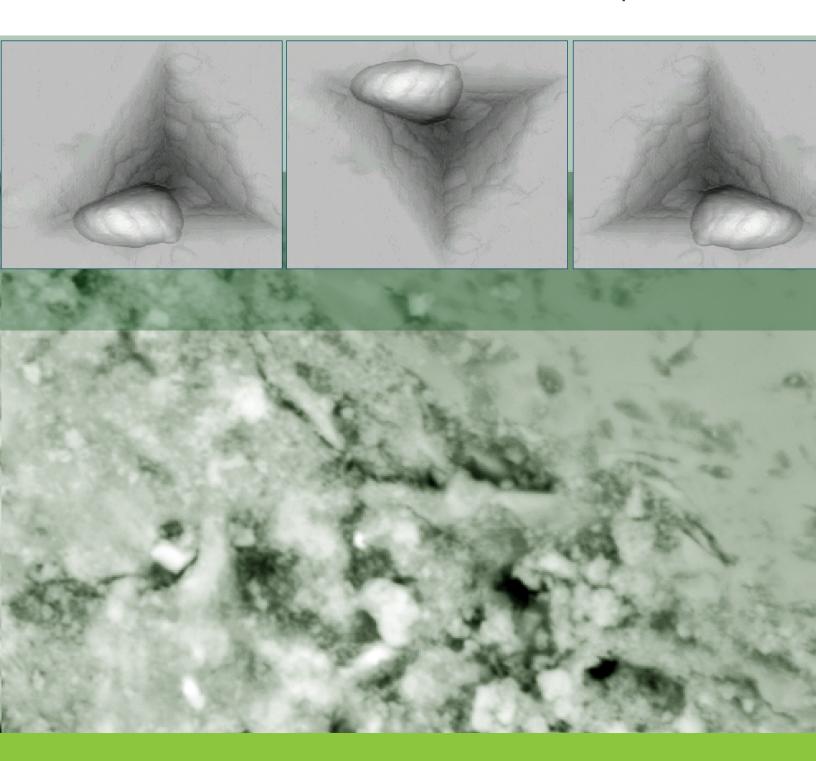
Workshop on _____

Nanotechnology for Cement and Concrete

September 5, 2007



Report of the Workshop on Nanotechnology for Cement and Concrete

September 5, 2007

Peter Taylor Krishna Rajan Bjorn Birgisson Tom Cackler

Sponsored by The National Concrete Pavement Technology Center and the National Science Foundation, in Cooperation with the Nanoscale Science, Engineering, and Technology (NSET) Subcommittee of the U.S. National Science and Technology Council, through the National Nanotechnology Coordination Office

Acknowledgments

The workshop was sponsored by The National Concrete Pavement Technology Center and the National Science Foundation, in Cooperation with the Nanoscale Science, Engineering, and Technology (NSET) Subcommittee of the U.S. National Science and Technology Council, through the National Nanotechnology Coordination Office.

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Thanks go to the presenters for permission to reproduce their presentations.

Workshop on Nanotechnology for Cement and Concrete

Preface

This document summarizes the discussions and findings of a workshop held in Arlington, VA, on September 5, 2007. The objective of the meeting was to provide national direction on areas of priority interest and collaboration between industry and public agencies specifically for applications of nanotechnology to cement and concrete.

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Introduction

The Challenge

Concrete as a material is the most commonly used material (other than water) on the planet. Its significance to the basic infrastructure of modern civilization is immeasurable, and it is difficult to imagine life without it. However, concrete as a material has changed relatively little since its first usage in its current form one hundred years ago. As increasingly higher performance demands are placed on the product, the limitations of modern concrete as a construction material become increasingly apparent.

One significant need of the concrete construction material is to significantly increase reliability. It is estimated that up to 10% of concrete placed in a given year fails prematurely or is below standard from the beginning. Considering that concrete construction is a 700 billion dollar industry worldwide, even a small reduction in the number of problems would amount to significant economic savings and performance benefits. A lot of attention is focused on dealing with the currently accepted risks inherent in construction, along with the associated high levels of litigation. The industry is generally conservative because the consequences of failure are devastating, leading to significant overdesign of many facilities. There is a movement to move away from prescriptive specifications to performance-based specifications; however, it is also generally accepted that adequate test methods and tools to measure performance are lacking at present. An improvement in reliability of concrete systems will have a multibillion dollar impact on the economy.

Another issue is that while the production of concrete is efficient in terms of emissions and embodied energy, the shear volumes of concrete produced worldwide mean that attention has to be paid to make the material more sustainable and impose a lower burden on the environment. Concrete produces lower emissions and has lower embodied energy than other materials. Published data are varied, but typically concrete is reported to have lower embodied energy per square foot of floor area for office buildings than steel¹. Portland Cement Association (PCA) reports that 2.310 million metric tons of cement were produced in 2005² worldwide, meaning that up to 2.08 million metric tons of CO₂ were released (based on the assumption that for each ton of cement, 0.9 tons of CO₂ are released).

A challenge facing materials engineers working in concrete is that most other modern systems are several orders of magnitude smaller and cheaper than they were a few decades ago, but the same is not true of structures. This is partially so because buildings still have to be big enough for us to fit into. Even so, section thicknesses in structures have not changed significantly over time.

Concrete as a construction material is unique because it is a commodity, fabricated on site by generally low-paid workers with a modicum of quality control. Imagine a material made out of abundant raw materials available almost everywhere by a very energy-efficient process. By mixing this material with water, you get a construction material that is workable for many hours, that can be formed into any geometrical shape, and that hardens and develops high strength. It is used in a relatively crude way in the field. Nanotechnology has the potential to enhance the desirable properties of concrete while helping to address some of the challenges facing the construction industry.

¹ Yohanis, Y.G., and Norton, B., "Life-cycle operational and embodied energy for a generic single-storey office building in the UK", Energy, Volume 27, Issue 1, January 2002, Pages 77-92.

North American Cement Industry, Annual Yearbook, 2006, Skokie, IL, Portland Cement Association, ER365, 2007

Background

The study of cementitious systems has not gained much attention in materials science and materials engineering circles, possibly because it is not a carbohydrate and because it is less predictable than metals. Also, in many ways, current knowledge has been good enough for it to be economically functional. It has been abuser friendly, and because strength was the only parameter of concern, a fundamental understanding of how the system works has not been aggressively pursued. However, concrete systems are growing increasingly complex, changing from mixes with four basic ingredients (cement, water, sand, and stone) to mixes with nine or more ingredients with the addition of multiple chemical admixtures and supplementary cementitious materials. With increasing number of ingredients come increasing complexity and risks of problems, as illustrated by a new-found emphasis on incompatibility that was not seen ten years ago. Additionally, as previously noted, engineers are moving toward requiring performance that is based on durability and crack resistance, rather than simply strength.

Fundamentally, hydrated cement paste (HCP) is a nanomaterial (Figure 1)³. The structure of calcium silicate hydrate is much like a clay, with thin layers of solids separated by gel pores filled with interlayer and adsorbed water (Figure 2)⁴. This has significant impact on the

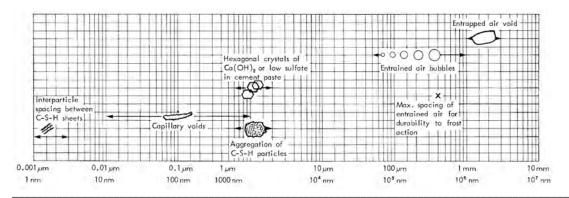


Figure 1. Dimensional range of solids and pores in a hydrated cement paste

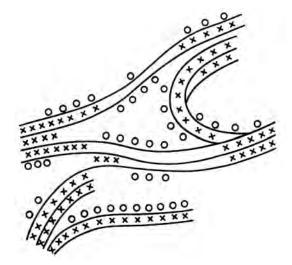


Figure 2. A model of the structure of C-S-H, showing C-S-H layers (lines), interlayer water molecules (crosses), and adsorbed water molecules (circles).

³ Mehta, P.K., "Concrete Structure, Properties and Materials," Engelwood Cliffs, NJ, Prentice-Hall, 1986.

⁴ Taylor, H.F.W., "Cement Chemistry," 2nd Edition, London, Thomas Telford, 1997.

performance of concrete because HCP is sensitive to moisture movement, which can lead to shrinkage and consequent cracking if accommodations in element sizes are not made⁵.

As computing capabilities grow and nanotechniques are developed, we now are starting to improve the tools and skills that we need to take a fundamental look at the hydrated cementitious system. Based on this new knowledge, it is therefore feasible to consider how to modify the cementitious system to address the issues confronting working construction sites, including shrinkage and knowing/controlling the degree of hydration.

The concrete construction industry is not the only industry looking at using nanoscience and technology to enhance their products. Notable overlaps with our work are roadmaps developed for forest products and chemical products. Forestry is looking at ways to manipulate and use lignin, which is a primary ingredient in concrete admixtures, while the chemical products industry is adopting an approach of starting with their needs and then using nanotechnology to meet those needs, which is the same approach being adopted in this meeting.

A workshop at the University of Florida in August 2006 was attended by over 70 participants, with over 30 presentations⁶. The meeting focused on the development of a Roadmap for Research for Concrete-Based Materials. The roadmap is destination oriented with clearly defined outcomes that will greatly enhance concrete technology and the uses of concrete in structures, including housing, bridges, tunnels, and pavements. The needs expressed during the 2006 workshop are as follows:

- Development of high-performance cement and concrete materials as measured by their mechanical, durability, and shrinkage properties.
- Development of sustainable and safe concrete materials and structures through engineering concrete for different adverse environments, reducing energy consumption during cement production, and enhancing safety with nano-engineering of concrete materials.
- Development of intelligent concrete materials through the integration of nanotechnology-based self-sensing and self-powered materials and cyber infrastructure technologies.
- Development of novel concrete materials through nanotechnology-based innovative processing of cement and cement paste.
- Development of fundamental multiscale model(s) for concrete through advanced characterization and modeling of concrete at the nano-, micro-, meso-, and macroscales.

The aim of the 2007 workshop was to build on the 2006 workshop and to seek input from industry regarding needs that should be addressed now, based on what is required, and what is conceivably possible in the near term. Input to the discussions also included examples of successes already achieved and guidance from those currently working in technology on what is feasible based on current knowledge. In attendance were representatives of the concrete construction industry, product manufacturers, government agencies, including owners of concrete structures and regulators of such, and academia. One of the presentations included a representative of Nanocem, a European initiative that is funded primarily by industry with the stated goal of conducting fundamental research on cementitious materials with an emphasis on understanding cement hydration at a molecular level.

The meeting included ten presentations, a roundtable discussion, and six breakout group discussions. The material covered in all of these sessions follows.

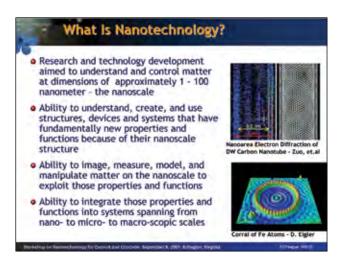
⁵ Jennings, H.M., Thomas, J.J., Gevrenov. J.S., Constantinides, G., and Ulm, F-J., "A multi-technique investigation of the nanoporosity of cement paste," Cement and Concrete Research, Vol. 37., 2007, pp. 329–336.

⁶ http://www.ce.ufl.edu/nanoworkshop/program.html, 2007

Workshop on Nanotechnology for Cement and Concrete

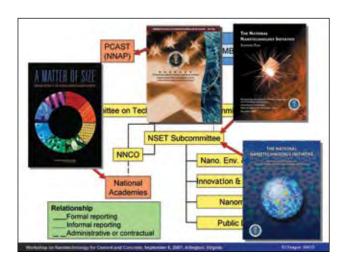
Presentations

- 1. Snapshot of the National Nanotechnology Initiative—Dr. Clayton Teague
- 2. Nano House—Dr. Mike Roco
- 3. Nanocem—European Efforts—Vagn Johansen
- 4. The Future of Concrete—Dr. Felek Jachimowicz
- 5. Nanoscience of Highway Construction Materials—Dr. Richard Livingston
- 6. New Functionalities for the Building Industry—Dr. Laurent Bonafous
- 7. The Nano-Engineering of UHPC & Structures—Vic Perry
- 8. Roadmap for Research—Dr. Bjorn Birgisson











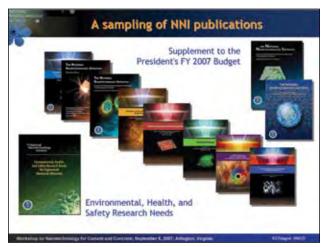
Snapshot of the National Nanotechnology Initiative

Dr. Clayton Teague

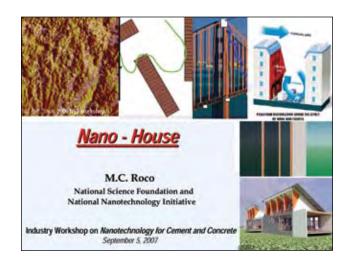












Topics

- Context: global nanotechnology development
- NSF/NNI support to industry
- Nano House: research opportunities
- Funding: NSF, NNI, international
- · Goals of the workshop

AND BOOK OR

Several particularities for cement and concrete research

- <u>Less investment in research</u>, including for nanotechnology, in the last decades as compared to other major technologies
- Basic phenomena at the nanoscale (nanoparticle behavior, nanoscale processes) can be addressed now for topics such as: low energy cement; novel binders; ductile and tougher concrete; sensors; less corrosive; coatings.
- Dynamic behavior is over several length and time scales: suitable to a multidisciplinary systemic approach
- Connected to various application domains: houses, sensors, energy, materials (polymers, ceramics, etc.)
- Begin with nanoscale in terminology and standards

C No. in

Benchmark with experts in over 20 countries
"Nanostructure Science and Technology"

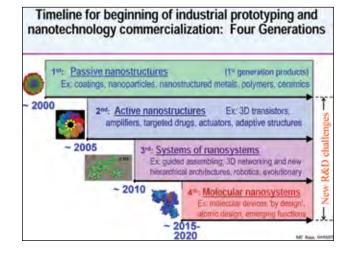
Book Springer, 1999

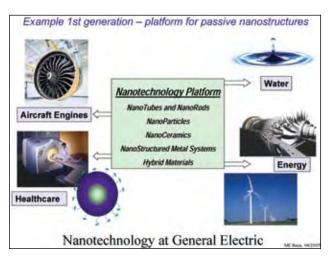
Nanotechnology

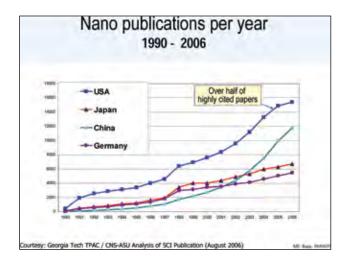
is the control and restructuring of matter at dimensions of roughly 1 to 100 nanometers (from atomic size to about 100 molecular diameters),

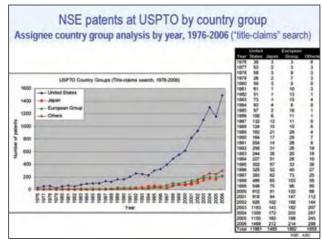
where new phenomena enable new applications.

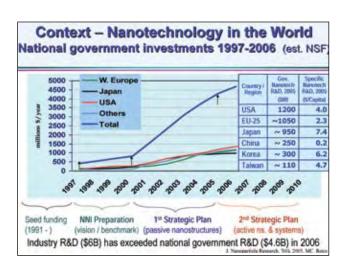
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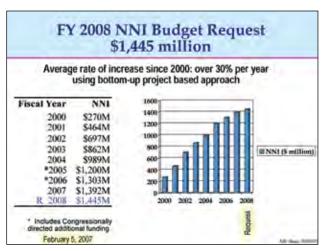


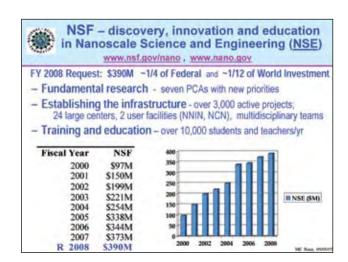












FY 2006-2008 NNI areas of investment "Program Component Areas" 1. Fundamental Nanoscale Phenomena and Processes 2. Nanomaterials — Cement and concrete materials 3. Nanoscale Devices and Systems 4. Instrumentation Research, Metrology, and Standards for Nanotechnology 5. Nanomanufacturing 6. Major Research Facilities and Instrumentation Acquisition 7. Societal Dimensions One of the 9 NNI Grand Challenges in 2001 was: - Economic and Safe Transportation



NNI: Support partnerships with industry

- Grand challenges / PCAs to create the technology base

Ex: Nanomanufacturing – NSF program >\$20 million/yr since FY 2002 - MARCO center; government –university – industry; NIST – Facilities

- Infrastructure for instrumentation, tools, laboratories

Ex.: 5 DOE labs, NSF's NNIN and NCN; over 70 centers and networks; NCI; NIST metrology and standards; NSF instrumentation program

Prepare the workforce at all levels

Ex: NCLT; Technological, Community Colleges and in PA (PFI award)

Various mechanisms for interaction with industry

Ex. Fund collaborations with industrial partners (GOALI, center collab.); Provide the NNI results to industry (ex. with SIA, CCR); Provide user facilities; Assistance for instrumentation, standards, manufacturing; Direct technology transfer and funding industrial projects: SBIR/STTR awardees by all agencies (>\$70 million/yt)

MC Resi

NNI-Industry Consultative Boards for Advancing Nanotech

Key for development of nanotechnology, Reciprocal gains

□ NNI-Electronic Industry (SRC lead), 10/2003 -Collaborative activities in key R&D areas

Collaborative activities in key R&D areas 5 working groups, Periodical joint actions and reports NSF-SRC agreement for joint funding; other joint funding

■ NNI-Chemical Industry (CCR lead)

Joint road map for nanomaterials R&D; Report in 2004 2 working groups, including on EHS Use of NNI R&D results, and identify R&D opportunities

NNI - Organizations and business (IRI lead)

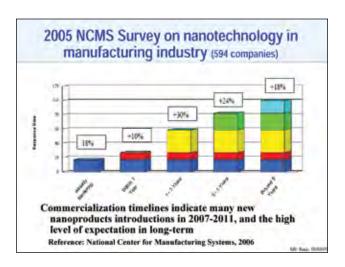
Joint activities in R&D technology management 2 working groups (nanotech in industry, EHS) Exchange information, use NNI results, support new topics

□ NNI – Forestry and paper products (FS lead), 10/2004-Workshop / roadmap for R&D

2 working groups (nanotech in industry, EHS) Exchange information, use NNI results, support new topic

Sampling of Current Regional, State, & Local Initiatives in Nanotechnology

| Comparison | Compa



NNI- Electronic Industry CBAN

Five consultative working groups (CWG), 2003 -

- Post CMOS information processing technologies
- Novel materials and assembly methods for extending charge-based technology to its ultimate limit
- III Multi-scale, multi-phenomena modeling and simulation
- Novel nano-architectures
- V Nano Environmental, Health and Safety

Six priorities:

Computational state other than electron charge

Non-equilibrium systems Novel short range IT mechanisms

Nano architecture

Nanoscale thermal management

Directed selfassembling

Nano - House - related interest -

- CSIRO project in Australia
- EC project, Denmark project
- NSF: programs and awards ENG/CMMI and MPS/DMR
- Potential interest from DOE, DOT, DOD, NASA, NIST
- Potential industry partners: cement and concrete, windows, heat-electrical energy transformers, ...

MC Rook States

Nano - House Where nanotechnology may be used?

Materials for construction:

for house, roads, infrastructure in nanostructured materials, coatings, windows,...

- Energy: heat exchange, lighting, solar/heat energy
- Life cycle and environment
- Sensors
- Coatings
- Connecting to electronics
- Water filtration

de face for





Workshop on Nano-modification of Cementitous Materials

Recommendations

U. Florida, NSF support, 2006; http://www.ce.ufl.edu/nanoworkshop/program.html

- High performance nanomaterials: reduce shrinkage, higher tensile strength, self-healing micro-cracks
- Sustainable and safe concrete: controlling heat of hydration, moisture movement, electrical conductivity, harsh environments
- Intelligent concrete materials: sensors for recording loadings on roads and bridges, chemical sensors for earlier warning, use IT
- Novel concrete materials: functional nanoparticles, composites, control rheology
- Nanoscale based multiscale modeling of concrete: predicting behavior and test new solutions (see NSF-industry functional nanomaterials workshop in October 2007)

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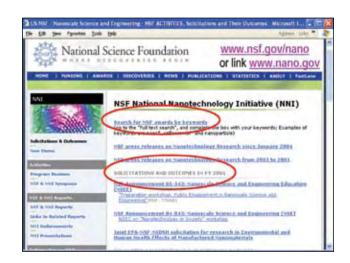
Examples of active NSF awards (September 2007)

Award Number	Title (searched by keywords www.nsf.gov/nano: 'nano and cement')	NSF Organiz,	Principal Investigator
408427	Sensing Intrinsic Nano-Alicrostructural Characteristics of Handening Concrete with High-Frequency Transverse Waives	CMM	Shah, Surendra
409114	Precast Concrete Coupling Beams for RC Walts	CMM	Kurami, Yahya
510854	Multi-Scale Kinetics-Based Model for Predicting Mechanical Property Development of Concrete Containing Supplementary Cementitious Materials	CMMI	Harses, Wi
555053	Effect of Inclusions on Material Performance-Investigation Through Micro- Continuum, Discontinuum and Nano-Indentation Approaches	CMM	Einstein, Hortest
625927	Unified Approach for Mutacale Characterization, Modeling, and Simulation for Stone-based Infrastructure Materials	CMA	Wang. Linking
637297	STTR Phase I: Demonstration of Enhanced Corrosion Resistance using a Nano-composite Thermal Barrier Coating	IP-	Cuttirm, Michael
654263	Collaborative Research: Measuring, Monitoring, and Modeling the Setting Properties of Concrete	CMM	Sun, Zhihui
700219	Design of "Crack-free" Concrete Materials with Robust Self-healing Functionality	CMAR	II. Votor
700524	Dielectric & Mech. Spectra Assistad Multi-Scale Study of Early Stage Concrete	CMM	Ye, Xinng

Examples of active NSF awards (September 2007)

Award Number	Title (searched by keywords www.nsf.gov/nano: "nano and concrete")	MSF Organization	Principal Investigato
510654	Muti-Scale Kinetics-Based Model for Predicting Mechanical Property Development of Concrete Containing Supplementary Centertitious Materials	CNM	Harsen, Wil
547024	CAREER: An Integrated Research and Education Program in Long-Term Durability of Nano-Structured Cement-Based Materials during Environmental Weathering	CMM	Sanchez, Florence
625927	Unified Approach for Multiscale Characterization, Modeling, and Simulation for Stone-based Infrastructure Materials	CMM	Wang. Linking
853869	Collaborative Research: Measuring, Monitoring, and Modeling the Setting Properties of Concrete	CMM	Shah, Surendra
654263	Collaborative Research: Measuring, Monitoring, and Modeling the Setting Properties of Concrete	CMM	Sun, Zhihui
700524	Dielectric and Mechanical Spectra Assisted Multi-Scale Study of Early Stage Concrete	CWM	Yu. Xiang

MC Rest, 1985



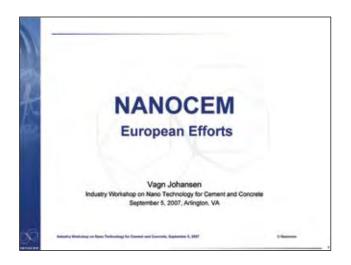
Five ways nanotechnology will change business

- Competitive advantage by improved products now
- <u>Create S&T nanotech platforms</u> for revolutionary new products (over 50% of new chemical/ electronic/ pharmaceutical/ advanced materials products by 2015)
- Opportunities for innovation. Convergence with biomedical, electronics, cognition, others
- New organization and business models "horizontal" information, S&T clusters, distributed production
- Global governance: strong collaboration and competition; address multi-stakeholders and responsible development

This workshop

- Timely contribution for application of nanotechnology in cement and concrete applications
- Address basic concepts specific for nano: research opportunities, necessary infrastructure, education, and sharing information
- Need for collaborative effort: industry- academe – government; interagency, various professional communities; international

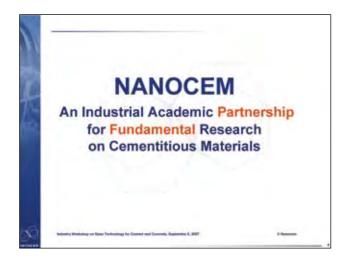
C Sam Johns

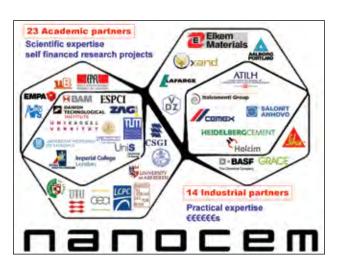


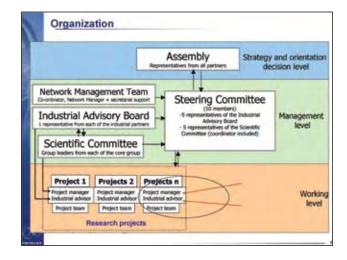


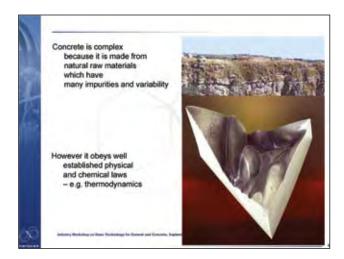




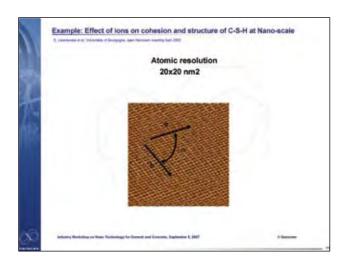


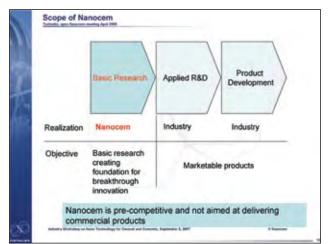


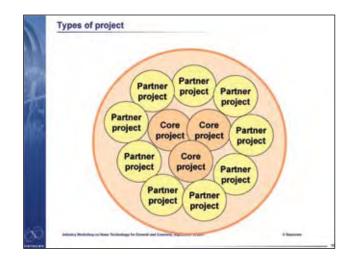




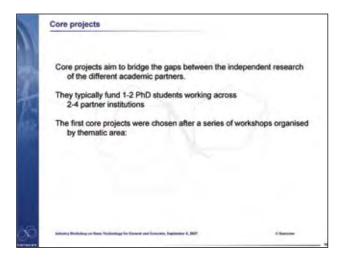


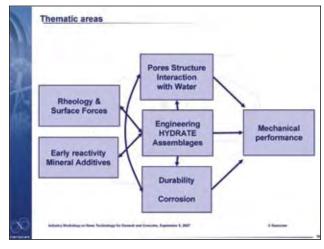


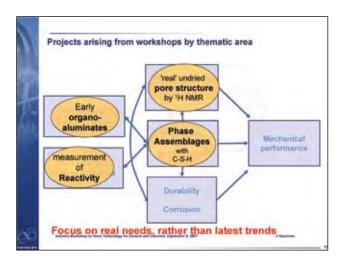


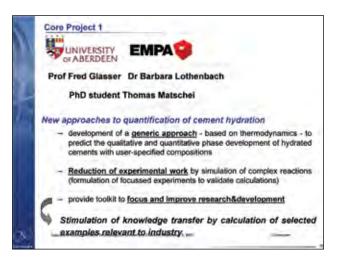


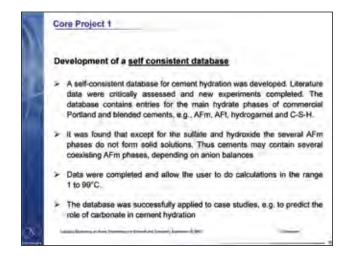


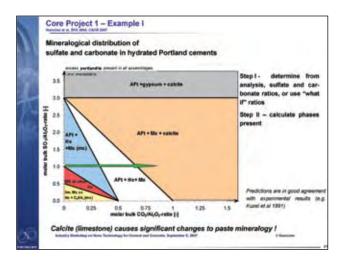


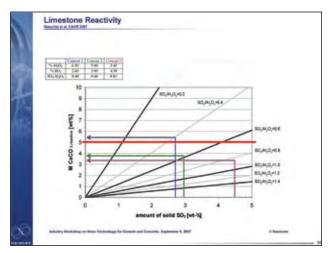


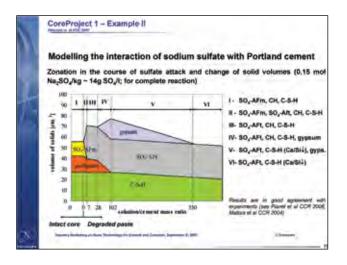


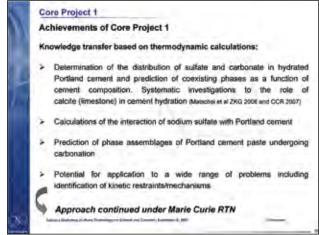


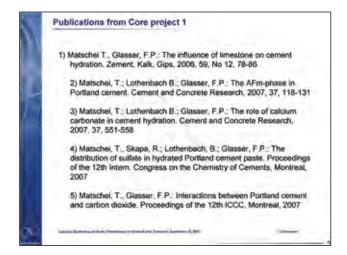




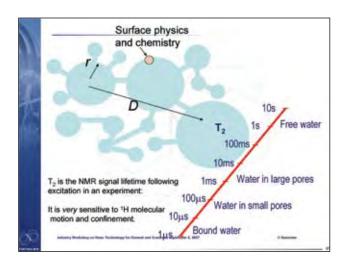


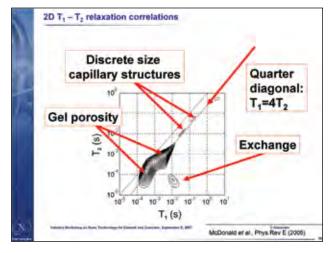






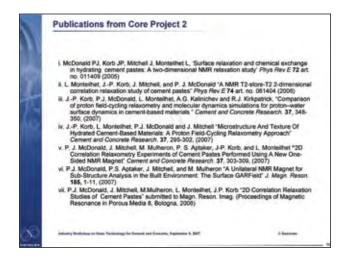


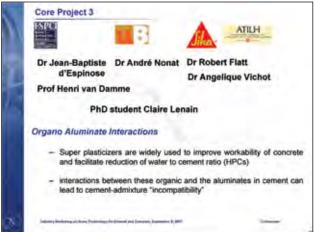


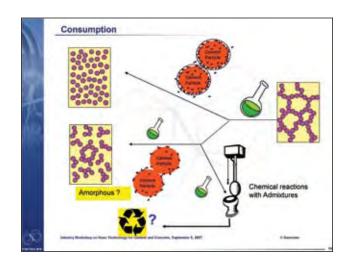


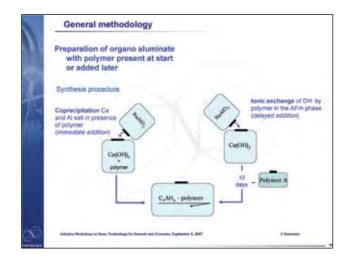


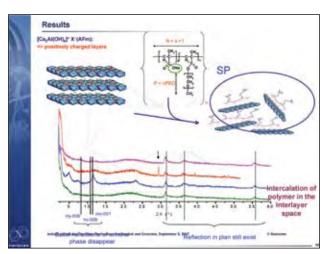


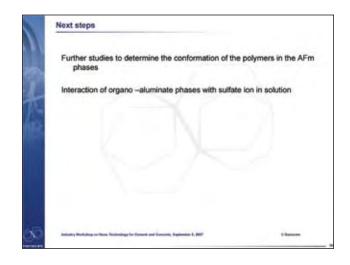




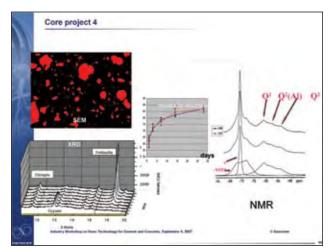


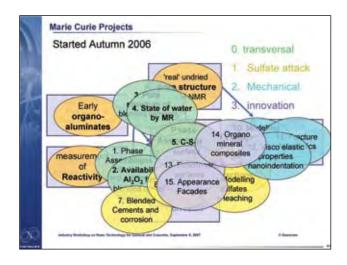












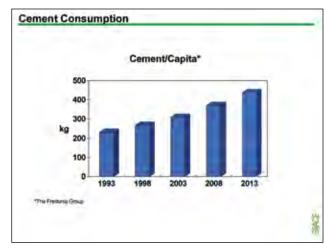


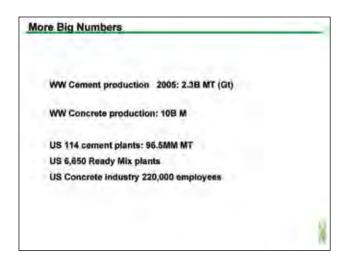
Nanocem - European Efforts

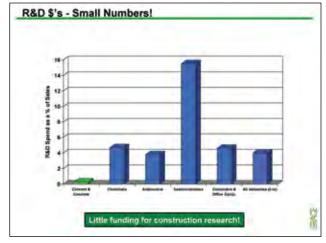
Vagn Johansen

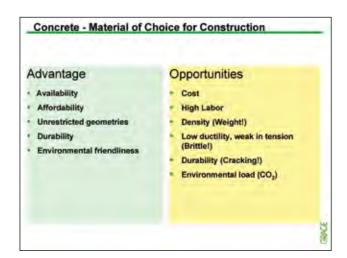


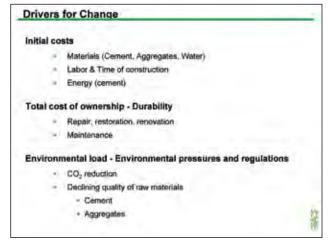


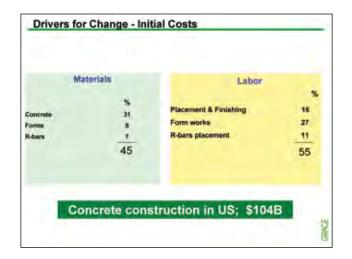




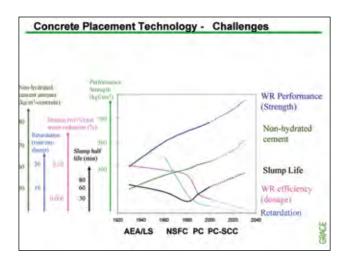


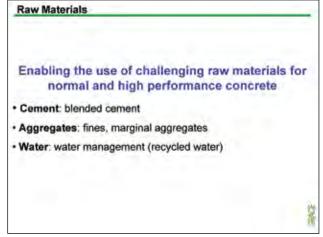


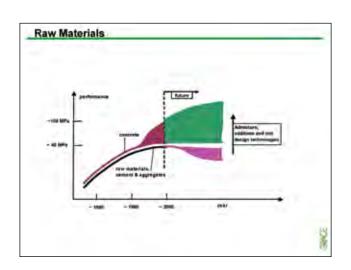


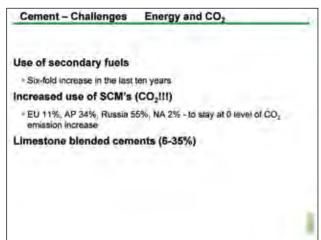


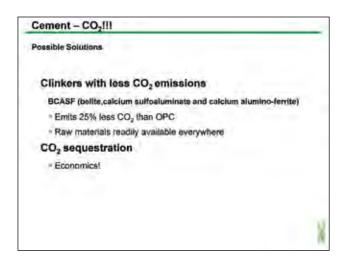


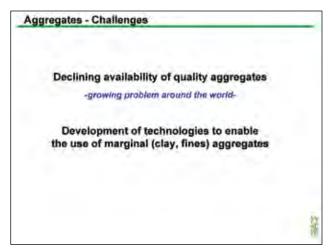


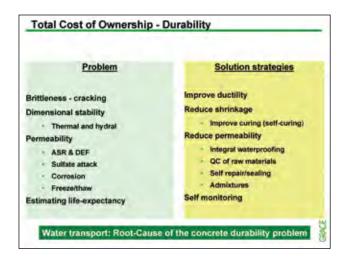


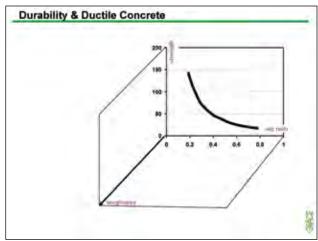


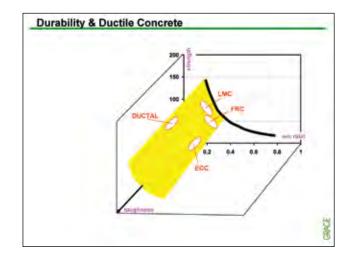


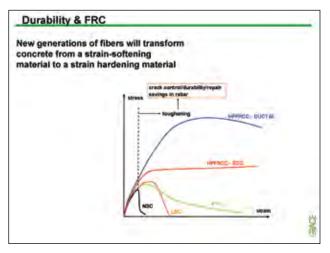




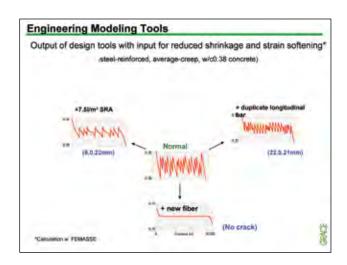


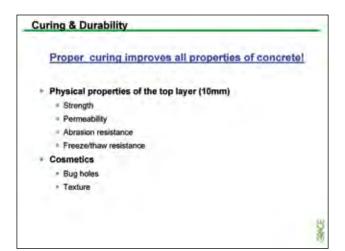


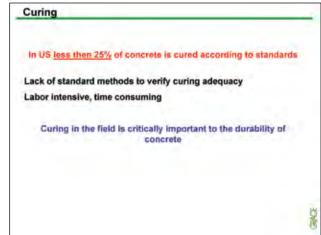


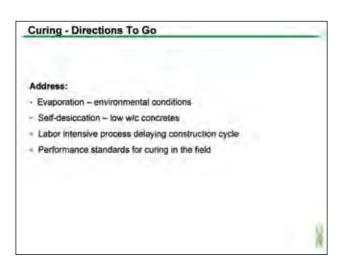


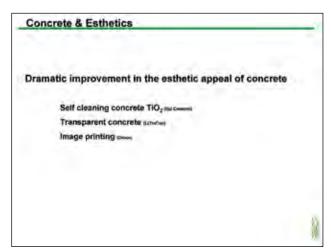
Building code will adapt advanced modeling tools to design with ductile concrete - Seismic improvement - Reduction of convernional reinforcement - Thinner seasons - Crack control and prevention - Durabaty











Future - Interactive/Smart Concrete

QC - (e.g., monitoring of w/c in place)

- · Electronic & chemical sensors
- In-place non destructive testing

Self repair

- *Triggered inorganic reactions
- Triggered organic/biological reactions

Future

- Ductile, flexible, breathable, permeable or impermeable. Properties
- · Dial-in set, strength, permeability, etc.
- Engineered materials: Maximize what you have locally, avoid un-necessary transport
- · Immune to freeze-thaw, corrosion, sulfate and other environmental
- Specialty: (blast resistant, conductive...)

Nano & Concrete

Understanding of cement chemistry and concrete microstructure

- · Dynamic properties hydration
- · Static (durability)
- · Elevating concrete's toughness (ductility)
 - · Nano reinforcement
 - · Nano-bridging of organic and cementitious materials.
- · Reduce permeability
- · Interface management
- · statementalismentalism

Barriers and Issues

- . Lack of adequate R&D funding
- Slow adoption rates of new technologies
- Low level of collaboration for multidisciplinary problems
- Prescriptive vs. performance based standards
- Low level of QC technologies
- Lip service to life-time costs
- Poor image of coment-based materials III

What Can Government Do?

Designate more funds for basic research

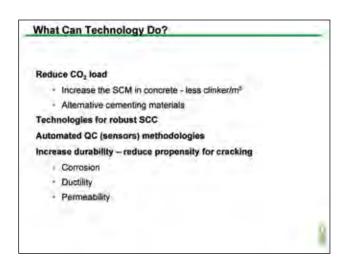
- Predictive modeling
- · Nano-scale manipulation of cement hydration and microstructure
- · Mechanistic understanding at the molecular level

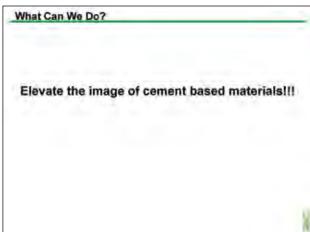
Encourage elevation of QC of concrete

What Can Industry Do?

- · Aggressive approach to codes and specifications
- · Embrace "green"
- · Focus on performance standards
- Stronger enforcement
- · Accelerate development/introduction of new technologies

What Can Science Do?





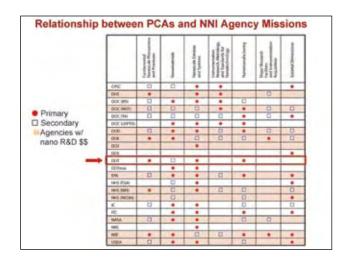
Nanoscience of Highway Construction Materials

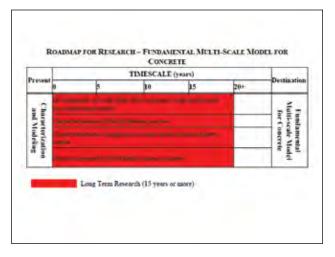
Richard A. Livingston Office of Infrastructure R&D Federal Highway Administration

Workshop on Nano Technology for Cement and Concrete September 5, 2007

Outline

- · Introduction
- · Cement Hydration Kinetics
- · Fly Ash Reactivity
- Nano-composites
- Self-Healing Materials
- Conclusions





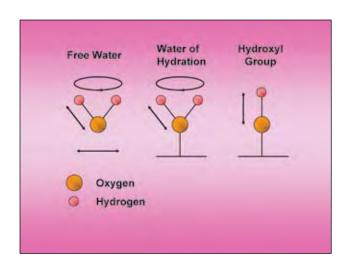
Concrete Microstructure

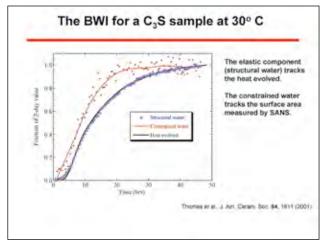
High Performance Materials

- · Higher strength
- · Greater durability
- · Increased speed of construction
- Reduced environmental impact

Standard Specifications Desired Effect Type of Admixture Haduce the water content by 5 to 10%, while maintening stump theraptenistics. fladuce the water content by 12% to 30%, while maintaining sturto. ASTM C 494 (AASHTO M 194) To decrease the rate of hydration of cornert. To increase the rate of hydration of cereins. Reduce drying shrinkage (and related cracking) in Shrinkage-reducing admixtures Minumos steel reinforcement complice







Nucleation and Growth model

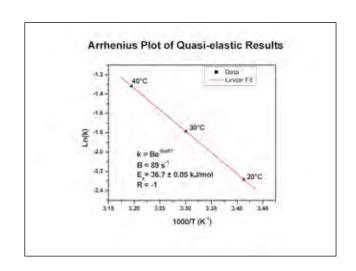
$$\beta(t) = \beta(t_o) + A\left(1 - \exp\left\{-\left[k\left(t - t_o\right)\right]^m\right\}\right)$$

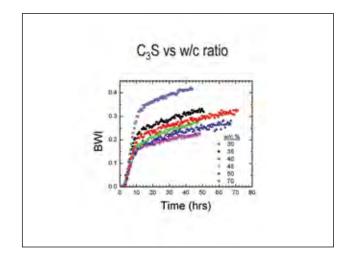
 $\beta(t)$ = boundwater fraction

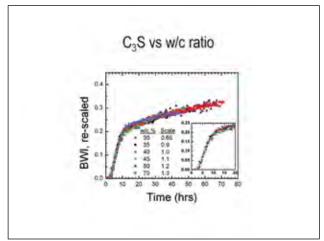
to = induction time

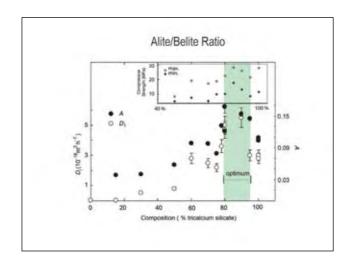
= asymptotic volume fraction

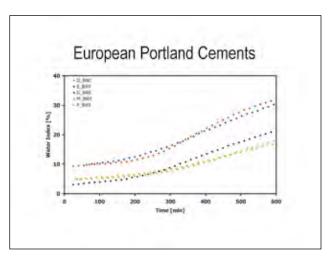
= rate constant m = dimensionality

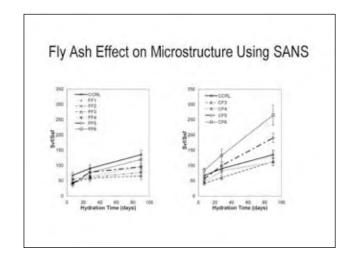


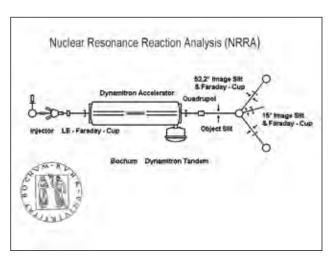


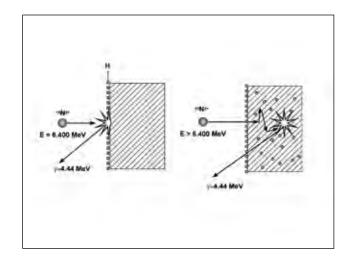




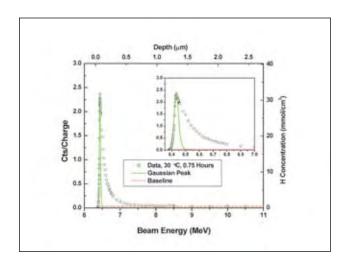


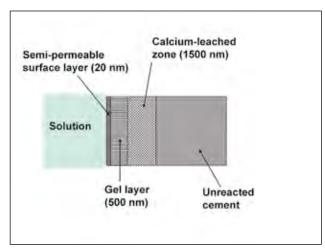


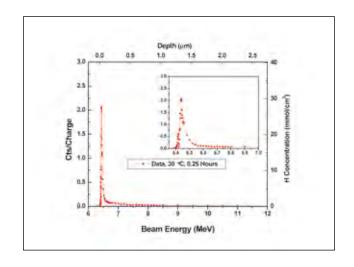


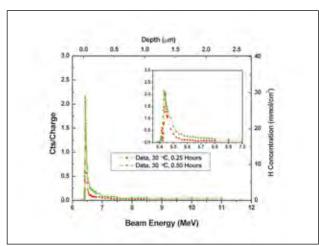


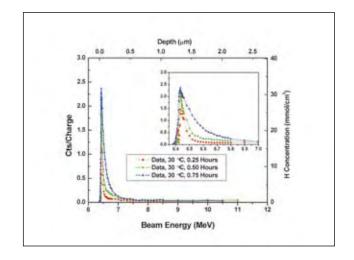


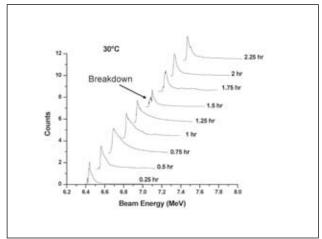


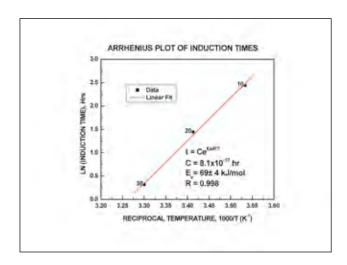


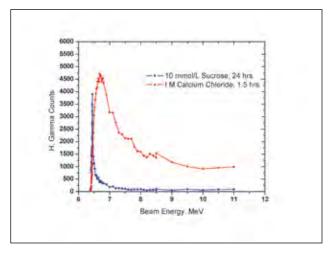


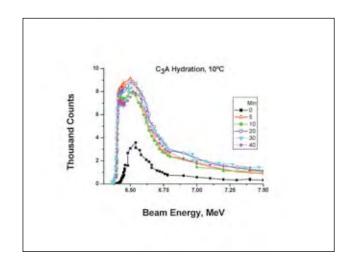


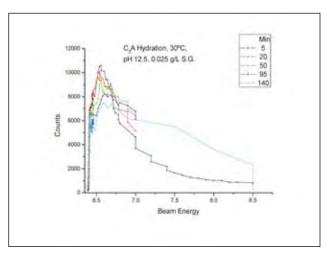


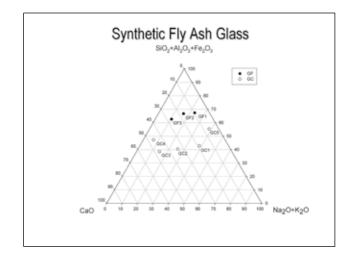


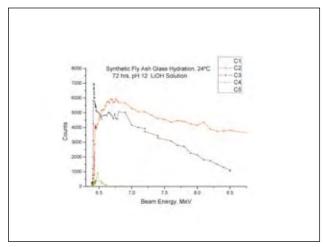


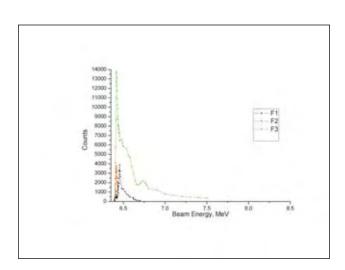


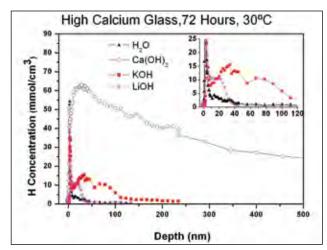






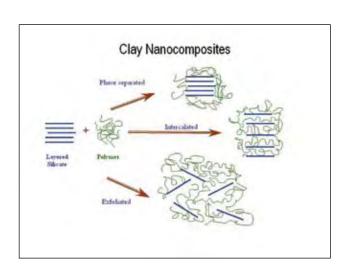


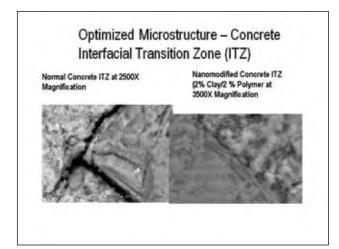




Nanoparticles

- Nanosilica
- Ca(OH)₂
- · CaCO₃
- TiO₂
- · Carbon nanotubes
- · Nanoclays







Self-Healing Approaches

- · Shape memory alloys
- · Tri-block co-polymers
- · Embedded microcapsules



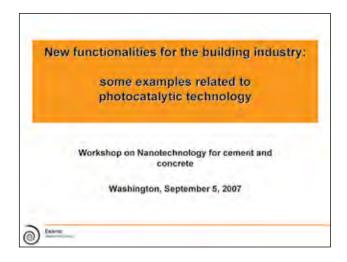
Other Nanomaterials

- Asphalt
- Steel
- · Coatings

Illinois Rt. 83 over the Canadian National Railroad tracks, Lake Villa, IL

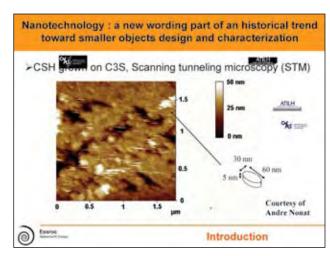
Conclusions

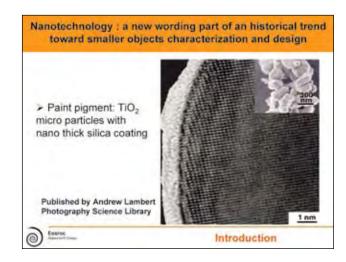
- · Highway materials are nanostructured
- · Nanoscience knowledge is still incomplete
- Nanoscience investigations require advanced materials characterization methods
- · Nanomodified steel has achieved field use
- · Other nanomodified highway materials still at the laboratory stage

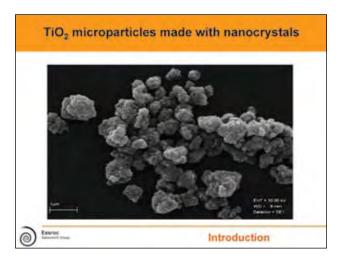












6. New Functionalities for the Building Industry



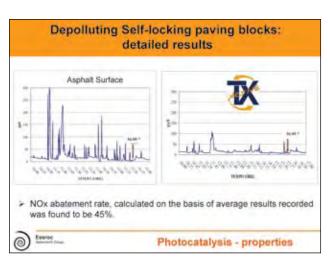


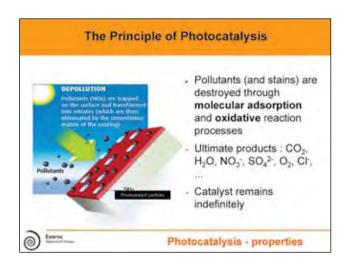
Dr. Laurent Bonafous

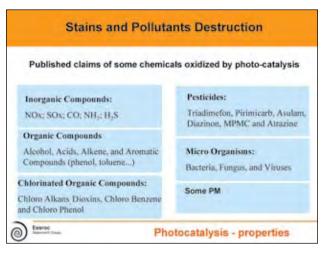


















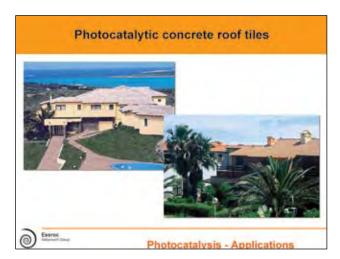


6. New Functionalities for the Building Industry

Dr. Laurent Bonafous



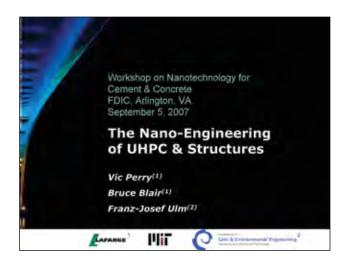


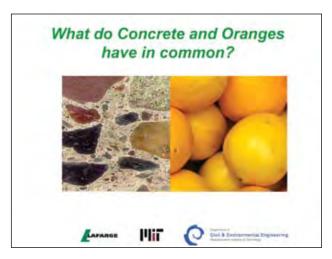


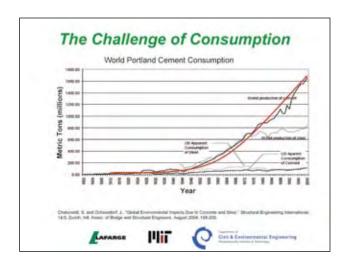
Reduced levels of several environmental pollutants. Continuous oxidizing action results in a clean building for the lifetime of the structure. Lower lifecycle maintenance costs. Potential for numerous LEED point credits Photocatalysis - Conclusion

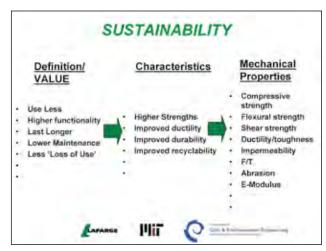
And opening towards future developments Research in nanotechnologies has been progressing for over three decades. The technology is adaptable to existing design and systems Nanotechnology new applications will continue to appear with time, becoming more and more available and cost effective.

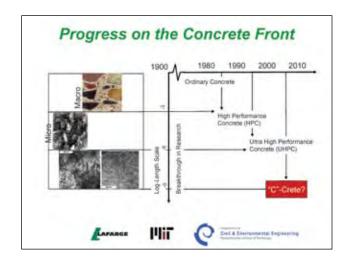
Nanotechnology - prospective

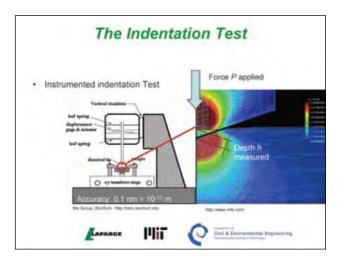






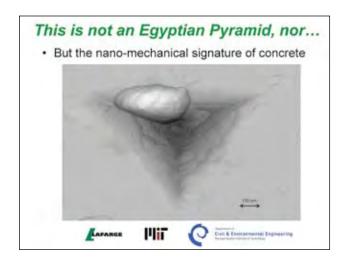


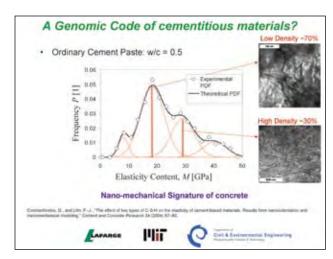




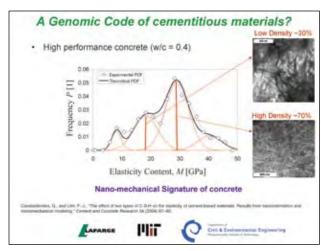
7. The Nano-Engineering of UHPC & Structures

Vic Perry

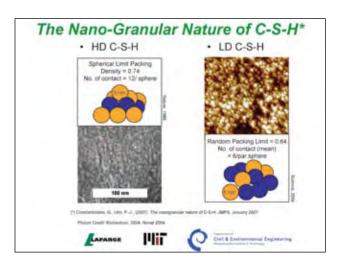


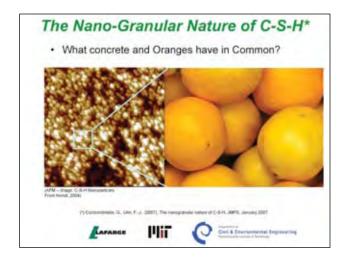


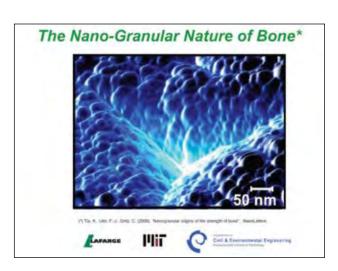




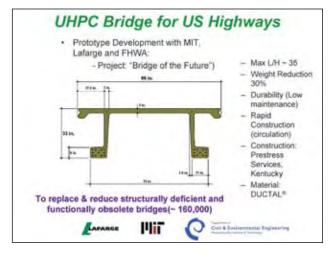


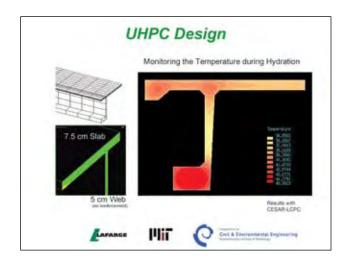


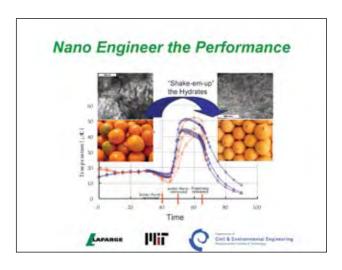










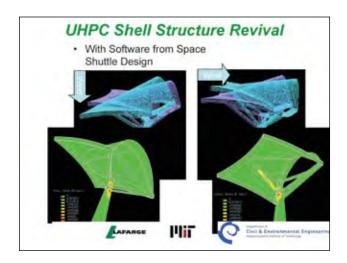


7. The Nano-Engineering of UHPC & Structures

Vic Perry











ROADMAP FOR RESEARCH

Nanotechnology in Concrete-Based Materials

Dr. Bjorn Birgisson, P.E., Professor and Division Chair of Highway and Railway Engineering

> School of Civil & Architectural Engineering The Royal Institute of Technology (KTH) Stockholm, Sweden

Pending Infrastructure Crisis

- Transportation Infrastructure:
 - ASCE (2003) estimated it would cost \$1.3 trillion dollars and in 2005 ASCE estimated it would cost \$1.5 trillion dollars to upgrade infrastructure to acceptable levels
 - AASHTO (2007) estimates that yearly capital outlays by federal & state governments would have to increase by
 42 % to reach the "Cost to Marisan Level"
 94 % to reach the "Cost to Improve Level".
 - The federal transportation bill for 2005 (SAFETEA-LU) authorized around \$43 billion/yr for the nations highway programs.
 - AASHTO (2007) predicts a 4 billion dollar shortfall in the National Highway Trust Fund by 2009, which could lead to a cut in federal-aid highway program from a planned obligation level of \$43.2 billion to \$25.7 billion for flocal year 2009.

Pending Infrastructure Crisis

In a recent call for action to aid the U.S. transportation system, AASHTO also found that:

- Although the U.S. population grew by 130 million people between 1955 when the Interstate Highway system was being debated and 2005, the national population is expected to rise by an even greater number - by 140 million over the next 50 years.
- Vehicles on U.S. highways have gone up from 65 million cars and trucks in 1955 to 246 million today and that number could rise to nearly 400 million by the year 2055.
- To fund what is needed, all levels of government will have to continue to do their part.

Pending Infrastructure Crisis

- · Examples
 - Congestion costs to motorist ~\$51 billion per year, worse impact on national productivity
 - 27.1 % of the nation's bridges are structurally deficient or functionally obsolete (i.e. 160,570 bridges are deficient, 2003).
 - The NTSB has recently (2004) issued a report stating that ALL bridges should be fitted with:

 - An Impact warning system, and
 Sensors that detect level of damage due to impact
 - The Dept. of Homeland Security has identified (2005) that bridge impact is a major security & economical threat to America

Nanotechnology for Safe and Sustainable Infrastructure

- Slowly deteriorating transportation infrastructure due to lack of sufficient funds implies a strong need for:
 - Developing advanced technologies that allow for the intelligent replacement of our transportation infrastructure with materials and systems that last at least twice as long as current bridges and
 - · Developing of effective long term monitoring techniques for warning of
 - Early material/structural degradation
 - Potential safety hazards

Nanotechnology for Safe and Sustainable Infrastructure

- Doing so will:
 - enhance the safety of the traveling public,
 - reduce fuel consumption due to congestion and rough roads, and
 - ensure continued economic competitiveness.

The NINE GRAND CHALLENGES in the Original National Nanotechnology Initiative Plan

- Nanostructured Materials by Design
- 2 Nano-electronics, Optoelectronics, and Magnetics
- Advanced Healthcare, Therapeutics, and Diagnostics
- Nanoscale Processes for Environmental Improvement
- Efficient Energy Conversion and Storage
- Microspacecraft exploration and Industrialization 6.
- Bio-nanosensors for Communicable Disease and Biological
- **Economic and Safe Transportation**
- **National Security**

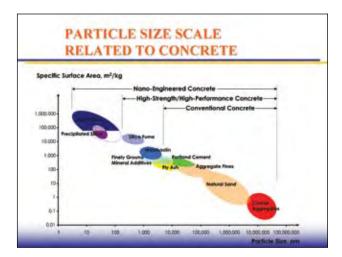
Initial Efforts Modification of Concrete

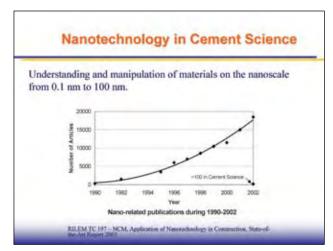
Why concrete?

The most heavily used construction material in the world

We currently use more than one cubic yard per person per year

The basic building blocks of concrete are nanosize (C-S-H crystals are about 5 nm long) - Lends itself to nanomodification and "bottom-up" engineering





NSF Workshop, August 8-11, 2006

- Objective: Develop a National Roadmap for Research in this emerging area
- Co-sponsored by

 - University of Florida The Defense Threat Reduction Agency
- The U.S. Army Corps of Engineers
- Portland Cement Association
- Florida Concrete and Products Association
- Affiliated Agencies

 - Federal Highway Administration
 The Florida Dept. of Transportation
- Twenty Nine Presentations
- Participants from the United States, Europe, Canada, Mexico
- All major federal agencies, the military, industries, and academic interests are represented

Pre-Workshop Meeting. Orlando, July 20th, 2006 **Participants**

- · Univ. of Florida
- Northwestern Univ.
- · Iowa State Univ. (NCPT Center)
- Army Research Center
- Federal Highway Administration (FHWA)
- Florida DOT
- Transportation Research Board (TRB)
- American Concrete Pavement Assoc. (ACPA)
- Florida Concrete & Products Assoc. (FCPA)

Pre-2006 Workshop Meeting

* Objective:

Develop Framework for a whitepaper on implementation of Nano research results.

· Discussion:

- Technology needs
- State of Nano research and early successes
- Consortium and collaborative effort
- Interaction and exposure

ROADMAP

- The Roadmap will serve to support the identification of resources needed to facilitate the technical innovation that will lead to:
 - the creation of new technologies
 - addition of knowledge-based and high tech jobs/companies,
 - associated technology transfer of the research findings to other fields, including homeland security.

ROADMAP FEATURES

 The Roadmap is "destination oriented" with clearly defined outcomes that will greatly enhance concrete technology and the uses of concrete in structures ranging from housing, bridges, tunnels, and pavements.

ROADMAP FEATURES

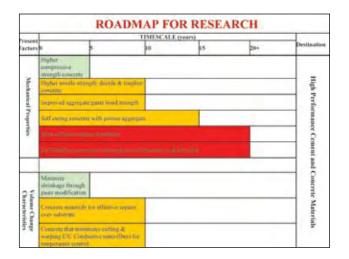
- Under each of these key outcomes are listed a number of research focus areas and topics.
- These research areas are arranged according to their time horizon to completion from today:
 - "Short term" activities lasting less than 5 years,
 - "Intermediate term" activities lasting between 5 and 15 years, and
 - "Long term" activities with a time horizon greater than 15 years.

IDENTIFIED TECHNOLOGY OUTCOMES FOR CONCRETE

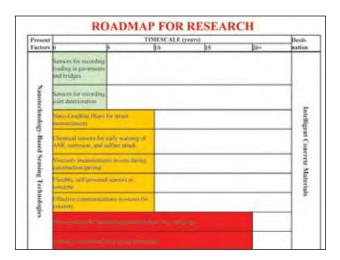
- High Performance Cement and Concrete Materials as measured by their:
 - mechanical
 - durability, and
 - shrinkage properties.
- Sustainable and Safe Concrete Materials and Structures through:
 - engineering concrete for different adverse environments,
 - reducing energy consumption during cement production, and
 - enhancing safety with nano-engineering of concrete materials.
- Intelligent Concrete Materials through integration of nanotechnology-based:
 - self-sensing and self-powered materials, and
 - cyber infrastructure technologie

IDENTIFIED TECHNOLOGY OUTCOMES FOR CONCRETE

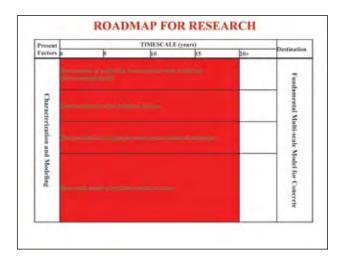
- · Novel Concrete Materials through:
 - nanotechnology-based innovative processing of cement and cement paste (Ex. cement-based ceramics, etc.)
- Fundamental Multi-scale Model(s) for Concrete through advanced characterization and modeling of concrete at the nano-, micro-, meso-, and macroscales.

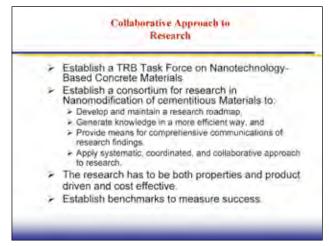












Interaction and Exposure

- Close interaction and sharing of information through specialty conferences and symposiums.
- Coordinate technical activities with NSF, ARMY ERDC, DTRA, FHWA, AASHTO, TRB, ACI, PCA, NRMCA, RILEM, and other research organizations and industry associations.



Roundtable Discussion

A roundtable discussion was held over a one-hour period, facilitated by Dr. Krishna Rajan. The aim was to allow all those present the opportunity to express their opinion/position on the needs of the construction industry (including some prioritization), and to identify those needs that could be met using nanotechnology and nanoscience. The discussion points can be divided into three categories: constraints, background, and needs. Each of these categories is summarized below.

Constraints

It is perceived at present that any work conducted or innovations developed will likely be constrained by the following before they will find broad application in the construction industry:

- Concrete is a commodity material, typically sold and placed under low-bid contracts. This means that the system is extremely cost sensitive, particularly with respect to first cost.
- Despite the emphasis on first cost from a budget standpoint, attention must be paid
 to the full life cycle of a concrete mixture, including disposal or recycling costs from a
 sustainability point of view.
- People involved in making and placing concrete generally do not understand the material
 well; therefore, the mixture has to be insensitive to mistakes and variability, and education
 has to accompany changes in technology.
- Contracts tend to be inflexible, often limiting the acceptability of innovative approaches
 or materials. For example, many specifications will not allow lower cement contents in
 concrete, therefore removing any motivation to make cement hydration more efficient.
 Policy changes are needed to help remedy this constraint.
- Costs of moving bulk raw materials are high, meaning that, in general, users are
 constrained into using locally available materials (particularly aggregates) regardless of their
 technical acceptability. Educational efforts and policy directives are required to address this
 constraint.
- Construction tends to be labor intensive and is generally outdoors, meaning that nanomodified materials will have to be examined for their effects on health and the environment should they be released or leached from the concrete.
- Emphasis should be placed on seeking solutions that are practical and achievable in the short term.

Background

In comparison to other materials, relatively little work has been conducted on understanding the nano-and microstructure of cementitious systems in comparison to other materials. A bibliography of reported work in this field is being developed by American Concrete Institute Committee 236. It was noted that the state of knowledge has effectively been good enough for the cases where concrete materials are used. The following, better understood, materials types are analogous to hydrated cement paste and may provide a useful background for further work:

- Hydrated cement pastes may be compared to polymeric materials in their structural form in that they are complex and amorphous multiphase mixtures.
- They are also analogous to clays because calcium-silicate-hydrate has a layered structure that is sensitive to moisture movement within the gel pores.
- In contrast, cement paste is also compared to ceramic systems because it is inherently brittle with low toughness and tensile strength.

Needs

It was suggested that consideration should be given to developing the list of properties needed for a mixture and then engineering the materials to provide those properties. For the concrete construction industry to flourish, the following needs should be addressed:

- Test methods and tools to assess the quality and state of a mixture are essential. If suitable tests and limits are available, then specifications can move toward calling out performance requirements and away from recipe book approaches.
- Control systems to modify the performance of a mixture on the fly are desirable.
- A better understanding of cementitious materials and their hydration mechanisms is required if they are to be fundamentally and scientifically modified.
- Usage of clinker has to become significantly more efficient from an environmental point of view, either by mixing with other materials, and/or by increasing the performance of the material (a 15% increase was discussed). It may also be noted that performance of cement may be measured using a number of parameters. Engineers historically depend on strength as a criterion, but this may not be appropriate when durability is likely to become a more important consideration.
- Means are needed to make concrete and its ingredients more uniform and stable. Many
 failures are due to unexpected materials being included in the mix or unexpected reactions
 occurring within it.
- Materials should be sought that reduce or control the timing of shrinkage in concrete in order to reduce the risk of cracking.
- Methods to make use of marginal aggregates are required if concrete construction is to be sustainable.
- Immediate and practical requirements are needed for improved control over workability (and how it changes with time) and durability.
- Advances in high performance computing should be taken advantage of to model cementitious systems at a nanoscale and to facilitate modifying concrete systems.

Breakout Sessions

Six breakout sessions were held, covering three topics: "Sustainability," "High Performance," and "Durability." Each topic was discussed by two groups in order to keep the groups small and to observe similarities and differences between their findings. Individuals were pre-assigned to each group to ensure that groups included representatives from government, product manufacturers, associations, and academia. The groups met for approximately one hour, followed by an hour of reporting and discussion. Each group of approximately nine people was asked to address their topic around the following questions:

- What do we need?
- How can nanotechnology help us get there?
- Who can do it and how?
- What is the low-hanging fruit?

The following is a summary of the findings of each group.

Sustainability 1

Invited

Steve Kosmatka (Facilitator), James Alleman, Jim Armaghani, Fred Hejl, Al Innis, Vagn Johansen, Daniel Rardon, Clayton Teague, Jerry Voigt

General

- When developing goals, it is important to quantify the targets to assist the researchers and to inform the funding agencies.
- Innovations and new developments must be cost neutral. The improvements, for instance thinner pavements, should balance higher prices for materials.
- Specifications should move away from prescriptive to performance-based approaches to allow innovations to be implemented.
- Collaboration with other industries/government bodies will assist in finding solutions to the following issues.
- All interested parties, from manufacturers, consumers, and owners to regulators and researchers, will have to be involved in defining the needs in detail and in funding and developing the solutions to them.

Need

There is a critical need to reduce CO₂ production from cement plants.
 (Cement manufacture reportedly generates about 1.5% of man-made CO₂ in the United States.)⁷ Demand on the cement manufacturers is to produce more cement with less CO₂ from the same raw materials.

Solutions

– Increase the life of highways and structures which will lead to lower cement consumption and thereby less CO₂ emission and lower consumption of raw materials. This would address all issues related to sustainability. Factors important for lifetime were listed as materials degradation from exposure to harsh environments, exposure to chemicals and ingress of aggressive fluids, and fatigue. Tensile failure of the paste is an important factor in deterioration; therefore, if the ratio of tensile strength to compressive strength could be

⁷ PCA, http://www.cement.org/concretethinking/FAQ.asp

increased, the situation would be greatly improved. Nanotechnology could be used to improve durability (resistance to environment) and tensile strength. The technology could also be used to control, improve, and/or monitor the degree of cement hydration.

- Use CO₂ to carbonate concrete to modify early properties and to consume CO₂. Nanotechnology could be used to assist in carrying out the process and in monitoring it.
- Reduce clinker contents in concrete while maintaining desired properties, thereby using thinner concrete and less material. Nanomaterials could be used in small quantities to enhance concrete properties.
- Sequester or harvest CO₂ from cement plants into a useful product using nanotechnology.
- Have a nanocatalyst to split CO₂ into O₂ and C. This should be a project across many industries, including power industry. (In the September 8–14, 2007 issue, The Economist has an article about CO₂ capture from a power plant exhaust gas by growing algae.)
- Use nanotechnology to develop concrete surfaces with less rolling resistance, which will lead to lower fuel consumption and lower emissions.

Need

With increasing demand for sustainable development, it is necessary to be able to increase the use of materials (particularly aggregates) currently considered marginal or unacceptable.

Solutions

- Improve the quality of the paste, allowing lower grade aggregates to be acceptable. A key to this will, again, be the ability to improve the degree of hydration of the cement.
- Consider two-layer pavement construction with poorer grade materials in the lower layer and high-grade materials in the wearing surface.
- Use nanoclays to improve concrete properties.
- Investigate the concept of nanomodification of poor-quality aggregates.

Low Fruit

- Quantification of needed tensile strengths.
- Development of methods to monitor and control cementitious materials hydration.
- Communication of industry research goals to government.

Sustainability 2

Invited

Richard Livingston (Facilitator), John Brighton, Tom Cackler, Rita Chow, Peter Deem, Kevin McMullen, Uwe Schutz, Leif Wathne

Needs

- Ways to reduce CO₂ footprint from the production of cement.
- Methods to reduce clinker content in concrete because it is the production of clinker that produces CO₂ and consumes energy.

- Means of improving fuel consumption in cement manufacturing, concrete production, and in transportation systems.
- Tools to reduce energy consumption, particularly in cement manufacturing.

Solutions

- Develop energy-efficient insulating construction systems in order to improve thermal characteristics in buildings, especially housing.
- Use nanotechnology to modify cements so that they are more efficient, which will lead to lower consumption rates.
- Investigate means to produce concrete with sufficient strength, flexibility, and potential durability to ensure longer life and less need for repair and replacement.
- Use nanomaterials to improve use of marginal and recycled aggregates in portland cement concrete. This would include methods to allow use of aggregates with currently excessive clay contents, poor soundness characteristics, and poor abrasion resistance.
- Develop methods to reduce the amount of water needed to wash or prepare aggregates and to make concrete mixture workable.
- Find ways to use "gray" or recycled water by using nanotechnology to control the amounts of contaminants in the water, or to limit their effects.
- Improve CO₂ sequestration properties of concrete to reduce the total CO₂ burden.
- Ensure that concrete can be recycled at the end of its functional life.

High Performance 1 -

Invited

Kevin MacDonald (Facilitator), Mike Beacham, Bjorn Birgisson, Laurent Bonafous, David Carson, Brian Green, Randell Riley, Mike Roco, Tyson Rupnow

General

- Method specifications are less desirable in this context than performance specifications.
- We need to get the information from the academic world to the real world quickly.
- HPC is defined as concrete fit for its intended use.

Needs

- Control shrinkage in concrete by modifying the nature of the hydrated cement paste.
- Produce a more uniform and controlled hydration product.
- Use marginal aggregates or reclaimed concrete aggregates.
- Control rheological properties of fresh concrete.
- Control concrete surface characteristics for skid resistance and noise characteristics.

- Develop innovative procedures for measurement of key parameters such as potential durability.
- Modify portland cement concrete processing to make it less sensitive to human error.

Solutions

- Use nanomaterials as uniformly distributed nucleation seeds for hydration.
- Use nanomaterials incorporating color change for indicating water control during early hydration in order to flag when sawing, texturing, or curing can start or end.
- Beneficiate aggregates by coating them with nanomaterials to improve bonding characteristics and inhibit deterioration mechanisms.
- Use clays to modify hydration product structures.

Who

Cement and admixture companies, ACPA, FHWA, NSF, anyone with funding and/or problems to solve.

Low fruit

We need to identify what is available in the nano world now and take from those industries and apply to transportation/infrastructure needs.

High Performance 2 -

Invited

Suneel Vanikar (Facilitator), Clark Cooper, Geoffrey Holdridge, Jack Holley, Felek Jachimowicz, John Melander, Krishna Rajan, Joe Tedesco, Don Weir

Needs

- Enhanced mechanical properties.
- Greater consistency in raw materials and in process control.
- Improved characteristics of raw materials.
- Improved constructability.
- Greater cost-effectiveness.
- Ability to recycle.

Solutions

- Develop affordable nanomeasurement technologies to monitor, control, and minimize water content in cement and concrete.
- Use embedded sensors in raw materials and finished concrete to enhance production consistency, predictability, and robustness.
- Identify nanoparticles for enhancement of mechanical properties.
- Establish computational nanotechnology techniques for modeling hydrated cementitious systems.

Who

- Consortia.
- Group/Industry/Academia.
- Roadmap—International Technology Roadmap for Semiconductors.

- Semiconductors and Semiconductor Research Corporation.
- Trained workforce.

Low Fruit

- Self-healing, self-curing concrete.
- Dimensional stability.

Durability 1

Invited

Colin Lobo (Facilitator), Mike Byers, Vic Perry, Bruce Blair, Panneer Selvan, Ed Garboczi, Jim Grove

Needs

- Improved paste quality to limit water transport through the paste.
- Control of degradation mechanisms in aggregates.
- Significantly extended life until the first major rehabilitation.
- New quality control means to monitor the pavement during and after construction.
- Tests to predict performance based on understanding the mechanisms that cause the deterioration.
- Tests to evaluate properties of ultra-high performance concrete (UHPC).
- Improved mixing and curing techniques and monitoring methods.
- Reduced shrinking and cracking.
- Greater use of marginal aggregates.
- Improved knowledge about the properties required for durability and the mechanisms behind them.

Solutions

- Monitor the rheological properties of fresh concrete with nanomonitors.
- Use nanomonitors to understand and monitor the migration of water in concrete.
- Use nanomaterials to improve self-curing.
- Use nanomaterials to create self-healing mechanisms when cracks occur.
- Use nanotechniques to develop better understanding of freeze-thaw, sulfate attack, and alkali silica reaction mechanisms.
- Develop nanoinstruments to monitor the mechanisms of degradation.
- Use nanoscale devices to monitor and modify concrete performance.

Who

- Multidisciplined consortia to do the work.
- NSF funding is needed.
- Liaison with Nanocem to prevent overlap.

Low Fruit

- Development of sensors and high-tech equipment.
- Chemistry and computational nano-level modeling.

Durability 2 -

Invited

Peter Taylor (Facilitator), Perumalsamy Balaguru, Teck Chua, Julie Garbini, Gary Henderson, Gary Knight, Shashi Nambisan

Needs

- Test methods that can be used to rapidly predict performance and correlate results with the life of the system.
- Improved understanding of attack mechanisms—alkali silica reaction, delayed ettringite formation, sulfate attack
- Improved understanding of fluid transport in concrete
- Improved understanding, control, and monitoring of cement hydration
- The ability to turn on and off the hydration process as desired
- Better control of entrained air stability
- Improved dimensional stability measurement and control
- Improved durability for new and existing structures
- The ability to fill or seal cracks and micropores
- Concrete that has a limited functional life.

Solutions

- Nanotracking and nanoinstrumentation can help address issues related to understanding hydration in the lab.
- Nanosensors could be used to measure various properties in the field. These
 would include monitoring mechanisms such as cracking and infiltration of
 aggressive chemicals.
- Nanomaterials could also be used for activation of desired processes such as improved curing/hydration.

Priorities

- Test methods based on better understanding of attack mechanisms.
- Improving durability of in-place existing structures through filling micro cracks and voids.
- Improved understanding of hydration systems.
- Faster, better durability test methods using nano-sensing.
- Turn on and off hydration of cement.
- Control percent hydration of concrete.
- Forced internal curing.

Summary

In collating the information from the groups, it was found that some themes were common to many of them. Likewise, several topics were only addressed by some groups, but they are critically important to the future of the concrete construction industry. The following sections summarize both of these sets of topics.

Reduction of CO2 loading on the environment

As a significant producer of CO_2 , the cement industry is under considerable pressure to reduce the amount of CO_2 they release to the atmosphere. This can be achieved by doing the following:

- Increasing efficiency of cement along with improving the quality and durability of concrete, leading to lower consumption.
- Supplementing clinker with other materials.
- Accounting for or encouraging sequestration of CO₂ into hardened concrete.
- Capturing and beneficiating CO₂ during the manufacturing process.

All of these have potential solutions through the use of nanotechnology.

Use of marginal and recycled materials

This topic encompasses modification of aggregates and recycled materials that would otherwise interfere with the fresh properties (constructability) or the long-term properties (durability) of the concrete. It is believed that nanotechnology will be able to provide systems to coat or modify problem systems so that they become usable. This will have a significant effect on sustainability of construction as traditional sources of high-quality materials are consumed.

Shrinkage

Volume change in concrete due to temperature changes and moisture loss over time accounts for a large percentage of defects observed in concrete systems, particularly in pavements and slabs on grade. Shrinkage is a direct cause of cracking and warping leading to faulting and premature serviceability failure in a large number of pavements around the country. If this movement within the concrete could be prevented, reduced, or at least made more predictable in terms of timing and extent, millions of dollars would be saved in slabs being removed and replaced, or repaired. Losses to contractors and owners of pavements would be significantly reduced. It is likely that nanotechnology will be able to offer tools to monitor and/or modify the shrinkage of hydrated cement systems. It should be noted that commercially available shrinkage-reducing admixtures are available today that modify the surface tension of capillary pore fluids. These have not yet found wide acceptance in the pavement construction industry.

Permeability

All failure mechanisms associated with concrete durability involve the transportation of fluids through the concrete microstructure. At present, there are a limited number of tests appropriate for assessing these transport mechanisms, and none has found general acceptance in the construction industry. Again, the use of nanotechnology-based tools to monitor and nanomaterials to modify the permeability of a given concrete system will immediately lead to longer lasting concrete structures. Methods to help develop better understanding of some of the still intractable deterioration mechanisms, such as alkali silica reaction, will also be of great value.

Modification of cement hydration

Cement hydration is a complex set of interrelated chemical reactions leading to stiffening of the fresh concrete, followed by strength gain and decreased permeability. This system of reactions is relatively poorly understood and generally uncontrolled once it has been initiated. Rates are affected by the materials within the system and by the environment to which it is exposed. Unexpected changes in stiffening and or strength gain regularly impact the quality of finished products. Development of a better understanding of the processes involved, associated with tools to monitor hydration and, preferably, means to control the rates of hydration, will significantly enhance construction reliability and efficiency.

Curing

A property associated with hydration is the provision of so-called "internal curing" to cementitious systems. Hydration of portland cement is relatively slow compared to other industrial materials, and the need to keep a concrete wet and warm for several weeks often runs counter to the construction schedule and economics. Curing is required to provide an environment for hydration to continue. If nanotechnology is able to provide a means to effectively provide moisture for hydration from internal sources rather than external, then the use of concrete for construction will be significantly simplified.

Computational Modeling and Nanodevices and Sensors

Hydrated cement paste is heterogenous and complex both at a nanometer scale and at a meter scale. A large amount of computing power is required to properly model the material across several orders of magnitude. Such computational resources are now becoming available, allowing for the development of more rigorous models that describe and predict the performance of different cementitious sytems. Work is needed to continue developing and validating these models in order to improve understanding of the materials and predict future performance. Tied to these models is the need to characterize and monitor the critical performance parameters. Once again, development of nanodevices that can report the in-situ properties of a system as hydration progresses will greatly ease the ability to build and maintain durable concrete structures and pavements.

Closing

All of these topics were identified in the roadmap developed at the workshop held in 2006. This session has been able to update the topics and priorities based on need and accessibility, largely from the point of view of materials manufacturers and users.

Outcomes

Common Themes and Priorities

Several common/important themes were apparent as immediate needs for the concrete construction industry that must be addressed through scientific exploration:

- Reduction of CO₂ loading on the environment,
- Use of marginal and recycled materials,
- Crack prevention (Shrinkage),
- Reduced permeability,
- Modification of cement hydration,
- Provision of curing, and
- Improved modeling of properties and performance.

It was believed that nanotechnology and nanoscience would have the means to make significant inroads into the aforementioned needs in the near term.

When prioritizing these needs, several factors need to be considered. Concrete is a heterogenous mixture of multiphase constituents. There are significant variances in composition and properties of each of the constituents, not the least of which is the paste fraction. Hydrated cement paste that forms near coarse aggregate particles tends to be weaker and more porous than that formed 50 μm away from the aggregate surface. Aggregate particles vary in size from μm sizes up to tens of mm. The "critical flaw" size of most concrete mixtures is in the tens or hundreds of μm , making the need to study nanoproperties of concrete as a whole somewhat questionable.

On the other hand, the structure and hydration mechanics of the individual phases of portland cement paste falls firmly into the realm of nanotechnology, and the tools and potential manipulations of this system may make significant contributions to addressing the needs described above.

Likewise, there appears to be great potential in investigating and modifying the raw materials of concrete. Chemical admixtures that are used to modify workability of the mixture, entrain air, or modify shrinkage behavior are ripe for nanomodification to optimize their performance. The use of supplementary cementitious materials and the study of their direct effects on hydration mechanics will likely further enhance sustainability and durability of concrete. Even cement grains may benefit from modification of their surfaces to enhance the hydration process by accelerating the phases that contribute to performance and limiting the processes responsible for unexpected stiffening. Development of improved materials to help reduce the surface permeability of concrete and so increase its durability will be invaluable.

The other arena where nanotechnology has the potential to significantly change concrete technology is in the realm of modeling and sensors. Many tests currently conducted on concrete for quality control purposes are empirical and have poor repeatability. Measurement of critical parameters, such as crack risk and durability, is unreliable. Devices that provide a means of tracking a mixture degree of hydration in real time would reduce the risk of premature

failure significantly. Tools that use numerical models to predict system performance will lead to improved reliability and more rapid development of innovative materials and combinations.

The other aspect to this consideration is that of sustainability. A car built in 2007 is significantly different from one built in 1960. The changes in design and manufacturing processes have been driven by the need for better safety and reliability, reduced emissions, and by competition from global manufacturers. The U.S. concrete construction industry is now starting to face the same demands in that CO_2 is now a global problem impacting many industries, aggregate sources are declining, and leading technology is being reported from elsewhere. These are likely to be the prime drivers in the near term, making the CO_2 issue the highest priority from the above list.

A Vision

A scenario for the future may be visualized by referring to one construction system—concrete slipform paving.

At present, a relatively stiff mixture is delivered to its point of placement. Because it is stiff, it has been difficult to ensure adequate and/or uniform mixing and to entrain a sufficiency of fine air bubbles needed for frost protection. Standard test methods do not reliably indicate the workability of the mixture or the state of the air void system. No means are available to confirm whether the mixture contains the correct ingredients within reasonable bounds of the designed mixture proportions. This stiff mixture is forced into its final shape using heavy equipment, and significant energy is required to fill the forms and remove large voids. Vibration is applied to remove oversized air bubbles, with the associated risk that desirable air bubbles are also removed. Only rarely are tests conducted once the paving machine moves past the concrete to confirm the state of hydration and the in-place quality of the air void system. Once the paver moves past the concrete, it is hoped that the concrete retains its shape. If the mixture is too wet, then edge slump will occur, compromising the integrity of the pavement. We are therefore walking a delicate balance between fluid enough to be handled and consolidated, but dry enough to retain shape when unsupported. If uncontrolled chemical reactions occur between the mixture ingredients, then the mixture may stiffen between the time of batching and final handling, making it difficult to consolidate.

Voids on the surface are filled (or covered over) by hand and the surface is then textured to provide skid resistance. After some time of exposure to the atmosphere, curing compounds are applied to seal in water for curing. No additional water is provided. If the weather is hot and evaporation rates are high, then cracking is probable. The mixture is exothermic and gets hot during early hydration, often causing the slab to set at well above ambient temperature. Joints are sawn into the surface a few hours later to allow the slab to shrink due to the initial temperature drop and later moisture loss. If sawing is too late, then random cracking occurs, leading to loss of serviceability. If sawing is too early, then the joints are raveled, reducing ride quality and increasing the risk of joint-related failures later. Often the decision on when to start sawing is based on an estimate by an experienced operator. No further treatment is applied to the surface to assist with permeability. Generally, it is assumed that a well-hydrated, well-proportioned mixture with an adequate air void system will be able to withstand the environment, and often this is true. However, there is no good way to be sure of this, short of waiting for several years for signs of distress.

This description has sought to indicate that slipform paving is a series of compromises and making critical decisions based on limited information, with significant implications on the life of the pavement if bad decisions are made. Adding to the risk is that these decisions are often made by people who have not received adequate training for the task, and who have limited knowledge of the complexities behind the system they are working with. However, we do manage to produce many hundreds of miles of successful concrete paving each year, and, despite the potential pitfalls, the system is economically and technically viable.

Consider then an alternative approach that may, indeed, be possible with the assistance of nanotechnology.

A very fluid mixture that has been easily mixed in transit is delivered to the point of placement. Internal monitoring nanodevices provide continual logging of the air void system and the degree of hydration. Hydration has actually been stopped by nanomaterials mixed into the concrete and the mixture is not stiffening. The mixture is handled by light equipment and relatively easily formed into its final position. Minimal vibration is required to remove unwanted large air voids, and vibration is stopped as soon as the internal nanosensors report the required air void parameters have been achieved. At this time, a signal is sent to the hydration control nanoparticles, and hydration is initiated and accelerated to cause the concrete to stiffen significantly before it is exposed by the paving machine. Edge slump does not occur. Sensors continue to report the state of the mixture behind the paver providing the basis for quality control and quality assurance. Texturing is applied and another signal further accelerates hydration to cause final setting and initial strength development.

Another set of nanoparticles are then applied to the surface. Their small size allows them to penetrate a few millimeters into the surface, where they interact with the hydrated cement paste to seal it up and prevent future fluid penetration and durability-related failure. Indeed, if a sufficiently robust sealant can be developed, then the need for entrained air may become redundant. This sealant would be below the surface; therefore, the skid resistance of the concrete would not be compromised. Internal curing molecules then promote hydration to a state where the concrete is ready to carry the intended traffic for the designed time. Other nanomaterials control the structure of the hydrated cement paste so that drying shrinkage is reduced or eliminated, thus significantly reducing the need for, or increasing the spacing of, joints and controlling warping. Ideally, methods to control temperature variations can also be incorporated to minimize thermal stresses in the slab, further reducing the risk of warping, cracking, and the need for joints. The sensors embedded in the system continue to report the state of the concrete, and should cracks or deleterious reactions occur, they can be reported early to facilitate planning for repair or mitigation.

Based on this vision, one can conceive that nanotechnology may fundamentally change the way that concrete pavements are constructed, resulting in increased reliability for all parties involved. Realistically, if we can deal with workability control, shrinkage, and permeability, then many of the failures currently occurring will be significantly reduced.

Collaborative effort

Based on the figures discussed in the introduction, it is not unreasonable to estimate that a savings of \$7 billion per annum, worldwide, can be achieved by meeting the needs discussed in this report. In 1992, it was estimated that replacement of the deteriorating built environment

⁷ NSF Civil Infrastructure (CIS) Strategic Issues, NSF 94-129

was going to cost \$20.6 trillion in the US⁷. Mitigation of this need in new construction by preventing premature failures would therefore be in the order of several billion per annum. Thus, the value of pursuing this work is clearly justified from an economic viewpoint alone. However, the work also offers significant environmental and societal benefits.

When considering the magnitude of the issues, it is clear that the needs can only be addressed by collaborative efforts in order to leverage the resources available. Collaboration is required between

- Funding agencies to allow sufficient resources to be available for the research to be conducted at the highest level.
- Research institutions to ensure that the best available minds and resources can be brought to bear.
- Specification authorities to allow innovations to be acceptable in contract documents.
- Education institutions to teach users of the new technologies how they may be utilized safely and effectively—both at an operator level, and for future researchers to continue the work.
- Information providers so that there is appropriate sharing of findings to ensure that seminal work is not repeated unnecessarily.
- Other industries to take every opportunity to make use of findings and approaches developed for other materials that will be of benefit to the study of cementitious systems.

The above discussion points to the need for a neutral, central, clearing-house resource where any of the above agencies can find partners and share data, resources, and needs.

Plans for the future

The following plans have been developed:

- Establish an Industry board to help steer future decisions regarding research in this field. It is planned that this board will develop into a National Nanotechnology Initiative Consultative Board for Advancing Nanotechnology (NNI CBAN) as appropriate. The board will include representatives of the cement and chemical admixture industries, readymix concrete industry, federal agencies, and researchers in this area.
- Establish an international university-based research consortium to promote and lead nanotechnology-based concrete research. It is extremely important to form a coalition of key research entities that bring together the broad knowledge needed for the breakthroughs in nanotechnology-based cement and concrete research. This consortium will include experts on construction materials, including concrete paving materials, material scientists with expertise in polymers and innovative material processing, as well as experts on computational modeling and thin films and coatings.
- Plan another workshop for the summer/fall of 2008 to provide an opportunity for scientists working in nanotechnology and nanoscience to discuss their work and their possible approaches to the needs raised at this workshop.
- Commence work on developing detailed work statements aimed at addressing the needs and issues raised at this meeting. This work will also include conducting extensive literature reviews of work conducted in other fields and industries to seek methods and approaches that may accelerate the proposed activities.
- Establish an Internet-based central database and clearinghouse on key research in progress and research outcomes, which will also allow secure communications between researchers during research in progress.
- Develop a consortium-based approach to foster research efforts through the international, university-based research consortium, with a focus on short-term and intermediate-term research outcomes. Organize larger consortia around grand challenge problems, such as the development of a model for the hydration process.

In addition, the key priority research areas identified in this workshop will be used as focal points for research consortia, where technical input and funding will be sought from industry and key funding agencies within the United States and Europe. The following topics will be covered by these research miniconsortia:

- Use of nanotechnology to reduce CO₂ loading from cement plants on the environment.
- Development of innovative technologies to enhance the use of marginal and recycled materials in portland cement concrete.
- Nanotechnology for reduced shrinkage behavior of portland cement concrete.
- Nanomodification of portland cement concrete to reduce permeability.
- Development of nanotechnology-based solutions to monitor and modify rates of hydration in portland cement concrete.
- Computational modeling and sensor systems to monitor and describe system performance.

Workshop on Nanotechnology for Cement and Concrete

Appendices

Appendix A: Agenda

Workshop on Nano Technology for Cement and Concrete September 5, 2007

FDIC, 3501 North Fairfax Drive, Arlington, VA

Sponsors: The National Concrete Pavement Technology Center and the National Science Foundation, in Cooperation with the Nanoscale Science, Engineering, and Technology (NSET) Subcommittee of the U.S. National Science and Technology Council, through the National Nanotechnology Coordination Office

Objective: Provide national direction on areas of priority interest and collaboration between industry and public agencies specifically for cement and concrete.

8:00 am – 8:30 am	Coffee	
8:30 am – 8:45 am	Welcome Tom Cackler, CP Tech Center, Iowa State Univ.	
8:45 am – 8:55 am	Snapshot of the National Nanotechnology Initiative Dr. Clayton Teague, National Nanotechnology Coordination Office	
8:55 am – 9:15 am	Nano House Dr. Mike Roco, National Nanotechnology Initiative	
9:15 am – 9:25 am	FHWA Perspective on Nanotechnology in Concrete Gary Henderson, FHWA.	
9:25 am- 9:45 am	Nanocem - European Efforts Vagn Johansen, Nanocem	
9:45 am – 10:15 am	Break	
10:15 am – 10:45 am	The Future of Concrete Dr. Felek Jachimowicz, Vice President of Research, WR Grace	
10:45 am – 11:00 am	Nanoscience of Highway Construction Materials Dr. Richard Livingston, FHWA	
11:00am – 11:30 am	New Functionalities for the Building Industry Dr. Laurent Bonafous – Essroc-Italcementi	
11:30am - 12:00 am	The Nano-Engineering of UHPC & Structures Vic Perry, Bruce Blair – Lafarge & Dr. Franz-Josef Ulm - MIT	
12:00 – 1:00 pm	Lunch	
1:00 pm – 1:45 pm	Round table discussion (Each participant group [agency/company] should be prepared to share brief comments [3 to 5 minutes] on main overarching themes of their agencies'/companies' areas of interest)	

1:45 pm – 2:15 pm	Roadmap for Research		
	Dr. Bjorn Birgisson, Royal Institute of Technology		
2:15 pm – 3:15 pm	Break		
3:15 pm – 3:45 pm	Breakout sessions to identify priority topics (Two groups per topic)		
	• Durability		
	High Performance		
	Sustainability		
3:45 pm – 4:45 pm	Reports from breakout teams (Goal is to prioritize several good topics for collaboration)		
4:45 pm – 5:00 pm	Next steps: Discussion Tom Cackler, CP Tech Center		
5:00 pm	Meeting Adjourned		

Appendix B: Attendees

James Alleman Iowa State University

Jamshid Armaghani Florida Concrete Products

Perumalsamy Balaguru Rutgers University Mike Beacham Pipe Association

Charles Beatty University of Florida

Bjorn Birgisson Royal Institute of Technology-Sweden

Bruce Blair Lafarge

Laurent Bonafous Essroc-Italcementi
John Brighton Iowa State University

Jeffrey Bullard National Institute of Standards and Technology

Mike Byers Indiana Chapter American Concrete Pavement Association

Tom Cackler National Concrete Pavement Technology Center

David Carson Environmental Protection Agency
Rita Chow Environmental Protection Agency

Teck Chua Florida Rock Industries

Clark Cooper National Science Foundation-Civil, Mechanical and Manufacturing

Innovation/Engineering

Peter Deem Holcim

Julie Garbini Ready Mix Concrete Research and Education Foundation

Ed Garboczi National Institute of Standards and Technology

Brian Green US Army Corps of Engineers-Engineering Research and Development

Center

Jim Grove National Concrete Pavement Technology Center and Transportation

Research Board Task Force on Nanotechnology-Based Concrete

Materials

Fred Hejl Transportation Research Board
Gary Henderson Federal Highway Administration

Geoffrey Holdridge National Nanotechnology Coordination Office

Jack Holley Lafarge
Al Innis Holcim
Felek Jachimowicz WR Grace
Vagn Johansen Nanocem
Gary Knight Heidelberg

Steve Kosmatka Portland Cement Association

Richard Livingston Federal Highway Administration

Colin Lobo National Ready Mix Concrete Association

Kevin MacDonald Cemstone Products

Kevin McMullen Wisconsin Chapter American Concrete Pavement Association

Shahran Mehrvarzi Federal Rail Administration
John Melander Portland Cement Association

Shashi Nambisan Iowa State University

Vic Perry Lafarge

Krishna Rajan Iowa State University

Daniel Rardon PPG Industries

Randell Riley Illinois Chapter American Concrete Pavement Association

Mike Roco National Science Foundation

Tyson Rupnow National Concrete Pavement Technology Center

Uwe Schutz St. Lawrence Cement
Panneer Selvam University of Arkansas

Peter Taylor National Concrete Pavement Technology Center
Clayton Teague National Nanotechnology Coordination Office

Joe Tedesco University of Florida

Suneel Vanikar Federal Highway Administration

Jerry Voigt American Concrete Pavement Association
Leif Wathne American Concrete Pavement Association

Don Weir Giant Cement



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