

Novel uses for cement – brief review and outlook.

Dr Phil Purnell, School of Civil Engineering, University of Leeds

1. Introduction

It's an unassuming material, yet it surrounds us every day. If you're reading this on your office computer, you might well be completely surrounded by it except for the windows. If you've got a window, have a look outside; unless you have a rural outlook, you can probably see thousands of tonnes of it and thousands more will be buried underneath you. Cement, more than any other material, supports and defines the edifices of modern urban life. Each year, 2.7 billion tonnes is manufactured globally [1], which in turn will make around 20 billion tonnes of structural concrete, building blocks, mortar, roof tiles, roads, foundations and so on.

Cement is produced in every industrialised country in the world, mainly because the raw materials – limestone, clay and gypsum – for its most common variety, Portland cement, are readily available everywhere. Limestone and clay are mined and crushed, then blended in a ratio of about 80 parts limestone to 15 parts clay and preheated to around 600°C to drive off water and decompose the limestone into lime and carbon dioxide. The material then enters a rotary kiln, which heats it up to 1450°C fusing the calcium in the limestone and the silicon in the clay into calcium silicates. The resulting golf-ball sized 'clinker' is then cooled, ground to an average particle size of 2 – 80 µm and 5% gypsum added to control setting.

The cement may then be blended with up to 5 – 90% other materials, such as powdered limestone or waste materials containing active silica such as fly ash (recovered from power station chimneys) or ground blast-furnace slag, for both economic and technical reasons, to produce a range of different cements for various applications. Cements for specialist applications may use different calcium compounds (e.g. aluminates, sulpho-aluminates or phosphates) or exploit non-calcium chemistry (e.g. magnesium oxychlorides) but the basic manufacturing process is the same. Related materials include so-called 'geo-polymers' (siliceous materials activated by alkali solutions) and glass-ionomer cements (glass powders activated by organic acid solutions). All these have most of the following features in common:

- They are ceramic powders activated by (normally inorganic) aqueous solutions; the cement and water are simply mixed together to form a 'green' paste.
- They can be formed into any shape with or without aggregates; the green paste can be poured, cast, injected, moulded or sprayed, and aggregates can be added both to reduce cost and enhance functional or structural properties.
- They are normally cured without recourse to elevated temperatures or pressures; unlike metals or polymers, no melting, high-pressure moulding, or heat curing is required for the green paste to form a hardened component.
- The green paste hardens via hydration or water-catalysed reactions to form strong, insoluble solid components; cements do not dry, they cure and the hardened mass will not simply revert to 'mush' when it comes back into contact

- with the activating liquid (i.e. gets wet). This is what distinguishes cements from plaster or materials such as solvent-based polymer cements and glues.
- The hardened microstructure is dominated by an amorphous gel and/or network of micro-crystals with intrinsic and extrinsic porosity on all scales from <10 nm up to microns. For example, in Portland cement, the calcium silicates (Ca_3SiO_5 and Ca_2SiO_4) react with water to form an amorphous calcium-silicate-hydrate gel interspersed with micron-sized calcium hydroxide crystals. The gel is intrinsically nano-porous but essentially impermeable, with pore sizes of $\sim 0.5 - 5$ nm and total porosity of about 28%. Its structure is generally likened to a mixture of crumpled foil with a mass of fibrillar features [2]. This gel or micro-crystalline phase has an enormous surface area and a forgiving molecular structure that allows it to easily incorporate lots of different ions, either by adsorption, reaction or solid solution. In addition to this gel porosity, there is also ‘capillary porosity’ which is the space left behind when the water has reacted, ranging from 10 nm to 1 μm .
 - The pore size distribution, total porosity and connectivity of the capillary porosity can be controlled over a wide range simply by varying the water/cement (w/c) ratio; e.g. for Portland cement, from $<10\%$ at $w/c < 0.30$ with a maximum pore size of ~ 75 nm, to perhaps 50% at $w/c=1$ with a maximum pore size of $>1\mu\text{m}$. The permeability would change from $\sim 10^{-12}$ to $\sim 10^{-9}$ m/s over the same range of w/c. Since the structural and functional properties of the hardened paste, from strength and stiffness to permeability and adsorptive ability, are controlled by the porosity, this allows properties to be easily ‘fine tuned’ for specialist applications. To a lesser extent, the gel porosity can be tailored by adjusting the cement chemistry and hydration conditions.
 - They are widely available and, in the case of PC-based products, globally available and cheap.

This unique combination of process, functional and structural properties is found in no other class of materials. It is perhaps surprising then that so little attention has been paid to exploiting cements in other fields. Over 99% of cement manufactured is used in construction; even in that seemingly simple application, it is a multifunctional material. As well as acting as the ‘glue’ in concrete, giving it compressive strengths of up to 150 MPa, it also acts as a physical barrier to prevent ingress of deleterious substances such as chlorides that can corrode reinforcing steel, and as a chemical barrier whose high pH maintains the chemical passivity of the steel (the pH of saturated concrete is generally 12 – 13 as a result of soluble alkali impurities from the clay used as raw material, buffered by the calcium hydroxide formed during hydration). There may be many applications in which it could perform in a similarly multifunctional manner. The commercial drivers to search for such applications have not been strong; until now, perhaps.

1.1. Cement: economics and environment

The environmental impact of cement production is well documented. Manufacturing a tonne of Portland cement releases 600 – 800 kg of CO_2 . Energy use accounts for 30-40% of this, while the rest is produced when limestone (the main raw material) decomposes [e.g. 3-7]. Depending on whose figures you believe, cement production accounts for around 5% of global CO_2 emissions. As such, it is likely to be hit hard by impending

emissions legislation, particularly when carbon emission credit markets become fully operational i.e. no free credits will be issued by governments, as they are at the moment. On the EU carbon permit market, the price per emitted tonne of CO₂ varied between €18 – €30 in 2008 and is expected to rise to at least €44 [8]; a significant proportion of the current retail price of cement (around €100/tonne). Rising energy and raw material prices, plus environmentally driven extraction taxes, also add further indirect pressure. Given the relatively restricted market conditions for cement (low specific value, impracticality of import/export, government price controls in some jurisdictions to prevent economic stifling of construction sector etc) it is difficult to see how the industry's long-term viability can be maintained without either:

- significant price hikes,
- introduction of low energy/low CO₂ cement formulations, or
- the development of novel uses for cement and new, specialised, high specific value markets.

This report concentrates on the last of these three issues, by reviewing existing non-traditional uses for cement and then proposing areas of research into possible new applications.

2. Established novel uses

There are a few fields outside of construction where cements are already used. These are reviewed very briefly below, in the approximate order in which they became established. Some are widely accepted, while some are still niche or experimental materials, so the literature available is variable both in breadth, depth and quality. Most of the references mentioned are reviews and are mainly intended as readily available starting points for the interested reader.

2.1. Refractory materials

The hydrated phases in Portland cement pastes begin to degrade at around 150°C and become structurally unsound above 450°C. Calcium aluminate cements (CAC) hydrate to form mixtures of microcrystalline CAH₁₀, C₃AH₆ and amorphous AH₃. Above 300°C, these also begin to break down, but at around 700°C the dehydrated minerals begin to fuse together, with ceramic bonds replacing hydrated bonds. Provided the right aggregates are used, heat-resistant concrete – often called refractory castables – can be made using CAC cements. These are used widely in industry for high-temperature insulation, furnace bodies and chimney linings where traditional refractory bricks do not give sufficient performance, either because of heat or gas loss through the joints, or because complex shapes are required.

The temperature at which refractory concrete can be used increases with the alumina content and purity of the CAC and also with the amount of aggregate used. The cement:aggregate ratio for normal 'dense' and high-performance 'ultra-low cement' refractory castables is 15-25% and 3-5% respectively. The type of aggregate chosen is also important. Quartz and limestone aggregates are to be avoided as they undergo phase changes at 573°C and ~600°C respectively. Concrete with basalt aggregate and low-grade

CAC can be used up to 800°C, while high-purity (80%-Al₂O₃) CAC with fused alumina aggregate can potentially resist 1850°C [9]. A key technological challenge is to keep the shrinkage of concrete components to an acceptable minimum (about 1.5%). Some phosphate cements, particularly those based on magnesium, can also be used in high-temperature applications.

2.2. Waste management

Cements are widely used in waste management applications to immobilise pollutant ions as they offer a unique combination of:

- physical solidification of slurries, granular materials or weak solids by mixing with cement and subsequent hardening;
- absorption mechanisms, where pollutant ions such as heavy metals are chemisorbed or adsorbed into the gel phases, by virtue of their enormous surface areas and their capacity to provide a wide variety of reaction sites onto which ions can bond;
- chemical stabilisation or immobilisation, since the solubility of many pollutants is severely reduced by the high pH environment within a cement paste.

Many different waste streams, from specific (e.g. air pollution control residues) to general (e.g. contaminated land) are suitable for treatment. The aim may be either to remediate the waste by solidification and stabilisation prior to landfill disposal or recycling, or to encapsulate it *in situ* to prevent it moving into uncontaminated ground, or some combination of both approaches. The approach taken will depend on the combination of contaminants that need to be dealt with. For example, the dominant mechanism in immobilisation of heavy metals such as zinc, cadmium and lead is chemical precipitation of insoluble hydroxides in the high-pH environment of a cement grout. Copper, chromium and zinc can form double hydroxides with the calcium in the cement. Cobalt and nickel can substitute for calcium in the C-S-H, and chromium can substitute for both calcium and silicon [10]. Thus adjusting the chemical and hydration characteristics of the cement blends used can tailor a solution to a particular situation. Often, there is a trade-off between physical and chemical immobilisation. Silica fume is added to cements used to immobilise lead in lime-based air pollution control residues to reduce the pH and improve leaching behaviour, but adding too much reduces the strength of the stabilised waste, which can lead to cracking and physical deterioration [11]. Many common contaminants, particularly heavy metals, can affect hydration of the cement. Copper lead and chromium all accelerate hydration, while zinc can retard it. Other interactions can change the structure of the hydrated paste in poorly understood ways. The choice of cement system to use is not at all straightforward.

For in-situ land remediation applications, ‘cut-off’ walls are used. A trench is dug around the contaminated area and progressively filled with a slurry of cement (Portland cement with pfa or bfs) plus 20-30% clay, typically bentonite. The clay adds thixotropy to the slurry, allowing the excavation to proceed through the slurry but ensuring that the trench is self-supporting. It also reduces the permeability to $10^{-8} - 10^{-9} \text{ m s}^{-1}$ and adds extra sorptive capacity. The slurry eventually hardens, reaching strengths of 0.1 – 1 MPa. Common contaminants can affect the integrity of the barrier; acids, magnesium and

aluminium salts, sulphates and organics such as phenol can all degrade the hardened slurry and are often present in contaminated land [12]. The long-term behaviour of such systems is not well understood [11].

2.2.1. Radioactive waste

Intermediate and low level radioactive wastes – i.e., those that generate little or no heat during storage – are usually encapsulated in cement, within stainless steel drums, prior to interim storage and eventual disposal. As well as the immobilisation mechanisms given above, cement is favoured as it is readily available, has controllable diffusion characteristics, acts as radiation shielding [13] and can cope with a wide range of ions; Evans [14] lists 29 in his review. Portland cement grout is normally used, combined with slow-reacting pozzolans such as pfa or bfs to reduce both the heat generated during hydration and the eventual permeability. Nano-structured additives such as clays or zeolites may also be used, e.g. to reduce leaching of metals such as caesium that remain soluble at high pH [15]. Other cements, such as calcium aluminate or sulpho-aluminate, geopolymer, and glass-ionomer systems, may be suitable for particular applications (e.g. where a lower pH is chemically useful) but industrial users concentrate almost entirely on PC-based encapsulation.

The very long storage time – measured in thousands of years – expected of cements used for radioactive waste encapsulation requires that the long-term changes in their chemistry and microstructure are carefully modelled and studied. Recent re-examination of 20-year old systems suggests that physical and chemical changes are still occurring in the gel phases over such timescales [16]. The amount, location and composition of the ‘free water’ in the pores of such systems is also time-dependent and controls how metallic wastes such as aluminium and magnesium will corrode. The effects of common concrete deterioration processes such as carbonation, are also uncertain [14]. Models of these changes are currently ‘in their infancy’ [13] and long-term data to calibrate these models is very scarce. This hampers research into the use of novel cement systems for radioactive waste management, as users tend to be extremely reluctant to move away from apparently ‘tried and tested’ PC-based solutions, which in fact are used more for heritage reasons than as a result of any objective certainty regarding long-term behaviour.

2.3. Biomaterials

The engineering properties of a cement – in particular, the ability to remain plastic for a defined period in order to be shaped and subsequently harden – are attractive in a number of surgical situations, from spinal repair to dental prosthesis. Fortunately, there are a wide range of cements that are chemically compatible with the human body and can offer both technical and economic benefits over competing materials such as polymers, amalgams or ‘denatured’ bone from cadavers. Use of these biocements has grown rapidly in recent years in response to advances in surgical requirements and cost/availability issues. It now represents by far the highest value market for cementitious materials and so is discussed in some detail here. Three main classes of biocement are in use: ‘mineral trioxide aggregate’ (which is effectively a mixture of Portland cement and bismuth oxide), glass ionomer cement and various calcium phosphate cements. The first two are used in dental

applications, while the last is used for bone repair and drug delivery, often simultaneously i.e. localised application of osteological drugs.

2.3.1. Dental cements.

Glass-ionomer cements (GIC) are fluoro-alumino-silicate glass powders activated with organic acids. They are enormously versatile and can be used in almost all aspects of dental reconstruction, including post luting, lining cavities, long-term sealing and physical restoration [17]. Biocompatibility is excellent; very little heat is produced during hydration and no harmful toxins are produced (in contrast to many dental resins, which produce benzene bromine and benzene iodine); in fact, GIC slowly releases fluoride over time, aiding remineralisation of the repaired area. The chemical and mechanical bond with the substrate tooth is strong but poorly understood [18]. As with construction cements, the powder-liquid ratio (p/l) and the mixing process controls the hardened cement properties. Although many manufacturers supply ‘pre-proportioned’ powder and liquid, many practitioners prefer to mix their own paste either for cost reasons or technical preference. Studies of the variation of GIC properties with p/l have been undertaken [e.g. 19] but the interpretation of the results, which attribute strength loss to decreased aggregate fraction, would be interpreted rather differently by traditional cement researchers in the light of over 100 years of experience of essentially identical systems. Changes in porosity on several scales caused by a combination of poor compaction at high p/l and excess liquid at low p/l, would be a more likely cause, leading to an ‘optimum’ p/l dependent on the placing technique as identified by Feret in 1896 [20]. Another dental cement used in root canal surgery, known as ‘mineral trioxide aggregate’, is a mixture of Portland cement and bismuth oxide. The calcium hydroxide produced during the Portland cement hydration encourages beneficial cell growth around the repair. Research into modifying its hydration chemistry and properties seems to be undertaken with almost no reference to the huge body of civil engineering materials literature on the subject [e.g. 21]. There is clearly scope for mutual knowledge transfer between the biocement and construction cement research communities.

2.3.2. Bone cements

Inorganic bone cements (as opposed to the poly-methyl methacrylate – PMMA – polymer ‘cements’ to which the term is often applied) are based on calcium phosphates, activated either with water, orthophosphoric acid or pyrophosphoric acid. Calcium phosphate cements (CPC) essentially boil down to three types: those that hydrate to form hydroxyapatite (HA, the main mineral in natural bone); those that hydrate to brushite and those that form dicalcium pyrophosphate (DCPP). There is a great deal of overlap between the classes, and hydration products may be microcrystalline or amorphous depending on many parameters including the original cement particle size and the pH of the reactant solution. The solid phase assemblage of many systems is not well understood. Setting times of 3 – 15 minutes are desirable and set modifiers such as citrates are frequently added to achieve this. Repairs may be placed in ‘open’ surgery where surgeons manipulate a partially stiffened paste into place with their fingertips, or by ‘minimally invasive’ injection via a cannular directly into bone defects [22, 23]. All CPC cements are reabsorbed by the body fairly quickly, with colonization by bone cells within 2 weeks and complete resorption within 3 – 36 months, depending on the system

used [24]. Brushite is absorbed more quickly than HA, while HA has better mechanical properties; DCPD systems are too novel for firm *in vivo* results to be available but are likely to be similar. This is the major advantage of CPC cements over competitor materials such as PMMA; other advantages and disadvantages are given in table 1.

Advantages	Disadvantages
<ol style="list-style-type: none"> 1. Self setting ability <i>in vivo</i> 2. Good injectability allows cement implantation by minimally invasive surgical techniques. 3. Good osteoconductivity and occasional osteoinductivity 4. Can be replaced by newly formed bone after a period of time (osteotransductivity). 5. Moldability: the perfect fit to the implant site, which assures good bone-material contact, even in geometrically complex defects. 6. Excellent biocompatibility and bioactivity. 7. No toxicity 8. Low cost (relative to other biological materials) 9. Ease of preparation and handling 10. Setting at body temperature (i.e. no localised necrosis as caused by polymer curing) 11. Forms chemical bonds to the host bone 12. Powder components are clinically safe 13. Can be used to deliver antibiotics, anti-inflammatory drugs, growth factors, morphogenic proteins, etc. at local sites, which are able to stimulate certain biological responses. 	<ol style="list-style-type: none"> 1. Mechanical weakness: limited use due to potential collapse of material followed by soft-tissue formation instead of bone formation (loaded areas). Until cements with adequate shear strength are available, most complex fractures that can be repaired with cement also will require metal supports. 2. Can be washed out from surgical defect if excess of blood. 3. Lack of macroporosity (especially interconnected pores), which prevents fast bone ingrowth and the cements degrade layer-by-layer from the outside to the inside only. 4. The <i>in vivo</i> biodegradation of many formulations is slower than the growth rate of a newly forming bone.

Table 1: Advantages and disadvantages of CPC systems (adapted from Dorozhkin 2008)

The total porosity of most systems is around 40-50% with an average pore size of 8 – 12 μm . This is large enough for nutrient transport to encourage bone growth around implants, but too small to allow intergrowth, so porogens (soluble aggregate inclusions or air entrainment agents) are often added to allow bone to grow into an implant, although this is at the expense of mechanical strength [25]. This trade-off between strength and porosity is the limiting factor in use of CPC bone cements. Although their compressive strength is comparable to that of trabecular bone (i.e. 10 – 100 MPa), their tensile and shear strength – in common with traditional concretes – is much lower, generally 1 – 10 MPa, limiting use to non-load bearing repairs such as maxillo-facial and cranial surgery, unless the repair is supported by e.g. stainless steel frameworks. As with the dental cements above, interpretation of p/l vs. strength and porosity results would be interpreted rather differently by traditional cement researchers. Faster progress could be made in addressing this problem by collaboration between the two research communities.

CPC repairs can also be ‘doped’ with drugs that slowly release directly into the trauma site over weeks or months. Although this is possible with pre-cast sintered implants, with CPC the drug can be dispersed throughout the entire volume of the implant, rather than just at the surface, leading to more prolonged release times. The micro- or nano-porosity of set CPC is the key to this and must be carefully adjusted to tailor the release rate for a given patient. The technique is particularly effective for localised delivery of growth

factors, for which injections are ineffective since the proteins are dispersed too rapidly away from the injection site to have significant effect [26].

The economic driving force for using CPC in bone replacement is huge. The scarcity of human bone for grafts is such that criminal scavenging of bones from cadavers is increasingly common [27]. If the economies of scale that could be gained by encouraging traditional cement producers to add biocements to their products lines could be realised, such ghoulish anachronisms could become a thing of the past.

2.4. Sculpture

Although cements and concrete have been used in the ‘craft’ sculpture market for many years, gnomes are not a technically demanding application and are thus not reviewed here. However, in recent years, fine art sculptors - including Turner Prize-winners Antony Gormley (*Allotment*, 1993) and Rachel Whiteread (*House*, 1993) – have turned to concrete as a material in which they can realise combinations of concept, line, shape and form that are impractical to create in other media. Creating large sculptures using concrete often brings challenges, such as heat management of very thick sections and control of colour and surface finish that, while not unique to sculpting, place unusual restrictions on placing and curing. Unfortunately, little seems to be published on how these problems are overcome in this field, perhaps because of the wish to retain artistic know-how or a lack of a communication channel, and bringing the technical expertise of concrete experts to bear on sculptural issues might increase the use of the material in this field, perhaps developing specialist cements and/or concretes that combine low heat output, light weight, excellent surface finish and stable, controllable colouring.

2.5. Rapid prototyping

Rapid prototyping and manufacture is a rapidly expanding field. Traditional manufacturing techniques, such as die compression or injection moulding, require the manufacture of expensive dies, tools and moulds to make components. This makes production of bespoke or short run components by these methods economically unviable, and it becomes the domain of the craftsperson, whose availability is diminishing and price inflating accordingly. Methods have thus been developed that allow direct manufacture of a component from a CAD model. Techniques include micro-stereolithography and laser sintering, but the quickest and cheapest is 3D printing. This uses simple inkjet printer technology to spray liquid activator onto successive layers of powder substrate, building up a 3D shape of arbitrary complexity limited only by the resolution of the system. The major drawback is that the parts manufactured tend to be very weak i.e. barely able to be handled – the powder substrate used is generally bassinite (i.e. Plaster of Paris) – and only suitable for aesthetic prototype purposes [28].

Replacing the plaster-based powder with cement should allow much stronger, functional items to be printed. This is an emerging application for cements and little work is available. Proof of concept has been demonstrated with both Portland cements [29] and biocements [30], with flexural strengths of 1 – 3 MPa reported for both systems depending on processing parameters. Of particular interest for biomedical systems is the ability to directly print macro-porosity to encourage bone ingrowth, removing the need

for porogenic agents in the cement. The capability to print extremely complex, bespoke shapes such as orbital or maxillary bone prostheses, which are difficult to form ‘by hand’ in theatre, is also attractive. A great deal more research is required to optimise these systems.

3. Proposed applications

It is not easy for cement scientists to identify new applications for this versatile material, as in a modern research environment it is almost impossible to have an overview of material requirements on a wide enough range of fields. Part of the purpose of this review is to provide a document that can be read by those outside the field who (not being familiar with cement) might become aware of the unique combination of pore structure, chemistry, ease of processing and structural properties it offers and recognise another use to which it might be put. However, below are two proposals that might help spur original thought.

3.1. Personal ballistic protection

High-end personal ballistic protection systems – ‘flak jackets’ – use ceramic core plates encased in a plastic spall liner, placed into a jacket made from aramid fibres. Shattering the core plate, deforming the projectile and transferring energy to the spall liner dissipates the energy of a projectile [31]. Core plates are currently made from sintered alumina, which is expensive, extremely energy intensive and time-consuming to form (requiring sintering at 1700°C for up to two weeks), and only rectangular plate shapes are available. Current world demand for these plates has expanded from primarily military sources to include the whole range of NGOs and other organisations working in strife-torn areas around the world and within our cities. Cement-based ceramics have a number of advantages in this respect: they are easy to form into any shape, manufacture is simpler and less energy intensive, and a wide variety of aggregates can be used to tailor the fracture properties. Fibres, such as carbon, can be included to dramatically increase toughness. Advanced processing and materials can help attain strengths of up to 400 MPa [32]. Viable ballistic protection composites could be tailored for particular applications by using correct combinations of aggregates, fibres and integral spall liners. Recent advances in textile-reinforced cement composites [33] bode well for this application. No studies have examined cements in this context; only limited tests on bulk concrete seem to have been carried out [34].

The range of science that could be applied to the problem is very wide. Fibre/matrix bond is crucial; surface science could help design the correct interface. Chemistry can predict new cement systems to be investigated. Statistics has a huge role in describing the stochastic properties of such complex materials under violent loading, and how the formation of crack patterns can be described and optimised. The physics of high-speed granular flow is important; industrial testing houses frequently report that plates resist projectiles better after previous rounds have shattered the ceramic plates – what mechanism is at work here? How can we exploit it? Inter-disciplinary work is essential in this area.

3.2. Solid Adsorption Refrigeration (AR)

AR is a low-energy sustainable refrigeration system, with no moving parts. Natural refrigerants (e.g. water, ammonia or methanol, which do not contain CFCs or other ozone-depleting and/or greenhouse effect enhancing common refrigerants) in a closed system is adsorbed by a solid substrate at low temperatures and desorbed at higher temperatures. The solid adsorbent performs the same function as a compressor in a normal fridge. A heat source provides the only energy input. The key properties of any absorbent are significant porosity with pore sizes both in the nanometre (for sorption) and micrometer (for transport of gas) ranges. Commonly used solid adsorbents are natural zeolites, activated carbon and silica gel [35]. C-S-H gel has a very similar nanostructure to natural zeolites, and the transport properties of hcp can be tailored by varying the water-cement ratio. Also, it is well known that water absorbs and desorbs freely from cement paste. Thus cements could be candidates as substrates for AR and are rather cheaper than other materials. No work has been carried out to assess this. Collaboration would be essential in establishing this research by bringing together physicists and chemists to model the affinity of various refrigerants for the C-S-H gel surface and diagnose the various levels of porosity required for the correct combination of properties.

4. Conclusions

Cement is one of the world's most important materials, but a step-change in our attitude to the environmental impact of its manufacture may drive manufacturers to look for new, high-specific value applications outside of construction. Fortunately, cements have such an enormous range of chemical compositions, controllable functional properties and structural strength that it is in fact surprising that they are not more widely used in alternative applications. Existing niche applications such as waste management and biomaterials are well established but a great deal of work is required to optimise the systems used; progress in these fields would be greatly accelerated by collaboration with cement and concrete scientists. Emerging applications such as rapid prototyping show promise. New applications that can exploit the unique combination of properties provided by cement will need to come from collaboration with communities outside cement and concrete research who have previously only had cement in their peripheral vision and never perceived it in the context of controllable, functional, nanomaterial.

5. References

1. HG van Oss, Mineral and Commodity Summaries. United States Geological Survey 2008, pp44-45.
2. IG Richardson, The nature of C-S-H in hardened cements. Cement and Concrete Research 29 (1999) 1131-1147.
3. E Worrell, L Price, N Martin et al, Carbon dioxide emissions from the global cement industry. Annu. Rev. Energy. Environ. 2001 (26) 303-329.
4. J Sjunnesson, Life Cycle assessment of concrete, Master Thesis, Department of Technology and Society, Lund University, September 2005.
5. Castle Cement, Sustainability. UK, Castle Cement, May 2005. 26pp. wall material. Construction and Building Materials 13 1999. 329-341.
6. J. R. Prusinski, M. L. Marceau, and M. G. VanGreen, Life cycle inventory of slag cement concrete, Eighth CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete: Proceedings of the Technical Papers Organized by the U. S. Advisory Committee, EPRI, Palo Alto, CA: 2004. 1010913. pp65-80.

7. E. Farahi, *Advanced Calcareous Ceramics via Novel Green Processing and Super-Critical Carbonation*. PhD thesis, University of Warwick, 2009.
8. CP Rogers, All you ever wanted to know about carbon trading 6.0: On the up. JP Morgan Europe Equity Research, 1 July 2008, 30pp.
9. I Odler, *Special Inorganic Cements*. UK, Spon, 2000, 395pp.
10. QY Chen, M Tyrer, CD Hills, XM Yang, P Carey, Immobilisation of heavy metal in cement-based solidification/stabilisation: A review. *Waste Management* 29 (2009) 390–403.
11. D Geysen, C Vandecasteele, M Jaspers, G Wauters, Comparison of immobilisation of air pollution control residues with cement and with silica. *Journal of Hazardous Materials B107* (2004) 131–143.
12. SL Garvin, CS Hayles, The chemical compatibility of cement-bentonite cut-off wall material. *Construction and Building Materials* 13 (1999) 329-341.
13. JH Sharp, J Hill, N.B. Milestone, E.W. Miller, Cementitious systems for encapsulation of intermediate level waste. *Proceedings of ICEM03 (9th Int. Conf. Radioactive Waste Mgt. and Environmental Remediation, Oxford, 2003)*. ASME, 2003 paper Icem03-4554, 9pp.
14. NDM Evans, Binding mechanisms of radionuclides to cement, *Cement and Concrete Research* 38 (2008) 543–553.
15. J Li, J Wang, Advances in cement solidification technology for waste radioactive ion exchange resins: A review. *Journal of Hazardous Materials B135* (2006) 443–448
16. R Taylor, IG Richardson, RMD Bryson, Nature of C-S-H in 20 year old neat ordinary Portland cement and 10% Portland cement-90% ground granulated blast furnace slag pastes. *Advances in Applied Ceramics* 106 (2007) 294-301.
17. GJ Mount, Clinical performance of glass-ionomers, *Biomaterials* 19 (1998) 573-579.
18. MAA De Bruyne, RJH De Moor, The use of glass ionomer cements in both conventional and surgical endodontics. *International Endodontic Journal* 37 (2004) 91-104.
19. GJP Fleming, AA Farooq, JE Barralet, Influence of powder/liquid mixing ratio on the performance of a restorative glass-ionomer dental cement. *Biomaterials* 24 (2003) 4173-4179.
20. PLJ Domone, Chapter 20 Strength and failure of concrete, in *Construction Materials (3rd Ed)*, eds. JM Illston & PLJ Domone. UK Spon/Taylor & Francis, 2001 pp161-175.
21. J Camilleri, Characterization and chemical activity of Portland cement and two experimental cements with potential for use in dentistry. *International Endodontic Journal* 41 (2008) 791–799
22. SV Dorozhkin, Calcium orthophosphate cements for biomedical application. *Journal of Materials Science* 43 (2008) 3028-3057.
23. LM Grover, U Gburek, AJ Wright, JE Barralet. Cement formulations in the calcium phosphate $H_2O - H_3PO_4 - H_4P_2O_7$ system. *Journal of the American Ceramic Society* 88 (2005) 3096 – 3103.
24. AJ Ambard, L Mueninghoff, Calcium phosphate cement: review of mechanical and biological properties. *Journal of Prosthodontics* 15 (2006) 321-328.
25. WJEM Habraken, JGC Wolke, JA Jansen, Ceramic composites as matrices and scaffolds for drug delivery in tissue engineering. *Advanced Drug Delivery Reviews* 59 (2007) 234-248.
26. MP Ginebra, T Traykova, JA Planell, Calcium phosphate cements as bone drug delivery systems: A review. *Journal of Controlled Release* 113 (2006) 102-110.
27. Anon, Ring boss admits theft of bones. UK News section, *The Guardian* 19 March 2008 p13.
28. J Stampfl, R Liska, New materials for rapid prototyping applications. *Macromolecular Chemistry and Physics* 206 (2005) 1253-1256.
29. P Purnell, R Williams, G Gibbons, E Farahi, 3D printing of cement composites: preliminary experiments. *Extended Abstracts, Cement and Concrete Science, University of Manchester, UK* 15-16 Sep. 2008 pp113-118.
30. U Gburek, T Hölzel, U Klammert, K Würzler, FA Müller, JE Barralet, Resorbable dicalcium phosphate bone substitutes prepared by 3D powder printing. *Advanced Functional Materials* 17 (2007) 3940-3945.
31. BA Gama, TA Bogetti, BK Fink et al., Aluminium foam integral armour: a new dimension in armour design. *Composite Structures* 52 (2001) 381-395.
32. A Loukili, A Khelidj, P Richard, Hydration kinetics, change of relative humidity, and autogenous shrinkage of ultra-high-strength concrete. *Cement and Concrete Research* 29 (1999) 577-584
33. W Bramshuber (ed), *State Of The Art Report: RILEM TC 201 “Textile Reinforced Concrete (TRC)”*. RILEM, Bagneux, France, (2006).

34. MH Zhang, VPW Shim, G Lu, CW Chew, Resistance of high-strength concrete to projectile impact. *International Journal of Impact Engineering* 31 (2005) 825-841.
35. E.E. Anyanwu, Review of solid adsorption solar refrigeration: *Energy Conversion and Management* 44 (2003) 301–312 (pt. I) and 45 (2004) 1279–1295 (pt. II)

DRAFT

15 Jun 09

DRAFT

15 May 09