

Novel Cements: Low energy, low carbon cements

Background and introduction

Sustainability and the UK cement industry

Traditional Portland cement-based concrete forms the 'bedrock' of 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 continuously 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. The BCA 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 (CO₂) 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 a BCA 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 1450°C. 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 interground in order to control the setting time of the product. The overall process is energy-intensive and CO₂ 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 production of composite 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 natural pozzolanas. These constituents are interground 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 CO₂-intensive i.e. the low energy, low carbon route.

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

Novel, or 'new', cements based on non-traditional processes or raw materials and which are generally non-Portland, are several and diverse. In general, they tend to embody less energy and emit less CO₂ 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, though, 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 or under development and can fulfil the above characteristics to varying degrees. They are:

- geopolymeric cements (Australia);
- low energy CSA-belite cements (China);
- cements based on magnesium oxide derived from carbonates (e.g. 'eco-cement', Tasmania) or from silicates (UK);
- 'ecocement' based on municipal solid waste incinerator ash, MSWIA, (Japan);
- C-Fix cement (The Netherlands).

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. Even a significant inroad is unlikely 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 CO₂ 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. However, 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? 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 2½ billion tonnes/year worldwide in 2007 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 geopolymers cements?

Geopolymeric cements are particular examples of 'alkali-activated pozzolanic cements' or 'alkali-activated latent hydraulic cements'. 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. The pozzolan/latent hydraulic binder component of the cement can be fly ash, municipal solid waste incinerator ash (MSWIA), metakaolin, 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 will tend to have lower embodied energy/carbon footprints than Portland cements (up to 80-90% but 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 and possibly, China and precast concrete products based on these cements are, apparently, available.

Can geopolymers cements be manufactured in the UK?

Geopolymeric cements could be manufactured in the UK. There are no intrinsic technical, process or material supply barriers to their production if the primary sources of alumina are by-products such as fly ash. However, extensive applied research and plant-level pilot studies would be needed to verify that available materials and plant could produce consistent high quality product.

What are CSA-belite cements^[9]?

Manufactured and used on an industrial scale in China for about 20 years, (calcium sulfo-aluminate) CSA - belite cements are made by heating/sintering industrial wastes such as fly ash, gypsum and limestone at 1200°C – 1250°C in rotary kilns.

CSA-belite (β -C₂S 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 %.

In comparison with Portland cement CEM I, energy savings can be as high as 25 %, with limestone reductions of 60 % together with reductions in CO₂ 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, as for any new cement, and as outlined above for geopolymers cements, the same measures 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: magnesium carbonates (e.g. the mineral magnesite) or magnesium silicates. In each case, the cementing substance will be reactive magnesium oxide but this will be produced by heating (pyro-processing) different raw materials and this will

fundamentally influence the cement's 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 CO₂ to be emitted. Conversely, a fairly large quantity of CO₂ 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 (sequester atmospheric CO₂) during its whole life cycle.

In terms of technical properties and performance, reactive magnesium oxide cements have a high water demand and this could lead to initial high porosity in high content materials. This tends to suggest that these cements are unlikely 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.

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

Magnesium oxide cements derived from magnesium carbonates^[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, preferably as the mineral magnesite, to its dissociation temperature of about 650°C. At the same time a fairly large quantity of CO₂ 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.

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 CO₂ 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, however, also occurs with hydrated Portland cement but at intermediate humidity, most significantly, in porous products such as concrete blocks, or masonry mortar but, aggregated over all uses and the whole life cycle, can compensate for about 20% of that liberated during manufacture.

Magnesium oxide cements derived from magnesium silicates^[11]

Engineers at Imperial College in the UK have developed, and intend to pilot, a magnesium oxide-based cement derived from mineral silicates. The technical properties and performance will be governed by the form of the reactive magnesia and how/whether this cement is to be used in combination with other binders (see above). However, they are unlikely to be significantly different to any similar cement derived from carbonate minerals but until research results are in the public domain, this will remain a conjecture.

Rather, the more interesting feature of this form of the cement is its potential to absorb more CO₂ from the atmosphere than is emitted from the production process (fuels, electricity etc) in which the raw materials are heated to around 650°C. Imperial College calculates that the manufacturing process would emit around 0.5 tonnes of CO₂ per tonne of cement produced whereas in the service condition, the cement has the potential, chemically speaking, to absorb about 1.1 tonnes of CO₂ per tonne of magnesium oxide cement. If this potential were to be reached, it is not clear to BCA what effect this would have on the volume stability of concrete containing the cement, however, the overall carbon footprint would be negative and CO₂ would be sequestered from the atmosphere by use of the cement. Even if practice were not to correspond exactly with theory, there is a significant likelihood that this cement could be 'zero carbon' or better.

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

Magnesium silicate minerals (e.g. 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 BCA whether or not magnesium oxide-based cements derived from silicates could be manufactured on a commercial scale in the UK. Funds, however, are said to be in place (early 2009) to build a pilot plant.

Manufacturing the same, or a similar, cement 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 cement works as magnesium oxide is a potentially deleterious inclusion in Portland cement. Traffic of raw materials would, therefore, 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 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 eco-cements 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 eco-cements 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 to be 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 is 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 petroleum-tar based binder produced as a waste/residue when crude oil is 'cracked' (fractionally distilled). The raw material for C-Fix has historically been burnt to avoid waste-handling measures but, in so doing, contributed CO₂ 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 tar is completely discounted.

C Fix is a thermoplastic material (it softens when heated and hardens again when cooled), as such, within 'concrete' it is temperature and pressure sensitive and has a much higher creep-related

deformation under load than Portland cement-based concretes; this property makes it unsuitable for critical structural work.

C-Fix will be unable to replace Portland cement in the generality of construction because of its thermoplastic character but it may well 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 the BCA and so it is not possible to say here whether it would be viable to manufacture C-Fix in the UK.

What position does the BCA take on low energy, low carbon cements?

The BCA 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 CO₂ – currently at around 2% of the total in UK^[12] – and to the amount of energy embodied in its cement 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, BCA's Member Companies are carrying out their own confidential laboratory-based research. The Portland cement industry has the objective of remaining in business into 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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Document No: ST/FS/12	Revision No: 3
Author: M G Taylor	Drafted: 25 May 2006
	Last revised: 16 March 2009