MPA Cement Fact Sheet 12

Novel cements: low energy, low carbon cements

Background and introduction

Sustainability and the UK cement industry

Traditional Portland cement-based concrete provides the foundation for the built environment. Buildings constructed appropriately and imaginatively from this material can and do exhibit an impressive array of properties [1] especially those that have been designed to optimise the thermal mass of concrete [2]. This type of concrete building is expected to adapt best to the UK's changing climate [3, 4].

The demands of 'sustainable development', however, place a responsibility on the construction sector to continually improve existing processes, products and practices, and to innovate in order to reduce both energy used in service and embodied energy in products together with emission of greenhouse gases during manufacture. MPA Cement and its Member Companies have their part to play in responding to this sustainability agenda and have a vision [5] for delivering a sustainable cement industry into the future, incorporating a 'carbon strategy' [6] for reduction of carbon dioxide (CO_2) emitted from the manufacturing process. The industry's activities are monitored within an Environment Agency 'Sector Plan' and performance against the plan is published annually in an MPA Cement report called '*Performance*' [7].

Part of the industry's contribution to sustainability is the recognition that it must evaluate the viability of potential alternatives to Portland cement CEM I, the fundamental ingredient needed to produce traditional concretes.

Making Portland cement CEM I

To provide a reference point, we first need to know how Portland cements are made. The manufacture of Portland cement CEM I involves precise blending of limestone or chalk with clay or shale (quarried and finely-ground), and heating the resultant mixture in a rotary kiln to 1450ºC. At that temperature, a chemical change takes place and the raw materials turn into a hard, nodular solid known as clinker. After cooling, the clinker is ground in a ball or roller mill to produce cement powder. Approximately five percent gypsum (calcium sulfate) is also inter-ground in order to control the setting time of the product. The overall process is energy-intensive and CO_2 is emitted during the chemical changes in the kiln.

Reducing the energy/carbon footprints of Portland cements

Several measures are taken to reduce specific energy/carbon footprints of Portland-based cements, including optimising the energy efficiency of clinker production, increasing the use of carbon neutral biomass fuels and other non fossil fuels and the production of factory-made composite cements (see MPA Cement Fact Sheets 14a and 14b – Modern cements) at the cement plant, in addition to the production of equivalent combinations by the downstream concrete producer. These composite cements and combinations incorporate secondary cementitious materials such as granulated blastfurnace slag, power station fly ash and limestone. These constituents are inter-ground with clinker or blended with CEM I cement to manufacture cement types CEM II, III, IV and V (or CII III and IV combinations). An alternative option, however, is to explore more 'novel' products and processes that are inherently less energy and CO_2-intensive i.e. the low energy, low carbon route.

What are 'novel', low energy, low carbon cements?

There are several diverse novel or 'new' cements which are generally non-Portland, based on non-traditional processes or raw materials. They tend to embody less energy and emit less CO_2 during manufacture than 'Portland cement CEM I' (formerly called ordinary Portland cement) although there is no precise definition for what constitutes a low energy, low carbon cement. Typically they would have some or all of the following characteristics. They would:

- embody less energy than traditional Portland cements, including those that contain additional inorganic/mineral constituents;
- be manufactured using a novel process that ideally utilises waste-derived fuels and raw materials;
- be expected to reduce both waste and emissions, in particular the greenhouse gas carbon dioxide.

This Fact Sheet examines five of the more interesting novel cement types and reviews their prospects for manufacture and acceptance in the UK. They are either already in production in some part of the world or under development and can fulfil the above characteristics to varying degrees. They are:

- alkali-activated cements including geopolymeric cements (e.g. Zeobond/e-crete, Blue World Crete/Geo-Blue Crete, banah/banahCEM)
- low energy CSA-belite cements (e.g. Aether);
- cements based on magnesium oxide derived from carbonates or from silicates (e.g. Eco-cement, Calix/Novacem);
- 'ecocement' based on municipal solid waste incinerator ash (MSWIA);
- thermoplastic carbon-based cements (e.g. C-Fix cement).

For a fuller discussion of the scientific and societal issues involved in developing new cements, see Gartner [8].

Are any of the non-Portland cements, described herein, realistic alternatives to Portland cements?

The simple answer is no, not yet. Some could well occupy valuable niche positions in specialised applications and, by doing so, would displace Portland cements that might otherwise have been adapted to fulfil such roles. Some may have the potential to make much greater inroads into the wide spectrum of uses for Portland cements. However, it is unlikely that Portland cements can ever be completely replaced, in a cost-effective manner, in mainstream (i.e. load-bearing) construction. No significant inroads are likely to occur in the short/medium-term because of the scale of operations needed, together with the attendant high capital/process costs of manufacturing and the requirement for rigorous technical validation.

Clearly, since a fundamental aspect of sustainability must be durability, any new cement will also have to have performance and durability characteristics at least as good as the current generation of Portland cements and probably even better, since it is likely to be initially more expensive, if it is to have any real impact on global construction industry-related CO_2 emissions.

Simply put, it is the geological availability and global distribution of suitable natural resources, coupled with the extensive validation needed to confirm fitness-for-purpose, that are the critical factors that will determine if any cement is a realistic alternative to Portland cement.

What 'end-use' barriers will a novel cement have to overcome to become a realistic alternative to Portland cements?

The construction sector is often perceived to be conservative in its attitude to new ideas, products and processes. Such an attitude arises from moral and legal obligations on architects, design engineers and regulatory authorities to minimise the risk of structural failure in order to safeguard society. Innovators, however, will experience this conservatism and its associated demands as a considerable barrier and may believe it has been raised simply to frustrate their objectives.

Establishing fitness-for-purpose for any cement, whether described as novel, alternative, non-Portland, low energy/low carbon, green, eco or otherwise; is neither a simple nor a linear undertaking and the more unfamiliar the cement type the more exacting will be the validation process. Justifiably, all stakeholders expect buildings and the infrastructure to be safe, long-lasting and without need of excessive maintenance.

Undoubtedly, a new type of cement would face an arduous route to acceptance. Unfamiliarity with process and product would demand a rigorous, independent technical validation, leading, at an initial stage, to some kind of formal certification. National or European standardisation would, if sought, follow much later when the product had established itself as 'tried and tested' i.e. as sufficiently durable under a wide range of exposure conditions. Even when appropriately validated, use of the cement in structural applications could well meet with resistance, particularly from specifiers as the representatives of the user-community. Specifiers would be aware that existing Codes of Practice and national construction regulations do not recognise the unfamiliar cement and cannot, therefore, provide a ‘deemed to satisfy’ solution. Confidence building measures would be needed and early use in non-structural, less demanding applications, would be obligatory until a ‘track record’ had been established. Use in structural applications could well require the sponsors to underwrite performance by way of insurance bonds/indemnities within demonstration projects. Use in general construction would require acceptance as a permitted material in the relevant concrete, mortar etc (i.e. end-use) standards and in engineering Codes of Practice.

How long might all this take before mainstream acceptance could be achieved for use of a new cement in general construction? Unfortunately, it is not possible to say on an evidential basis because there are no contemporary precedents.

Are new cements likely to be more expensive than Portland cements?

On any cost comparison basis, Portland cements benefit greatly from the 'economies of scale' implied by production of around 3.8 billion tonnes/year worldwide (2012) and from the many costs which have been amortised, such as the expense of historical validation. Unit cost may, however, increase as a consequence of international emission trading schemes for greenhouse gases but it is unlikely that any non-Portland cement could compete on a cost per unit volume/mass basis unless or until it had become an accepted mainstream binder produced in industrial quantities. Hence, new cements will generally be more expensive initially, mass/mass, than Portland cements, even where they derive from less energy intensive processes, and are likely to remain so for the foreseeable future.

Inventory of cements

What are alkali activated cements and geopolymeric cements?

Alkali-activated cements gain their strength, and other properties, via chemical reaction between a source of alkali (soluble base activator) and aluminate-rich materials. The alkali used as the activator tends to be an alkali silicate solution such as sodium silicate (waterglass) but can also be sodium hydroxide solution, or a combination of the two, or other source of alkali (such as lime). The aluminate-containing material - the pozzolan/latent hydraulic binder component of the cement - can be coal fly ash, municipal solid waste incinerator ash (MSWIA), metakaolin, blastfurnace slag, steel slag or other slags, or other alumina-rich materials. Use of sodium silicate gives a low temperature sodium aluminosilicate glass, chemically similar to naturally occurring zeolites (a special class of hydrated aluminosilicates). Geopolymeric cements are particular examples of 'alkali-activated pozzolanic cements' or 'alkali-activated latent hydraulic cements'.

All alkali-activated cements tend to have lower embodied energy/carbon footprints than Portland cements (up to 80-90% but this is pozzolan dependent). Historically, short, erratic setting times restricted the use of these cements, although predictable performance in the fresh wet state is now claimed. Manufacture on a commercial basis is underway in Australia, USA and possibly, China and precast/prefabricated concrete products based on these cements are apparently available.

Can alkali-activated/geopolymeric cements be manufactured in the UK?

Alkali-activated/geopolymeric cements are manufactured in the UK. There are no intrinsic technical, process or material supply barriers to their production. The primary sources of alumina tend to be by-products such as fly ash or blastfurnace slag. However, extensive applied research and plant-level pilot studies are still taking place to verify that available materials and plant produce consistent high quality product. The manufacture of these cements for use in general construction is increasing annually and there are many examples of pilot/demonstration projects, particularly in Australia.

What are CSA-belite cements [9]?

Manufactured and used on an industrial scale in China for over 35 years, (calcium sulfo-aluminate) CSA-belite cements are made by heating/sintering industrial wastes such as coal fly ash, gypsum and limestone at 1200°C – 1250°C in rotary kilns. CSA-belite (β-C_2S i.e. dicalcium silicate) cements are made in a range of compositions but the structural grades made in China comprise a predominant phase of CSA of 35 %– 70 %, a belite content below 30% and a ‘ferrite’ (calcium ferroaluminate) phase of 10 % – 30 %. Similar cements are now being produced at pilot plant level in Europe as part of the Aether project (www.aether-cement.eu).

In comparison with Portland cement CEM I, energy savings can be as high as 25 %, with limestone reductions of 60 % together with reductions in CO_2 emissions of around 20 %.

Strength development broadly equivalent to Portland cement appears feasible and early strength may be enhanced by adjustments to composition.

Can CSA-belite cements be manufactured in the UK?

In principle, CSA-belite cements could be manufactured in the UK. There are no intrinsic technical, process or material supply barriers to their production. However, the same measures outlined above for alkali-activated/geopolymeric cements would need to be in place to ensure consistent high quality product and to reassure construction sector stakeholders.

What are magnesium oxide-based cements?

The magnesium oxide-based cements that are currently manufactured or are under development are derived from two distinct chemical/mineralogical forms (and associated processes): magnesium carbonates (e.g. the mineral magnesite) or magnesium silicates. In the first case, the cementing substance is a reactive magnesium oxide but in the second case (see later) it is a mixture of magnesium oxide and hydrated magnesium carbonates.

In order to produce these two different types of magnesium-oxide based cements, a heating stage (pyro-processing) is involved but the different starting materials (and processes) fundamentally influence the cement's intrinsic environmental credentials. Magnesium oxide-based cements derived from silicate raw materials will have intrinsically smaller 'carbon footprints' than those derived from carbonates because when silicates are heated there is no chemically-bound CO_2 to be emitted. Conversely, a fairly large quantity of CO_2 is given off as a reaction product where magnesium carbonates are heated. In this latter case, the cement's environmental credentials rely crucially on how easily and completely such a cement can re-carbonate (sequestrate atmospheric CO_2) during its whole life cycle.

These different types of magnesium oxide-based cement are described below.

Magnesium oxide cements <u>derived from magnesium carbonates</u> [10]

'Eco-cements', derived from magnesium carbonate precursors, have been invented in Tasmania. There are two practical forms of these eco-cements. A type in which the main constituent is reactive magnesium oxide, mixed with industrial by-products such as fly ash or blastfurnace slag and a type where reactive magnesium oxide is mixed with Portland cement clinker and a pozzolan to form a type of ‘composite cement’.

The reactive magnesium oxide is produced by heating magnesium carbonate at atmospheric pressure, preferably as the mineral magnesite, to its dissociation temperature of about 650°C. At the same time a fairly large quantity of CO_2 is given off as a further reaction product and the viability of a magnesium oxide cement made in this way will depend heavily on its environmental characteristics assessed over its whole life.

These magnesium oxide-based eco-cements hydrate to form magnesium hydroxide (brucite), the main binding phase. Strength, especially at exposed surfaces, is said to be enhanced by rapid atmospheric carbonation (re-carbonation), a process claimed to be able to absorb most of the mass of CO_2 liberated during manufacture. It is, however, known that high humidity is required for significant re-carbonation of these cements and, to date, the validity of the claim remains to be independently verified for the cements in end-use products subject to natural/ambient carbon dioxide levels.

This same (atmospheric) carbonation process also occurs with hydrated Portland cement but at intermediate humidity, most significantly in porous products such as concrete blocks or masonry mortar. Aggregated over all uses and the whole life cycle, this can compensate for about 20% of that liberated during manufacture.

In terms of technical properties and performance, reactive magnesium oxide cements tend to have a high water demand and this could lead to initial high porosity in high content materials. This suggests that these cements are unlikely, in practice, to be 'standalone' products. They are more likely to be used in combination with quantities of Portland cement and additional materials such as coal/power-station fly ash or blastfurnace slag in order to increase solid volume for pore-filling.

Magnesium oxide cements derived from magnesium silicates [11]

In around 2005/6, engineers at Imperial College in the UK developed a magnesium oxide-based cement derived from mineral silicates. Both the starting materials and manufacturing process are novel in that magnesium silicates are first carbonated under elevated temperature (170ºC) and pressure (150 bar) to produce magnesium carbonate. This is heated (700ºC) under atmospheric pressure to its dissociation temperature to produce reactive magnesium oxide; part of this is (re-)carbonated to produce hydrated magnesium carbonates [i.e. $4MgCO_3.Mg(OH)_2.4H_2O$] which are blended with reactive magnesium oxide to produce the final cement. The resulting composition/chemistry is still new and so the technical properties and performance of this cement will remain a matter for conjecture until research results are in the public domain. However, there have been credible claims that concrete strengths of 50 – 60 MPa can be achieved but with further optimization trials needed.

Perhaps the most interesting feature of this new cement is its potential to become a carbon-negative product, because:

- magnesium silicates are, intrinsically, CO_2-free;
- CO_2 generated in the process is recycled back into the process;
- fuels with low energy content or carbon intensity (i.e. biomass) can be used;
- the production of the hydrated magnesium carbonates absorbs CO_2.

The inventors have observed that the production process to make 1 tonne of cement absorbs up to 100 kg more CO_2 than it emits, making it carbon negative.

Can magnesium oxide-based cements be manufactured in the UK?

Magnesium silicate minerals (e.g. pyroxenes, olivine/forsterite, serpentine and talc) are abundant worldwide but are less so in UK and deposits tend to be located in environmentally sensitive regions. Accordingly, it is not clear to MPA Cement whether or not magnesium oxide-based cements derived from silicates could be manufactured on a commercial scale in the UK. The research effort/pilot studies ceased in UK (in 2012) and the technology moved overseas. Pilot plant is still needed in order to determine if the process can be scaled up to a commercially viable level.

Manufacturing magnesium oxide-based cements from magnesium carbonates in the UK would seem unlikely due to lack of significant magnesite deposits. Magnesium carbonate occurs mainly in the UK as dolomitic limestone, deposits of which are remote from Portland cement plants because magnesium oxide is a potentially deleterious inclusion in Portland cement. If the current Portland cement makers were to contemplate such manufacture, then traffic of raw materials would have to increase or new plant would have to be built close to suitable deposits. Either option would involve significant environmental impacts and costs which might be difficult to justify.

What are 'ecocements' based on municipal solid waste incinerator ash (MSWIA) [12]?

Municipal solid waste incinerator ash (MSWIA) can be used in one of two ways to make a novel cement. As described in the section on geopolymeric cements, it can be used as the major component of an alkali-activated pozzolanic/geopolymeric cement or it can be used as a major raw material within a novel process to produce a traditional Portland cement. It is this latter usage, so far only in Japan within so called 'ecocements', which is explored here.

These types of ecocement are manufactured in Japan and are traditional Portland cements in their mineralogical composition but processed from raw materials where 50% has been replaced by MSWIA, and/or sewage sludge, and where waste oils, non-recyclable plastics and refuse-derived fuels have replaced fossil-fuels. MSWIA ecocements are also lower energy cements in that 'clinkering' takes place in a rotary kiln at 1350°C rather than at 1450°C, as is the case for traditional Portland cement clinker. With the exception of a specialised rapid-hardening, high chloride type produced for particular applications but unsuitable for use in structural concretes, these ecocements are virtually indistinguishable from Portland cement CEM I and consequently have the same properties, performance and applications.

What about chlorides and dioxins in MSWIA?

MSWIA generally contains high concentrations of chlorides as well as small amounts of toxic substances such as dioxins and heavy metals. In consequence, both the process and the product are engineered to be safe with respect to human health and impacts on the environment. To this end, any dioxins initially present are completely decomposed above 800°C, so that the product is free from them and kiln exhaust gases are quickly cooled below 250°C to prevent re-formation of dioxins in the cement kiln dust (CKD). Some volatile heavy metals, such as lead, zinc, copper and cadmium vaporize during clinkering in the form of chloride salts and are trapped in the CKD. The metals are then extracted from the CKD via a metal recovery process and delivered to smelters for refining.

Can cements based on MSWIA as a raw material be manufactured in the UK?

There would seem to be no obvious technical barriers to production in the UK. However, manufacture would be critically dependent on the availability of MSWIA and its proximity to existing cement works, if Portland cement manufacturers were to contemplate producing such cements. Currently, MSWIA is in short and irregular supply in the UK but even if this were not the case, public perception issues could arise far outweighing other considerations. Hence the likelihood of producing a familiar Portland cement by this process in present social, economic and regulatory conditions would seem to be low.

What are thermoplastic carbon-based cements such as C-Fix cement?

Unlike most cements used in buildings, and unlike those previously described herein, C-Fix (the name is derived from *carbon fixation*) is an organic cement, i.e. carbon-based, rather than an inorganic cement. It is a processed, black, thermoplastic binder produced as a waste/residue when crude oil is 'cracked'. The raw material for C-Fix has historically been burnt to avoid waste-handling measures but, in so doing, contributed CO_2 to atmosphere. C-Fix was developed by Shell and the University of Delft (NL) and needs to be heated to 200°C before being added to aggregates/fillers to make a 'carbon concrete'. It has properties in common with both asphalt and cement-based concretes but is mixed and applied using asphalt techniques.

The developers claim that the carbon footprint of C-Fix concrete is 3½ times lower than that for Portland cement-based concrete but this is only credible when the energy/carbon footprint of the refining process that gives rise to the residue is completely discounted.

C Fix is a thermoplastic material (it softens when heated and hardens again when cooled), and as such, within 'concrete' it is temperature and pressure sensitive. In consequence, it has a much higher creep-related deformation under load than Portland cement-based concretes therefore C-Fix will be unable to replace Portland cement in the generality of construction. It may prove to be a useful material in certain applications in the search for more sustainable cements/concretes. It could have considerable potential as a replacement for asphalt in road-surfacing work, concrete in industrial flooring/paving and use in the marine and chemically extreme environments. The overall potential of C Fix will only become clear with time.

Can C-Fix be manufactured in the UK?

In principle, C-Fix could be manufactured wherever crude oil is cracked but the factors governing commercial viability are unknown to MPA Cement and so it is not possible to say here whether it would be viable to manufacture C-Fix in the UK.

What position does MPA Cement take on low energy, low carbon cements?

MPA Cement welcomes, and aims to be involved with, any initiatives that could lead to a reduction both in the Portland cement industry's contribution to environmental impacts such as emissions of CO_2 – currently at around 2% of the total in UK [12] – and to the amount of energy embodied in its cements and, hence, in concrete, buildings and structures.

The Portland cement industry has conducted its own review [8] into the scientific and societal issues involved in developing inorganically-based non-Portland alternatives and, on this basis MPA Cement's Member Companies are carrying out their own confidential laboratory-based research. The Portland cement industry has the objective of remaining in business in the long-term and although the demands of the climate change agenda and free competition will drive the search for alternatives to current processes and products, the industry will ensure that it only manufactures cements that are safe and fit-for-purpose.

Where can I find out more?

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