

Nanotechnology in Construction: A Roadmap for Development

by P.J.M. Bartos

Synopsis: Compared with other major industrial sectors, the construction industry has lagged behind in awareness of the potential for exploitation of nanotechnology. Both the awareness and actual exploitation in construction are now increasing; however, progress is uneven, especially in the current early stages of its practical exploitation. A roadmap then becomes a useful tool, a template, for predictions of trends and developments connecting nanotechnology and construction. The Roadmap for Nanotechnology in Construction (RoNaC) outlined in this paper is aimed at facilitating identifications of desirable aims/destinations for construction research and technical development (RTD) over a short-to-medium timescale (up to 25 years). The RoNaC was developed as an aid for forecasting research and investment directions. It provides guidance to construction industry, investors, and national/international bodies supporting research and development about the diverse pathways toward current nanotechnology-linked expectations, aims, and targets in this very large and economically significant domain. The complexity of the construction domain is such that a single overall chart would be far too general in a scale so large that it would become incomprehensible. Sectorial or “topical” charts have been developed instead of a single “map”, and three examples of such charts have been worked out to illustrate this approach. Requirements for adequate research infrastructures, effects of appropriate drivers, and diverse vehicles for RTD are considered together with an assessment of the “environment” conducive to progress along the pathways and directions indicated in the charts.

Keywords: construction; forecasting; guidance; nanotechnology; research and development; roadmap; trends and aims

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1. **INTRODUCTION**

Nanotechnology is a recently developed, major enabling tool, already well established in several sectors of science, which is expanding rapidly into applied sciences, technology and engineering. Nanotechnology enhances our understanding of “origins” of key properties of everyday materials and structures; of manufacturing processes and interactions between materials, structures, external elements and internal components. It leads to development of advanced characterisation and eventual prediction and control of properties of materials at a sub-micron level. Its potential for development is such that it is often considered as the industrial revolution of the 21st century. Applications of Nanotechnology are expected to lead to better, cleaner, cheaper, faster and smarter products. In addition, much more effective use of basic resources and development of environmentally sustainable production processes is predicted.

The purpose of a Roadmap is to chart of trends and developments, which, in this case, link nanotechnology and construction and provide a useful tool, a template, for their predictions. The Roadmap for Nanotechnology in Construction (RoNaC) has been aimed at facilitating identifications of desirable aims/destinations for construction RTD over a short-medium timescale (up to 25 years). The RoNaC was developed as an aid in forecasting RTD directions and helping to inform and guide construction industry, investors and national/international bodies supporting research and development about the diverse pathways towards current nanotechnology linked expectations, aims and targets in this very large and economically very significant domain.

The Roadmap for Nanotechnology in Construction was initially developed at the Scottish Centre for Nanotechnology in Construction Materials, attached to the Advanced Concrete and Masonry Centre of the University of Paisley. It had been a deliverable of the 5th FP project “NANOCONEX” (2002-2003) [1], which was subsequently presented to and consulted with membership of RILEM International Technical Committee TC 197-NCM on Nanotechnology in Construction Materials (2002-2007). Its earliest version was introduced as part of the E-CORE & ECCREDI conference on “Building for a European Future – Strategies & Alliances for Construction Innovation”, held in Maastricht, the Netherlands, in October 2004 and presented at the 2nd International Symposium on Nanotechnology in Construction (NICOM2) in Bilbao, Spain, in November 2005.

The RoNaC is also based on a State of the Art report [2] which was prepared by the Scottish Centre for Nanotechnology in Construction Materials (Dr. W. Zhu, Prof. P.J.M. Bartos) as part of the European 5th FP project “NANOCONEX” (2002-2003) and later

adopted by the RILEM TC197-NCM on Nanotechnology in Construction Materials [3]. The State-of-the-Art report [2, 3] examined and evaluated current development and applications, awareness and perceptions, and future potential of nanotechnology in the construction industry by surveying construction professionals and leading researchers and by studying publications and reports in relevant fields.

Information and data from the State-of-the-Art report [2] helped to establish the benchmarks for the development of the RoNaC. With the 5th FP European project NANOCONEX running and a proposed 6th FP Network of Excellence on Nanotechnology in Construction (project EXINAC) being considered, the original survey gave priority to Europe. However this was later complemented by a study of a global range of sources on existing knowledge, proposed and current R&D activities in nanotechnology that are potentially applicable to any part of the construction sector. Contributions presented at the 1st International Symposium on Nanotechnology in Construction, Paisley, UK, June 2003 [4], active links with the TC-197 NCM on Nanotechnology in Construction Materials, established under the auspices of RILEM in 2002, and events organised and documents produced by the UK Institute of Nanotechnology [5] and other organisations were reviewed and their conclusions considered. The 2nd International Symposium on Nanotechnology in Construction (NICON2) in Bilbao, Spain in November 2005 confirmed the emerging trends and indicated several new projects exploiting nanotechnology [6]. The 3rd Symposium (NICOM3), to be held in Prague in spring of 2009, will provide new information and a forum for discussion and updating of the RoNaC [7].

Construction industry differs from many other sectors of industry in that it is not connected directly to research and development of the new nano-scale tools, which was stimulated by nano-science, usually in the more fundamental scientific domain. Construction has only recently started to appreciate the potential impact of Nanotechnology on a significant scale. Compared to many other industrial sectors, relatively few instances have been reported where Nanotechnology has been already successfully exploited and a major product has already reached open markets. Awareness of the potential for exploitation of Nanotechnology in construction has improved over the last few years, but much more remains to be done. Nano-related RTD in construction has been recently established in a few sectors; however, it can be still described as “emerging”. Advances are very non-uniform, leading to a particularly pronounced fragmentation and often to a distinct isolation of current centres of nano-related construction research and development. These are very important, construction-industry specific circumstances, accounted for in the RoNaC.

Detailed analysis of the fragmented nature of nano-related RTD in construction is provided in the NANOCONEX/RILEM TC197-NCM State-of-the-Art report [2, 3].

Four underlying reasons for this situation are identified, relating to:

- ***Inherently different nature of the construction industry.*** This leads to many inventions being adapted from other industries or from related sciences, rather

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than invented within the construction industry itself. Construction tends to be much more an exploiter of ideas and inventions than their creator. This partly due to specific characteristics of its final products, which tend to be very complex, non-mass produced and requiring a relatively long service life. Such characteristics differ greatly from those of products from microelectronics, IT or even automotive industries.

- **Very low historic level of investment into construction RTD.** This represents a major hindrance in exploitation of nanotechnology. In many countries the level of investment in construction research has been distinctly the lowest across the whole of the manufacturing industry. Margins of profitability within construction and in related industries have been always very small. Such a situation slows down progress and hinders particularly advance along the development paths/routes exploiting nanotechnology, which already exist and in a creation of new ones.
- **Very high initial capital investment invariably required in nano-related RTD.** This is a major obstacle, applicable to all industrial sectors. The rate of obsolescence of nano-instrumentation is equally very high. Any substantial commercial returns are not being available earlier than within a mid- to long-term time-scale.

2. ROUTES AND PATHWAYS

The RoNaC charts are plotted against a timescale, which provides a measure of how distant the required or desirable research/development destinations are from a situation in 2004, which is considered as the starting point at the baseline. The timescale extends to 25+ years ahead. However, the greater is the extension of the time interval into the future, the greater are the potential errors and the lesser is the reliability of forecasts in this rapidly and very unevenly developing field.

It has been found entirely impracticable to produce one all-encompassing single map for all of the construction in which all the routes and /pathways of progress would be shown. The reason for this was the existence of a multitude of “pathways”, criss-crossing each other. Many are seen today as relatively “thin”, faint and indistinct ones, which is how they are seen today, but which, in future, they may (or may not!) become well-established, densely “trafficked” wide principal routes/highways of progress and development. An early attempt to show them all in one chart/roadmap, with all the numerous possible intersections, interactions and feedbacks, produced a tangled mass of connections resulting in and an illegible and incomprehensible document.

Solution of this problem of presentation appears to have been found in the creation of a number of simpler charts in which the nano-related construction research pathways and/or routes, heading towards a common specific “destination”, have been clustered. An example is the Chart 2: “Buildings of Future”, where the destination has been defined in a number of highly desirable goals and outcomes summarised and presented in the chart. Some of the pathways shown appear in another chart(s). This is to be expected, as Nanotechnology is fundamentally an “enabling technology”, where one advance, especially when it is a major advance, is very likely to underpin progress towards

desirable goals in more sectors than in its original one. It would be also possible to indicate the current status of the pathways as is common for traditional roadmaps (e.g. note which roads were existing, under construction or just planned), but this was felt to be the next stage in the RoNaC development. The activities shown in the specimen charts have colour coding to indicate existing pathways (red).

3. TIMESCALE

The RoNaC charts were plotted against a timescale, which provides a measure of how distant the required or desirable research and development destinations were from a “benchmark” situation in 2004, which was considered as the starting point at the baseline. The timescale extends to 25+ years ahead. However, the greater is the extension of the time interval into the future, the greater are the potential errors and the lesser is the reliability of forecasts in this rapidly and very unevenly developing field.

There are three specific Charts shown in this document. However, these should be also considered as examples of how to construct a RoNaC chart. It is possible to re-define the goals/aims, introduce new, additional goals/aims over the time-scale, re-trace the pathways and re-assess the information available, leading to new lists of activities, pathways and known (or expected) connections to selected “common” goals. There is sufficient information already available in the State-of-the-Art reports [2, 3] the proceedings of the 1st and 2nd International Symposia on Nanotechnology in Construction [4, 6], from the soon to be published final documentation from the RILEM TC 197 NCM and other more specific papers and sources, to provide data for production of new charts in a similar format.

It is important to appreciate that the “routes/pathways” shown in the charts are in many instances only now being formed or traced. Additional ones may develop in due course, and may not even exist as yet. It would be possible to indicate their current status as is common for traditional roadmaps (roads existing, under construction or just planned), but this was felt to be the next stage in the RoNaC development.

4. RESEARCH INFRASTRUCTURES

The very existence, or the construction, of roads and pathways critically relies on the availability of relevant supporting infrastructure, which itself has to be upgraded and developed with passage of time, to maintain it in an active, effective shape, fulfilling their role in supporting research, development and practical exploitation of nanotechnology. Progress towards highly desirable but inevitably only medium-long term goals will slow down very much, perhaps even stop entirely, if the necessary infrastructures were not maintained and periodically upgraded, mainly because of inadequate funding provisions.

The research infrastructures, which “pave the way” include:

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- Instrumentation and methodologies for nano-scale investigations, e.g. for characterisation of properties at nano-scale, nano-assembly and fabrication, analytical techniques and imaging at molecular/atomic scale.
- Descriptive and eventually predictive numerical models, which include a linkage across the whole scale, from nano-to-macro size.
- Standardisation of basic nano-scale metrology equipment and provision of means for an assessment of their performance. Development of new, more effective tools for a meaningful nano-scale characterisation of materials.

Instrumentation and metrology at nano-scale are developing at a very fast pace, which inevitably brings with it a rapid rate of obsolescence. The rate of obsolescence is comparable to that seen in the IT sector; however “hardware” costs of nano-scale instrumentation and costs of its maintenance/calibration/upgrading, even on only a moderate scale, are much higher than in the IT sector.

5. VEHICLES, DRIVERS, KNOWLEDGE AND BUSINESS ENVIRONMENT

Not all of the pathways/routes, including their intersections, shown on the attached Charts, may be immediately very clear and recognisable to potential developers and exploiters. The choice and understanding of the research “vehicles” needed to pursue specific goals and the capability of their “drivers” to steer them along correct routes to desired outcomes and destinations, require adequate prior **knowledge** of both Nanotechnology and the relevant sector(s) of construction industry in all instances.

The greatest impact on the construction industry and the economy within the timescale of the Roadmap is likely to come from an enhancement in performance of materials arising from an improved understanding and control of their structure on micro-to-nano-scale and from an improvement of their production processes. The eventual total impact will be almost always very substantial, due not necessarily to radical technological leaps forward but mainly to massive quantities in which basic (“bulk”) construction materials are used. Most of the advances along the specific research routes and pathways of RTD are predicted to be incremental, leading to a relatively steady progress related to existing, namely the “bulk” materials and technologies. Such a relatively steady progress will be strongly influenced by developments in the research “infrastructure”, such as in equipment. It may be that some of the expected improvements will not take place and there will be a waiting period with only a small or even zero advances, until a breakthrough occurs and the capability of the equipment (infrastructure) is instantly and significantly upgraded.

An improved understanding of structure-properties relationships and an ability to control the structure of many materials on the nano-scale will provide opportunities for major advances in materials science. Such breakthroughs will enable the “materials by design” approach to replace the traditional “trial and error” one, enabling properties of a material to be tailored for a specific requirement. It will also lead to development of new

approaches to extend the life of existing structures and to prevent/arrest deterioration in the new build.

Many of the basic and most significant drivers such as market pull, venture capital involvement, competitiveness and prospects of higher financial returns will be either weak or not established if an environment conducive to acquisition of adequate and relevant knowledge is not present. All the drivers of progress in this area rely critically on knowledge and information.

Construction industry is a very substantial domain, in Europe alone its turnover is estimated at about 1000 billion Euros [8]. However, it is also estimated that 97% of employees working within it are employed by enterprises with less than 10 staff. In such circumstances, acquiring the required minimum of knowledge, which is at present inadequate if not entirely largely absent, will be unacceptably slow without it being facilitated by a targeted national or supra-national support.

The way ahead - an exploitation of the directions such as those shown in the specimen RoNaC charts will be not be easy and straightforward as the knowledge required at different levels of construction-related staff tends to lag behind the advance of nanotechnology.

There is strong evidence that in the absence of an environment conducive to acquisition of adequate knowledge through education and training, many of the basic and most significant drivers such as market pull, venture capital involvement, competitiveness and prospects of higher financial returns will be either weak or not established. Numbers of skilled research related personnel at both the scientific/supervisory level and at the supporting staff/technician level, who possess the required combination of knowledge related to construction and nanotechnology, appear to be still too low to provide the manpower required to steer and move efficiently forward the “vehicles” for expansion of nano-related RTD in construction.

Indications are that countries leading the development and exploitation of Nanotechnology, such as the USA and European Union (in both overall and national programmes [8, 9], have realised the necessity of providing a major financial support from state/government sources. The US government set up the National Nanotechnology Initiative in the year 2000, which has committed an initial funding over one billion US dollars of public funds to facilitate the additional commitment of private venture capital for specific developments through its different agencies [8]. Unfortunately, all but a very small fraction of the public funding for nano-related RTD appears to have been channelled either into non-construction industries or into development of the nano-scale research infrastructure used primarily to support non-construction research.

Investment into research infrastructure can be of benefit for construction and it can “smooth/pave” some of the development paths shown in the Charts. However, in practice, such facilities tend to be under non-construction related management and many of the already established access routes are already crowded by nano-science related research “vehicles” with very little or no construction linkage. Benefit to construction

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from such nanotechnology related investments is therefore likely to be disproportionately low compared with the economic significance of construction, which, in EU contributes approximately 10% of GDP. Other significant drivers are emerging, which gain significance in terms of construction and nanotechnology. These include climate change and the associated issues on a global scale and urban redevelopment and in some countries.

6. ROADMAP AND CHARTS

A roadmap for the whole of construction, including all the existing and proposed pathways for development would be illegible. The “scale” would have to be adjusted, but then the roadmap would become too coarse to make it comprehensive and legible. As a result, such a complex overall chart would not reveal adequately details necessary for an appreciation and understanding of the links, relationships and dependencies of varied significance between the pathways shown.

The RoNaC should therefore comprise a collection of “sectorial” charts such as the examples attached, each focused on a coherent cluster of aims and destinations. Aims and destinations, which are expected to be of significance for construction in the medium-long term 3 include:

- Understanding basic phenomena (interactions, processes) at nanoscale: e.g. cement hydration and formation of nanostructures, origins of adhesion and bond, pore structure and interfaces in concrete, mechanisms of degradation, relevant modelling/simulation based design tools, etc.
- Bulk “traditional” construction materials with a modified nano-structure: e.g. concrete, bitumen, plastics modified with nanoparticulate additives, special admixtures and new processing techniques modifying internal nanostructures etc.
- New high performance structural materials: e.g. carbon nanotubes, new fibre reinforcements, nanocomposites, advanced steels and concrete/cement composites, biomimetic materials, etc. Materials with extended durability in extreme service conditions.
- High performance new coatings, paints and thin films: e.g. wear-resistant coating, durable paints, self-cleaning/anti-bacteria and anti-graffiti coatings, smart thin films, etc.
- New multi-functional materials and components: e.g. aerogel based insulating materials, efficient filters/membranes and catalysts, self-sensing/healing materials, etc.
- New production techniques, tools and controls: e.g. more energy efficient and environmental friendly production of materials and structures, novel processes with more intelligent and integrated control systems, etc.
- Intelligent structures and use of micro/nano sensors: e.g. nano-electromechanical systems, biomimetic sensors, paint-on sensors, and self-activating structures/components, etc.

- Integrated monitoring and diagnostic systems: e.g. for monitoring structure defects and reinforcement corrosion, environmental changes/conditions, and detecting security risks, etc.
- Energy saving lighting, fuel cells and communication devices: e.g. efficient and cheap fuel cells and photovoltaics, LED based lighting, etc.

Three Charts are shown as examples of the “clustering” of aims/destinations. The paths emerge from a baseline to the left of the Chart. If appropriate, the baseline can be split into separate “blocks”, indicating that it comprises distinctly different sub-areas of research. Each sub-area may consist of several recognised and related research streams/directions.

Progress forecast along each of the identified nano-related RTD activity paths is shown against a linear timescale from 0 to 25+ years. Activities, which are shown to begin within the interval of 0-32 years, are already being pursued or about to commence. Aims/destinations, common to each of the charts, are shown on the right hand side and basic characteristics/parameters of the aims are also listed there.

Each research activity is represented by a simple elongated rectangular box, which may suggest a very precise and sudden start and finish, and a uniform intensity of the activity throughout its expected duration. However, this is a simplification, which has been adopted for the sake of clarity, and because it is impossible to predict the inevitable variations in the intensity/magnitude of research during each of the activities. There may be ups and downs, and even breaks/discontinuities, when funding may drop below the level required to sustain advance. Unexpected and at that time perhaps temporarily insuperable technological problem, may be encountered on the path followed, or even an unexpected dead end may be encountered, for example by discovery of a hitherto unknown ecological or health & safety threat or danger. It is also realistic to expect that each of the activities will gradually develop in its intensity and volume. Some of the activities showing early starts are already being pursued.

Each “activity box” is therefore presented in a simplified linear and parallel direction, with only major interactions indicated as “diagonal” connecting lines. As has been mentioned before, some of the activities will be using common paths/routes and share the infrastructure. There are therefore many overall “integrating” features because of the commonality of some of the nano-scale approaches, a feature likely to be well appreciated, representing the inherent multi-disciplinarity of RTD exploiting advances in nanotechnology.

A general activity, which is beginning to be much more appreciated, and which will become soon an integral part of any of the specific (“boxed”) activities shown is an **evaluation of health and safety**, both during the process of research and development and regarding practical products/applications. There are concerns especially about the capability of nanoparticles to pass through natural bio-boundaries in living organisms and safety precautions must be maintained even though evidence on adverse effects on health is still limited. It is now therefore very urgent to provide an adequate national and

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international legislative cover for nanotechnology and avoid potential health and safety problems which would undermine confidence in nanotechnology in general and dramatically slow progress.

7. SPECIMEN CHARTS

Chart 1: Traditional Bulk Construction Materials

This chart (Fig. 1) covers basic existing construction materials. Here, even incremental improvements achieved by the exploitation of nanotechnology will lead to big commercial and environmental/societal gains because of the extremely high “multiplying factors” attached to such materials. Activities shown follow generally the “top-down” approach, in which an existing material is improved through knowledge and modifications carried out down at the micro-nano level.

Chart 2: Buildings of Future

This chart (Fig. 2) shows activities leading to a much higher standard and much more environmentally acceptable, and eventually fully sustainable, building construction. Achievements reached by routes shown in Charts 1 and 3 will be associated with activities shown in this Chart.

Chart 3: Novel Construction Materials

This chart (Fig. 3) follows primarily the “bottom-up” development direction, where materials of substantially altered properties and much high performance are “built” or “assembled” from the basic nano-scale constituents (molecular - atomic level). Related activities are shown in same colour coding.

It is important in all cases to note the “unforeseen developments”, a box that covers developments not even thought of at present.

8. CONCLUSIONS

Nanotechnology in construction remains in an “emerging, early development” state. Its uneven progress, prevailing fragmentation and the specific nature of the construction industry limit the accuracy of the forecasts shown in the RoNaC.

The RoNaC presented includes three specimen charts covering the most common “clusters” of construction research activities, where nano-based research and development activities are already carried out and several routes/pathways are already established. Additional charts can be developed for specific activities or aims/destinations.

Reliability of predictions regarding commencement, duration and end of activity decreases rapidly as the commencement time becomes more distant from present (time zero).

Integration of the currently fragmented nano-related research in construction and the use of common “vehicles” at national or international levels would speed up progress along the pathways outlined in the RoNaC.

Most of the overall construction output is through Small and Medium Enterprises, however, the SMEs in construction domain have negligible research and development capabilities. They cannot be therefore considered as effective vehicles for progress in exploitation of nanotechnology in construction, however, they need to be associated with the RTD and their awareness of developments improved and maintained.

Activities concerned with monitoring and evaluation of ecological, environmental and health and safety aspects of materials and processes both during research at nanoscale and for development of marketable products are expected to become an essential part of all activities considered.

The RoNaC charts provide a “snapshot” of the current situation in only three sub-sectors of construction. It is suggested that the same “template” is used to develop further charts focused on different sub-sectors or topics, and the charts are updated every 3-5 years. The nearest opportunity will be at the 3rd International Symposium on Nanotechnology in Construction (NICOM-3) to be held in Prague in spring of 2009.

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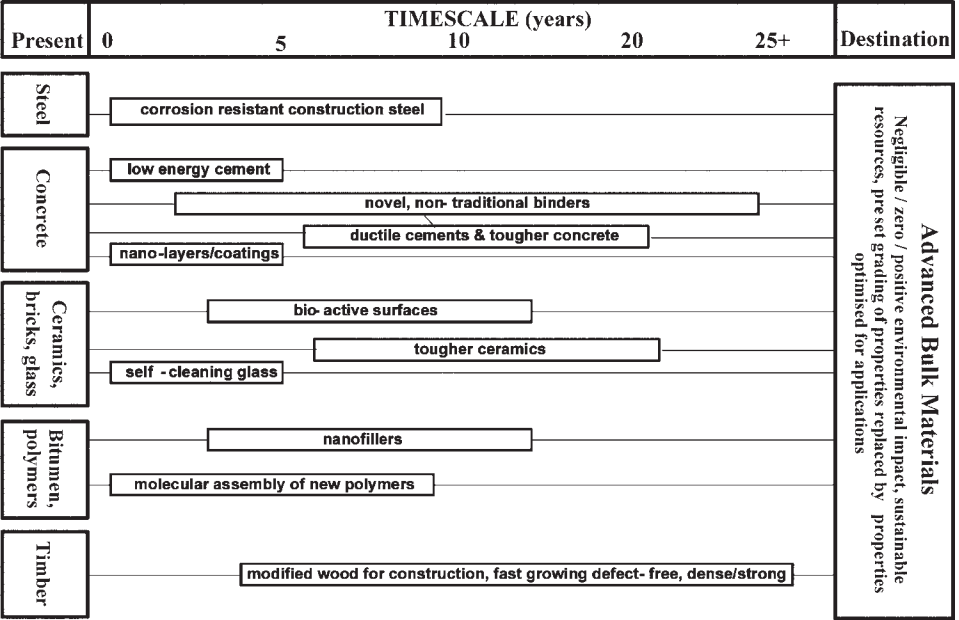


Fig. 1. NANOCONEX roadmap chart 1: bulk construction materials.

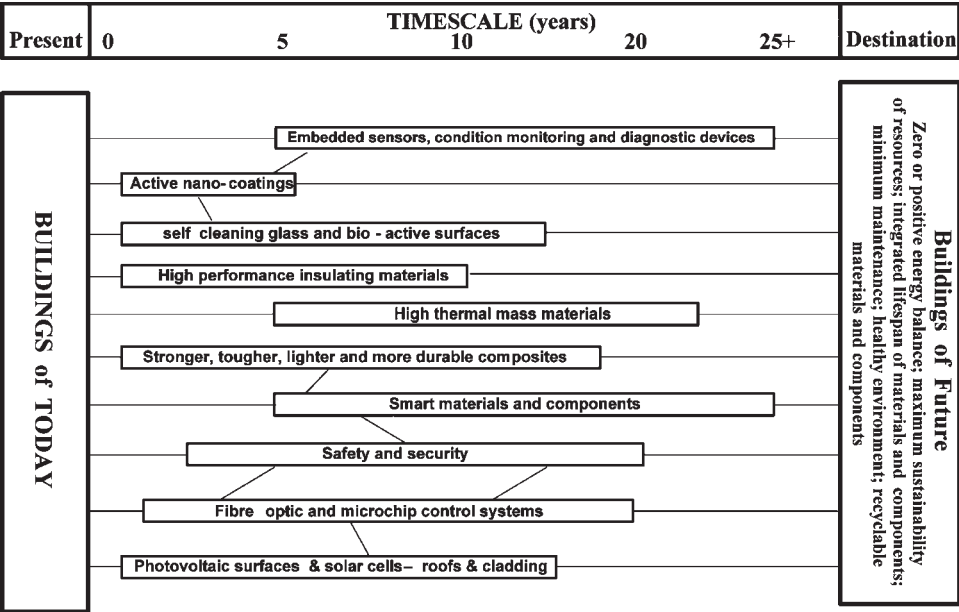


Fig. 2. NANOCONEX roadmap chart 2: buildings of future.

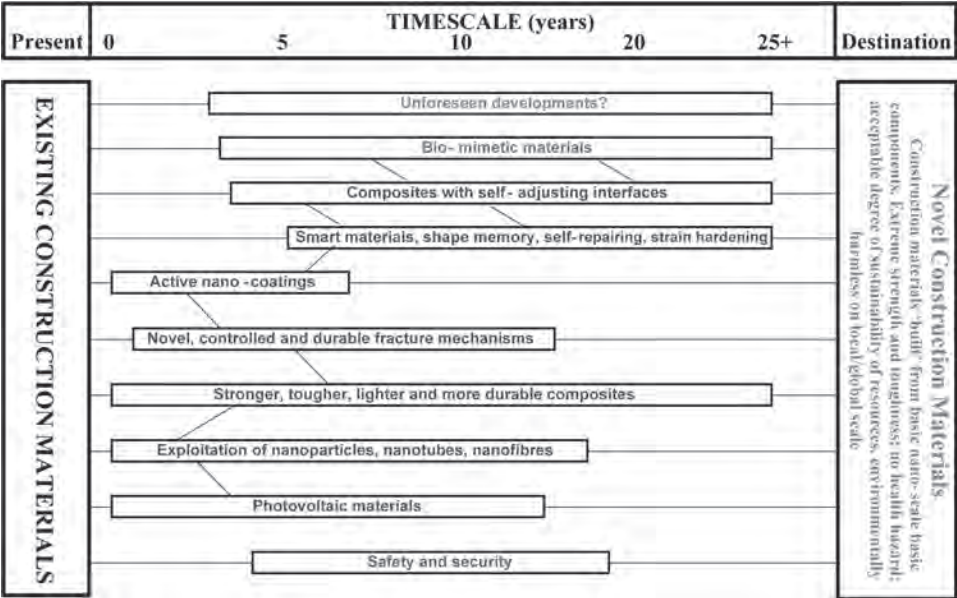


Fig. 3. NANOCONEX roadmap chart 3: novel construction materials.

Nanotechnology and Concrete: Research Opportunities

by P. Balaguru and K. Chong

Synopsis: Nanotechnology is one of the most active research areas that encompasses a number of disciplines including civil engineering and construction materials. The most active fields are electronics, biomechanics, and coatings. Interest in nanotechnology concept for portland-cement composites is steadily growing. Currently, the most active research areas dealing with cement and concrete are: understanding of the hydration of cement particles and the use of nano-size ingredients such as alumina and silica particles. There are also a limited number of investigations dealing with the manufacture of nanocement. If cement with nano-size particles can be manufactured and processed, it will open up a large number of opportunities in the fields of ceramics, high-strength composites, and electronic applications. This will elevate the status of portland cement to a high-tech material in addition to its current status of the most widely used construction material. Very few inorganic cementing materials can match the capabilities of portland cement in terms of cost and availability. The main objective of this paper is to outline promising research areas. Basic background information on nanotechnology research, state of the art on use of this technology in concrete, opportunities, and challenges are discussed.

Keywords: carbon; composites; nano portland cement; nanotubes

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1. INTRODUCTION

Nanotechnology is a very active research field and has applications in a number of areas. Currently this technology is being used for the creation of new materials, devices and systems at molecular, nano- and micro-level [1-8]. Various government agencies in the United States of America are supporting nanotechnology exceeding billion dollars per year. National Science Foundation (NSF) is one of the active participants with a major share of research funding.

Areas of investment for the fiscal year 2006 were:

- Fundamental Nano-scale Phenomena and Processes;
- Nano-materials;
- Nano-scale Devices and Systems;
- Instrumentation Research, Metrology, and Standards for Nanotechnology;
- Nano-manufacturing;
- Major Research Facilities and Instrumentation Acquisition;
- Societal Dimensions.

Program emphases for fiscal year 2007 are:

- Increased focus on complex large nano-systems. Research on nano-scale devices and system architecture, dynamic and emerging behavior, and their respective fabrication, will be emphasized;
- Increased focus on three-dimensional measurements of domains of engineering relevance with good time resolution;

- Converging science, engineering and technology from the nano-scale, by integrating nano-systems into applications (in manufacturing, information systems, medicine, environment, etc.);
- Expanded joint research program addressing potential implications of nanotechnology with other federal agencies;
- Earlier educational programs and teaching materials, including for K-12, by using remote access to NSF educational networks; and
- Expand partnerships of academic researchers with industry, medical facilities and states.

As of 2007, there are more than 700 active research projects supported by NSF. The primary objective of this paper is to present the possibilities of using nanotechnology for portland cement-based composites including nano- and micro-concrete.

Portland cement is the most common and widely used construction material and its current production is estimated as 8 billion cubic yards per year [18]. The major advantages of this material are: availability of raw materials for production all over the world, low cost, room temperature setting, ease of construction, readily available properties and performance data for design and construction. In addition modern day concrete has a very good performance record for a period of more than 175 years. Portland cement is typically used as cementing materials with fine and coarse aggregates to create products that are a few mm to several meters thick. Average size of portland cement particle is about 50 microns (1.97×10^{-3} in.). In applications that require thinner final products and faster setting time, micro cement with a maximum particle size of about 5 microns (1.97×10^{-4} in.) is being used [10]. Therefore the particle size has to be reduced by an order of magnitude to obtain nano-portland cement. If these nano-cement particles can be processed with nano-tubes and reactive nano-size silica particles; conductive, strong, tough and room temperature processed ceramics can be developed both for electronic applications and coatings. Since carbon oxidizes at temperatures above 400 °C (750 °F), room temperature processing will be a boon to retain the mechanical properties of carbon nano-tubes. Since most ceramics are processed at temperatures much higher than 400 °C (750 °F), carbon fibers can not be used with these processes.

At the micro level, there is also a very good analogy between reinforced concrete and fiber composites. The lessons learned on fiber reinforced concrete can also be effectively used for composites made using short discrete fibers, both at micro and nano-level. For example, considerable amount of fiber reinforced concrete containing 0.5% of steel fibers are being used in actual construction. The enhancement of properties provided by this 0.5% of steel fibers to concrete matrix are not that much different from the enhancement provided by 0.5% of carbon nano-tubes in high performance composites [9-10]. Note that carbon fibers provide enhancement to both mechanical and electrical properties.

2. DEFINITION OF NANO-CONCRETE

For discussions presented in this paper, nano-concrete is defined as a concrete made with portland cement particles that are less than 500 nano-meters (1.97×10^{-5} in.) as the

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cementing agent. Currently cement particle sizes range from a few nano-meters to a maximum of about 100 micrometers. In the case of micro-cement the average particle size is reduced to 5 micrometers. An order of magnitude reduction is needed to produce nano-cement.

3. IS THERE A NEED FOR NANO-CONCRETE?

The authors believe that the answer is Yes. Certain unique properties of portland cement such as: room temperature processing, low shrinkage, temperature resistance up to 600 °C (1,115 °F), compatibility with a number of fiber types including carbon fibers, reaction capability with currently available nano-materials such as nano-silica and non toxic characteristics can be effectively used to create unique products. It can also be molded to complex shapes; heat cured and coated with other nano-materials.

If processable nano-cement is synthesized, micro-meter thick plates and other shapes such as cylinders can be manufactured for various applications including electronic components and high temperature sensors. Carbon nano-tubes can be used for both strengthening and creating electric circuits. Another major large volume application is in the area of coatings. Current portland cement-based coatings are not popular because they need to be thick and polymer additions are needed to improve adhesion. Nano-cement will create a new paradigm in this area of application. Crack-free decks will be a reality instead of a dream.

4. STATE-OF-THE-ART

4.1. Concrete and Nanotechnology

One can claim that concrete utilizes nanotechnology because it contains nano-particles as ingredients including nano-water particles and nano-air voids. However, to claim the use of nanotechnology, we should be able to control the amount and the locations of these nano- ingredients inside the final products. The scales of various constituent materials of concrete are shown in Fig. 1. If we can create chemical or mechanical tools to control nano-scale pores and the placement of calcium-silicate hydration products then concrete becomes a product of nanotechnology.

Current research activities of nanotechnology in concrete include: characterization of cement hydration, influence of the addition of nano-size silica to concrete, synthesis of cement using nano-particles and coatings (that contain nano-size particles) applied to protect concrete. These activities are briefly described in the following sections.

4.2. Cement Reactivity Nano-Structure

A collaborative research activity supported by Federal Highway Administration (FHWA) and NSF is being conducted at University of Connecticut to study cement hydration at a nano-scale level. In this study US and German scientists are using nuclear resonance reaction analysis (NRR) to investigate what takes place on the surface of the cement

particle as it hydrates. A beam of nitrogen atoms is used to probe a reacting cement grain to locate hydrogen atoms, a necessary component of water, or reaction by-products. Location of these hydrogen atoms are used to create a hydrogen depth profile, which shows the rate of water penetration as well as the arrangement of various surface layers formed during the reaction.

The researchers identified four components that are active during cement hydration, Fig. 2. The following section provides a short summary of their observations. The 20-nanometer-thick (7.87×10^{-7} in.) semi-permeable surface layer allows water to enter the cement grain and leaches out calcium ions. The larger silicate ions in the cement are trapped behind this layer. As the reaction continues, a silicate gel forms there, causing swelling within the cement grain. This leads to eventual breakdown of the outermost layer. The surface disintegration then releases accumulated silicate into the surrounding solution. The silicate reacts with calcium ions to form a calcium-silicate hydrate gel, which binds cement grains together and sets the concrete.

The evolution of the hydrogen profile shows the timing of the surface layer's breakdown. This information can be used to study the concrete setting process as a function of time, temperature, cement chemistry, and other factors. For example, researchers used NRRA to determine that in cement hydrating at 30°C (86°F); the breakdown occurs at 1.5 hours [7].

4.3. Nano-Scale Silica Fume for Improving Concrete Performance

Ultra-fine amorphous colloidal silica was found to be much more efficient than micron sized silica for improving the performance such as permeability, and subsequently, durability [5]. In addition, reduced amount of about 15 to 20 kg (33 to 44 lbs) of nano-silica was found to provide same strength as 60 kg (132 lbs) of regular or micro silica.

4.4. Alkali-Silicate Reaction (ASR) Studies

ASR results in the formation of alkali/silica gel, which expands and causes significant material damage. The gel is formed due to the reaction between cement alkalis and a reactive form of silica from aggregates or supplementary additions. FHWA researchers are using neutron scattering and positron annihilation spectroscopy to measure nano-scale changes in gel microstructure as a function of gel chemistry, temperature and relative humidity [7].

4.5. Fly Ash Reactivity Characterization

FHWA is also funding a research study to examine interactions between fly ash and portland cement gel nano-structure. Small-angle neutron scattering is being used to quantify the changes on a nano-scale as a function of time and fly ash composition.

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4.6 Cement Hydration Kinetics

Conventional analytical methods are unable to provide an accurate model for the rate of cement's reaction with water as a function of temperature, water/cement ratio, and grain size because the reactions occur in the nano-scale pores of the cement gel. Therefore, scientists from National Institute for Standards & Technology's (NIST) Center for Cold Neutron Research and FHWA are using neutron scattering methods to measure motions and reactions of water at a nano-scale. This study is expected to explain the effects of various factors on the rate of development of cement's fractal nano-scale structure.

4.7 Synthesis of Cement Using Nano-Particles

In a project supported by National Science Foundation, it has been synthesized the components of portland cement Type I using nano-particles and compared their properties with that of commercial cement. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) equipment were used to evaluate the morphology and structure of synthesized tricalcium silicate (C_3S) components. Conglomerated nano-particles with crystalline structures containing quantities of tri- and di- calcium silicate compounds as well as copper oxide were found to be present in the synthesized cement. Hydration tests indicated that the nano-cement had a more rapid hydration rate than portland cement Types I and III. Compressive strength of the cement synthesized using nano-particles was found to be less than that of ordinary portland cement. The authors attributed this reduction to a number of factors including: particle aggregation, rapid hydration, a high water to cement ratio, and the lack of gypsum [14].

4.8. Carbon Nano-Tubes

Since carbon nano-tubes have excellent potential for use in cement composites, basic mechanical properties of these tubes are presented in the following sections [4-6]. More details can be found in reference 4.

4.8.1. General Description

The most popular nano-tubes are carbon nano-tubes, discovered by the Japanese Scientist Sumio Iijima in 1991 [6]. Within a short period, arc-evaporation techniques were used to produce bulk quantities of nano-tubes. These tubes were multilayered structures. A single layer nano-tube was synthesized in 1993 by adding metals such as Cobalt to Graphite electrodes. In 1996, Smalley's group in Texas, USA developed a method that resulted in high yield of single walled tubes with unusually uniform diameters. These uniform tubes had a tendency to form aligned bundles compared to those prepared using arc-evaporation. The bundled nano-tubes are sometimes referred to as nano "ropes".

Other forms of carbon nano-tubes are: nano-horns, nano-test tubes and nano-fibers. Nano-horns are single walled carbon cones with remarkable adsorptive and catalytic properties. They have excellent potential for use in fuel cells. Nano test tubes have potential for use in a number of applications, including medical fields. These tubes can be

filled with materials including biological molecules. Nano-fibers could become the ultimate carbon fibers because of their very high strength, stiffness, aspect ratio and purity.

Single layer nano-tube can be considered as the perfect thin walled cylinder because of the uniformity in thickness, accurate geometry and linear elastic material behavior. The challenge is to test them to obtain strength, stiffness and stability properties. A number of techniques are being developed to use electro-mechanical devices to induce force and measure responses. The forces are measured in nano Newtons and the displacements are measured in fractions of nano meters. Structural properties of single walled (single layered) tubes, multi walled tubes and single wall bundled tubes are needed for effective utilization of these materials in electronic and bio applications and development of nano/micro composites. The following sections provide some basic information on geometric dimensions and mechanical properties of carbon nano-tubes. Since this is a very active research area, the reader is advised to refer to latest journals for up to date information.

4.8.2. Dimensions of Carbon Nano-Tubes

The first nano-tubes discovered were multi-walled tubes [11]. Transmission electron microscopy studies indicate that these tubes look like nested shells with an interlayer spacing of about 0.34 nm (1.34×10^{-8} in.). The equivalent diameter of the tubes is in the range of 10 to 50 nm (3.94×10^{-7} to 1.97×10^{-6} in.). The typical length varies from 100 to 1000 nm (3.94×10^{-6} to 3.94×10^{-5} in.). Single layer tube has a much smaller diameter [1 to 3 nm (3.94×10^{-8} to 1.18×10^{-7} in.)] and length [about 300 nm (1.18×10^{-5} in.)]. The single layer tubes are often manufactured in “rope” or “bundled” form, where many individual tubes are close-packed in parallel.

4.8.3. Mechanical Properties of Nano-Tubes

The basic information needed for analysis are elastic modulus, stress-strain behavior, strain capacity in compression and tension, shear modulus and strengths in various modes. These values can be obtained using either experimental techniques or theoretical formulations. The small dimensions of the tubes impose a tremendous challenge for experimental study. Various types of high-resolution microscopes with the recent innovative developments in the area of nano manipulation have helped to obtain quantitative results. However, the numbers reported on strengths and modulus values vary widely. The modulus values reported range from 270 to 3600 GPa (39,200 to 522,100 ksi). Theoretical predictions indicate that the modulus can be as high as 5000 GPa (725,200 ksi). Typical stress-strain plots reported two investigators are shown in Fig. 3 [10]. The stresses were estimated assuming a uniform thickness of 0.34 nm (1.34×10^{-8} in.) for the single tube. The strains reported are engineering strains.

In tension mode, the reported strain at failure is as high as 12% and the strengths vary from 10 to 63 GPa (1450 to 9140 ksi). The strengths of very long [about 2 mm (0.08 in.)] ropes were found to be in the range of 1.72 ± 0.64 GPa (250 ± 93 ksi) [12].

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4.9. Nano Composites

Nano-tubes can be used to fabricate fiber composites that can inherit some of the outstanding properties of the nano-tubes. For example, carbon nano-tubes can be mixed with aluminosilicates to produce very thin wafers that are very strong and highly conductive. The composite can also be used as a tough, durable, high temperature and low-friction coating. Current aluminosilicate formulations consist of silica particles in the range of 50 to 100 nm (1.97×10^{-6} to 3.94×10^{-6} in.) [8]. It is possible to refine the process to reduce the maximum particle size in the matrix to 5 or 10 nm (1.97×10^{-7} or 3.94×10^{-7} in.). These matrices can be reinforced with as low as 0.5% of nano-tubes and still produce extraordinary strength and electrical conductivity improvements.

Researchers at NIST and university of Pennsylvania have been building nano-clay filled polymers that can improve fire resistance as well as mechanical properties [15]. Metal oxide nano-particles have also been used in coatings for protection of UV light, self-disinfecting surfaces, solar cells, indoor air cleaners, etc. Other nano-composites have superior structural performance.

4.10. Nano Sensors for Concrete Structures

The feasibility of Cyberliths, or Smart Aggregates, as wireless sensors embedded in concrete is being evaluated [16]. In the future these micro sensors might be reduced to dust-particle size, with the ability to coat an entire bridge with Smart Dust for optimum monitoring capabilities via a smart sensor net. These sensors can be used to remotely monitor the condition of the concrete and reinforcement without damaging the structures.

5. FUNDAMENTAL CEMENT HYDRATION CONCEPTS RELATED TO NANO-CEMENT

A large and in-depth knowledge base has been developed regarding the behavior of concrete over the past 150 years [8]. Possible issues related to nano-size cement particles are discussed in this section. The first and major issue is the synthesis of nano-cement. As mentioned earlier the particle size has to be reduced by an order of magnitude. Possible avenues are chemical synthesis and separation of nano-size particles from micro cement using mechanical means. Attempts have been made in both fronts but published information is not available in the open literature.

The second major issue is the structure of hydrated cement. Heat of hydration and fabrication techniques are related to this subject area. The following facts that we learned from cement hydration will play an important role in understanding the hydration of nano-cement paste:

- One cubic mm (6.10×10^{-5} in.³) of cement occupies about 2 cubic mm (1.22×10^{-4} in.³) of space after complete hydration.
- Three major solid components of hydrated cement paste are: Calcium Silicate Hydrate (CSH), Calcium Hydroxide crystals (CH or portlandite) and Calcium Sulfo-Aluminates (CS or ettringite). CSH occupies about 50 to 60 percent of the

volume where as CH and CS occupies 20 to 25 percent and 15 to 20 percent respectively.

- The size of CSH sheet is less than 2 nm (7.87×10^{-8} in.) and the space between the sheets vary from 0.5 to 2.5 nm (1.97×10^{-8} to 9.84×10^{-8} in.). Aggregation of poorly crystalline CSH particles could occupy 1 to 100 nm (3.94×10^{-8} to 3.94×10^{-6} in.). Inter-particle spacing within an aggregation vary from 0.5 to 3 nm (1.97×10^{-8} to 1.18×10^{-7} in.).
- CSH has a large surface area [100 to 700 m²/g (30,515 to 213,600 ft²/oz)] and the strength of this material is attributed to van der Waals forces.
- CH products are typically large with a width of about 1000 nm (3.94×10^{-5} in.).
- CS has needle type structure and is unstable.
- Hydrated cement paste can contain adsorbed water. Up to six molecular layers of water, about 1.5 nm (5.91×10^{-8} in.) thick can be held by hydrogen bonding. Major part of this water can be removed by drying at 30 percent relative humidity.
- Size of capillary voids range from 10 to 1000 nm (3.94×10^{-7} to 3.94×10^{-5} in.). However in well hydrated paste with a low water-cement ratio the pore size is typically less than 100 nm (3.94×10^{-6} in.).
- Small CSH crystals, hexagonal calcium aluminate hydrates and calcium sulfo aluminates posses large surface areas and adhesive capability. They also adhere to un-hydrated cement grains and aggregate particles.
- Pozzolanic reaction results in reduced capillary voids and replacement of calcium hydroxide with CSH.
- Heat of hydration is strongly influenced by particle size of cement. Blaine of cement varies from 320 m²/kg (1,562 ft²/lb) for normal cement to 900 m²/kg (4394 ft²/lb) for ultra high early strength cement.
- C₃A generates the most heat and C₂S generates the least amount of heat.
- Heat of hydration has two peaks, one occurs during the dissolution stage and the second occurs during the formation of compounds.
- Active hydration zone is about 2000 nm (7.87×10^{-5} in.) thick, [Fig. 2].
- Of the two mechanisms of hydration through-solution hydration is more suitable for nano-cements. In this mechanism, complete dissolution of anhydrous compounds to their ionic constituents and eventual precipitation of hydrates are assumed to take place.
- Aluminates hydrate much faster than silicates. Silicates, which make up about 75 percent of cement, play a dominant role on strength development.

5.1. Possible Performance and Fabrication Techniques

A careful review of the aforementioned facts and figures on portland cement can be used to envision the performance of nano-cement:

- Irrespective of the mode of manufacturing, the gypsum content has to be engineered to control the heat of hydration and strength development.
- It is possible to mix nano-carbon tube bundles in nano-cement slurry. For certain applications even regular carbon whiskers can be used.

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- Only nano-size pozzolans and fillers should be used for nano-cement composites. Note that silica fume and titanium oxide are readily available in nano-sizes.
- The techniques used to manufacture asbestos cement sheets can be used to fabricate micro-meter thick carbon-cement sheets. Filtering technique of asbestos sheet manufacturing needs to be combined with vacuum bagging technique used for fabrication of aircraft structural components.
-

5.2. Fundamental Questions

Some of the fundamental questions that need to be answered are:

- Is the influence of water-cement ratio same for nano-cement?
- Will the strength and strain capacity remain same?
- Is it possible to use metallic nano-fibers?
- Will it be possible to dry process the cement-filler-fiber mix and cure using steam impregnation?

6. SOME OPPORTUNITIES AND CHALLENGES

6.1. Cement composites

If portland cement can be formulated with nano-size cement particles, it will open up a large number of opportunities. For example, the cement can be used as an inorganic adhesive with carbon fibers. Currently the micron size cement particles are not conducive for use with 7 micron (2.75×10^{-4} in.) diameter carbon fibers. The cement will not only be more economical than organic polymers but also will be fire resistant. In addition it will not emit any volatile organic compounds (voc) and the composites can be attached to parent concrete substrate using a compatible adhesive. It will be also very competitive with current inorganic composites because they have to be processed at high temperature.

A number of investigations have been carried out for developing smart concrete using carbon fibers [17]. This will become a reality with nano-cement because nano-carbon tubes are much more effective than carbon fibers. The thickness of the composite can be reduced to microns and hence flexible and smart cement composite can be manufactured.

The primary challenge is to manufacture nano-size cement particles. Chemical vapor deposition shows promise [14]. Other avenue is high tech grinding. The second challenge is the heat of hydration. Special organic and inorganic additives need to be developed to control the setting and heat of hydration. Even though this is a risky and tough venture, the authors believe that the risk is worth taking.

6.2. Coatings for Concrete

Coatings are routinely used as protective barriers against abrasion, chemical attack, hydro-thermal variations and to improve aesthetics. Currently, most of these coatings are in the micrometer range. New materials and techniques are being developed to develop

nano-meter thick coatings that are durable and generate less heat due to reduced friction. Coatings could be self-cleaning and self-healing. In most cases the performance of these coatings are evaluated using experimental techniques. The major parameters evaluated are: durability of coatings under various exposure conditions, abrasion resistance, friction resistance, high temperature resistance and electrical characteristics. Performance of the (coating) film and the interface between the film and the parent material play important role in the overall durability of the system. The authors believe that analytical models are needed to predict the performance of various types of coatings, so that optimum design approaches can be developed. The models could become quite complex because of the interaction of the coating-film with the parent material through the interface. For most cases, the mechanical properties of parent surfaces and some of the available coating materials are known. But very little is known about the performance of the interface under mechanical, hygrothermal and magnetic forces. For the nano coatings, the properties of the coatings themselves need investigation.

Brittle coatings usually fail by cracking, delaminating and spalling rather than “wearing out”. Robust analytical models are needed to predict the initiation and growth of cracks and their contribution to final degradation. We believe that the knowledge-base developed to analyze the thin walled structures can be effectively used to develop the aforementioned analytical models. Most existing coatings tend to accumulate grime reducing aesthetics. The deposited materials also degrade the parent surface over time. Coatings with a nano-scale of roughness that will repel water and dirt, modeled after the coating of the lotus leaf are being created. The lotus leaf has extraordinary ability to keep itself clean and dry. Now nanotechnology is being used to mimic the lotus leaf surface and create new products that outperform existing no-stick products. Typically, on a hydrophobic or water-repellent surface, particles of dirt are removed by moving water. But on a Lotus simulated surface, dirt particles are collected by water drops and rinsed off. Fig. 4 shows self cleaning properties of a coating made using nano-particles. It can be seen that the coated surface is totally free of mold that is present adjacent to the coated surface [13].

7. CONCLUSIONS

Large amounts of funds and effort are being utilized to develop nanotechnology. Even though cement and concrete may constitute only a small part of this overall effort, research in this area could pay enormous dividends in the areas of technological breakthroughs and economic benefits.

Current efforts are focused on understanding cement particle hydration, nano-size silica and sensors. Unique opportunity exists for the development of nano-cement that can lead to major long standing contributions.

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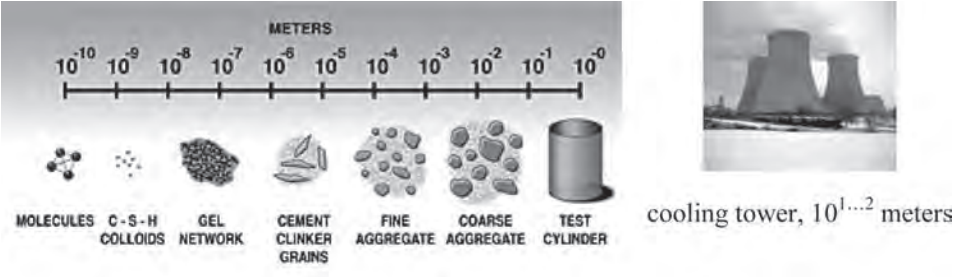


Fig. 1—Scales of various constituents of concrete and a typical application.^[7]

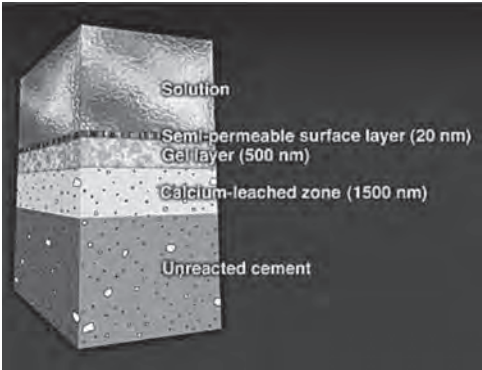


Fig. 2—Details of hydrating cement grain at nano-scale.^[7]

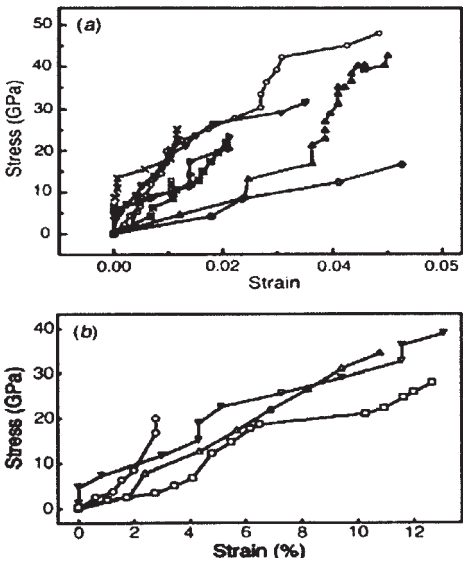


Fig. 3—Stress-strain relationships of nano-tubes.^[11]



Fig. 4—Self-cleaning coating made of nano-particles.^[13]

Molecular Engineering of the Cohesion in Neat and Hybrid Cement Hydrates

by A. Gmira, J. Minet, A. Franceschini, N. Lequeux, R.J.-M. Pellenq, and H. Van Damme

Synopsis: On the basis of recent molecular simulation or experimental studies, we discuss two possible strategies for improving the mechanical properties of cementitious materials by modifying the bonding scheme in the hydrates at molecular level. We focus on the calcium silicate hydrates (C-S-H). A first strategy would be based on the strengthening of the cohesion forces acting between the individual C-S-H lamellae or between their crystallites. Monte Carlo simulations in the primitive model framework and ab initio atomistic calculations suggest that the cohesion of C-S-H is mainly due to a combination of sub-nano range ionic-covalent forces and meso-range ionic correlation forces. Both types of forces may be modified, at least in theory, by changing the nature of the interstitial ions, their hydration state, or the charge density on the C-S-H lamellae.

A second strategy, akin to a bio-mimetic or tissue engineering approach, would be to hybridize the hydrates by grafting organic moieties on the mineral lamellae. We show that this is easily achieved by controlled hydrolysis of mixtures of organo-silane precursors. The outcome may be a material with improved fracture energy.

Keywords: C-S-H; cohesion forces; hybrid hydrates; molecular simulation

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1. INTRODUCTION

One possible way to improve the sustainability of concrete use is to improve the mechanical performance of the binder, cement. Progress in this direction in the last decades have been mainly achieved by reducing porosity, either by optimizing the granular composition towards fine particles and/or lowering the water/solid ratio thanks to the use of organic admixtures.

In the present paper, we discuss a radically different approach, based on the engineering of the bonding scheme in the hydrates at molecular or quasi-molecular level. In this approach, C-S-H is undoubtedly the main target since it is the major source of cohesion in materials made from ordinary portland cement.

A first possible strategy, which is expected to increase rigidity and strength while maintaining an essentially brittle behaviour, could be the optimization of the surface forces which are giving C-S-H its remarkable cohesion, in spite of its porous structure and in spite of the presence of water between the individual nano-particles. The prerequisite for this is to know quite accurately the nature of those surface forces and the chemical parameters which are controlling them.

A second possible strategy, leading to an increase of strength, toughness, and possibly to ductile behaviour, could be to hybridize the hydrates by introducing some soft matter between the hydrate nano-particles. This strategy is extensively used by nature whenever the fracture energy of an otherwise very brittle material, like calcite or aragonite for instance, has to be improved. Nacre (mother-of-pearl) is a well-known case which owes its toughness to the alternation of μm -thick hard aragonite crystals and nm-thick soft protein layers.

We are not yet at the point where these strategies could be implemented in the real construction world, but the basis for it are being built. The point in the present paper is, first, to review our present knowledge of the cohesion forces in C-S-H, largely based on molecular simulation studies and, based on that, to think about possible ways to increase the overall cohesion. Second, we will show that the use of sol-gel techniques opens a way towards the synthesis of truly hybrid hydrates in which the mineral lamellae are separated from each other by covalently bonded organic chains.

2. THE COHESION OF C-S-H

In spite of intense investigations over several decades, the structure of C-S-H is still a matter of some debate [1]. However, it is widely recognized that it has a layered crystal structure and that, at short length scales, the layers form compact domains in which the distance between individual C-S-H nanolayers is of the order of a few tenths of nm, i.e. of the same order as the interlayer distance in a tobermorite crystal with a 1.1 or 1.4 nm (4.33×10^{-8} or 5.51×10^{-8} in.) repeat distance for instance (Fig. 1). These ordered stacks or “crystallites” have been clearly evidenced by atomic force microscopy [2]. The calcium ions in these very confined (“sub-nano”) spaces may be expected to be strongly interacting with the negative surface groups of the silica chains of the C-S-H layers. It is also admitted that, at larger (“meso”) length scales, these compact stacks form three-dimensional porous agglomerates [3], in which the average inter-“crystallite” distance is larger than the interlayer distance within the crystallites, except at the contact spots. The calcium ions in those regions should be fully hydrated and highly mobile.

We will now analyze the cohesion forces which may be acting in these two types of environments. As discussed elsewhere, van der Waals and capillary forces contribute probably only marginally to the cohesion of hardened cement [4]. We will therefore concentrate on the forces generated by the presence of charged ions, starting from the meso-scale porous regions where a continuum approach seems acceptable, and switching thereafter to the very confined sub-nm regions where a molecular description is compelling.

2.1. Cohesion at Meso-Scale

It becomes increasingly clear that a system composed of two charged particles with like charges, separated by charge-balancing ions in water, may generate strongly attractive configurations due to purely electrostatic interactions [4]. At interlayer distances in the nm range, these attractive forces may be considerably stronger than van der Waals forces.

A clear example is the restricted swelling of Ca^{2+} -montmorillonite, compared to the Na^{+} -exchanged form. Montmorillonite belongs to the family of the so-called swelling or smectite clays [4]. The individual layers have a thickness similar to that of C-S-H layers, but their lateral extension is much larger, typically in the μm range. The layers are negatively charged like in the case of C-S-H, but the charge stems from ionic substitutions in the central octahedral backbone, which leads to a surface charge density which should be much more diffuse than in C-S-H where the negative charge is localized on the ionized silica tetrahedra. As shown by Kjellander et al. [5, 6], the restricted swelling of Ca^{2+} -montmorillonite is due to the so-called ionic correlation forces. In the Poisson-Boltzmann treatment of two identically charged surfaces with an intervening electrolyte solution, the two halves of the cell are symmetrical and both are neutral, so that no electric field is induced by one cell into the other. In a real system, the overwhelming majority of instantaneous ionic configurations do not achieve this ideal situation (Fig. 2). On the average, the electric field generated by one half of the lamellar system is still zero in the other half, but for every configuration there is a spatially varying field. The charges of the second half respond to this instantaneous field by adopting configurations of lower energy, different from the mean field configuration. These correlated polarizations of the ionic clouds give rise to an ionic van der Waals type force, much in the same way as correlations between fluctuating electronic dipoles give rise to the London dispersion force. These attractive forces are not taken into account in the DLVO theory of colloid stability.

Ionic correlation forces increase with the surface charge density and with the charge of the interlayer ions. Using Monte Carlo simulations, Pellenq and co-workers [7-9] carried out a systematic study of correlation forces between charged planar surfaces in water in a broad range of charge densities, within the framework of the so-called primitive model (smooth surfaces separated by ions in a dielectric continuum). Charge densities going from less than one charge per 2 nm^2 ($3.10 \times 10^{-15}\text{ in.}^2$) to one charge per 0.2 nm^2 ($3.10 \times 10^{-16}\text{ in.}^2$) were explored. The pressure was calculated for separation distances going from one to five ionic diameters. For the sake of comparison, both the case of Na^{+} and Ca^{2+} counterions were studied. Neglecting van der Waals interactions, the z-component (z axis perpendicular to the surfaces) of the pressure can be written as the sum of three terms:

$$P_{\text{total}}(D) = P_{\text{elec}}(D) + P_{\text{contact}}(D) + P_{\text{ideal}}(D) \quad (1)$$

The first term is the force resulting from the sum of all the ion-ion, ion-lamella and lamella-lamella coulombic interactions through a plane at $z = 0$ (mid-plane). It is obtained from the z-derivative of the energy. This term is always attractive (negative). It takes into account the ionic correlations due to electrostatic interactions. The second,

repulsive contact term is the hard core contact pressure, which is a consequence of using ions with a finite and realistic size, instead of point charges. It is proportional to the number of ions in contact (collisions) through the plane located at $z = 0$ and takes automatically into account steric correlations. The third ideal term is nothing but the repulsive osmotic pressure, $\rho(0)kT$, due to the kinetic contribution of the confined ions. It is obtained from the ionic density $\rho(0)$ in a volume of thickness δx around the mid-plane. A first result was that the total ionic pressure is always repulsive with Na^+ counterions, even at the largest charge densities, showing that ionic correlations are negligible with small monovalent ions in water. The pressure values are also in good agreement, at moderate charge densities, with the mean field PB treatment.

Second and more important, one or more attractive pressure wells were obtained with Ca^{2+} ions for all parameters sets investigated. For charge densities corresponding to montmorillonite, the pressure well is of the order of -1 MPa (-145 psi) at a separation distance of 1.4 nm (5.51×10^{-8} in.) (Fig. 4), in agreement with theory. But for charge densities of one charge per 0.33 nm^2 (5.12×10^{-16} in.²), the depth of the well increases to -60 MPa (8700 psi) at a separation of 0.7 nm (2.76×10^{-8} in.) (Fig. 3), which is more than one order of magnitude larger than the van der Waals pressure at the same distance. Those are the most attractive conditions.

At still higher charge densities, repulsive contact interactions in the crowded interlayer space start to compensate the electrostatic attraction. Remarkably, the charge density at which the maximum attractive pressure is obtained corresponds to that of a C-S-H lamella with all its OH groups ionized. A pressure vs. distance map is shown in Fig. 3. It is worth mentioning here that what has been said for correlation forces in C-S-H might also apply to aluminate hydrates. Indeed, mono-sulfo-aluminate hydrates have also a layered crystal structure, with positively charged lamellae and interlamellar divalent anions. Thus, *mutatis mutandis*, they may be considered as a charge-symmetrical version of C-S-H and, within the framework of the primitive model (which ignores the atomic details of the lamellae) and Monte Carlo computations should yield comparable results

2.2. Cohesion at Sub-Nano Scale

The previous modeling approach implies that the distance between surfaces is large enough to consider that water is a continuum. It implies also that the ions are highly mobile. These assumptions are definitely no longer valid when the distance between walls becomes of the order of two water molecule diameters. A correct modelling of this requires atomic level simulations, using either potential energy minimization or direct quantum methods.

In potential energy minimization, starting from a reasonably good approximation of the structure and suitable expressions for the short- and long-range interaction potentials in the system, the total potential energy is minimized with respect to all degrees of freedom of the system in configuration space. This approach yields results comparable to those of molecular dynamics in which, using interatomic potentials, the equations of motion of each atom are solved.

Potential energy minimization has recently been applied to tobermorite, with a Ca/Si ratio of 1 and 4 water molecules per unit cell [10, 11]. Several energy minima are obtained at 1.1, 1.225, and 1.4 nm (4.33×10^{-8} , 4.82×10^{-8} , and 5.51×10^{-8} in.) (repeat distance, i.e. layer thickness plus interlayer distance), respectively, the later being less stable than the formers. The first derivative of these curves with respect to distance gives the interlayer pressure. A strongly cohesive behaviour is obtained, with attractive pressures around the equilibrium positions which may be up to 100 times larger than those calculated from the ion correlation forces (previous section). The bulk- and Young's modulus values obtained from these calculations are in good agreement with experimental values.

Ab initio quantum calculations performed on the same structure (tobermorite with Ca/Si=1; 4 H₂O/u.c.) [16, 17] show the partial electronic charge on the atoms does not depend on the interlamellar distance, which means that the nature of the inter- and intra-lamellar bonds remains unchanged.

The numerical values obtained for the charge on the oxygen, calcium and silicon atoms in the lamellae show that the ionic character of the bonds in the lamellae is close to 60%. The charge on the interlamellar calcium ions is +1.38, which is slightly higher than for the ions within the lamellae, but still much lower than the value expected for a purely ionic bond. If the ions were really hydrated and totally free to diffuse in the electric double layer, as assumed in the primitive model, they would have a charge +2. Furthermore, the distance between the interlamellar calcium ions and the oxygen atoms of the lamellae is very close to the Ca-O distance within the lamellae. This is very important because it shows that the interlamellar calcium ions are linked to the lamellae by a strongly ionic-covalent bond (30% covalent character) and are really part of the lamellae structure, in agreement with the structure obtained by energy minimization (Fig. 5). This is the reason for the low exchangeable character of these ions.

The interlamellar distance dependence of the cohesion energy, neglecting the electronic correlations (dispersion or London contribution to van der Waals interactions), is close to the curve obtained by energy minimization (Fig. 6), with a main minimum at 1.2 nm (4.72×10^{-8} in.). The attractive contribution of electronic dispersion interactions (van der Waals forces) adds about 20% to this energy.

2.3. Overall Picture and Prospects for Improvement

The results summarized in the previous sections show that short- and medium-range attractive electrostatic forces are the essential components of the cohesion of C-S-H. At short sub-nm distance (one or two water molecule diameters), the C-S-H layers are trapped into an extremely deep potential well corresponding to a configuration involving quasi-individual interlamellar water molecules and calcium ions which are bonded to the closest lamella by a partly covalent bond. At larger (a few nm) distance, the lamellae or stacks of lamellae are trapped in less deep potential wells generated by ionic correlation forces involving mobile ions in liquid water films.

It is hard to establish *a priori* the respective contribution of these two types of forces without having a very detailed model for the fabric of the C-S-H layers at length scales going from the shortest interlayer distances to the size of a mechanically representative volume, which may be orders of magnitude larger. There is little doubt that within the locally ordered stacks the ionic-covalent forces are dominating. The same holds for the spots where two stacks come in “contact”. However, the structural conditions for having these strong interactions are very stringent. The ion correlation forces are weaker but they require much less stringent structural conditions. Considering the very disordered character of the C-S-H “gel” in a dense cement paste, it is likely that these forces generate a kind of background attractive pressure contributing significantly to the overall cohesion.

The levers that we have in our hands in order to improve this cohesion are the parameters which control the forces. As far as ion correlation forces are concerned, increasing the charge density of the C-S-H layer by ionic substitution in the layers (substitution of Ca^{2+} by Al^{3+} for instance) may be considered but, in parallel, the size of the interlayer ions would have to be lowered in order to avoid hard core repulsions. On the other hand, changing the interlayer ions would also modify – in one way or another – the strength of the short-range ionic-covalent bonds between the interlayer ions and the oxygen atoms of the layers. The main problem is that it is notoriously difficult to dope the C-S-H layers and to ion-exchange their interlayer ions.

Another route would be to try to modify the growth of the individual layers in such a way as to favour entanglement rather than perfect stacking. This would largely improve the continuity of the bonding scheme and the overall cohesion. However, very little basic knowledge has been gathered on this so far. Progress is definitely needed.

3. TOWARDS HYBRID HYDRATES

There are several ways to synthesize C-S-H. The most important in practice is for obvious reasons the hydration of C_3S . Alternative routes may involve the so-called pozzolanic reaction between reactive silica and lime solutions, or the direct precipitation from a solution containing silicate ions and lime at high pH [12, 13]. It has recently been shown that co-precipitation of a mixture of organotrialkoxysilane, tetraethoxysilane (TEOS) and a calcium salt in aqueous/ethanol base solution leads can lead to a variety of solids including neat C-S-H, a layered calcium organo-silicate hybrid with a clay-like structure [18], or truly hybrid C-S-H with varying amounts of organic groups in the interlayer space, directly linked to the silicate chains [19].

In the absence of organotrialkoxysilane (that is, using only TEOS), a relatively well crystallized C-S-H is obtained. At the opposite, hydrolysis with 100% organotrialkoxysilane leads to a layered calcium alkyl-silicate in which the silica tetrahedral are forming a continuous layer on each side of a central brucite-like calcium octahedral layer. The alkyl chains, covalently bonded to the silica sheets, are forming a bi-layer in the interlayer space (Fig. 5). As expected, the basal distance is increasing linearly with the length of the alkyl chains.

The most interesting materials as far as cementitious binders are concerned are those obtained at intermediate substitutions of TEOS by the organotrialkoxysilane. The structural data obtained by X-ray diffraction and by 1D and 2D solid-state NMR show that the silica tetrahedral recover the chain structure typical of C-S-H and that the organic groups are covalently to the inorganic framework (Fig. 6). This was so far achieved with short organic chains (ethyl, n-butyl or 3-aminopropyl), but encouraging results with silylated polymers have recently been obtained. The mechanical properties of these materials, after compaction, are currently being investigated.

4. CONCLUSIONS

In this paper, we reported about two approaches which may ultimately prove to open new ways for improving the mechanical performances of cementitious materials.

One is based on the possible engineering of the surface forces which insure the cohesion of the hydrates. The other, bio-inspired, is based on the covalent hybridization of the hydrates with small organic groups or with polymeric chains. In spite of a sound scientific basis, both approaches require further fundamental studies before they could be implemented. In particular, it appears essential to improve our understanding of the parameters controlling the doping and/or the ion exchange of C-S-H by foreign ions. Equally crucial are a basic understanding of the parameters controlling lamellae growth in dense systems, and a theory of the mechanical behaviour of nano-hybrid materials.

When taken together, these two strategies could form the basis for what would be a truly nanotechnological roadmap for cementitious construction materials.

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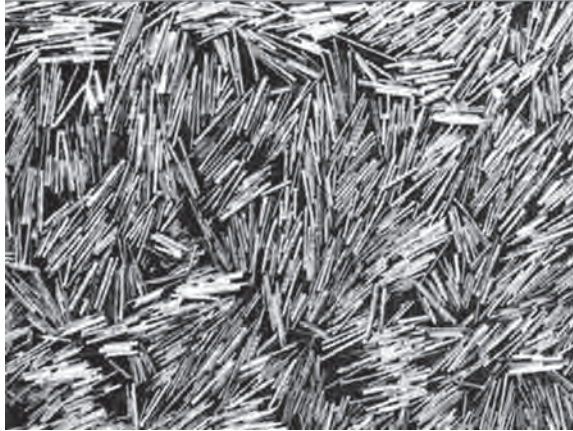


Fig. 1—The microstructural model of C-S-H, with locally dense quasi-1D layer stacks and less dense 3D assemblies.

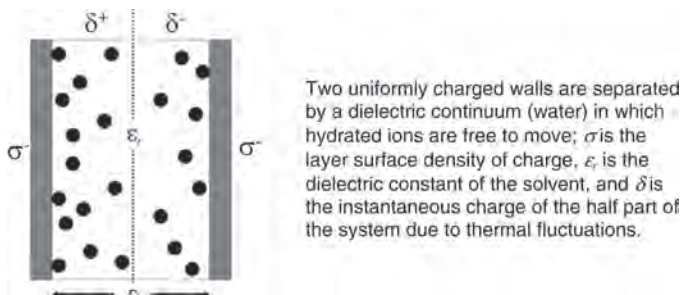


Fig. 2—Sketch of the configuration used to calculate the double layer interactions by Monte Carlo simulation, using the so-called primitive model.

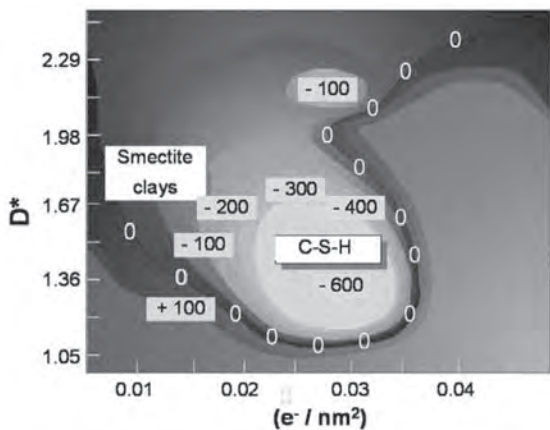


Fig. 3—Isobaric contour map for the interaction between two negatively charged surfaces facing each other, with calcium counterions in water (adapted from Pellenq et al., [7]).

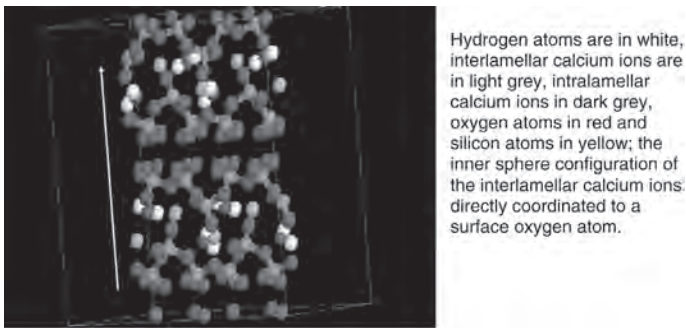


Fig. 4—A relaxed configuration of tobermorite-like C-S-H (Hamid's structure); after potential energy minimization, at $\text{Ca/Si} = 0.83$ and four water molecules per unit cell in the interlamellar space.

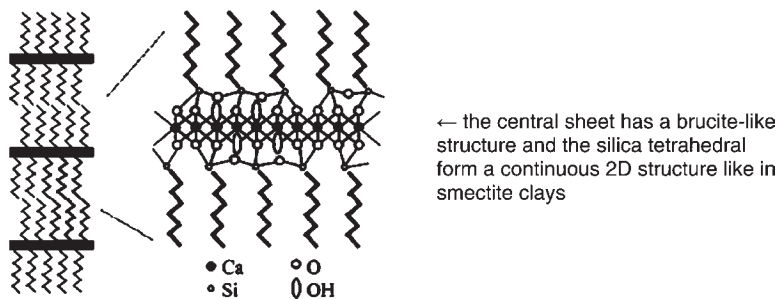


Fig. 5—Structure of the clay-like layered calcium alkyl-silicates obtained by the hydrolysis of organotrialkoxysilane.

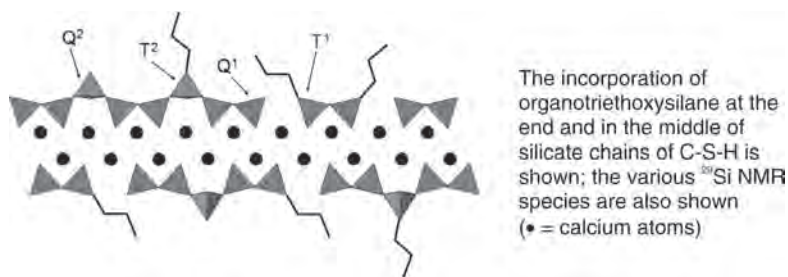


Fig. 6—Schematic model of a layer of hybrid calcium-silicate materials.

Use of Atomic Force Microscopy and Nanoindentation for Characterization of Cementitious Materials at the Nanoscale

by P. Mondal, S.P. Shah, and L.D. Marks

Synopsis: In this research, sample preparation techniques were developed to image the nano- and microstructure of hardened cement paste and to determine local mechanical properties. An atomic force microscope (AFM) was used to image the nanostructure of hardened cement paste. AFM and a Hysitron Triboindenter equipped with an in-situ scanning probe microscopy were used to determine the Young's modulus of cement paste at the nanoscale.

Keywords: atomic force microscope; cement paste nanostructure; mechanical properties; nanoindentation

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1. INTRODUCTION

The fundamental properties of concrete are affected by material properties at the nanoscale. Thus, characterization at the nanoscale is essential to improve cement and concrete properties [1, 2]. It is necessary to understand the nanostructure and how this relates to certain properties, such as local mechanical properties.

In the recent past, atomic force microscopy (AFM) [3] has been used to study the nanostructure of cementitious materials [4-10]. As a few examples, it has been used to study: (a) the surface changes of cement clinker immersed initially in saturated calcium hydroxide solution, followed by immersion in water and sucrose solution [4]; (b) the change in hydrated cement paste microstructure with exposure to different humidity levels [5]; (c) the carbonation process of calcium hydroxide present in hydrated cement paste [6] and (d) for imaging the denser microstructure of the cement paste with silica fume or fly ash [7].

It has also been used in force mode to study how the adhesion changes with use of different superplasticizer [8]. Its local probe can in principle determine local mechanical properties along with high resolution imaging. This has been successfully implemented for different soft materials [11], but in general it only provides qualitative information

and proportional values for the elastic modulus [12, 13]. AFM has also been used to determine mechanical properties at ultrasonic frequencies [14-16].

Nanoindentation is another technique that has proven reliable to quantitatively determine local mechanical properties [17-24]. However, the absence of any imaging ability is an issue for heterogeneous materials such as cement paste. To overcome this problem, in some recent nanoindentation studies a large number of indentations were performed on a hydrated cement paste sample and the calculated modulus values were grouped statistically to get the moduli of different phases present [21, 22]. In another study, in order to make the experiment more reliable, a cold field emission scanning electron microscope (CFE-SEM) has been used to add an imaging capability [18].

In this paper, an atomic force microscope was used to image the nanostructure of cement paste. Two different methods were considered for the determination of nanoscale local mechanical properties. The basic idea behind both the approaches was to be able to image the sample first to identify different phases and then determine local mechanical properties for the same. AFM was employed due to its ability to be used in force mode with a special diamond indenter probe to extract nanoscale local mechanical properties along with high resolution imaging. An effort was made to determine the nanoscale elastic modulus of hardened cement paste. Also, a Hysitron Triboindenter was used, which combines nanoindentation to determine the local mechanical properties at the nanoscale with AFM-like high resolution in-situ scanning probe microscopy (SPM) imaging that allows pre- and post-test observation of the sample. A Triboindenter allows for a more direct approach, where one can identify different phases in cement paste through imaging and determine the local mechanical properties of the same phases with minimal ambiguity. This unique advantage has already been exploited in the case of other materials [10]. This paper presents results of nano-mechanical testing on cement paste.

2. RESEARCH SIGNIFICANCE

This is an interdisciplinary research with a goal to improve the understanding of the basic properties of concrete and cementitious materials. In this paper, a novel idea of combining nano-mechanical testing with imaging at the nanoscale is reported. It furnishes the effectiveness of two different techniques in determining nanoscale local mechanical properties. Further research is in progress, which will provide better understanding of the nanostructure of cement paste and inputs for modeling the nanoscale properties of cementitious materials in the future.

3. SAMPLE PREPARATION

The cubes of cement paste 25.4 mm × 25.4 mm × 25.4 mm (1 in. × 1 in. × 1 in.) were made out of Type I Portland cement with a water to cement ratio of 0.5. Samples were demolded after 24 hours, and then cured at 25°C (77 °F) under water for 6 months. Next, thin sections were cut out of these specimens and polished to get a very flat surface. This is a very important step since having a smooth surface is critical to determine local mechanical properties using an AFM or a nanoindenter. Different polishing techniques were studied to understand the effectiveness of these techniques and estimate the

damaging effect that might be associated with them. Finally the technique mentioned in this section was selected since it gave the best result. Samples were dry polished using Beuhler-Met II paper discs of gradation $34.2\text{ }\mu\text{m}$ (1.35×10^{-3} in.), $22.1\text{ }\mu\text{m}$ (8.7×10^{-4} in.), $14.5\text{ }\mu\text{m}$ (5.71×10^{-4} in.), and $6.5\text{ }\mu\text{m}$ (2.56×10^{-4} in.). During polishing, water was avoided since it weakens the porous microstructure of cement paste samples. The effect can be evident in the form of pull offs (peeling of the top layer in patches) on the surface. After polishing on each paper, a Nikon Epiphot Microscope was used to check the effectiveness of the polishing. Diamond lapping films from Allied High Tech Products Inc. of gradation $6\text{ }\mu\text{m}$ and $3\text{ }\mu\text{m}$ (2.36×10^{-4} in. and 1.18×10^{-4} in.) were used to polish samples down to $3\text{ }\mu\text{m}$ (1.18×10^{-4} in.). Then, a $0.1\text{ }\mu\text{m}$ (3.94×10^{-6} in.) diamond suspension in water was used to polish samples down to $0.1\text{ }\mu\text{m}$ (3.94×10^{-6} in.). As a final step, 2 mm (0.08 in.) thick polished samples were ultrasonically cleaned for 1 minute in water to remove polishing debris. During sample preparation, water was avoided for most of the polishing steps. Otherwise, effects, if there were any, due to the use of water were always tested against methods without any water. For longer storage, samples were placed in nitrogen to avoid any change in the microstructure due to atmospheric exposure.

4. IMAGING HARDENED CEMENT PASTE AT THE NANOSCALE

4.1. Experimental Details

A FEI Quanta 600 sFEG environmental scanning electron microscope was used in low-vacuum mode to find representative areas of the sample after polishing. Use of SEM along with a Digital Instrument Nanoscope MultiMode Scanning Probe Microscope also provided surface information from the millimeter to the nanometer scale. AFM was used in both contact and tapping mode, although tapping mode was found to be more effective. AFM images of samples before and after SEM imaging were compared. This was to make sure that AFM images were not affected by any possible damage that the low-vacuum used in SEM might have on the sample.

4.2. Experimental Results

Images of C-S-H gel show nearly spherical particles of different sizes in different areas. Fig. 1 is a $4.7\text{ }\mu\text{m} \times 4.7\text{ }\mu\text{m}$ ($1.85 \times 10^{-4} \times 1.85 \times 10^{-4}$ in.) AFM image of C-S-H gel which clearly shows particles of size 200 nm to 350 nm (7.87×10^{-6} to 1.38×10^{-5} in.). The image was captured in tapping mode. The left image shows the topography or the coarse height variations of the sample, brighter regions being higher than darker ones. The right one is the amplitude image that shows local variations in height after removal of the coarse topography variations. This is in effect a high-pass filtered image. With the most effective polishing technique, it was possible to explore the structure of C-S-H gel at a scale of 40 - 50 nm (1.59×10^{-6} - 1.97×10^{-6} in.). Fig. 2 is a $1.5\text{ }\mu\text{m} \times 1.5\text{ }\mu\text{m}$ ($5.91 \times 10^{-5} \times 5.91 \times 10^{-5}$ in.) AFM image which shows spherical particles of size in the range of 40 nm. It should be noted that the feature size in an AFM image of a somewhat rough material such as this should only be interpreted as an upper bound on the true feature size

in the object; in many cases the images are a convolution of the tip shape and the sample roughness.

4.3. SEM and AFM study on fractured surface

An effort was made to compare scanning electron microscopy images with atomic force microscopy images. Secondary electron imaging using SEM on a polished sample does not reveal much information on the morphology due to the extreme smoothness of the sample. Therefore, it was decided to consider a fractured surface in this context.

Fig.3 shows the SEM image of a fractured surface of cement paste. However, with fractured surfaces, it was very difficult to get atomic force microscopy images. On a fractured surface, surface roughness is generally so high that it suppresses the capability of imaging small inherent structure of the material in AFM. After much effort, relatively smaller areas have been successfully imaged using AFM. Figs. 4 and 5 are atomic force microscopy images of the fractured surface. Images compare well with the SEM image showing the foil or crumble-like structure of C-S-H. It also shows that these foil-like structures are made up of spherical particles which only the sensitive AFM probe can capture.

5. DETERMINATION OF MECHANICAL PROPERTIES AT THE NANOSCALE

5.1. Review of Nanoindentation Theory

In any indentation technique, one material of known properties is used to indent the material of interest whose mechanical properties such as elastic modulus and hardness are unknown. This technique has its origins in Mohs hardness scale developed in 1822 in which one material is said to be harder if it can leave a permanent scratch on another material. In nanoindentation, an indenter is pushed into a sample while load applied by the indenter is plotted continuously with the displacement of the indenter into the sample. This kind of plot is commonly known as load-indentation plot or, simply p-h plot. The data obtained is then analyzed to estimate elastic modulus, E , and hardness, H . This analysis procedure is essentially based on the solution of elastic contact problem developed by Boussinesq and Hertz in late 19th century. In early 1970's, Buylchev, Alekhin, Shorshorov used instrumented microhardness testing machines to obtain load-displacement plot and analyzed the data using the following equation which is known as Buylchev-Alekhin-Shorshorov equation or in short BASH equation:

$$S = \frac{dp}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A} \quad (1)$$

In this equation, $S = dp/dh$ is the experimentally measured stiffness for the upper portion of the unloading data, E_r is the indentation modulus which is related to the elastic modulus and poisson's ratio of the sample and A is the projected area of the elastic contact

which was assumed to be equal to the optically measured area of the hardness impression. E_r can be calculated using equation (2) where E and ν are the elastic modulus and poisson's ratio of the sample, and E' and ν' are the elastic modulus and poisson's ratio of the indenter respectively:

$$\frac{1}{E_r} = \frac{1 - \nu^2}{E} + \frac{1 - \nu'^2}{E'} \quad (2)$$

In 1992, Oliver and Pharr [20] proposed a method of analysis based on analytical solutions. This accounts for the curvature in the unloading data. They also mentioned that the direct measurement of the contact area is not always accurate and convenient and proposed a procedure to determine the contact area based on the depth of indentation and indenter shape function. Such a method is sometimes called "depth-sensing indentation testing".

5.2. Experimental Details using Atomic Force Microscopy

Indentation and subsequent determination of nanoscale mechanical properties of a material can be done using an AFM in force mode. In this study, a Digital Instruments D3000 scanning probe microscope was used to produce force curves on a hardened cement paste sample. A special diamond-tipped indentation probe was used as shown schematically in Fig. 6. The diamond tip had an approximate tip radius of 25 nm (9.84×10^{-7} in.) which was attached to a stainless steel cantilever that had approximate width of 100 μm (3.94×10^{-3} in.), thicknesses of approximately 13 μm (5.12×10^{-4} in.), and lengths of approximately 350 μm (1.38×10^{-2} in.). The effective spring constant was estimated to be 150 N/m (2.19 lb/ft) (as supplied by Digital Instruments). During experiment in AFM force mode, the probe tip is first lowered into contact with the sample, then an indentation is made into the surface, and finally the tip is lifted off of the sample surface. The probe tip deflection is measured concurrently and a plot of tip deflection versus piezo motion, called a force curve, is generated.

A typical force plot is shown in Fig. 7 where force can be calculated as difference in piezo movement (ΔZ) times the spring constant. As the piezo moves toward the sample surface (or vice-versa, depending on the system), the tip deflection remains constant until the probe tip touches the sample surface (A to B in Fig. 7). Now, just before contact, the tip can be pulled down to the surface by attractive forces, causing a small decrease in tip deflection (B to C in Fig. 7). Further decrease in the piezo height causes indentation into the sample surface and at the same time, the cantilever deflects in the opposite direction, increasing the tip deflection from C to D as shown in the figure. During unloading, cantilever deflection reduces (D to E in Fig. 7) while the piezo retracts. Due to the tip-sample adhesion, the cantilever deflects further down (E to F) and finally jumps out of contact. For an infinitely stiff sample with respect to the probe, no indentation will occur. This can be used to calibrate the AFM probe under the operating conditions. In this study, a force curve was first recorded on a sapphire sample. It was assumed that no indentation was made in this case. Then indentation was made on a cement paste sample. Fig. 8

shows a force plot recorded from three different indentations on the sample, and the difference in elastic properties can be inferred from the difference in the slope of the unloading part (refer Eq. (1) of section 5.1). Fig. 9 shows an AFM image captured after making several indents on the cement paste sample. From the test data, a relative Young's modulus was determined. It was found that the testing procedure was not sensitive enough for stiff material like hardened cement paste to determine quantitative values.

5.3. Experimental Details using Triboindenter

A Hysitron Triboindenter as shown in Fig. 10 with a Berkovich tip (total included angle of 142.3°) was used to determine the nano-mechanical properties. The indenter tip itself was used to capture the AFM image of a sample. Since the tip radius of the indenter mentioned above is in the range of 100 - 200 nm (3.94×10^{-6} – 7.87×10^{-6} in.), image resolution was not as high as with a conventional AFM [tip radius typically in the range of 5 - 15 nm (1.97×10^{-7} – 5.91×10^{-7} in.)]. Thus, images of the same area from a Quanta Environmental Scanning Electron Microscope and a Digital Instrument AFM were compared with the AFM images from the Triboindenter to establish the protocol of identifying different phases of cement paste using the Triboindenter only. Once good correlation was established, the desired test location [maximum area being $60 \mu\text{m} \times 60 \mu\text{m}$ ($2.36 \times 10^{-3} \times 2.36 \times 10^{-3}$ in.)] was imaged in AFM mode of the Triboindenter using the indenter tip. Then indents were made on about 50 test locations with specified maximum load and loading rate. Multiple cycles of partial loading and unloading were used to make each indent. This eliminates the creep effects and the size effects [19].

Fig. 11 shows a typical load displacement plot recorded from nanoindentation on C-S-H in a hardened cement paste sample. In different tests, the maximum load used for indentation on C-S-H was varied from 500 μN to 1500 μN (1.12×10^{-4} to 3.37×10^{-4} lb) at a loading rate of 100 $\mu\text{N/s}$ to 300 $\mu\text{N/s}$ (2.25×10^{-5} to 6.74×10^{-5} lb/s). Corresponding variations in the depth of indentation were from 250 nm to 500 nm (9.84×10^{-6} to 1.97×10^{-5} in.). Elastic properties were evaluated using the Oliver and Pharr method [20] from the final unloading region of the load vs. indentation curve.

5.4. Analysis of the Results from Triboindenter

Fig. 12 shows a $60 \mu\text{m} \times 60 \mu\text{m}$ ($2.36 \times 10^{-3} \times 3.36 \times 10^{-3}$ lb) image of cement paste with a bright, residual cement particle near the center. It also shows the modulus values calculated from the indentation data. Values are written at the respective indent locations on the image. Observed mechanical properties of the C-S-H gel in different areas varied in a wide range [~ 10 - 35 GPa (1450 – 5077 ksi)]. Statistical analysis showed that a normal distribution can be fitted for the variation in modulus with a mean of 19 GPa (2756 ksi) and standard deviation of 7.2 GPa (1044 ksi). Fig. 13(a) shows a normal probability plot, where the linear nature (correlation coefficient = 0.96) of the plot indicates normality of the data. Fig. 13(b) compares the cumulative distributions of the experimental data and the fitted normal distribution. In this case the P-values for the