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Current themes in cement research

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1. Introduction

Cement is one of few modern processed materials known worldwide to layman and expert alike. There are few people in the world who have not watched a brick laid, a wall rendered or a fencepost set. The large fraction of the world's population who live in urban areas are often surrounded by concrete – a composite ceramic of hydrated cement and aggregate – throughout their working day and their evening rest. Cement, more than any other material, defines modern urban life. Annually, 2.7 billion tonnes are manufactured around the world[1], which in turn makes 20 billion tonnes of structural concrete, foundations, blocks and paving slabs, mortar and rendering, roof tiles and other products.

Familiarity, it is said, breeds contempt and this ubiquity has indeed fostered a few popular and technical misconceptions about cement and concrete. The first, and perhaps most pernicious, is that such a mature technology – Joseph Aspdin patented Portland cement in Leeds, England in 1824 – must be completely understood. What can there possibly be left to learn about such an omnipresent and venerable material? A brief look at the parlous state of many of the relatively modern concrete buildings that blight your nearest city should alert your suspicions in this regard. Secondly, cement is normally only associated with construction projects, from the simple mortar maintaining the brickwork of our houses to the complex concrete used in large civil engineering infrastructure components such as bridges. But why should a material so useful on such a grand range of scales remain the sole preserve of the construction industry? In fact, it is not; for example, your dentist may well have put some in your teeth… Thirdly, even within the wide remit of its traditional uses, there is an enormous diversity of classes, blends, formulations and recipes of cement and concrete. We often talk about cement and concrete as though they were simple, invariable, materials with generic attributes and properties, yet the variety of cements and concretes used in construction today - and thus the ability to tailor a concrete to perfectly fit a given situation – far outstrips that of timber or steel.

Here, we highlight recent research that dispels these myths and misconceptions, showcasing cement and concrete as vibrant, hi-tech, bespoke materials providing cost-effective and technically appropriate solutions to both traditional and modern problems. In particular, we will review some of the wide variety of cutting-edge research presented over the last few years at the annual Cement & Concrete Science

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As is traditional when discussing cementitious systems, which are generally compounds and combinations of metallic oxides, we use a shorthand notation to refer to cement phases: C = CaO, S = SiO_2, A = Al_2O_3, F = Fe_2O_3, H = H_2O, P = P_2O_5, Š = SO_3 and Č = CO_3. For example, the main reactive phase in Portland cement, alite Ca_3SiO_5, is referred to as C_3S and the minor hydration product portlandite $Ca(OH)_2$ is referred to as CH.

Innovative analysis and characterisation

As Professor John Sharp said in his Mellor lecture and paper, “We know all about cement - don’t we?”[2] The question mark throws this assertion into doubt. If we knew all there was to know about this most ubiquitous material then there would be no need for any further research. There would be no need to use transmission electron microscopy to examine the structure of calcium silicate hydrate – the built environment’s glue[3]. We would not be using dynamic SEM to view the hydration of cement on the micro-scale[4] or *in-situ* Raman spectroscopy to observe the real-time formation of hydration products on clinker mineral surfaces[5]. All of this work has helped to give valuable insights into the complex interplay of the chemical and the physical in the development of hydrated cement pastes.

Cement and concrete science has moved beyond the days of parametric studies, mixing cubes and testing them to destruction - the traditional make ‘em and break ‘em approach. Nowadays a wide variety of different analytical techniques is used to probe the fine, complex, highly heterogeneous structure of cement clinker and hydrated cement paste.

Conventional analytical methods have been used extensively for many years in cement science, including thermal analysis, x-ray diffraction and fluorescence, scanning electron microscopy and wet chemical methods. Whilst these were all valuable, they all left unanswered questions, being restricted to, say, bulk analysis, identification of crystalline compounds only, or otherwise missing the fine interplay of the myriad of species present cement or concrete. Technological advances have enabled us to probe, in ever finer detail, some of the complex minutiae within cement and concrete, increasing our understanding of the structure and performance of the world’s key construction material.

It is known that the principal binding phase in hydrated Portland cement is calcium silicate hydrate, commonly abbreviated to C-S-H according to the standard cement chemistry notation. It is also known that this C-S-H is poorly ordered, and that its composition depends on curing conditions and the presence of additional materials such as fly ash or slag[6]. However, the precise structure of C-S-H remains elusive, and there has been considerable discussion, disagreement even, within the scientific literature as to its structure. Early models suggested a mixture of nanometer sized 14 Å tobermorite ($Ca_5[H_2Si_6O_{18}].8H_2O$) and jennite ($Ca_9[H_2Si_6O_{18}](OH)_8.6H_2O$) domains[7], with subsequent models based on solid solutions of tobermorite and portlandite ($Ca(OH)_2$)[8] or isolated silicate chains of variable length and OH content, intergrown with $Ca(OH)_2$[9]. In fact, the precise structure of C–S–H depends upon the system in question, but appears to be a combination of the tobermorite–jennite model and the tobermorite–portlandite model[6]. However, determination of the structure of C-S-H has been a driving force in the field for many years.

The use of neutron scattering in its many guises led to the proposition that C-S-H could be represented as comprising high and low density regions[10], and subsequently revealed variations in the distribution of the water around the C-S-H grains[11]. Similarly, nano-indentation has been used to characterise cement hydration products and also shown a bimodal distribution[12]. Both nano-indentation and neutron scattering have been used to validate a recently revised model for calcium silicate hydrate[13]. However, the interpretation of the nanoindentation data has recently been questioned[14].

A more conventional probe of hydrate structure is nuclear magnetic resonance (NMR) spectroscopy. Skibsted and Hall gave a thorough review of the capabilities of NMR in cement science[15], showing how ^{29}Si and ^{27}Al MAS NMR can be used to determine average silicate chain length and the degree of aluminium incorporation into the (alumina)-silicate structure[16,17]. The low natural abundance of suitable isotopes of other elements has limited the application of NMR primarily to Al and Si, although there has been isolated work, for example, ^{33}S NMR[18]. A valuable use of NMR is in conjunction with transmission electron microscopy (TEM) to provide valuable information on C-S-H composition and structure[3,16,19,20,21]. The combination of morphological and compositional information which can be obtained from this combination of techniques has shed light on the composition of hydrated phases in cement.

Other approaches have been employed to study hydrated phase structure. Building on work in the field of mineralogy, x-ray photoelectron spectroscopy has been used to examine the earliest stages of cement hydration[22] and probe the silicate structure of fresh[23] and aged[24] C-S-H phases, and now in this issue for the first time hydrated aluminate phases formed upon the exposure of cement clinker to water vapour[25]. The extreme surface sensitivity of this technique has been employed to look at the earliest stages of both hydration and sample ageing.

XPS and NMR studies have all shown that C-S-H ageing leads to silicate polymerisation, with fresh pastes comprising dimers, (Q^1), which transform to chains (Q^2) upon further hydration[26]. Subsequent polymerisation of the C–S–H gels to sheets (Q^3) and 3D structures (Q^4) is possible in mature and partly carbonated cement pastes[27].

A great many other techniques have been used to investigate the structure of hydrated cements and changes occurring during ageing. These include vibrational spectroscopic techniques such as Raman and Fourier Transform Infra-red (FTIR) spectroscopy and microstructural probes such as transmission electron microscopy (TEM), focussed ion beam (FIB) microscopy and x-ray microtomography. More recently has seen the advent of hyphenated techniques combining microscopy and molecular probes such as Raman-SEM.

FTIR has not found a great deal of application in cement science, primarily due to problems associated with the intense bands due to water often obscuring many of the fine bands in the spectra of hydrated cement pastes. However, there have been some isolated studies. Fletcher and Coveney used artificial neural networks and FTIR spectra to predict the thickening times of cement pastes[28], whilst Ylmen used FTIR and other techniques, to follow the early stages of cement hydration, with the changes in spectra being related to changes in silicate structure[29]. García Lodeiro *et al*. have also used FTIR to study the structure of C-S-H gels, plus the phases found in geopolymer systems (vide infra), i.e. calcium aluminate silicate hydrate (C-A-S-H) and sodium aluminate silicate hydrate (N-A-S-H) gels[30-32].

A complementary technique to FTIR is Raman spectroscopy, pioneered in the 1970s by Bensted[33], and then with isolated exceptions[34] ignored until recently, when instrumental advances made the technique more favourable. Recent years have seen the burgeoning use of Raman spectroscopy as a molecular probe, taking advantage of the technique's ability to 'see' through water by following hydration [5,35-38], or then using the information gleaned from the spectra to look at changes in structure with changes in either composition or ageing[39,40]. The high spatial resolution available from modern spectrometers has also opened up new possibilities, obtaining information from heterogeneous cement pastes, both traditional, e.g. Portland cement[36,41] or lime[42], and more developmental, e.g. calcium sulphoaluminate cements[43], or then looking at traditional cements in novel environments, such as the use of Portland cement as a dental material[44]. There is then also the aforementioned work using the latest development, attaching a Raman spectrometer onto a low vacuum scanning electron microscope to enable combined structural information (from the Raman spectra) with morphological and chemical information from the SEM and EDX system. The technique was proved suitable for clinker analysis[45], but the potential is there to examine now the complex interplay of chemistry and morphology in hydrated systems.

The ability to probe the microstructure of cementitious systems is a key aspect of modern research, with paste morphology playing a key role in defining transport properties and therefore durability. Transmission electron microscopy has been used on many occasions to investigate the nanostructure and elemental composition of C-S-H formed under different conditions. Richardson showed how C-S-H could be foil-like or fibrillar depending upon hydration conditions or the presence of slag or pfa[6], with the microstructure of the C-S-H becoming finer over time[3], and being dependent upon temperature[21]. Moving from the nanoscale to the microscale there have been numerous uses of electron microscopy, but that of Gallucci and Scrivener was particularly interesting in that it was the first demonstration of wet SEM technology in cement science[4]. Here, the use of a thin electron transparent film held over a hydrating cement paste enabled hydration to be followed almost in real time. Edwards *et al*. meanwhile used focussed ion beam microscopy to examine the microstructures of lime-waste glass blends[42], whilst x-ray microtomography has been used to examine the three dimensional arrangement of cement paste, aggregates and pores in a hydrated concrete[46].

In summary, the section above is by no means exhaustive, and yet is shows clearly that characterisation of cement and concrete is a field exploiting some of the recent advances in materials characterisation to the full, and given the continual evolution of both analytical equipment and cements themselves, this is likely to continue for a long time to come.

Cementing the future: novel applications for cement

It is difficult to obtain figures on the proportion of the cement manufactured annually that is used outside the construction industry, but it seems reasonable to assume that it would be less than 1% in terms of weight or volume. Nevertheless, in terms of value, there is a rather more significant market for cement and related materials in novel applications. Established alternative markets include refractory materials and the management of various pernicious waste streams, from contaminated ‘brownfield’ land remediation to encapsulation of intermediate level radioactive waste for long-term repository storage. There is a rapidly emerging market in specialised cements for medical applications, especially in dental and bone surgery. Concrete is increasingly used by sculptors and artists to realise forms and concepts that cannot be achieved by other media. Research groups around the world are turning to cements for applications as diverse as rapid prototyping, rainwater harvesting and storage in the developing world, or retrieval of sea-bed instrumentation. These and other applications exploit some combination of cement’s unique suite of properties – activation by aqueous solution; initial fluidity; room-temperature/pressure curing; complex, microstructure combining amorphous and crystalline phases; tunable chemistry, strength, stiffness, porosity and adsorptivity; and relative cheapness and abundance – to provide solutions that cannot be economically achieved with other materials.

3.1. Refractory materials

Refractory cements exploit the ability of calcium aluminate cements to form ceramics that retain their integrity at high temperatures. Calcium aluminate cements (CAC) hydrate to form mixtures of microcrystalline CAH_{10}, C_3AH_6 and amorphous AH_3. Above 300°C, these compounds dehydroxylate; at around 700°C the residual minerals fuse, replacing hydrated bonds with ceramic bonds. Combined with appropriate aggregates, heat-resistant concrete can thus be made. This is used for high-temperature insulation, furnace bodies and chimney linings in preference to traditional refractory bricks, either to prevent heat and/or gas loss joints, or to form more complex functional shapes. Simple refractory castables are stable up to 800°C while more specialised, complex formulations can be used up to 1850°C[47].

3.2. Waste management

Cement is crucial to many waste management technologies. It has a unique three-pronged ability to immobilise pollutants; physically solidify the waste by physico-chemical adsorption of pollutant ions by the poorly crystalline hydrated phases, and reduce the solubility of heavy metals by virtue of the cement pore solution chemistry. For example, zinc, lead and cadmium are immobilised by chemical precipitation, since in the high-pH environment of a cement grout they form insoluble hydroxides. Copper, zinc and chromium can react with the calcium in the cement to form double hydroxides. Many ions can be incorporated into the hydrated gel phases by substitution; nickel and cobalt for calcium, and chromium for either calcium or silicon[48]. This makes it particularly well suited for situations where a wide or poorly characterised range of problematic ions may be encountered, such as in contaminated brownfield sites.

A particularly well established application is in the stabilisation of intermediate-level radioactive waste. As well as the attributes listed above, cement provides an encapsulant with low permeability and a degree of radiation shielding. It can cope with most of the huge range of ions encountered, particularly in those poorly-characterised wastes associated with legacy and research reactors; Evans lists 29 in his review[49]. The standard approach is to place the waste into large (~0.5 – 3 m^3) stainless steel containers, which are then filled with a fluid Portland cement based grout modified with up to 90% w/w pozzolanic (reactive silica-bearing) powders such as pulverised fuel ash or ground granulated blast-furnace slag. These additives slow the reaction rate and thus heat output, reducing the risk of thermal gradient-induced cracking, and also reduce the permeability of the cemented wasteform. Although these simple PC-based systems have been successfully used for many years, they are not ideal for all applications. For example, there are some concerns over the long-term stability of reactive metal wastes such as magnesium and aluminium derived from fuel rod casings[50]. These can react with the free OH^- ions in the cement pore solution to produce gaseous hydrogen and special modifiers such as sulphates may be added to the cement to modify the corrosion behaviour[51]. Other problems, include interference with the hydration reactions by certain ions (e.g. phosphates, zinc and tin) causing retarded setting and hardening, reactions with iron flocs in the waste forming porous hydration products, and degradation of cellulose. Fortunately, there are a large range of cement chemistries – e.g. calcium aluminates, calcium and/or magnesium phosphates, calcium sulpho-aluminates – that can be investigated for encapsulating any given waste, and employing a diverse ‘toolbox’ of different cement systems can help to cope with a wide range of immobilisation challenges[52]. Alkali activated systems, such as the so-called 'geopolymers', could potentially be particularly useful for ions such as caesium whose high solubility at any pH makes encapsulation in cement problematic. By using CsOH as the activating alkali, preliminary work suggests that 50-75% of the Cs used is sufficiently well incorporated into the ceramic structure to be prevented from leaching out[53]. However, knowledge the long-term behaviour of both novel and traditional systems – measured in thousands of years for radioactive waste immobilisation – is still incomplete. Even in well characterised systems, examination of the microstructure of the cements after 20 years shows they are still changing, contrary to popular belief[3].

3.3. Biomaterials

The ability to mould a soft material into shape and then let it harden into a functional component is as attractive to surgeons as it is to structural engineers. There are many cement systems that are compatible with the human body and thus a range of inorganic biocements are available to compete with traditional repair materials such as dental amalgams, polymethylmethacrylate bone cements and surgical steel. Cements for therapeutic use fall into three chemical families; calcium phosphates (CP), glass-ionomers and those based on traditional cements or plasters. The most extensively researched are probably the various inorganic bone cements used in orthopaedic surgery and reconstruction. These are calcium phosphate powders activated either with water, ortho- or pyro-phosphoric acid. They may hydrate to form a range of calcium phosphate minerals, including hydroxapatite ($Ca_{10}(PO_4)_6(OH)_2$, the mineral component of bone), brushite ($CaHPO_4.2H_2O$) or DCPP (dicalcium pyrophosphate) ($Ca_2P_2O_7$). The degree of crystallinity and size of crystals formed is controlled by, among other things, the pH of the activating solution and the size of the precursor powders. CP cements have many advantages over polymers, their main competitors: they can be placed either by hand or by injection; they are non-toxic, being based on bone chemistry; they have comparatively minimal temperature rise during setting; they bond well to parent bone; and are relatively low cost[54,55]. However, the unique selling point of CP cements is that they are absorbed by the body over time, acting as a scaffold for – and eventually replaced by – natural bone. The timescale of replacement varies from 3 – 36 months, depending on the cement chemistry and hydrated porosity[56]. Attempts have been made to further increase the biocompatibility by using blood plasma as the hydrating fluid but this can affect setting and hardening behaviour[57]. The inherent porosity of most hydrated CP cements (~40-50% at an average of 8 – 15 μm)[56],[58] permits sufficient nutrient transport for surface bone growth but does not allow intergrowth, so artificial pore-forming agents are often added to encourage bone to colonise the implant. These have a detrimental effect on strength, particularly tensile strength, which is generally only 1 – 10 MPa (despite the compressive strength being comparable to that of bone, 10 – 100 MPa). This is currently the major limit on the applications in which CP cements can be used, restricting it to non-primary load bearing repairs (e.g. maxillofacial surgery) unless reinforced with stainless steel frameworks. Attempts to increase the inherent strength by e.g. using organic polymer acids as the activating liquid to produce a polymer-modified cement have had limited success so far[59]. Strengthening continues to be a focal research area. An alternative approach is to use the CP cement system to make precursor green forms for implants which are subsequently sintered to give high strength. It is particularly useful for forming calcium pyrophosphate ceramic implants, which are more bioactive than hydroxyapatite ceramics. This approach is quicker and easier than the traditional method of producing green forms (high pressure slurry compaction at ~300 MPa) which cannot form complex organic shapes and is associated with significant shrinkage[60].

The inherent porosity of CP cement systems does however combine with their low hardening temperature to offer a unique advantage over other systems; the ability to be impregnated with drugs and then slowly release them at the repair site in a controlled manner. As in any system, tailoring the micro/nano scale porosity is the key to controlling the drug dose rate. Since this is easily done in cements by varying the powder/liquid ratio, they are an ideal slow-release, topical delivery mechanism. For example, growth factors can be delivered more effectively and safely by CP cements than injections[61] and two-stage control of the release rate of antibiotics can be achieved via a surface mechanism where release proportional to the square root of time (and thus presumably diffusion controlled), and a CP resorption release mechanism proportional to time[62].

Glass ionomer cements are widely used in almost all aspects of dentistry, from cavity lining to cosmetic reconstruction. They are fluoro-alumino-silicate glass powders activated with organic acids. As with CP systems, they compete with polymer-based materials, offering increased biocompatibility and greatly reduced toxicity and heat generation during hardening as their main advantages[63]. They also slowly release fluorides into the repaired tooth area, encouraging natural bonding and remineralisation, although the nature and formation of interface between the cement and tooth substrate is poorly understood[64]. Powder and liquid fractions may be supplied ‘pre-proportioned’, or dental professionals can mix their own cement formulations either to suit a particular application, for economic reasons or simply to retain greater control over the process. As with all cements, the powder-liquid ratio (p/l) controls the mechanical properties but biomaterials researchers often attribute the declining strength with increasing p/l to reduced relative aggregate fraction, e.g. [65], rather than to the well-known porosity effect first established for construction cements by Feret in 1896[66]; this seems unlikely and worthy of further research and clarification.

Some use is made of traditional cements and related materials in medical applications. Plaster of Paris is a well known example (although not strictly a cement, since it loses integrity when wet) but in general calcium sulphates dissolve too rapidly to be used inside the body[60]. They may be used to adjust the setting and hardening rates of other biocements[67]. Another dental material, the flamboyantly named ‘mineral trioxide aggregate’ (MTA)[68] is actually a simple mixture of ordinary Portland cement with bismuth oxide. It is used in root canal surgery, where it seems that the calcium hydroxide produced during its hydration acts both as an antiseptic and to encourage beneficial cell growth[69]. Research into its hydration chemistry and properties in a biomaterials context seems to be undertaken without reference to the 100 years worth of literature on Portland cement available to construction researchers; as with GI cements, there is clearly scope for synergies to be developed by increasing dialogue between these two communities.

3.4. Emerging applications

Cement and concrete are used in small quantities in other fields. Sculptors are increasingly turning to concrete as a unique medium in which novel and engaging forms can be created, including Turner Prize winners Antony Gormley (*Allotment*, 1993) and Rachel Whiteread (*House*, 1993). More recently, Royal Academician Anish Kapoor has experimented with using concrete for huge sculptures that blur the boundaries between architecture and art, including using a ‘concrete piping’ machine to create a series of sinuous, primaeval ‘wormcast’ sculptures at his 2009 Royal Academy exhibition. A more prosaic extension of this idea is the use of cement for 3D printing, a manufacturing/prototyping process that prints bespoke forms direct from a CAD model by using ink-jet technology to imprint successive thin layers of powder with liquid reactant (i.e. water). Commercial 3D printing systems use plaster-based powders and the resultant forms are weak and susceptible to moisture damage. By replacing the plaster with hydraulic cement, stronger and more durable forms can be produced. Proof-of-concept of this has been demonstrated, showing favourable strength-density correlations[70] although significant optimisation of process parameters still remains to be carried out. Some investigators have used novel processing methods for cementitious materials, such as compression moulding and supercritical carbonation, carried out with the aim of producing high-performance and/or sustainable ceramics for various applications [e.g. [71]. Others have taken a converse approach, exploiting our knowledge of a particular concrete deterioration mechanism – thaumasite attack – to produce a material with carefully controlled degradation behaviour, designed to release instruments from the seabed after a specified period[72]. Concrete is also finds uses in the developing world outside of construction. Cement mortars are used to build rainwater harvesting tanks placing the material in tension. Large local variations in material and artisanal quality require that robust design methodologies to determine optimum material and structural design parameters are established[73].

Cutting-edge construction: new cementitious materials for established applications

Whilst the Earth's geology[74] dictates that the most common cementitious material comprise primarily ofcalcium, silicon and aluminium, there are an increasing number of alternatives to Portland cement being reported in the literature, e.g. to name but a few; hydraulic lime[42,75] , geopolymers[76], activated slags[77] and sulphoaluminate cements[78-80]. A key driver in these developments appears to be a desire to reduce abiotic depletion and find a practical application for materials currently considered to be wastes[75, ,77 ,81]. There are also a number of approaches based on traditional, i,e. Portland cement, binders, but with a non-traditional pre- or post-treatment step, such as sol-gel synthesis[82] or hydrothermal treatment[83,84].

Hydraulic limes have been used for millennia, but it was Smeaton who perhaps pioneered their use in modern civil engineering during the construction of the Eddystone Lighthouse, realising that hydraulic behaviour was related to the clay content from which the lime was made. Recently, there has been a resurgent interest in hydraulic limes, particularly in the heritage sector where the material's perceived environmental benefits are touted. It may be argued that there is nothing novel in using technology available since Roman times, but more recent applications have strived to combine the use of hydraulic limes with novel materials such as ground glass cullet and other waste materials, using the lime to induce a pozzolanic reaction. Zawawi and Banfill effectively synthesised artificial hydraulic limes from a low-silica limestone blended with waste siliceous materials such as pfa, burnt shale and glass cullet[75]. They showed that ground glass reacted with the lime thus helping the mix to develop strength. Edwards *et al.* similarly investigated the behaviour of hydraulic lime mortars mixed with ground glass cullet, using a range of novel analytical techniques to show the formation of C-S-H as a binding phase[42].

Perhaps the opposite extreme to lime-based systems are geopolymers. When Davidovits coined the term he intended that it refer specifically to calcium-free materials[76]. However, the term is now used more liberally, being applied to both calcium-free and calcium-bearing materials formed by mixing concentrated alkalis (>8 M) with glassy aluminosilicates. Duxson *et al*. provided a thorough review of geopolymers and their applications[85], stating how their rapid strength development, dimensional stability and chemical resistance made them suitable for construction purposes. However, geopolymers have also been shown to have excellent thermal barrier properties[86] and, as mentioned earlier, be suitable for waste immobilisation[53]. Aside from alkali activation, 'geopolymeric' systems have also been made by activation with sodium silicate[77] or other activators, such as sulphate, as presented by Collier *et al*. later in this issue[51]. Many of these alternative systems strive to improve their environmental credentials by utilising waste materials such as slags, fly ash or other such wastes, thus reducing the depletion of the World's natural resources. This approach has also been used in the manufacture of Portland cements[87] and alternatives such as sulphoaluminate cements, which can be made in standard cement kilns, but at slightly lower temperatures and using waste as raw materials[78-80]. More recently, and still at the laboratory scale, Dovál et al. used a sol-gel process followed by thermal treatment at between 600 and 1250°C to synthesise highly reactive gehlenite (C_2AS) and C_2S.

Another approach to low energy construction systems is autoclave curing under saturated steam pressure where quartz, lime and clay react, with or without cement, at temperatures of 100 to 300°C. Such treatment often leads to the formation of crystalline calcium silicate hydrates such as tobermorite or xonotlite, and the resultant strong, yet porous, blocks find application for their insulating properties[88,89] or as a filler to improve the flexural properties of cement matrices[90]. Recently there have been studies looking at replacing calcium with magnesium without significant changes in either performance or morphology[83], or looking at changes in morphology with steam temperature or duration of treatment[84]. Research into hydrothermal treatments of silicate based systems is still ripe for further development, with a wide range of applications available for this low energy material.

Conclusions

This paper has shown that there is far more to cement and concrete science than is normally believed. Novelty comes in many guises, from the application of novel characterisation techniques, through novel applications of conventional cements to novel alternatives to Portland cement. The remaining articles in this Special Issue continue this theme, broadening cement and concrete science beyond its normal boundaries and encompassing the three themes given above. Dubina *et al*. have used a broad array of analytical techniques to look at the first stages of the interaction of cement minerals with water vapour, the process known as prehydration. Alternatives to Portland cements are discussed by Collier *et al*., looking at sulphate activated matrices for waste immobilisation, and by Tyrer *et al*. who investigate the potential for carbon reduction by the use of industrial wastes in cement and concrete. Finally, novel applications of cements are then covered by the remaining papers. Gibbons *et al*. show that 3D printing of cementitious materials is a possible route for rapid prototyping. Bolarinwa *et al*. discuss the application of phosphate cements in bone replacement, Xiang et al. investigate the use of super absorbent polymers to produce self-healing cement, and finally Justnes *et al*. have turned conventional concrete design on its head designing concrete blocks with service lives of only six months for very specific applications.

In summary, it's fair to say that even after all these years, "We don't know all about cement, do we!"

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