

Innovation in Use and Research on Cementitious Material

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ABSTRACT

In this paper we discuss innovations in concrete technology which are currently being applied in the field – namely high and ultra high performance (strength), and self consolidating concrete. We discuss the factors which have enabled these developments and ongoing needs in these areas. The importance of sustainability as the major driver for future innovations and prospects for development of new cementitious materials with lower environmental impact is briefly discussed. Finally the importance of innovation in research is examined. The dramatic development in experimental and computational techniques over recent year opens up wide-ranging possibilities for understanding the micro- and nano- scale chemical and physical processes which underlie performance at a macroscopic level. The example of computational approaches at the atomic and molecular scale is presented in detail. In order to exploit the opportunities presented by such new techniques, there needs to be greater efforts to structure interdisciplinary, multi-group research.

1. INTRODUCTION

In terms of volume used, cementitious materials, mainly in the form of concrete, are the most successful materials in the world. Every year more than 1 m^3 is produced per person worldwide. This success stems from the ease with which a mixture of grey powder and water can be transformed into a highly functional solid of readily manipulated shapes at room temperature. Furthermore it is a low cost, low energy material made from the most widely available elements on earth. However, despite having a lower environmental impact than most alternative construction materials, the huge volumes of cement and concrete produced mean that cement production accounts for some 5-8% of man-made CO_2 emissions. Therefore there is increasing pressure to innovate to improve sustainability.

More broadly, innovation is *the process of making improvements by introducing something new*. This is not easy for cementitious materials, whether these innovations are directed at improving performance or at increasing sustainability. There are 3 main barriers to innovation:

- i) **Structural Safety**: Building and structures have service lives of 50-100 years and more. They are expected to function for such long

periods without catastrophic failure and with little or no surveillance and maintenance. The dire consequences of catastrophic failure in terms of loss of life lead to a conservative approach to codes and standards and a need to demonstrate performance over long time scales.

- ii) **Empirical knowledge base:** Limitations in our knowledge of the physical and chemical processes underlying the performance of cementitious materials at the macroscopic level mean it is often necessary to test new materials iteratively at nearly full size. This leads to incremental development. This situation can be changed by investing in fundamental research to underpin new developments.
- iii) **Market Niche and Critical Mass:** The fundamental reason for such widespread use of cementitious materials is because they are *cheap*, very cheap! From a mechanical point of view, at least, the performance of cementitious materials is not marvellous. Innovations in performance that involve significant increases in cost, however, quickly bring them into the price range of competitive materials such as steel, with which it is difficult to compete on a basis of performance. This was one of the main reasons that so called macrodefect free, cements, MDF, have never really found commercial application. Solutions to the much talked about problem of moisture susceptibility of MDF can be found, but the high materials and processing costs mean that they have never been competitive with alternative materials – metals, plastics or ceramics.

This problem is further compounded by the need for an innovation to achieve critical mass. The production efficiency of cementitious materials increases tremendously with scale. The increases in such factors as cost and energy requirements in going from a small scale shaft kiln to a small rotary kiln to a large state-of-the-art plant are two to three fold. Furthermore, the efficiency of a modern plant is strongly related to the stable production of clinker of a constant composition. This means the cost and waste associated with producing “special cements” is very large. Even for fairly successful special cement, a years worth can be produced in a week or so. Changing the production conditions involves several days on either side of this, and the *transition* product must then be disposed of. Such production constraints alone can multiply costs several times.

The problem of critical mass is worsened by the business model of cement manufacturers being related to dealing with large scale production and cost optimisation. It is difficult to develop and nurture innovative products within this business ethic.

Having outlined the barriers to innovation, we should neither be too pessimistic about the prospects for improvement, nor too negative about

those innovations which have taken place. The imperatives behind the two main drivers for innovation: *sustainability* and *productivity* are stronger than ever and will continue to increase worldwide. Perhaps as important, we now have the experimental and theoretical tools that allow us to understand the relations between the macroscopic properties of cementitious materials and the micro- and nano-scale chemical and physical processes occurring in them.

In this paper we discuss the following:

- **recent innovations** in the technology of high and ultra high performance (strength) and self consolidating concrete that are currently being applied in the field, the factors that have enabled these developments, and further needs in these areas.
- **sustainability** as the major driver for future innovations and prospects for development of new cementitious materials with lower environmental impact (while noting that this topic is the subject of another keynote paper).
- The growing **need for a better understanding** of the micro- and nano-scale chemical and physical processes which underlie macroscopic performance and the ability of basic research to support current and future developments and the ever-increasing complexity of cementitious materials.

The rapid development of characterisation techniques and modelling provide the possibility to fulfil this need. Realising the potential of these modern approaches, however, depends significantly on better organisation of the research effort to better connect the information emerging from experimental studies and modelling approaches to applications, new materials and the acceptance of new materials..

2. RECENT INNOVATIONS IN CEMENTITIOUS MATERIALS

2.1 Increasing Strength – High and Ultra High Strength Concretes

The maximum strength of concrete used in demanding buildings and structures has increased steadily from about 40 MPa prior to 1980 to 130 MPa and more in some structures today. The strength of concrete is first and foremost a function of the spaces between the cement grains which have to be filled with hydration product. This in turn is determined by the amount of water added at the mixing stage (the water to cement ratio). The extent to which the amount of mixing water can be reduced is limited by the need to have a workable concrete that can be placed and compacted. Additives that improve the fluidity of concrete, plasticizers and superplasticisers, have been critical in the achievement of higher concrete strengths.

Early generations of cement dispersants were based on lignosulphonates or sulphonated melamine or naphthalene formaldehyde condensates. These are based on natural products, and there is little control of the basic chemical structure. Differences in performance are achieved based on molecular weight, purity, blending and the introduction of secondary chemicals to modify the properties. The most important innovation in recent years has been the introduction of PCE (polycarboxylate ether)-based plasticisers and superplasticisers. The molecular structure of PCE polymers is a comb with a backbone and side branches. By manipulation of the relative lengths of the chain backbone and side branches and the density of the side branches (Figure 1, [1]) the performance can be modified in relation to such concrete properties as workability, retention, cohesion and rate of strength development. The possibility of tailoring additives for specific purposes will likely be one of the most important sources of innovation for the future.

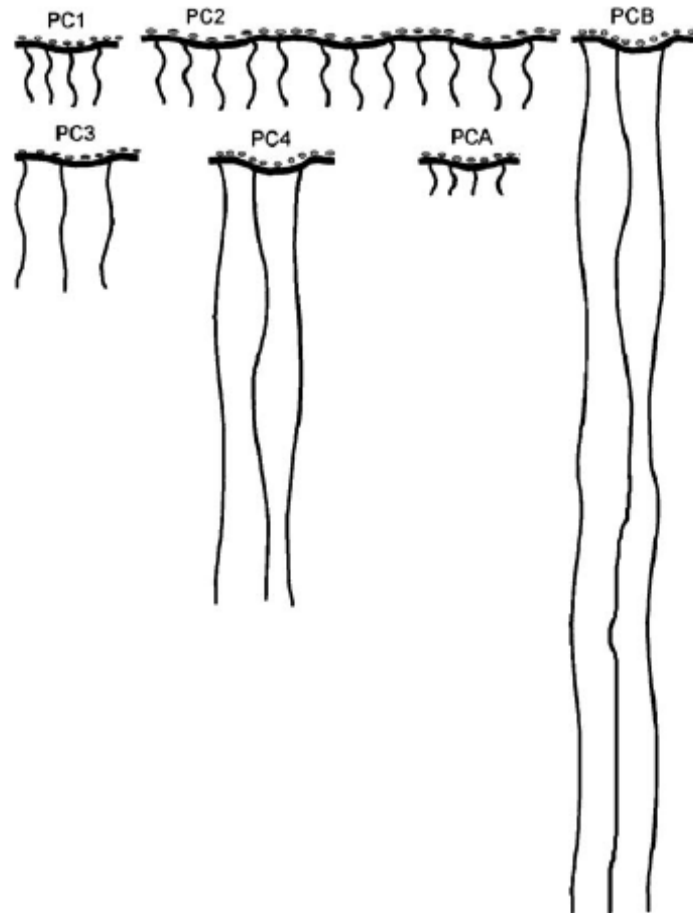


Figure 1 Schematic illustration of the molecular structure of comb-type copolymers with a negatively charged polycarboxylate backbone with grafted polyethyleneoxide side chains of different lengths. From [1]

High strength concretes also often incorporate silica fume. The main role of this additive is due to its small particle size (10-100 times less than cement grains), which allows it to fill the space between the cement grains, and increase the compactibility of the concrete. This principle of extending the range of particle sizes to improve space filling has a long history – in fact it was one of the principles used in building Roman roads. Over 100 years ago these ideas were applied to the aggregates in concrete by workers such as Ferret. However only more recently have the same concepts been applied to the binder phase. The classic idea of particle packing is based on the so called Apollonian concept, Figure 2a [2], where small particles fill the spaces left between the larger ones. However, in a concrete made strictly with such a packing arrangement, the particles cannot move, and it would be impossible to place. To combine high compactibility with good workability it is necessary to increase the proportion of fines to better separate the larger particles and allow them to move past each other, Figure 2b.

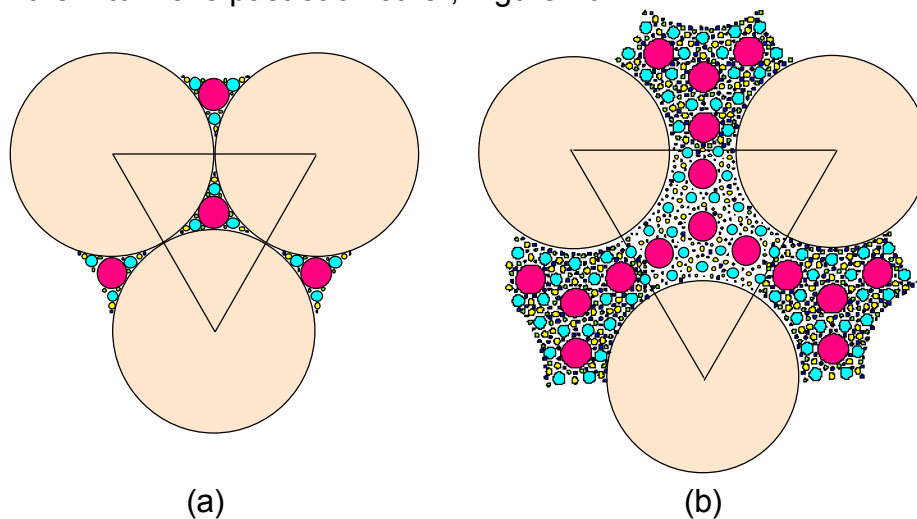


Figure 2. (a :Schematic of “Apollonian” packing, whereby the smaller particles exactly fit into the interstices left by the bigger particles.

(b : particles packing with the same packing density as in (a), but here the particles of the same class are spaced by the smaller ones, at each scale. From [2]

The optimisation of particle packing is taken to its current acme in so called reactive powder concretes. These ultra high strength concretes can have strengths up to 800 MPa in compression (when heat cured) and 50 MPa in tension [3]. They also incorporate fibres (~2% by volume), which make a crucial contribution to the increased tensile strength. Steel fibres are necessary to achieve the highest tensile strengths, but polymeric fibres – e.g. polypropylene or PVA – are also used in some cases. Indeed, mixes of two or more fibre types with differing lengths, aspect ratios, moduli, etc are increasingly being applied. Several groups are developing and promoting different varieties of such High Performance Fibre

Reinforced Cementitious Composites (HPFRCC) [4,5]. However more widespread application of such materials depends critically on the development of codes which do not rely solely on the basis of compressive strength. Interestingly, several applications of ultra high strength concrete, including the landmark foot bridge in Sherbrooke [6] have been constructed with steel tubes filled with UHPC.

Although the first motivation for the development of such concretes was improved mechanical properties, they are now usually referred to as high *performance* materials. The other aspect of performance which is improved by the reduction of water to cement ratio is the durability and hence service life, which is controlled by penetration of moisture, gas or ions through the pore structure. Many such materials contain essentially zero capillary porosity. However, concretes with low water to cement ratios are susceptible to early age cracking due to self desiccation, and the presence of cracks clearly facilitates the ingress of aggressive media. This problem has even lead to the introduction of *maximum* strengths in some applications. Some practitioners claim that early age cracking can be avoided by better water curing, and this is also a situation where the use of polymeric fibres seems to be effective.

2.2 Self Compacting (Consolidating) Concretes.

In terms of the history of concrete technology, the uptake of self compacting or consolidating concrete (SCCs) in the field has been extremely rapid. In some industrialized countries they now account for nearly 10% of ready mix concrete supplied. Self compacting concretes are attractive for several reasons.

- The concrete can be pumped straight into the forms, eliminating the need for vibrators and often also for hoisting concrete in batches to the forms. This can lead to a significant economy in manpower and reduction of construction time.
- Without vibrators, etc. there is a reduction of noise on the job site.
- The ease of consolidation of the concrete minimises defects on the concrete surface.

These materials were first demonstrated in Japan around 1988 at Tokyo University by Okamura and his students, including Ozawa and Maekawa, [7], although ironically the current use of SCCs is much lower in Japan than in Europe, for example. The main factor in the mix design of SCC is the increase in the powder content, to increase the separation of the aggregate particles, following the principle shown in Figure 2(b). As the use of cement for the entire powder fraction would be too expensive, limestone or fly ash are usually used. SCCs also rely on the use of superplasticisers and, often, viscosity modifying agents to prevent segregation. Due to the complexity of the mix design, with several admixtures the main challenge for self compacting concrete is achieving

robustness – minimisation of the variability of the concrete when there are small variations in the raw materials, temperature, humidity, etc.

3. SUSTAINABILITY AS A DRIVER FOR INNOVATION

The need to reduce the environmental impact of cementitious materials is, and will continue to be, a major driver for innovation. The use of supplementary materials is now so well established that the average clinker content of cements in Europe* is less than 80%. The most commonly used Supplementary Cementitious Materials (SCMs), blast furnace slag, fly ash, limestone, and silica fume, are industrial by-products that, by and large, can be obtained in large and regular amounts with a consistent composition. Many other materials containing reactive silica, reactive alumina or both can be used to similar effect. But these products are more variable or available in relatively small quantities. The present, empirically based approach to concrete innovation necessitates extensive testing for each individual material. Thus, while such materials may be suitable from a chemical standpoint, they are difficult to exploit practically. Better use of alternative SCMs depends on reducing testing needs by being able to predict their impact in blended systems through development of better understanding of their reaction mechanisms and better techniques for their characterisation.

A promising area of investigation for the future is the use of natural mineral deposits. Several sources of natural pozzolans are already used, but generally these are only available in certain localities. Other, minerals, notably kaolin, can be activated by thermal treatment, but often the cost of this processing makes them uncompetitive with the better established SCMs. This situation is likely to change in the future as the imperative to reduce CO₂ emissions increases (e.g. with the introduction of carbon taxes) and as the sources of traditional SCMs become fully utilised.

In fact, many sources of high quality traditional SCM are already fully utilised in concrete, and future developments in both steel and electric power production are likely to lead to lower quantities of blast furnace slag and fly ash. With regard to steel, there is intensive effort to find methods of production with lower associated CO₂ emission. Similarly, burning coal produces some of the highest amounts of greenhouse gases relative to the electricity produced. This puts into question the promotion of concrete containing very high volumes of SCMs, notably fly ash. Furthermore, there are questions about the extent to which pozzolans react at high levels of substitution (e.g. > 50% fly ash). Stoichiometric calculations show that 100g of Portland cement with a relatively high alite content of

* The figures for other countries, e.g. North America are not known. In North America it is normally the practice to add SCMs during the production of the concrete rather than cement.

70% will only produce enough calcium hydroxide to react with 12g of silica. This is consistent with the practical maximum additions of 10% silica fume and 30% fly ash (where the degree of reaction will be fairly low).

With respect to innovation, several researchers are looking beyond conventional blended cements to alkali activated cementitious systems and new clinker types. These are not discussed in detail here as they will undoubtedly be covered in the paper on Sustainability to be presented at this conference. However several points are worth noting:

- Although the feasibility of alkaline activated materials has been frequently demonstrated in the laboratory, their commercial exploitation has not been widespread due to: variability of performance, especially with changes in temperature; the high cost of the most effective alkaline activators (e.g. water glass) and the lack of robustness with cheaper activators. Alkaline activated systems are generally fast setting and the use of superplasticisers is not effective.
- Most new clinker types contain higher amounts of alumina and sulfate than Portland cement. It is difficult to find cheap sources of concentrated alumina, due to the demands of aluminium production for minerals such as bauxite. The use of high content of sulfate in the raw materials may lead to problems of controlling emissions causing acid rain.

4. RESEARCH NEEDS FOR INNOVATION

The most important thing to bear in mind is that cements and concrete are becoming more complex. The increasing range of admixtures and blending materials open up many possibilities for choice in final concrete. In order to exploit these choices we need tools to predict, for example:

- the flow and early age properties of the granular mixtures of materials;
- the phase assemblages which will form from the reaction of the different clinker minerals and SCMs;
- The pore structure which will be created
- The cohesive forces between phases and the resulting mechanical properties;
- The ingress and interaction of moisture, gases and ions into the materials and the consequences for durability;

A wide range of experimental and computational tools have become available in recent decades and are being increasingly applied to cementitious materials. Some notable examples are:

- Rietveld analysis of X-ray diffraction data to enable quantification of complex phase mixtures [e.g. 8,9,10,11]

- Scanning and transmission electron microscopies coupled with chemical microanalysis, to determine microstructural development and microchemistry of cementitious phases [e.g. 12,13]
- Nuclear Magnetic Resonance (NMR) techniques, which have provided invaluable information on C-S-H structure [e.g. 14,15,16] and the pore structure of cementitious materials [e.g. 17,18]
- Small angle neutron and X-ray scattering to probe the “mesostructure” or “gel” porosity of C-S-H [e.g. 19,20,21,22]
- Atomic Force Microscopy (AFM) [e.g. 23,24]
- Nanoindentation [e.g. 25]

The data and insight from these increasingly diverse characterisation techniques span many decades of length and time, and integrating the results into a comprehensive and predictive framework that spans the atomic to the macroscopic is one of the great challenges facing cement and concrete science and technology. Developing these approaches will require a sound theoretical and computational framework. We now discuss the current state of atomic and molecular scale computational modelling in concrete science. These methods will be essential to developing an integrated microscopic to macroscopic approach to predicting concrete properties and behaviour.

4.1 Computational Approaches at the Atomic and Molecular Scale

Atomic and molecular scale computational methods have been in existence for more than 60 years and are very highly developed. Quantum chemical and molecular potential based methods are routine components of research in chemistry, biology, and physics, but have made surprisingly little penetration into cement and concrete science. Current methods, however, can effectively address a broad range of structural, dynamical, and energetic questions that are central to understanding cementitious materials. Using this collection of techniques it is possible to effectively address questions related to the structure on lengths scales as large as 100s of nm. In this way, we can study molecular-scale dynamical properties and spectroscopic properties, diffusion and other transport properties, mechanical deformation, equilibrium energetics, and the atomic scale mechanisms controlling chemical reactivity and activation energies. As an example of the potential for innovation in research on cementitious materials, we briefly review these methods here and discuss recent applications to cements and related materials.

Computational approaches can be grouped into those based in quantum chemistry and those based on empirical or semi-empirical potentials between or among atomic or molecular entities. There are also methods, such as quantum molecular dynamics, that bridge this gap. Quantum (first principles) approaches involve solution of the Schrödinger equation

describing the interaction of electrons and atomic nuclei. The electrons are described by their wave functions, and the challenge is to adequately describe these functions in a computationally accessible way. The Schrödinger equation cannot be solved exactly except in the most limited cases. The Hartree-Fock approach involves an approximate solution to the exact Schrödinger equation, whereas Density Functional Theory (DFT) provides an exact solution to an approximate Schrödinger equation. Sherman [26] provides an accessible introduction to quantum methods and illustrations of applications to aqueous solutions.

Potential based methods, including Molecular Dynamics (MD) and Monte Carlo (MC) approaches, involve treating the atoms or molecules as classical (non-quantum) entities and computing their positions, motion, and energies as they interact with each other under the influence of potential functions. These functions describe, for instance, short range atomic repulsion, van der Waals forces, attractive and repulsive Coulombic interactions, and terms describing bond bending. MD methods follow the time evolution of the structure and energy of the computed system, thus allowing calculation of dynamical properties such as vibrational spectra. MC methods compute the relationship between the structure and energetics of the system by computing the energy of many different configurations. Cygan [27] and Gale [28] provide useful introductions to these methods. Kalinichev et al. [29] provide a more detailed discussion of applications of potential-based, molecular dynamics simulations to cement systems. Quantum (Car-Parrinello) MD (CPMD) is a potentially useful hybrid that calculates the interactions among atoms by quantum (normally DFT) methods but follows their interactions through time the way MD does [30,31,32]

Each of these methods has advantages and disadvantages, and the choice of which to apply depends on the nature of the problem. In their modern manifestations, all are computationally demanding. When well done, quantum methods are normally more accurate than potential based methods in describing atomic positions, interaction energies, and spectroscopic properties, but even with the most recent generation of supercomputers are limited to a few hundred atoms. In contrast, MD and MC trade accuracy for increased system size and reaction time. They can now be used for systems of the order of 10^6 atoms for a few ns. CPMD is very demanding, and can be effectively used for at most a few hundred atoms for a few ps.

4.2 Applications of Computational Approaches to Cementitious Materials: Current Results and Future Objectives

4.2.1 C-S-H Structure and Cement Paste Properties: One of the most important, long-standing needs in cement science (e.g.[33]) is a

quantitative understanding of the structure of C-S-H on the atomic to 100 nm scale and how the structures on this scale control the mechanical, transport, and chemical properties of hydrated cement paste. Without such understanding, it will not be possible to understand or rationally manipulate cement behaviour and such important properties as creep and drying shrinkage. Over the past two decades, spectroscopic methods, principally NMR, have provided a reasonably clear picture of C-S-H structure on the sub-nm scale. These results demonstrate that C-S-H has a local, sub-unit cell scale structure similar to layered Ca-silicates such as tobermorite and jennite and provide direct evidence for the ratios of silicon tetrahedra with different polymerizations and different numbers of Si and Al next-nearest atomic neighbours [e.g. 14-16]. These methods are, however, silent on longer range structure. In parallel, however, transmission electron microscopy (TEM) [e.g. 12,15,16] small-angle neutron and X-ray scattering (SAXS and SANS [19-22]), and ^1H NMR relaxation studies [e.g., 17] are providing direct data concerning particle morphology, surface area, pore size distribution, and fractal dimensionality on the 1 – 100 nm scale. Jennings [34] has recently developed an expanded colloidal model involving fundamental C-S-H particles with characteristic radii of the order of 5 nm and aggregates of these particles with characteristic radii of the order of 10 nm. He has applied the model to such problems as drying shrinkage, creep, and the effects of aging. The surface area and pore size distributions obtained from SAXS, SANS, and NMR relaxation studies are broadly consistent with this model. TEM observation of hydrated OPC and blended cement pastes are also generally consistent with these ideas, but show significant differences between the nanostructure of inner product and outer product C-S-H and also significant effects of the presence of blast furnace slag and fly ash [16]. For OPC pastes, the inner product C-S-H appears to consist of nearly equidimensional particles with characteristic dimensions less than 10 nm and significant inter-particle porosity on this scale. In contrast, outer product C-S-H has a more directional, fibrillar morphology on the 100 nm scale with a 3-dimensional, capillary pore system between. Each fibril consists of particles a few nm to 10s of nm long and “thicknesses” less than 5 nm, with significant inter-particle porosity.

Recently, Gmira et al. [35] (see also [36]) have used atomic-scale, potential-based energy minimization and quantum chemical calculations to investigate the mechanisms of cohesion in hydrated cement pastes based on tobermorite-like structural models. This study was based on an earlier Monte Carlo study that used simpler, non-atomistic potentials (e.g. 37, 38). The critical point with which they were most concerned is that although hardened cement pastes have strengths comparable to porous materials in which there is continuous interatomic bonding across particle boundaries (such as sandstones or bricks), nano-structural observations suggest that bonding between particles in cement paste is mediated by

the presence of water molecules. The energy minimization results show strong nm-scale cohesive forces due to hydrated Ca^{+2} ions that lead to computed bulk and Young's moduli in reasonable agreement with experimental results. The quantum chemical calculations support this conclusion and suggest that the bonding between interlayer Ca^{+2} and tobermorite-like silicate layers has substantial covalent character. The authors suggest that a combination of short range (~1-2 nm) chemical bonding and longer range (a few nm) attraction due to ion correlation effects provide for the strength of cement paste. They also suggest that the rapidly acting component of cement creep is the result of diffusion in the more open void space and the slower acting component is due to sliding of neighbouring C-S-H lamellae, perhaps by a dislocation-like process. The energy minimization techniques they used are comparable to those used in MD simulations, except that the dynamics was not followed through time.

With respect to C-S-H, the range of computational methods currently available can effectively address a broad range or related issues including the transport and chemical mechanisms of precipitation, the origin of the different nano-scale C-S-H structures, and the structural reorganization or lack thereof with time.

4.2.2 Aqueous Attack on Anhydrous Cement Phases: The attack of aqueous solutions on the surfaces of Portland cement and mineral additive grains is the critical, initiating step in hydration, but the molecular mechanisms are poorly understood. There is, however, a quite large literature describing experimental studies that show that dissolution rate increases with decreasing polymerization and that the charge balancing cation has an important secondary effect [e.g. 39,40]. Computational studies have used traditional quantum chemical approaches and have focused principally on H_2O , H_3O^+ , and OH^- attack on small molecules (up to as many as about 30 atoms) designed to simulate the Si-O and Al-O sites on the surfaces of SiO_2 and aluminosilicate phases. These studies date back as far as the 1980's (see review by Lasaga [41]), and the topic remains active [40,42,43]. These studies have shown, as expected, that both acid (H_3O^+) and base (OH^-) catalysis is highly effective in promoting dissolution relative to H_2O , and yield detailed, multi-step reaction paths and activation energies in reasonably good agreement with experimental values. Under the basic pH conditions most relevant to cement hydration, OH^- attack appears to occur by a sequence of steps involving deprotonation of a surface site that results in the attacking OH^- anion becoming an adsorbed water molecule, followed by formation of a negatively charged 5-coordinate Si species, and finally the rupture of the Si-O-Si bond.

The published studies of silicate dissolution clearly demonstrate the potential of the computational approach and pave the way to similar studies directed towards cement systems. Significant problems include not just the mechanisms of dissolution of the anhydrous phases, but the molecular speciation in solution (not just silicate polymerization, but ion pair/cluster formation), the mechanisms of precipitation of C-S-H, CH and the aluminate phases, and the mechanisms of chemical attack associated with the wide range of concrete deterioration processes.

4.2.3 Water at Surfaces and in Nano-Confinement: The physical and chemical properties of water on solid surfaces and in nano-confinement are critical and poorly understood issues in cement science. The water in AFm and AFt phases are classic examples of nano-confined structural water, and understanding the water between the 5 – 10 nm particles that apparently compose C-S-H in many situations is central to understanding the properties of cement and concrete. The study of cement cohesion by Gimra et al [35] discussed above and other studies of Cl⁻ binding in cement [44,45] and ASR gel expansion [46] are examples where computational methods have provided insight into important problems. There is a very large literature addressing general problems related to surface and confined water that is beyond the scope of this paper (e.g., 47,48,49). Kalinichev [50] and Wang et al. [51,52] provide useful reviews and introductions.

5. NANOTECHNOLOGY

A paper on innovation would not be complete without some consideration of the subject of nanotechnology. All around the world increasing amounts of research funding are being diverted into this field, which is claimed to have tremendous potential for the future. What is the importance of nanotechnology to cementitious materials?

As discussed above there is no doubt that the performance of cementitious materials is controlled by physical and chemical processes occurring at a nano level. Not least it is now widely accepted that C-S-H is composed of nanoparticles [53,54] and the intrinsic properties of these materials are beginning to be understood [55,56]. However this is more correctly “nanoscience”, whereas nanotechnology implies manipulation of structures at the nanometre level. In the area of admixtures the development of new superplasticisers is certainly taking place at this level as indicated earlier. However the potential of *nanotechnology*, in the strict sense of the term, rather than *born again chemistry*, is less clear. In other fields, notably consumer electronics, we see many innovations related to miniaturisation and multifunctionality. Such innovations come at a high cost, which is acceptable for such products in an increasingly affluent society. It seems feasible that with enough effort the nanostructure of C-S-H could be manipulated to change its properties. The question is at

what cost and whether the resulting properties would be sufficiently attractive relative to those of other materials.

For instance, one could imagine the use of nanoparticles as a way of further extending the concept of particle packing and manipulation of particle size distribution, as discussed above (Figure 2). In fact, silica fume, which may have particles as small as 100 nm, could already be considered a nanomaterial. However, as particles become smaller their relative surface increases, and already with silica fume it is necessary to add significant amounts of superplasticisers to ensure good fluidity. Furthermore, the whole essence of cement hydration is that the solid volume expands to fill the pore space, and this is already practically achieved with current UHPCs.

Another route for innovation by the addition of particles (nano or micro) is where these add new functions to concrete. Such applications are already seen with the addition of fine anatase, TiO₂ particles [57,58]. Anatase is photocatalytic, and through the absorption of sunlight has a strong oxidizing power. This prevents the build up of dirt and organic growth, preserving the clean appearance of the concrete for longer. This oxidising power can also breakdown NO_x and so contribute to reducing pollution.

The use of fibres in concrete was discussed earlier, and it is perhaps not surprising that some researchers are starting to look at the addition of carbon nanotubes to concrete. Carbon nanotubes have extremely high intrinsic stiffness and strength [e.g. 59]. However their surfaces have very low friction, so it is very difficult for them to bind together or to matrix materials to realise these extraordinary properties on a macroscopic scale. This is a field of very active development, and the current obstacles of high cost and poor binding are likely to decrease in the future. At present, however, such materials are not practical as an addition to concrete, and as already mentioned much work needs to be done on building codes even to allow widespread application of existing fibre containing concretes.

6. CONCLUDING REMARKS

Despite the obstacles, the past decades have seen significant innovation in cementitious materials. The most significant of these – high performance (strength) and self compacting concrete – have been achieved by the optimised packing of particles of different sizes, which is facilitated by the use of organic admixtures. These materials are likely to become more robust and easier to use through the possibility to design additives for different performances.

Sustainability will be the main driver for innovation in the near future and therefore we are likely to see an increasing range of supplementary

cementitious materials and even new clinker types emerging over the coming years.

Current and future innovations mean that cementitious materials are becoming more and more complex. In order to surmount the limitations of empirically based development, there is a pressing need to improve our understanding of the micro and nanoscale processes which determine the performance of cementitious materials at a macroscopic level. This is now possible through the dramatic, recent advances in materials characterisation techniques and will be facilitated by advanced computational approaches that span and connect the atomic to macroscopic length and time scales.

In order to benefit from the potential offered by such techniques, there needs to be a better organisation of research at the fundamental level to overcome fragmentation of effort. In this respect the European Network NANOCEM [60] is an example of bringing academic research groups together with the industry to carry out the basic research needed.

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