Concrete nanoscience and nanotechnology: Definitions and applications

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Abstract There are many improvements needed in concrete, especially for use in renewal and expansion of the world's infrastructure. Nanomodification can help solve many of these problems. However, concrete has been slow to catch on to the nanotechnology revolution. There are several reasons for this lag in the nanoscience and nanotechnology of concrete (NNC). First is the lack of a complete basic understanding of chemical and physical mechanisms and structure at the nanometer length scale. Another reason is the lack of a broad understanding of what nanomodification means to concrete, which is a liquid-solid composite. NNC ideas need to profit from, but not be bound by, experience with other materials. As an illustration of these ideas, a specific application will be given of using nano-size molecules in solution to affect the viscosity of the concrete pore solution so that ionic diffusion is slowed. A molecular-based understanding would help move this project towards true nanotechnology. A final section of this paper lists some possibly fruitful focus areas for the nanoscience and nanotechnology of concrete.

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1. Introduction - The Need for Research

There are many improvements needed in concrete, especially for use in renewal and expansion of the world's infrastructure, e.g. increased durability, decreased brittleness and increased tensile strength, and routine use of large volumes of non-traditional materials like fly ash. Nanomodification can probably help solve many of these problems. However, concrete has been slow to catch on to the revolution in the nanotechnology that is ongoing in many materials. There are several possible reasons for this lag in the nanoscience and nanotechnology of concrete (NNC).

The first reason is a lack of a basic understanding of chemical and physical mechanisms and structure at the nanometer length scale, without which any attempted modifications at this length scale are only empirically-based and cannot be fully successful. Greater use needs to be made of advances in instrumentation from other fields to help characterize concrete at the nano-scale. In conjunction with this experimental need is the need for improved modeling of concrete at the nanoscale.

To make this point crystal clear, imagine someone who knew absolutely nothing of cement, of chemistry, and of other chemicals being given the task of finding a new chemical admixture that will improve property X of concrete. He doesn't even know how to make concrete, much less apply chemistry to it or measure a property. The cement and concrete industrial and scientific community is not exactly in this situation when it comes to NNC, of course, but perhaps we are not as far from it as we might wish.

Another reason for the lag in NNC is the lack of a broad understanding of what nanomodification means to concrete, which is a liquid-solid composite. Concrete is a material that is quite different from many other materials, and so NNC ideas need to profit from, but not be bound by, experience with other materials. Simply trying to duplicate advances made in other materials without adaptation to concrete is hampering the field of NNC. Further details will be given in subsequent sections of this paper.

As an illustration of these ideas, a specific application will be given of using nano-size molecules in solution to affect the viscosity of the concrete pore solution so that ionic diffusion is slowed, thus increasing service life under diffusion-controlled scenarios (e.g. chloride penetration). The success of this application is an example of what can be done based on the understanding gained by years of fundamental research on transport in concrete pore solution. But a molecular-level understanding, which would lead to more intelligent material selection, is still elusive. A final section of this paper lists some possibly fruitful focus areas for the nanoscience and nanotechnology of concrete.

This is not a review paper, so references will be limited to just a few examples to illustrate points. In order to review the nanoscience of concrete, one would have to synthesize what is known about cement paste at the nanoscale, which would be a large task. To review the nanotechnology of concrete, which is defined here as “using understanding of concrete nanoscience to affect the technology of concrete at the nanolevel and so improve macroscale properties,” would unfortunately be a lot easier to review. A fairly recent and useful review exists, as well as a summary of some of the nanoscience of concrete work to date [1,2].

2. The Unique Material - Concrete

To simply speak of "nanomodification" of a material doesn't convey much information. The microstructure, much less the nanostructure, of materials differ widely. The typical nanotechnology application that one hears about in other materials is that of inserting nanosized solid particles into a solid matrix. However, one must broaden this understanding of what nanomodification means when one thinks of concrete.

Concrete is clearly a porous liquid-solid composite, which is quite different from almost all materials used in human technology. The cement paste binder includes water at the nanometer and higher length scales. If any of the aggregates is porous, then they may contain water as well. So for concrete, there are three places where nanomodification can be carried out: in any of the solid phases, in any of the liquid phases, or at any of the water:solid interfaces (see Figure 1). For instance, nano-size additives can be solid particles added to the solid phase, or nano-size molecules added in solution to the liquid phase that can affect either the liquid phase itself or the liquid-solid interface. Since concrete is a material that is quite different from many other materials, NNC ideas should profit from, but not be bound by, experience with other materials.

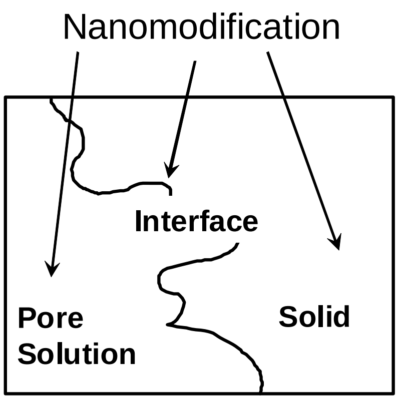

Fig 1: Schematic of concrete showing liquid-solid composite nature (no length scale is given).

In some sense, polymeric chemical admixtures in concrete, which have been used for decades, should be considered as NNC. For example, polymers that affect the nanoscale interaction forces between cement particles are nanosized molecules that are affecting nanoscale behavior by being added to the liquid phase. Shrinkage reducing admixtures affect the liquid-solid interface by reducing the surface tension in water:air menisci.

But what new types of nanoscale particles can be added to concrete? A fruitful area could be inorganic nanotubes [3,4]. Just adding carbon nanotubes does not seem to have a great effect on concrete properties, except perhaps for electrical conductivity, perhaps because the carbon nature of the nanotubes does not allow them to bond significantly with the calcium-silicate-hydrate (C-S-H) phase. But inorganic nanotubes, made of the correct material to interact strongly with the C-S-H phase, could lead to nanoreinforcement and other such, probably desirable, outcomes. Even carbon nanotubes, if they are appropriately functionalized [5], could also play a role. The point is that any nanoparticles that will be added to concrete must take into account the unique chemistry and physics of concrete.

3. Advances in Material Characterization to be Used

The list of modern experimental techniques that can give information at the nanoscale include atomic force microscopy (AFM) [6,7], transmission electron microscopy [8,9], nanotomography via dual ion focused beams [10], mechanical nanoindentation [11-13], although this gives information more on the hundreds of nanometer length scale, small-angle neutron scattering [14-16], nuclear resonance experiments [17], and synchrotron x-ray diffraction and other techniques, which are discussed in a recent review [18]. These references all list applications of these techniques to cement and concrete, and there are many more such references. The nanoscience understanding of cement and concrete is developing fairly rapidly. However, these techniques must be employed more routinely and in conjunction with each other, since no one experiment can give all the information necessary and desirable on which to base applications and models.

4. Advances in Models Needed

The experimental techniques of the last section rarely give a complete description of a system, so they must be coupled to computation to develop a self-consistent view. This will require nanoscale and molecular scale models for concrete, which are in their infancy. Not only do such models need to be developed and adapted to cement needs, there also needs to be advances made in the typical kinds of model used (e.g. molecular dynamics [19,20], ab initio [21]) so that they can be usefully employed on the randomness that is encountered in concrete at the nanoscale. The kinds of models that are typically used at this scale have been designed for relatively simple, small systems. To handle the complexities of cement paste, a systematic attempt needs to be made to use greater computer power (e.g. larger numbers of parallel processors) to be able to handle the larger numbers of types of atoms and molecules in these complex materials, the ubiquitity of water, the greater absolute number of atoms and molecules needed to be modeled, molecular reactions (an enormous complication over mere simulation of the movement of atoms and molecules), and the longer times that need to be modeled. The National Institute of Standards and Technology (NIST) has made strides in using massively parallel computers to help model concrete problems like rheology, where the large size range of particles on the micrometer and millimeter scale dictates the computational power needed [22], but not at the nanoscale. But even in the rheology problem, to go from 10 or 20 processors to 500 or 1000 processors required non-trivial changes in the code [22]. Similarly, there are public versions of molecular dynamics codes that are parallel [23], but to go to massively parallel versions will also require new computational structures.

To bring 3-D nanostructure simultaneously into such models, and not just thermodynamics and kinetics, something like HydratiCA [24,25], a 3-D model for simulating diffusion, reaction, and 3-D growth at the micrometer scale, also needs to be developed at the nanoscale. This is an achievable task. Although the Virtual Cement and Concrete Testing Laboratory (VCCTL) at NIST [26] does not model concrete at the nanoscale but only currently at the micrometer to millimeter length scales, nanoscale models could be incorporated (not easily, but readily) into the computational structure, directly linking nanoscale models with macro properties via multi-scale models.

5. An Example - Doubling the Service Life of Concrete

Past attempts to reduce the chloride diffusivity of concrete have focused on producing denser, less porous concretes. Unfortunately, these concrete formulations have a greater tendency to crack. A different approach was taken at NIST. Rather than change the size and density of the pores in concrete by working on the solid phase, a method was sought to change the *viscosity* of the pore solution in the concrete, using a soluble additive, to reduce the speed at which chloride ions and sulfates diffuse through the pore solution. Continuum transport equations that have been worked on for many years show that the speed of ionic diffusion through the pore solution is inversely proportional to viscosity of the pore solution [27]. These equations, however, do not give any guidance about molecular details.

In this research project, it was quickly found that the molecular size of the additive was critical for it to serve as a diffusion barrier. Larger molecules such as cellulose ether and xanthum gum increased viscosity greatly, but did not cut diffusion rates. Smaller molecules – of only a few nanometers in size – slowed ion diffusion. Several molecules of about the correct size were found to work, though some similar ones did not work, but the lack of molecular models do not allow predictivity so that any new such molecules still have to be found by trial and error. Such additives can be effective by being added directly to the concrete mixture as are current chemical admixtures, but even better performance is achieved when the additives are mixed into the concrete by saturating absorptive lightweight sand [28,29].

6. Some Possibly Fruitful Areas for NNC

Some areas in which concrete nanoscience could spawn some useful applications of nanotechnology are listed and briefly discussed below.

In autogeneous shrinkage, often a cause of early-age cracking, the reaction of cement and cementitious materials with water and each other induces chemical shrinkage because the reaction products take up less space than reactants. Chemical shrinkage results in air-water menisci (self-desiccation), especially in dense mixtures, where the excess water needed cannot get in quickly enough from the outside. These menisci, which are under tension, induce tensile stresses that can cause cracking. It has been shown [30] that shrinkage-reducing admixtures, among other chemicals, affect surface tension via nanometer-scale rearrangement of molecules. Understanding this phenomenon better at the nanometer-scale could lead to better ways of addressing autogeneous shrinkage, which is not a solved problem by any means.

The rheology of concrete is controlled by the rheology of cement paste, and the rheology of cement paste, while strongly dependent on parameters like particle size distribution, particle shape, and volume fraction, is also influenced strongly at the nanometer scale via interparticle forces. If these forces were understood better, the rheology could be controlled better via nanoscale chemical admixtures that were designed for their job, not just found by trial and error.

Another NNC area that has been exploited empirically but would greatly benefit from nanoscience understanding is the area of using chemical admixtures to affect the reactivity of cement particle surfaces. This is an NNC area, since the layer of dissolution/reaction at early ages is of the order of nanometers in size. Models and experiments at this level working together can lead the way to being able to design molecules for various purposes.

The whole area of concrete degradation via alkali-silicate reaction or sulfate attack, for example, involves ionic transport via the high ionic strength and high pH concrete pore solution, with surface complexation, followed by reaction, microstructure degradation that changes transport properties, and so on. Many key steps of these processes are at the nanoscale, and should be fruitful for nanotechnological applications once further nanoscience understanding is achieved.

Finally, probably the most important application of nanoscience and nanotechnology in concrete is affecting the C-S-H “glue” that holds concrete together. This is a nano-porous, nanostructured material that controls almost all the mechanical and transport properties of concrete. For example, the only reason concrete is viscoelastic is because C-S-H is viscoelastic. The mechanical properties of C-S-H set the scale for cement paste and therefore concrete elastic moduli and strength. Marrying inorganic nanotubes and/or particles with profound knowledge of C-S-H nanostructure, obtained from experiments that probe and models that accurately simulate this length scale should bring about significant NNC advancements, e.g. nanoscale tensile reinforcement and toughening. One should note, however, that the whole problem of adding nano-sized particles, reactive or otherwise, and their potential benefit, involves dispersing them properly. Only then does their reactivity really matter.

7. Summary and Conclusions

It is hopefully clear from this paper that one cannot just take a "practical engineering" approach to NNC, pull nanoparticles from other materials and throw them in the mix and hope for a miracle. There are unique aspects of concrete that must be taken into account in order to have successful NNC. Nanoscale research is needed to provide profound knowledge of the nanoscale to guide applications, since we have no intuitive "feel" for this length scale. One needs to let research knowledge be the guide to intelligently design concrete from the nanoscale up.

The NNC of concrete is well underway. There have been two previous NICOM conferences: NICOM 1 at Paisley and NICOM 2 at Bilbao, a US National Science Foundation-funded workshop on the nanomodification of concrete at the University of Florida in 2006, a workshop in March, 2009 in Spain focusing on nanoscale modeling, an upcoming (May, 2010) US Transportation Research Board (TRB) international conference entitled “Nanotechnology in Cement and Concrete” sponsored by the TRB task force on the nanotechnology of concrete, and undoubtedly there have been some other workshops and conference sessions that have been missed in this brief list. Note that the annual Computer Modeling Workshop held each summer at NIST has also touched upon nanoscale experiments and modeling (the 20th in the series is coming up in August, 2009, see http://ciks.cbt.nist.gov/monograph). The Nanocem consortium [31] in Europe has also made some strides in NNC research. Overall, the field of NNC needs to mature, to focus, to develop, and to make progress using experiments and models together in a synergistic way.

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