mainly in the belite/alite ratio. For RBPC the belite content is more than 40% (under Chinese standard GB200-2003 for low heat Portland cement) and alite normally less than 35%, making belite the most abundant phase in RBPC, as opposed to alite in OPC. The type of RBPC specified under GB200-2003 also differs significantly from the low heat Portland cements defined under ASTM C150 (type IV) and JIS R5210 in the aspect of 20MPa higher compressive strengths after 28 days of wet curing, which shows the higher reactivity of RBPC compared to conventional HBC.

The appendix to this report gives basic data for C₃S and C₂S and other clinker phases in terms of enthalpy of formation and RM-CO₂ emissions when manufactured from pure raw materials. FD-CO₂ emissions can be considered to be approximately proportional to the enthalpy of formation if efficient dry-process kilns are used. C₃S formation clearly requires more energy and emits more RM-CO₂ than C₂S. The manufacture of RBPC therefore leads to lower specific energy consumption and CO₂ emissions, and also has the additional practical advantage of requiring less high-grade (low-silica) limestone as a raw material.

Industrial production of RBPC in China has been conducted in various modern dry process rotary kilns with preheaters (from one to five stages) with or without precalciners. It uses the same types of raw materials as for OPC, but different raw mix designs. The ideal clinkering temperature for RBPC is usually close to 1350°C, which is about 100°C lower than the average for OPC, which can lead to somewhat lower kiln heat consumption and permit more use of low-grade kiln fuels. Physical or chemical activation, e.g. rapid clinker cooling or minor element doping, may be needed in some cases to make the belite sufficiently reactive. As an example, the use of 0.5-1.0% SO₃ in the raw meal combined with rapid clinker cooling can lead to the formation of reactive belite in the clinker. Specific kiln fuel requirements and CO₂ emissions are typically about 10% below those for OPC. Lower emissions of NO_x and SO_x are commonly observed when making RBPC, due mainly to the lower burning temperature. On the other hand, it requires about 5% more electric power to grind RBPC to the same fineness as OPC, due to the greater hardness of belite relative to alite.

RBPC cements typically exhibit similar setting times, lower water demands, better compatibility with most water reducers (due mainly to lower C_3A contents), lower heat evolution and early strength gain but higher later age strength, and lower drying shrinkage compared with OPC. Better resistance to sulfates and chlorides have also been shown for RBPC, mainly due to the smaller proportion of portlandite in the hydration products. RBPCs typically attain similar 28-day strengths to OPCs, and gain additional strength more rapidly than OPCs at later ages.[9]

The performance of cements is generally compared in standard tests at a fixed temperature (20°C in Chinese and European standards). But in real applications the concrete temperature can vary over a wide range. The temperature of concrete usually increases with time for at least the first few days after placing due to the heat released by cement hydration, the precise thermal behaviour being dependent on the environmental conditions and the dimensions of the concrete pour. This can have a significant effect on the rate of strength gain in practice. A major reason for using RBPC is its low heat of hydration, which results mainly from the fact that the heat of hydration of belite (on a mass basis) is only about half that of alite.[10] This means that maximum concrete temperatures reached with RBPC can be much lower than with OPC for equivalent concrete mix designs; and this lower maximum temperature is very desirable to avoid thermal cracking especially in large concrete pours (e.g. in mass concrete applications, such as dams). Nevertheless, the self-heating effect is by no means negligible even for RBPC concretes, and it can contribute significantly to accelerating the hydration of the cement above the rate observed in standard test at a fixed temperature. So it is interesting to note that, although RBPC and OPC both show higher rates of strength gain with increasing curing temperature, the effect is significantly stronger with RBPC. In addition, the 1-day strength of RBPC is equivalent to that of OPC when cured at 60°C or above.

The accelerating effect of increased temperature on concrete strength has its limits, however. For OPC-based concretes, curing at temperatures above 60°C tends to result in significant decreases in long-term strengths. It is believed that excessively fast hydration of alite at high curing temperature results in encapsulation of the cement particles in a dense hydrate shell which hinders their later hydration.[11] But the effect appears to be different with RBPC. For example, increasing the curing temperature results in a continuous increase in the 28-day strength for RBPC, while OPC typically gives the opposite result. This gives RBPC a significant performance advantage over OPC in applications such as mass concrete and very high strength concrete, as well as in many more common concrete applications in hot climates.[12]

The first successful use of RBPC in China was for the third phase of Three Gorges Hydropower Project (TGP), which was a mass concrete application in which RBPC concrete exhibited better cracking resistance than moderate heat Portland cement (MHC) concrete due to a lower temperature rise and lower shrinkage. The maximum temperature rise of RBPC concrete determined by on-site monitoring was more than 5°C lower than that of MHC concrete, which is a very significant improvement in terms of a reduced risk of thermal cracking. The use of RBPC also allowed significant energy and cost savings because, in the case of the TGP project, the massive concrete made with conventional MHC mixes required cooling to a temperature of 7°C for fresh concrete, (an expensive proposition,) which was not necessary for equivalent RBPC concretes. RBPC sales volumes now exceed those of MHC in China, and it has become the main cement used for mass concrete in China's hydraulic concrete structures. The important precondition is to blend same amount of SCMs with the cement when making the concrete. Otherwise the user will be very reluctant to accept RBPC due to the economic consideration. This

has been proven by lab results as well as field application such as the first successful application of RBPC in the third phase of the Three Gorges dam, where both MHC and RBPC-based concrete mixes were compared using the same amounts of fly ash (up to 40% additions).[13]

2.1.2 ***Belite-Ye'elimite-Ferrite (BYF) binder technology***

BYF technology is based on clinkers containing three essential phases:

Belite (di-calcium silicate, C_2S) - this is also an important phase in OPC

Ye'elimite (calcium sulfoaluminate, CSA, C_4A_3S) – this is the principal phase in CSA clinkers

Ferrite (calcium alumino-ferrite, brownmillerite, C_4AF) – this is also an important phase in OPC

The BYF approach can in many ways be considered intermediate between conventional OPC technology and the reasonably well-established technology for “conventional” CSA cements. As for CSA, BYF cements can be manufactured in standard Portland cement plants, which is a great advantage in terms of capital investment costs. The main difference between the BYF approach and the existing commercial technology for CSA cements is that CSA cements are currently aimed at the specialty cement markets, which demands special properties such as rapid strength development and shrinkage compensation, both of which derive mainly from the ye'elimite phase. Thus, current commercial CSA clinkers have high ye'elimite contents, leading to very high raw materials costs, which makes them very significantly more expensive than OPC and thus restricts them to specialty applications. The BYF approach was developed with the intention of reducing the manufacturing cost of CSA-based clinkers by allowing the use of less of the most expensive aluminium-rich raw materials while making products better suited than existing CSA cements for the production of ordinary concretes with a significantly lower carbon footprint than concretes of roughly equivalent performance made from conventional OPC-based cements.[14][15]

BYF clinkers usually contain their three main phases in the order of content $B > Y > F$ but can also contain other similar phases. For example, the phase “ternesite” (C_5S_2S , sulfate spurrite) can substitute for some of the belite,[16] and the ferrite phase(s) (there may be more than one) can have a wide range of compositions. Interestingly, the ferrite phase in BYF cements appears to be quite reactive compared to the ferrite phase in OPC, despite its high average iron content. In addition, the ye'elimite phase can include significant amounts of iron; and minor components such as boron can also be incorporated in order to increase belite reactivity and/or decrease ye'elimite reactivity. But, for commercial viability relative to OPC, BYF clinkers are most likely to contain more than 50% calcium silicates (belite plus ternesite) because this results in lower raw materials costs. Thus, the main technical differences between typical CSA and BYF clinkers is that the silicate phase(s) and also the ferrite phase(s) are far more abundant and more reactive in BYF clinkers.

The main manufacturing difference between BYF and OPC lies in the proportions of the various raw materials used to make the “kiln feed” - the finely-ground homogenized mixture of raw materials that is fed into the kiln system where clinker is formed. For both of them the principal raw material is limestone (comprising mainly calcium carbonate, $CaCO_3$) which provides most of the calcium. However, BYF clinkers require 20-30% less limestone than OPC, which is the main reason for their lower CO_2 emissions. Well over half of the CO_2 emitted by OPC kilns is RM- CO_2 from the calcination of limestone in the kiln feed, which reduces directly in proportion to the amount of limestone used, while much of the remainder is FD- CO_2 emitted by combustion of

fuels required to provide the heat needed to calcine that limestone, although there is also a modest additional fuel requirement to cover other heat losses from the kiln system.[15] Thus, for example, a 20% reduction in limestone use per unit of clinker manufactured usually translates into slightly less than a 20% CO₂ emissions reduction per mass of clinker.

On the other hand, BYF clinker manufacture requires more aluminium than OPC manufacture, so more aluminium-rich raw materials (bauxites, clays, coal combustion ashes, municipal waste incinerator ashes, etc.) are needed to make BYF clinkers, and this may often result in the need to bring in supplementary raw materials to the cement plant. Most existing cement plants are situated very close to a quarry which serves as the main source of suitable raw materials for making OPC, which itself requires far less aluminium in the raw materials than BYF. The cost of bringing in extra aluminium-rich raw materials is usually the main reason why BYF clinkers are more expensive to manufacture than OPC. In other respects, however, they are easier to manufacture. Since less energy is consumed per unit of clinker when making BYF, the production rate on a given kiln can be increased substantially. A 15% rate increase was demonstrated in full-scale tests under the EU's "Aether" Life+ project [17]. Moreover, thanks to the lower maximum kiln temperature (typically 1250-1350°C for BYF, compared to 1400-1500°C for OPC) the levels of NO_x in the kiln exit gases are much lower when making BYF, and the BYF clinkers also tend to be easier to grind than OPC, thus saving grinding energy when making the finished cement.

One further important difference is the importance of sulfur in the BYF system. BYF clinkers typically contain at least 3% sulfur (expressed as SO₃) most of it in the ye'elite phase. This is far more than typical OPC clinkers. The high sulfur content in the clinker will preferably come from very inexpensive sources, i.e. essentially sulfur-rich waste fuels such as high-sulfur petroleum cokes, or even elemental sulfur.[18] Calcium sulfate- and lime-rich ashes from fluidized-bed coal combustion systems, etc., also make excellent raw materials for BYF clinker manufacture. Since modern cement kiln systems are very efficient at SO₂-scrubbing, almost all of the sulfur remains in the clinker and very little is emitted to the atmosphere.

BYF cements are made from BYF clinkers in much the same way as Portland cements are made from PCC. The clinker is finely ground together with other ingredients, the principal additives being calcium sulfates such as gypsum and anhydrite. OPC-based cements are generally limited (by norms) to total sulfate contents of less than 4% (expressed as SO₃ per mass of cement,) in order to ensure durability; but BYF cements can tolerate much higher levels of SO₃ without any durability risks, so calcium sulfate addition levels in BYF cements can typically be about twice what they are in OPC-based cements (e.g. 10% vs. 5% in typical cases). This also helps reduce the CO₂ footprint of BYF cements. Other "supplementary cementitious materials" (SCMs) of the same types as permitted in OPC-based concretes (i.e. ground granulated slags, fly ashes, pozzolans, limestone powders, etc.) can also be used in conjunction with BYF clinkers in concrete, while maintaining acceptable performance. Thus, BYF clinkers could in principle replace OPC in many applications. BYF cements can gain strength at similar rates to OPC over a wide range of temperatures, and give acceptable durability in many standard tests, as shown in the performance and durability data from EU's "Aether" Life+ project.[19] They are suited for both precast products manufacture and ready-mixed concrete applications, as well as for site-mixed concretes; and BYF concretes protect mild steel against corrosion similarly to OPC-based concretes containing moderate-high SCM (clinker replacement) levels. However, as with any alternative binder, there are some subtle differences in behaviour that need to be considered when

training concrete makers how best to use them. For example, BYF cements tend to set rather rapidly compared to OPCs, although this tendency can be controlled by judicious use of chemical admixtures. Sophisticated levels of control of concrete setting and fresh concrete rheological properties can require specialized admixtures (already commercially available) and suitable training on the part of users. But BYF cements are also relatively insensitive to excess water, which may be an advantage over OPC in some situations.

2.1.3 **Carbonatable calcium silicate cements (CCSC)**

CCSC technology is based on the well-known fact that calcium silicates can harden by carbonation as well as by hydration. The simple lime-based binders used in ancient times, and still used today for certain types of mortar and renders, also harden principally by atmospheric carbonation. However, atmospheric carbonation is very slow, because ambient air only contains about 400ppm CO₂ - an increase of almost 50% on its value in ancient times, but still very dilute compared, for example, to water vapour. A second problem is that carbonation occurs inwards from the outside by a process of diffusion and reaction. This leads to an inhomogeneous hardening profile, often forming a dense skin on the outside. While this is not a problem for thin layers of lime-based mortar, it is can be very problematic for bulk concretes.

Development of CCSC technology has been advanced recently by improvements in the understanding of how to accelerate and control the carbonation hardening process in an industrial context without consuming excessive amounts of energy.[20] It has been shown that binders made from simple calcium silicates, such as the mineral wollastonite (CaSiO₃, CS,) can carbonate very rapidly in relatively pure CO₂ gas at atmospheric pressure, provided that the temperature and the relative humidity in the curing chamber are kept within fairly narrow limits. Thus, CCSC binders comprising wollastonite or other calcium silicates with low hydraulic reactivity can be used to make precast concrete articles in a factory if the simple thermal curing chambers conventionally used for OPC concretes are converted into (non-pressurized) carbon dioxide curing chambers with controlled ventilation, temperature and relative humidity. This is not too difficult but does involve some capital costs. There are non-negligible operating costs as well, because, although heating is not usually required because of the exothermicity of the carbonation reaction, the removal of water vapour (by condensation) from the circulating CO₂-rich atmosphere requires refrigeration.

The major advantages claimed [20] for CCSC technology are:

- (i) the low CO₂ emissions of the cement manufacturing process due to the low calcium content of the clinker, which leads to CO₂ emissions typically about 30% lower than for making OPC;
- (ii) the absorption of a large additional amount of CO₂ during curing (equivalent to essentially all of the RM-CO₂ released by the calcination of the calcium carbonate in the CCSC kiln feed);
- (iii) the ability to reach high (final) strengths in under 24 hours, often equivalent to or even exceeding the strengths reached by OPC concrete mixes of essentially identical mix design with 28 days of ambient temperature curing.
- (iv) The recapture of most of the mix water in the concrete by condensation during the curing process. Thus, the CCSC concrete manufacturing process consumes very little water overall.

However, there are also clearly severe limitations to the application of CCSC. It is suited mainly to the fabrication of precast articles, and they must not be too large in cross section, to permit thorough curing. Because of its low pH (≈ 9) the concrete does not protect mild steel against

443 corrosion in the presence of high humidity and even trace quantities of anions such as chloride or
444 sulfate.

2.1.4 **Magnesium oxides derived from magnesium silicates (MOMS)**

Magnesium oxide (MgO, periclase) is used in a variety of specialty industrial applications, such as basic refractories, etc. It is usually manufactured by calcining natural magnesite rock (MgCO_3) but it should be noted that this process releases a great deal of CO_2 because pure magnesite comprises about 52% RM- CO_2 by mass, which is all released, together with the CO_2 derived from the fuel required to drive this strongly endothermic reaction (see appendix). MgO hydrates in water to give magnesium hydroxide (brucite, $\text{Mg}(\text{OH})_2$), but this reaction gives pastes with very low mechanical strengths because brucite does not bond well, either to itself or to other solids. However, mixtures of MgO with various magnesium salts can give quite good cements because they form products with better binding properties and also because they bind more water during hydration than does pure MgO. For example, magnesium oxy-chloride or oxy-sulfate (“Sorel”) cements, made by mixing powdered MgO with aqueous magnesium chloride or sulfate solutions, have been used for over a century to make products such as light-weight building panels with better strengths and fire resistance than equivalent gypsum boards. However, like gypsum-based products, Sorel cement products lose strength rapidly at high RH or in water, so such cements are unsuited for humid environments.[21]

MgO plus various phosphate salt solutions can give very strong hydrated pastes with good water resistance; but phosphate is a scarce natural resource primarily needed for agricultural applications, so such systems are very expensive and thus unsuited to large-volume construction applications.

Recently, a new type of MgO-based hydraulic cement, based on mixtures of MgO with hydrated magnesium (hydroxy-) carbonates, was developed by Vlasopoulos and Cheeseman.[22] This reportedly has the advantages of good water resistance and also a relatively high level of sequestration of CO_2 in the hydration products, in theory capable of counterbalancing all of the CO_2 released in the manufacturing process. We refer to this type of hydraulic binder by the term “magnesium hydroxy-carbonate cements.” However, the benefit of the sequestered CO_2 was not sufficient to make such cements “low- CO_2 ” unless the MgO itself could be manufactured from natural magnesium sources which contain no RM- CO_2 . [5] A company, “Novacem,” was set up in the UK in 2008 to develop an industrial process for manufacturing such cements from basic magnesium silicate rocks, (e.g. serpentines or olivines, global reserves of which are enormous, although they are not as widely-distributed as limestones.) Unfortunately, the Novacem venture failed in 2012, due to lack of sufficient funding, without having been able to demonstrate an industrially-viable manufacturing process for MOMS binders. The IP from Novacem was purchased by an Australian company, Calix, so Novacem’s data are not currently open to public scrutiny.

Regardless of the technical feasibility of Novacem’s novel magnesium hydroxy-carbonate cement technology, it is also known that MgO can be hardened by direct carbonation at modest CO_2 pressures.[4] Such processes also offer the possibility of capturing a large amount of CO_2 into the hardened products, similar to the CCSC approach, e.g. for factory-produced articles. We will therefore also include carbonation-hardened binders under the broad “MOMS” heading. The key unresolved issue is the problem of how to manufacture MgO from basic magnesium silicate rocks in an energy-efficient manner on an industrial scale. This problem might be solved if sufficient funds were invested in the needed research.[23] We will therefore continue to consider the MOMS approach to be potentially interesting, as it in theory still has the possibility of making concrete binders with negative net CO_2 emissions (i.e. net CO_2 capture).

2.2 Robustness of the alternative clinker-based binder technologies

The table below compares the robustness of the four technologies, listed using the letter code established at the beginning of the paper (A = RBPC; B = BYF; C = CCSC; D = MOMS)

Is the technology suitable for use	Unknown	Proved Possible	Needs further development	Not possible
1) in poor and remote regions:		A	B,C,D	
2) by illiterate worker:			A,B,C,D	
3) with poor quality aggregates,	D		A,B,C	
4) with poor control of water content	D	A,B		C
5) without admixtures	D	A,B		C
6) in hot climates	D	A,B,C		
7) in concretes requiring stable workability at high temperatures	D	A,B,C		
8) in applications requiring high strengths at early ages (e.g. precast)	D	B,C	A	
9) in concretes containing common contaminants (clays, chlorides, etc.)	D	A,B	C	

3 Durability

3.1 RBPC:

RBPC is already in use in China, and meets Chinese standards for Portland Cements. In many respects RPBC concrete is expected to be more durable than average OPC concretes. For example, the resistance of unreinforced RBPC concretes to various aggressive aqueous salt solutions such as a 3% Na₂SO₄ solution, a 5% MgCl₂ solution, and artificial brine with 3 times the ionic concentration of natural sea water, has been shown to be better than that of equivalent OPC concretes.[24] RPBC concretes also show lower drying shrinkage. The ability of RBPC to protect reinforcing steel is similar to that of OPC, as evidenced by the facts that (i) the alkalinity of RPBC pore solution is the same as OPC after one hour of hydration [25] and (ii) both the RBPC and OPC show similar carbonation rates in concrete.[24]

3.2 BYF:

BYF binders are not yet in commercial production, and specific norms covering them do not yet exist apart from the small range of BYF compositions which fall under existing Chinese norms for CSA-based cements. Relatively few data have yet been published for the novel types of BYF cements currently being developed by certain European cement companies, except for performance and durability data obtained under the EU's "Life+" program's "Aether" project. These data, for tests run over up to two years on concretes and mortars made using Lafarge's "Aether™" cement technology, are published on the project website.[19] They show that the Aether™ cement tested under the project gave a very similar strength development rate to OPC in concrete. The Aether™ concretes showed better sulfate resistance than OPC, and, on average, better dimensional stability (they had only about half of the drying shrinkage of OPC, while their expansion under wet conditions was measurable but not excessive, and there was no sign of "delayed ettringite formation.") The Aether™ concretes also did not give any expansion due to alkali-aggregate reactions when tested under conditions in which OPC concretes often give deleterious expansions. Tests on other important aspects of concrete durability, such as the ability of Aether™

concretes to protect reinforcing steel against corrosion, are still under way; but preliminary results suggest that their carbonation resistance is similar to that of OPCs blended with sufficient fractions of supplementary cementitious materials (SCMs) so as to achieve similar carbon footprints. Frost resistance tests data are also not yet available.

3.3 CCSC:

There is not yet much information available on the durability of Solidia™ CCSC concretes, although chemical common sense dictates that they should not be susceptible to alkali-aggregate reactions or sulfate attack. An initial study of the freeze-thaw and salt-scaling resistance of air-entrained Solidia™ concretes has shown results that are comparable with or better than those of air-entrained Portland cement-based concretes with a moderate level (20%) of fly-ash replacement.[26] As pointed out earlier, however, such concretes are not expected to be capable of protecting conventional steel reinforcement against corrosion, and so appear best suited to non-reinforced applications, or applications where reinforcement other than mild steel is appropriate, such as in glass-fiber-reinforced panels, etc.

3.4 MOMS:

MOMS binders are still in the early research stage, so very little is yet known about their durability.

4 Stage of development and research needs

The table below compares the R&D needs of four technologies, listed using the letter code established at the beginning of the paper (A = RBPC; B = BYF; C = CCSC; D = MOMS)

Innovation Phase	1) Conceptual phase (research only)	D
	2) Development phase: Laboratory evidence	
	a) Unanimous	A
	b) Some debate	
	c) Important debate on fundamental issues	B,C
Demonstration	3) Pilot plant	B,C
Public Policy	4) Standardization	
	a) 1 country	
	b) Some countries	A
	c) International	
Market Penetration	5) Commercial	
	a) one company, one site	
	b) one company, many countries	
	c) Few companies, several countries	A*
	d) widely known	

*Note: Production of RBPC in China has been increasing in recent years due to the proven technological advantages and economic benefits of using the RBPC new materials solution for massive concrete in dams. The annual production of RBPC in 2014 in China was about 1 million tons. Japan is also using HBC for mass concrete and very high strength concrete.

5 Scale-up Potential

5.1 Raw materials

For **RBPC** and **CCSC**, the main raw material is limestone, which is essentially the same as for OPC, with the additional advantage that more limestones of lower purity (high silica content) can be used compared

to **OPC**. Thus, raw materials availability or cost issues are not likely to significantly limit the global scale-up potential of these two technologies.

For **BYF** cements, the main raw material is also limestone. However, important secondary raw materials must include relatively concentrated sources of aluminium and sulfur. Both of these elements are also needed for OPC production, but in significantly lower proportions, so their availability and cost may represent a practical limitation in some locations. In the case of aluminium, the nature of the raw material requirements depends strongly on the target BYF clinker composition. It is advantageous to target moderate clinker ye'elimite and ferrite phase contents (e.g. not more than about 20% and 15%, respectively) so as to permit the use of relatively cheap and abundant aluminium sources such as clays and coal ashes, which also contain a lot of silicon and some iron. If high ye'elimite contents are sought, as in conventional CSA cements, concentrated aluminium sources such as bauxites are needed, and these minerals are both relatively scarce and also in strong demand for the manufacture of aluminium metal plus various specialty products. This is the main reason why conventional CSA cements are only used in specialty applications. As for sulfur, BYF cements need considerably more sulfur than OPCs, both in the clinker and also (added separately as calcium sulfates) in the cement. This also may limit scale up in certain locations. On the other hand, the possibility exists of using large amounts of inexpensive sulfur-rich kiln fuels, such as low-grade petroleum cokes, and even elemental sulfur from oil and tar refining, to provide much of this sulfur.[18] The commercial potential of BYF technology will clearly be strongly dependent on raw materials costs, but considerably more R&D is still needed to optimise the composition range for cost-effectiveness.

As for **MOMS**, global reserves of basic magnesium silicates are more than sufficient for potential global cement demand; but they are much less well-distributed than limestones.[27] This is likely to limit MOMS production to specific geographic areas close to large deposits of suitable basic magnesium silicates. Moreover, magnesium-rich olivines have a significant advantage over serpentines as the main raw material, because they are (a) higher in MgO content and (b) lower in bound water content. Because of the relatively high bound water in serpentine, the enthalpy of extraction of MgO from serpentinite rocks will be significantly higher than the value of 0.86 GJ/t estimated in the appendix for pure magnesium olivine, which could add significantly to the carbon footprint of the manufacturing process.

6 Comparison with OPC

6.1 Binder manufacturing process

6.1.1 It has been clearly demonstrated that **RBPC** binders can be produced in conventional OPC manufacturing plants with no major changes in their mode of operation, although attention should be paid to the need to modify the raw mix design: the inclusion of certain minor elements requires a more homogenous kiln feed. Since kiln fuel requirements are lower, clinker production rates can potentially be increased on existing kilns, but attention should be paid to the clinker cooler's capacity to ensure sufficiently rapid cooling. Also since the clinker is harder to grind than OPC, the finish grinding capacity of the cement plant may not be sufficient to deal with an increase in kiln output and thus grinding may become a production bottleneck in some plants unless additional finish grinding capacity is installed. However, there are some additional related issues for any existing OPC plant that decides to start producing an additional clinker. Firstly, there are inefficiencies that result from changing the kiln feed composition (and possibly also the fuel mix) from one target clinker composition to another: changeover periods must be carefully planned to minimize their duration and frequency, as a significant loss of energy-efficiency and carbon-efficiency is to be expected during such changeovers. Secondly, there is the need for additional clinker and cement storage capacity for the new clinker and cement made from it, which is a capital expense. Thirdly, there may be a need to modify the grinding circuit settings. All of these factors can have a significant influence on production costs.

6.1.2 For **BYF**, comments very like those given above for RBPC apply; and production of BYF cements in conventional OPC plants has also been publicly demonstrated.[17] The main difference relative to RBPC is the need for significantly more aluminium, iron and sulfur in the clinker. The required additional raw materials sources will significantly change the raw mix composition, and this may have implications for the raw mix preparation and homogenization circuits, especially if the plant plans to manufacture both OPC and BYF clinkers on some kind of alternating schedule. But there is no inherent process problem with making BYF per se, other than the likely higher cost of the new raw materials. Regarding the need for more sulfur in the clinker, this may also be provided in the form of a high-sulfur kiln fuel, since the oxidized sulfur is effectively scrubbed from the combustion gases and ends up as sulfates in the clinker. Efficient and environmentally safe burning of high-sulfur fuels, such as petroleum cokes, or even pure sulfur from oil and tar refining processes, appears to be a very sustainable way of using these industrial by-products.

6.1.3 For **CCSC**, comments very similar to those given for RBPC and BYF also apply. Production of CCSC cements in conventional OPC plants has been demonstrated, and the technology is currently in the early stages of commercialization.[28] The raw materials required for CCSC cements are very close to those required for OPC, and in most cases no additional raw materials are likely to be needed. Furthermore, no calcium sulfate additions are required in the cement, unlike OPC, RBPC or BYF cements. On the other hand, the kiln fuel requirements may be somewhat more restrictive than for OPC, RBPC or BYF. In particular, fuel sulfur contents may have to be kept relatively low, and the burning of waste fuels (as is now common in OPC production) may not be appropriate.

6.1.4 For **MOMS** binders it is almost certain that the whole cement manufacturing process will be very different from that used for OPC, and thus that completely new plant will be required. However, as a practical industrial process for the energy- and carbon-efficient manufacture of MOMS binders has apparently not yet been invented, or at least not yet publicly disclosed, we cannot speculate on the likely costs of such plant, except perhaps to guess that they are unlikely to be less expensive than new plants for the manufacture of OPC. In addition, any such plant is likely to be situated close to a suitable raw materials deposit, i.e. a deposit of basic magnesium silicates, preferably based on magnesium-rich olivines. This may well correspond with an existing mining site, since such raw materials are often the host rocks for valuable minerals such as nickel and chromium ores, as well as for many old (discontinued) mining sites for chrysotile asbestos. Thus, any MOMS manufacturing process should ideally be capable of using as raw materials the extensive existing mine wastes from such deposits and, we hope, rendering them both useful and non-toxic in the form of MOMS binders. Since the manufacturing sites for MOMS will almost certainly be at a considerable distance from existing cement plants, the logistics of transporting the products to cement market may also be an important issue in the overall evaluation of this approach.

6.2 Concrete processing and applications

6.2.1 The use of **RBPC** in concrete presents no significant processing issues, as it falls within the accepted definition of Portland cement. However, the hydration rate at early ages is slower than that of conventional standard OPCs, which will influence the type of application targeted. RBPC is not well-suited to precast concrete manufacturing at normal curing temperature, but is well-suited to mass concrete and very high strength concrete applications. RBPC also has potential for making pavement concrete due to its higher flexural strength and lower dry shrinkage vs. OPC. Care should be taken not to remove the formwork too early for normal strength RBPC concrete due to its lower early strengths (e.g. up to 3 days). But this is not a significant concern when making high strength and very high strength concretes with RBPC. The rate of hardening can be greatly accelerated by moist curing at elevated temperatures, and as a result RBPC is well suited for applications in hot climates provided that any exposed concrete surfaces can be adequately protected against water loss during the critical curing period, possibly amounting to several days. The use of RBPC in concrete involves no new H&S issues relative to OPC.

6.2.2 The use of **BYF** binders in concrete has so far only been demonstrated in a limited number of applications, but in principle they can be made suitable for a very wide range of applications. They usually have setting and hardening times considerably shorter than for OPC, which can be an advantage in certain applications such as precast concretes; but the setting and hardening times can be controlled (retarded) by use of well-known chemical admixtures and thus can be made much longer if necessary, so they can also be used in Ready-Mix concrete applications. Because of their need for chemical admixtures in many applications, their sensitivity to temperature (e.g. in terms of workability and setting time) is somewhat higher than that of OPC, so their efficient use in many conventional applications will require additional training of concrete workers. However, the equipment needed will be the same as for OPC. As for contaminants, BYF binders are generally less sensitive to organic contaminants than OPC, but, on the other hand, they can be sensitive to contamination from OPC and OPC concrete residues, so some precautions may be required to avoid excessive intermixing of BYF materials with OPC materials in concrete. As for H&S issues, there are no generic issues that make them significantly different to OPC; but there may be specific BYF binders which contain specific minor components or elements not usually found in significant quantities in OPC. For example, in some proposed BYF clinker formulations the content of boron can reach several tenths of a percent. This is not of itself likely to make the resulting cement hazardous; the boron is mainly present as a form of calcium alumino-borate which is relatively unreactive in the hardened concrete. However, it is still a potential H&S issue which will have to be addressed if such boron-rich BYF binders are ever proposed for commercial applications. On the other hand, BYF cements generally give a significantly lower initial pH than OPC in fresh concrete, which makes BYF concretes less hazardous in terms of the risk of harmful skin contact.

6.2.3 The use of **CCSC** binders in concrete is very different to either RBPC or BYF binders because the latter two are both hydraulic binders (i.e. they harden by reaction with water, just as does conventional OPC,) whereas CCSC binders do not. CCSC binders harden by reaction with carbon dioxide gas (CO₂) during the curing process. This means that the manufacturing process used for CCSC concretes is very different from the conventional processes (for OPC concretes) that can be used for RBPC and BYF. CCSC concretes must be mixed and placed with some water (but preferably not too much) and then the moist concrete mix must be cured under an atmosphere rich in CO₂ until the cement has carbonated sufficiently to give the product its required final strength. Because the CO₂ reacts with the cement, a very significant amount of CO₂ is captured during this concrete curing process. In theory, most of the RM-CO₂ released from the limestone used to make the CCSC clinker can be recaptured this way. However, in order for the curing of typical concrete elements to be completed in an industrially-acceptable time frame, (ideally less than 24 hours for factory-cured articles,) it is necessary to use a curing atmosphere containing CO₂ at close to one atmosphere pressure, which implies the use of fairly pure CO₂ rather than the relatively dilute sources typical of industrial flue gases. In addition, most of the water contained in the fresh concrete mix, which serves both to facilitate the initial compaction of the fresh concrete during forming and then to catalyze the carbonation curing (hardening) reaction, must be allowed to evaporate during curing to avoid blocking the pores in the concrete through which the CO₂ gas can enter. So the relative humidity in the curing chamber must be maintained below 100% by condensing most of the water vapor that evaporates from the concrete during curing. Thus, the curing cycle requires careful control of gas composition, gas circulation, temperature and relative humidity. For this reason, specially adapted concrete curing chambers are required. This involves additional capital costs to the concrete manufacturer. Moreover, the concrete manufacturer must purchase relatively pure CO₂ as a consumable raw material, in addition to the CCSC cement plus conventional concrete aggregates. On the other hand, almost all of the mix water is recaptured (as pure water) by condensation and can be recycled, so the concrete-making process can be almost water-neutral.

It is clear from the above discussion of the manufacture of CCSC concretes that the process is only really suitable for articles that can be cured in suitable chambers, which in most cases is likely to limit applications to factory-made concrete articles. Since the curing can be done at atmospheric pressure if relatively pure CO₂ is used, the curing chamber does not need to be pressure-tight, so fairly simple materials can be used, such as moderately gas-tight fabrics. Thus, in principle, mobile curing equipment is feasible, so some on-site curing applications may be possible. However, there is also a limitation to the dimensions of the concrete articles that can be cured in an acceptable time, since the CO₂ gas must be able to diffuse in and the water to diffuse out. Thus, mass concrete applications cannot possibly be considered. But large precast articles can be cured provided that suitable access holes are provided to ensure uniform gas distribution inside the concrete.

6.2.4 The use of **MOMS** binders for concrete has not yet been seriously explored, although prototype “Novacem” concretes were demonstrated on a small scale.[29] It is too early to speculate on their practical limitations for concrete making, but they are in principle neither toxic nor corrosive, so it seems unlikely that they will give rise any significant H&S issues in use.

7 Costs of production

For RBPC, BYF and CCSC, the investment costs for additional clinker and cement production capacity are generally likely to be similar to that of OPC; but all three can be produced in conventional cement plants. As already noted, the raw materials costs for BYF are likely to be significantly higher than for OPC, whereas the raw materials costs for RBPC and CCSC are likely to be similar; and the total manufacturing costs for all such products will depend strongly on local fuel and raw materials costs. For CCSC one must also add the additional investment cost of the special curing chambers required to carbonate the concrete products, and the cost of purchasing and transporting the CO₂ required for curing, which is not insignificant.

For MOMS, it is too early to make an estimate of either investment or production costs, as there is not yet any well-defined manufacturing process to evaluate.

8 Simplified environmental assessments

There are apparently no independent published Life-Cycle Analyses of any of these alternative clinker technologies, so we have used a simple theoretical (thermodynamic) approach to assessing their potential for reductions in CO₂ emissions and primary energy consumption. This approach allows them to be compared with existing OPC clinker technology in a practically useful way before sufficient production data become available. Details of the calculations are provided in an appendix.

8.1 RBPC

Our calculations compare a typical OPC clinker containing 63% alite, 15% belite, 8% C₃A and 9% C₄AF with a RBPC clinker containing 62% belite, 16% alite, 8% C₃A and 9% C₄AF, (the remaining 5% in both cases being minor phases such as alkali sulfates, MgO, etc.) For simplicity, it is assumed that the raw materials in both cases are pure calcium carbonate, pure silica, pure alumina and pure iron oxide. (While not realistic, this assumption will not greatly affect the relative results of the calculation.) The calculations show that the manufacture of the OPC clinker emits about 541 kg of RM-CO₂ per tonne of clinker, whereas the manufacture of the high-belite clinker emits only 509 kg, a reduction of about 6% in RM-CO₂ emissions.

The actual kiln fuel consumption cannot be predicted very accurately on theoretical grounds, but the enthalpy of the clinker-forming reactions can be calculated accurately and it is reasonable to assume that the two should be roughly proportional. For the typical OPC shown above the enthalpy requirement is 1.63 GJ per tonne of clinker (GJ/t), and for the RBPC it is 1.39 GJ/t, a reduction of 15%. Since efficient modern cement kilns making OPC usually have kiln fuel energy requirements close to 3 GJ/t, i.e. a little under twice the theoretical enthalpy requirement calculated with the assumptions used here, one can estimate that the actual energy savings in switching from OPC to RBPC could be as much as 0.45 GJ/t; and, assuming that the kiln fuel is usually either coal or coke, (which emit about 90kg of CO₂ per GJ of fuel energy [15]) the resulting reduction in FD-CO₂ emissions is likely to be of the order 40kg per tonne of clinker, giving a total reduction of about 72 kg relative to a (roughly-estimated) 830kg average total of CO₂ emitted per tonne of OPC clinker, or about 9%. Thus, typical observations of ≈10% CO₂ emissions reductions on switching from OPC to RBPC are credible.

8.2 BYF

Using the same approach as above, and assuming a BYF clinker composition of about 46% belite, 35% ye'elimite and 17% ferrite we find a RM-CO₂ emission of about 409 kg per tonne of clinker, a reduction of about 24% relative to the standard OPC, and an enthalpy requirement of only 1.01 GJ/t, which is 38% less than for the OPC. Combining these in the same way as done above, this works out to a total CO₂

savings of about $(132 + 102) = 234$ kg/t, about a 28% CO₂ emissions reduction. The actual observed reductions in these trials were in the range of 25-30%, which is quite consistent with these estimations.[17] In addition, it should be noted that, in the Aether project production trials, most of the sulfur was provided in the form of calcium sulfate added with the raw materials. If a sulfur-rich kiln fuel has been used instead, additional kiln energy savings could no doubt have been achieved.

Note also that the BYF clinker composition used in these Aether industrial trials had a rather high ye'elimite content relative to what is likely to be needed in a fully-optimized BYF clinker. Reducing the ye'elimite content will reduce the CO₂ savings slightly, but will reduce the raw materials costs much more, because of a greatly reduced need for expensive raw materials such as bauxite, and so increase the chances that the technology will actually be applicable to a mass market, provided that the performance of the resulting cements is adequate. So we can compare the high-ye'elimite BYF clinker above with a low-ye'elimite BYF clinker composition containing about 60% belite, 20% ye'elimite and 17% ferrite. This gives a RM-CO₂ emission of about 440 kg per tonne of clinker, a reduction of about 19% relative to the standard OPC, and an enthalpy requirement of only 1.07 GJ/t, which is 35% less than for the OPC. Combining these in the same way as above, this works out to a total CO₂ savings of about $(101 + 105) = 215$ kg/t, or close to a 26% CO₂ emissions reduction compared to OPC, which is still a very good result.

We can also compare this low-ye'elimite, high belite BYF clinker with the RBPC clinker composition calculated in section 8.1, which contained about the same amount of belite. The 60%-belite BYF clinker in theory reduces CO₂ emissions by about 26% relative to OPC, whereas the RBPC with 62% belite in theory only reduces CO₂ emissions by about 9%, which shows the advantage of the BYF approach.

8.3 CCSC

A similar thermodynamic approach can in principle be applied to the manufacture of CCSC clinkers, if their compositions can be specified. However, such information is not currently available for any industrial products, so the simplest approach is to assume a clinker consisting primarily of wollastonite made, as in the other cases presented above, from pure raw materials (in this case, only calcium carbonate and silica). In that case, the raw-materials-derived CO₂ emissions will only be about 380 kg per tonne of clinker, and the enthalpy of formation is only about 0.77 GJ/t, about 53% less than for OPC, giving an overall reduction of about $(161 + 143) = 304$ kg CO₂ per tonne of clinker, or about 37% relative to OPC. This is significantly better than for BYF clinkers, but the actual clinker compositions in a commercial product are likely to be somewhat different (and probably higher in CO₂ emissions) than this. And, in any case, since the raw-materials-derived CO₂ is essentially all re-absorbed during carbonation-hardening of the binder, the only figure that really counts in this case is the kiln energy consumption, which is likely to be even less than that of BYF clinkers, and perhaps less than half that of typical OPC clinkers.

8.4 MOMS

There is as yet no known industrial process for making magnesium oxide from natural basic magnesium silicates in an energy-efficient manner, although it may well be possible to invent one given enough support for the necessary research. However, one can still do a basic thermodynamic calculation in roughly the same way as for calcium-based clinkers. If we assume that pure forsterite olivine, (Mg₂SiO₄), the most magnesium-rich mineral commonly found at or near to the Earth's surface, can be decomposed into its two oxide components, MgO and SiO₂, by means of some industrial process not yet specified, then the minimum energy requirement is given by the enthalpy change of that decomposition reaction, which is about 0.86 GJ per tonne of MgO produced, i.e. only half of the theoretical enthalpy requirement for making a typical OPC clinker. Thus, the theoretical potential exists for the manufacture of MgO from magnesium silicates in a relatively energy-efficient manner compared to making Portland clinkers from standard raw materials, and such a process in principle emits no raw-materials-derived CO₂ at all, as the

basic raw materials, magnesium silicates, contain no carbon. Given that MgO can harden either by hydration (e.g. in reaction with hydrated magnesium carbonates) or else simply by carbonation (to give magnesium carbonates,) it is conceivable that hardened MOMS-based binders could contain, in stable solid form, more CO₂ than emitted during the manufacturing process, in which case they would be “CO₂-negative,” i.e. a net sink for CO₂. If proven feasible, this could have very significant global implications in terms of CO₂ capture potential.

9 Barriers, incentives and research needs

9.1 RBPC

RBPC cements are already covered by existing norms in many parts of the world, and can be manufactured in existing cement plants at costs that may well be lower than for conventional OPCs. There are no significant additional health and safety issues relative to conventional OPCs, and the only technical barrier to the more widespread use of RBPC appears to be the lower rate of strength gain at early ages. However, the cement and concrete industries also have logistical cost barriers to the use of multiple cement types, such as, for example, the need to manufacture, deliver and stock more than one cement either at the cement plant or at the concrete making site, etc. For this reason, regardless of the technical advantages of any alternative cement, there is always a logistical cost barrier to the introduction of any new cement type, which tends to restrict its use only to very large jobs where the costs of additional storage, etc., can be justified by the size of the other savings (efficiencies) provided by its use. This is an issue for all alternative cements, but in the case of RBPC it may well be the only real remaining barrier to greater use.

9.2 BYF

BYF cements are not yet in commercial production anywhere, and are not yet covered by standards in most locations. The need to dope the clinker with boron in some cases might raise some additional health and safety concerns relative to OPC, but the raw materials cost issue is in any case a strong driver for not using such dopants. Thus, there is a need for additional research to develop better BYF clinker formulations that do not need such expensive dopants. Although BYF cement technology has been successfully demonstrated on an industrial scale, and does not require any new manufacturing plant, the relative raw materials costs are currently too high to justify the use of BYF cements as an alternative to OPCs under current CO₂ emissions regulations (e.g. in Europe) which put a relatively low price on emitted CO₂. But the relative cost of BYF cements can probably be reduced significantly by further R&D, so one can hope that the cost limitation to its use will slowly disappear. Standardization may take quite a long time, because there is not yet sufficient long-term performance data available; but, given that several different cement manufacturers, representing a significant fraction of the European-based cement industry, are still investing to a modest extent (with some EU support) in BYF technology development, the standardization process is still progressing, albeit slowly. There is also scope for using such binders in certain well-defined applications (especially precast) under specific local technical approvals without the need for full normalization.

9.3 CCSC

As far as we know, CCSC cements are currently only being developed seriously by a single US-based company, Solidia, via a close commercial relationship with a large cement manufacturer, LafargeHolcim. Commercial sales have already taken place on a small scale. Because the products are currently restricted to precast concrete articles, such products can be sold under local technical approvals without the need for standardization at the national level. However, in the long term, standards will also be sought.

There are clearly health and safety risks associated with the use of a concentrated CO₂ atmosphere for curing CCSC concretes - primarily, the risk of asphyxiation if ventilation is inadequate. But these risks are well understood and can be dealt with relatively easily in an industrial context.

9.4 MOMS

At this time research on MOMS approaches appears to be on hold. After the bankruptcy of the Novacem start-up venture in 2012, no industrial company has apparently been willing to finance additional research to try and solve the key scientific and technical problems. But, based on our simple thermodynamic analysis, we believe that this approach still holds long-term promise for creating a very low-CO₂ (and potentially even CO₂-negative) concrete binder technology. So, we encourage government and industry to support the relatively inexpensive basic research needed to get to the point where it can be determined scientifically whether or not industrial development of MOMS could ever be feasible.

10 Conclusions

Our analysis suggests that, with the exception of alkali-activated materials, which are treated in another paper in this issue,[1], there are only four classes of alternative clinker system that deserve serious attention with respect to global reductions in concrete-related CO₂ emissions:

- (A) Reactive Belite-rich Portland cement (RBPC) clinkers
- (B) Belite-Ye'elimite-Ferrite (BYF) clinkers
- (C) Carbonatable Calcium Silicate clinkers (CCSC)
- (D) Magnesium oxides derived from magnesium silicates (MOMS)

A and B are “hydraulic” clinkers, (i.e. clinkers which harden by reaction with water,) C is a “carbonatable” clinker, (i.e. one which hardens by reaction with CO₂ gas) and D falls into both categories. In summary:

- (A) RBPC clinkers are the most well-established. They can be made in existing PCC plants and cements made from them are covered to a large extent by existing norms for PCC-based cements. Thus, the only current limitation to their greater use is one of performance, as they harden relatively slowly compared to many Ordinary Portland cements (OPC). However, the potential CO₂ savings obtainable with RBPC technology are typically not more than about 10% relative to OPC.
- (B) BYF clinker is a fairly new approach which makes use of technology previously developed for specialty cements based on calcium sulfoaluminate (CSA). BYF clinker and cement technology is still in the R&D stage and is not yet commercialized or normalized. It offers potential CO₂ savings of 20-30%.
- (C) CCSC is another new approach which is at about the same level of technological advancement as the BYF approach, but is reportedly already in the early stages of commercialization. However, it is very different because it makes use of non-hydraulic carbonatable clinkers, which harden only by reaction with CO₂. This requires that the concretes be cured under an atmosphere very rich in CO₂, which in turn restricts its potential applications primarily to factory-made concrete products. It currently offers CO₂ savings of 30-40%, but savings could be as high as 70% if a circular CO₂ economy develops.
- (D) Unlike the first three approaches, which are based primarily on limestones as the main raw materials, the MOMS approach is based on magnesium silicate raw materials, which have the advantage,

relative to limestone, of containing no chemically bound (“fossil”) CO₂. This means that, unlike all the other approaches, MOMS, at least in theory, provides the possibility of making concretes with a significantly negative carbon footprint, especially if carbonation hardening is used. However, reaching this goal will require the development of a very energy-efficient industrial manufacturing process for MOMS, and it is not yet clear whether this might be possible. So, we encourage government and industry to support the relatively inexpensive basic research needed to get to the point where it can be scientifically determined whether or not industrial development of MOMS could ever be feasible.

904

905 **11 Appendix: Calculations of CO₂-efficiency of clinker production**

906 The actual CO₂ emissions of a clinker manufacturing process can be split into three main categories:

- 907 a. “Raw-materials-derived” (RM) CO₂ emissions, which come from “fossil” carbonate compounds
908 in the raw materials, and are thus not directly related to the burning of fuel to drive the process.
909 b. “Fuel-derived” (FD) CO₂ emissions, which come directly from the combustion of carbon-based
910 fuels as usually needed to drive the process.
911 c. “Tertiary” CO₂ emissions, which come, indirectly, from other inputs to the process, such as
912 power needed to drive fans, motors, etc. These emissions are more variable than the other two
913 because they depend on the carbon efficiency of the other inputs, which can vary greatly from
914 location to location. For example, electric power may be derived from coal (very high in CO₂
915 emissions,) or from hydro-power (very low in CO₂ emissions,) etc.

916 Because the tertiary emissions are so variable, we will exclude them from the calculations at this first
917 level of approximation. It is likely, in any case, that they will not vary all that much, on a relative basis,
918 per tonne of clinker produced, regardless of the type of clinker.

919 For the calculation of the first two classes of emission, we make the following simplifying assumptions:

920 All clinkers are assumed to be made from the following well-defined pure-phase raw materials:

921 Calcite (CaCO₃, the main component of limestone) as the only calcium source

922 Amorphous silica (SiO₂) as the only silicon source

923 Corundum (Al₂O₃) as the only aluminium source

924 Hematite (Fe₂O₃) as the only iron source

925 As the sulfur source, either anhydrite (CaSO₄) can be used as a component of the kiln feed, or else
926 elemental sulfur (S) can be used as a component of the kiln fuel, (since sulfur capture is very efficient in
927 modern dry-process cement kilns equipped with multi-stage preheater towers.)

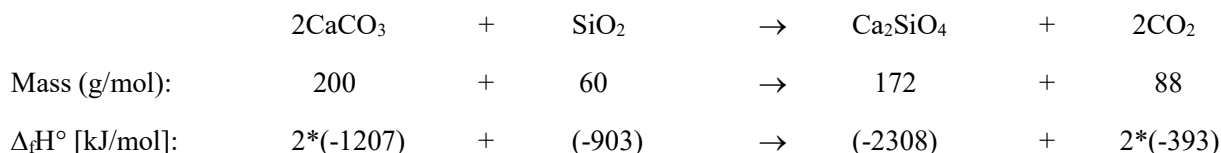
928 Forsterite olivine (Mg₂SiO₄) as the only magnesium source (for MOMS calculations only)

929 The only raw material listed above containing any carbon is calcite (e.g. limestone,) so all RM-CO₂
930 emissions are assumed to emanate from that raw material, and it is very simple to estimate them from a
931 mass balance once the raw materials proportions required to give a specified clinker composition are
932 calculated. But note that for sulfur we have two very different options. If we add it as anhydrite in the
933 kiln feed it adds no energy and emits no CO₂; but if we add it as a component of the fuel (e.g. from
934 petroleum coke) the oxides produced from the combustion of this sulfur will all react with CaCO₃ in the
935 cement kiln to give CaSO₄ (which remains in the clinker) plus one extra mole of emitted CO₂ per mole of
936 sulfur.

937 The calculation of FD-CO₂ emissions is more difficult because it depends on the thermal efficiency of the
938 kiln system and the type of kiln fuel used. So we use, instead, a simple thermodynamic approach, which
939 is to calculate the net enthalpy requirement of the reactions required to produce the desired clinker
940 composition from the above-listed raw materials. For this, we make use of the $\Delta_f H^\circ$ values (standard
941 enthalpies of formation from the elements in their standard states at 25°C) of the raw material and product
942 compounds from three different published sources. These data are summarized in the table below:

Compound	$-\Delta_f H^\circ$ [kJ/mol]	Data source
CaCO ₃ (calcite)	1207	[30]
SiO ₂ (amorphous silica)	903	[30]
Al ₂ O ₃ (corundum)	1662	[30]
Fe ₂ O ₃ (hematite)	821	[30]
CO ₂ (carbon dioxide gas)	393	[31]
CaSO ₄ (anhydrite)	1435	[30]
CaO (quicklime)	635	[31]
MgO (periclase)	602	[31]
MgCO ₃ (magnesite)	1111	[31]
CaSiO ₃ (wollastonite)	1630	[31]
Ca ₂ SiO ₄ (belite, dicalcium silicate, C ₂ S)	2308	[30]
Ca ₃ SiO ₅ (alite, tricalcium silicate, C ₃ S)	2931	[30]
Mg ₂ SiO ₄ (magnesium olivine, forsterite)	2176	[31]
Ca ₃ Al ₂ O ₆ (tricalcium aluminate, C ₃ A)	3561	[30]
Ca ₄ Al ₂ Fe ₂ O ₁₀ (brownmillerite, C ₄ AF)	5080	[30]
Ca ₄ Al ₆ O ₁₆ S (ye'elimite, CSA, C ₄ A ₃ S)	8406	[32]

The above data were used to calculate the enthalpies of manufacture of the main clinker compounds from the basis set of simple raw materials chosen. For example, to make belite, the reaction is:

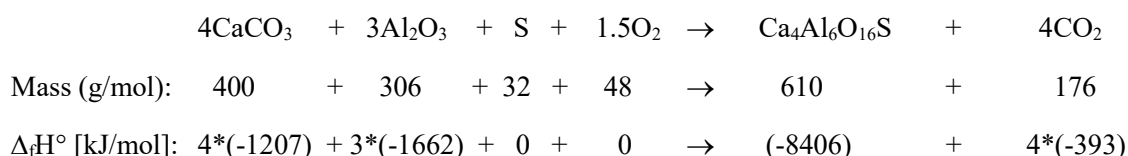


Thus, the net enthalpy requirement is +223 kJ/mol or 1.30 kJ per gram of belite (1.30 GJ/t).

Using the same approach, we calculated the enthalpies of manufacture of the other PC clinker phases:

Alite: 414 kJ/mol or 1.82 GJ/t; C₃A: 543 kJ/mol or 2.01 GJ/t; C₄AF: 659 kJ/mol or 1.36 GJ/t;

Note: in our manufacturing enthalpy calculation for C₄A₃S (ye'elimite) we conservatively assume that all of the sulfur is present in the raw materials as anhydrite (CaSO₄) rather than as elemental sulfur as assumed for the RM-CO₂ calculations. This assumption gives 465kJ/mol or 0.77GJ/t as the manufacturing enthalpy. However, if we run the calculation assuming elemental sulfur as the sole sulfur source, which is practically feasible in some cases, we must also allow for combustion of that sulfur in the kiln and subsequent reaction of the resulting sulfur trioxide with limestone, as shown in the reaction below:



The enthalpy required to make ye'elimite this way is much less: -164kJ/mol (-0.27GJ/t) i.e. heat is released by this reaction, rather than being consumed, because of the large amount of energy released by

burning sulfur in air. However, to be conservative, we have not used this value in the paper, and we have also used the more conservative RM-CO₂ figure (4 mols instead of 3). The manufacturing enthalpy and RM-CO₂ values calculated for clinker phases, as used in this paper, are summarized in the table below:

Clinker phase:	Manufacturing enthalpy, GJ/t	RM-CO ₂ emissions, kg/t
Alite, (C ₃ S)	1.82	579
Belite, (C ₂ S)	1.30	512
Aluminate, (C ₃ A)	2.01	489
Ferrite, (C ₄ AF)	1.36	362
Quicklime, (CaO)	3.20	786
Wollastonite, (CS)	0.77	379
Ye'elimite (C ₄ A ₃ S) [from CaSO ₄]	0.77	216
Ye'elimite (C ₄ A ₃ S) [from S]	-0.27	289
Periclase (MgO) [from MgCO ₃]	2.90	1100
Periclase (MgO) [from Mg ₂ SiO ₄]	0.86	0

Note that, to be more conservative, the values in italics for ye'elimite were not used in this paper.

Using the values from the above table, it is simple to estimate the manufacturing enthalpy and RM-CO₂ emissions for a clinker composed of any combination of the above phases. One simply adds the contributions weighted by the mass fraction in the clinker. Even if the total mass fractions add up to slightly less than 100% it can be reasonably assumed that the remaining unaccounted-for phases make no contribution to the totals.

It is less easy to predict what the FD-CO₂ emissions would be when making any of the above compounds from typical industrial raw materials in an industrial process, because that depends both on the specific raw materials used (and especially their water and CO₂ contents) and also on the energy-efficiency of the process itself. However, we note that the energy required to make a typical PCC in a modern, energy-efficient cement kiln can be as low as 3GJ/t for a process for which the theoretical enthalpy requirement is about 1.75GJ/t. This implies a thermal efficiency of about 58% as the upper limit in modern cement-making technology; and since the fuel is usually very carbon rich (either coal or coke) we can use about 90kg of FD-CO₂ emissions per GJ of fuel burned as a rough estimate of fuel-derived CO₂. [15] One can combine this information with the RM-CO₂ data from the table to roughly estimate the lowest likely total CO₂ emissions for making each clinker phase. For example, making MgO from dry magnesite in an energy-efficient kiln should require roughly (2.90/0.58) $\approx$ 5GJ/t of fuel energy, which is equivalent to roughly 450kg of FD-CO₂ per tonne of MgO. Adding this to the 1100 kg of raw materials CO₂ from the table, we get a rough estimate of 1550 kg of CO₂ per tonne of MgO for the total CO₂ emissions for making MgO from magnesite in an energy-efficient industrial kiln.

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