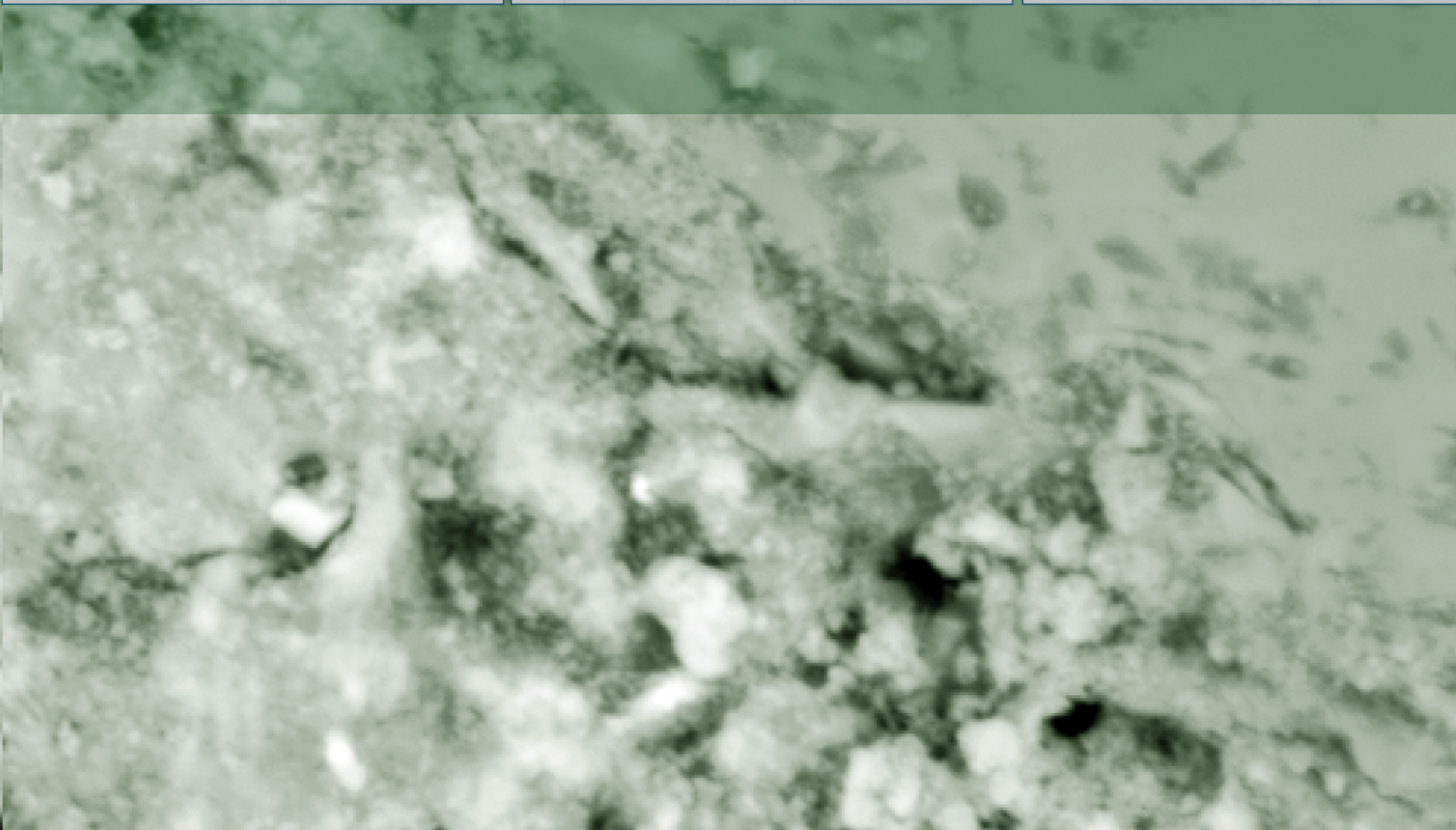
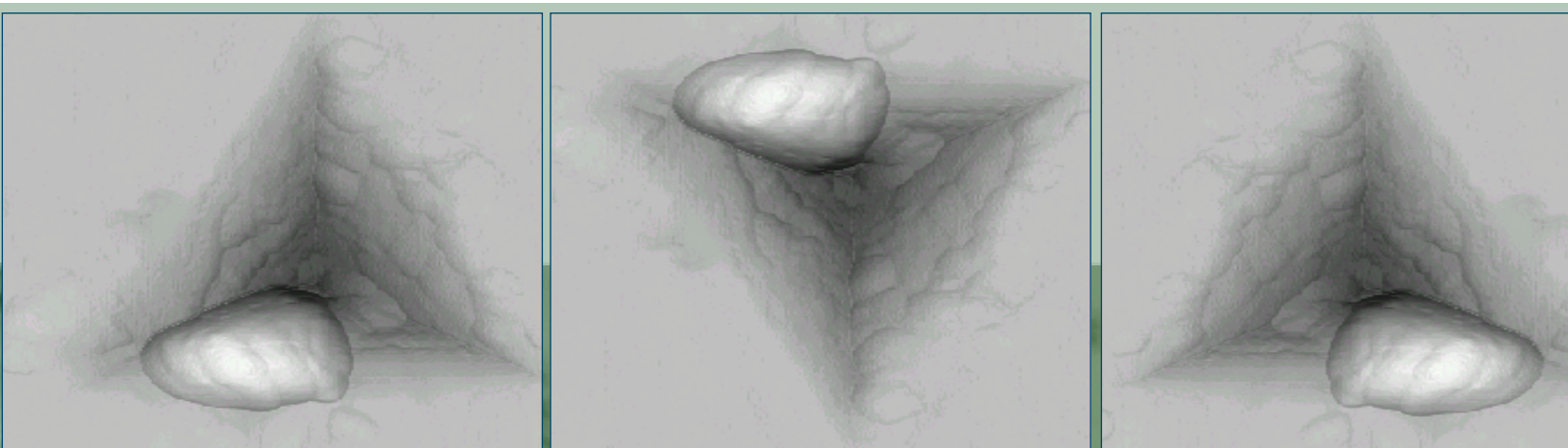


Workshop on _____

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.

Travel support for most state department of transportation and university attendees and support for development of this report were made possible by NSF Grant CMMI 0749499.

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

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

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 sheer 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.

² 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

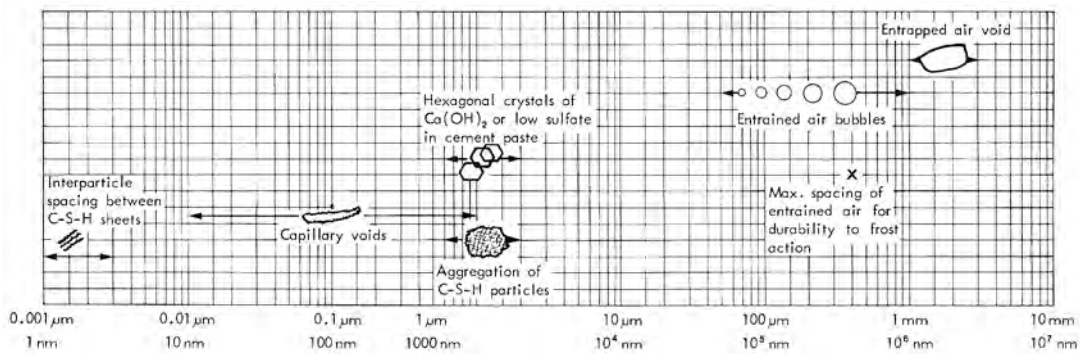


Figure 1. Dimensional range of solids and pores in a hydrated cement paste

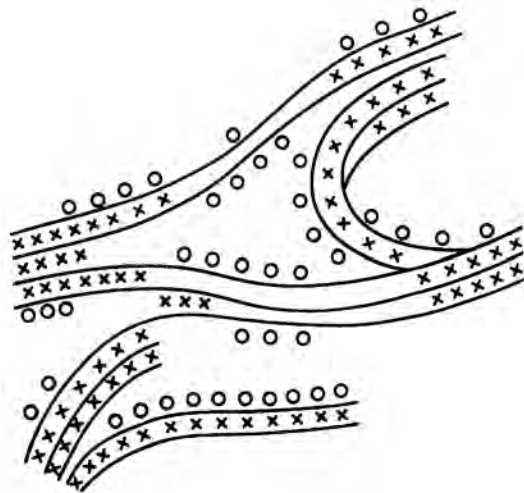


Figure 2. A model of the structure of C-S-H, showing C-S-H layers (lines), interlayer water molecules (crosses), and adsorbed water molecules (circles).

³ Mehta, P.K., "Concrete Structure, Properties and Materials," Englewood 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

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

Nano - House

M.C. Roco
 National Science Foundation and
 National Nanotechnology Initiative

Industry Workshop on *Nanotechnology for Cement and Concrete*
 September 5, 2007

Topics

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

Several particularities for cement and concrete research

- Less investment in research, 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

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.

Timeline for beginning of industrial prototyping and nanotechnology commercialization: Four Generations

- 1st: Passive nanostructures** (1st generation products)
 Ex: coatings, nanoparticles, nanostructured metals, polymers, ceramics
 ~ 2000
- 2nd: Active nanostructures**
 Ex: 3D transistors, amplifiers, targeted drugs, actuators, adaptive structures
 ~ 2005
- 3rd: Systems of nanosystems**
 Ex: guided assembling, 3D networking and new hierarchical architectures, robotics, evolutionary
 ~ 2010
- 4th: Molecular nanosystems**
 Ex: molecular devices 'by design', atomic design, emerging functions
 ~ 2015-2020

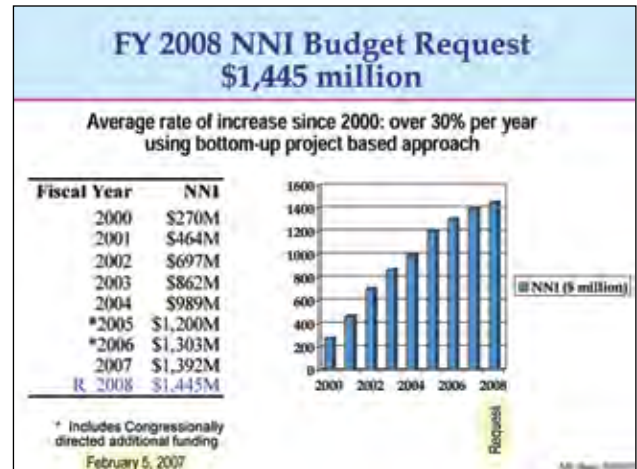
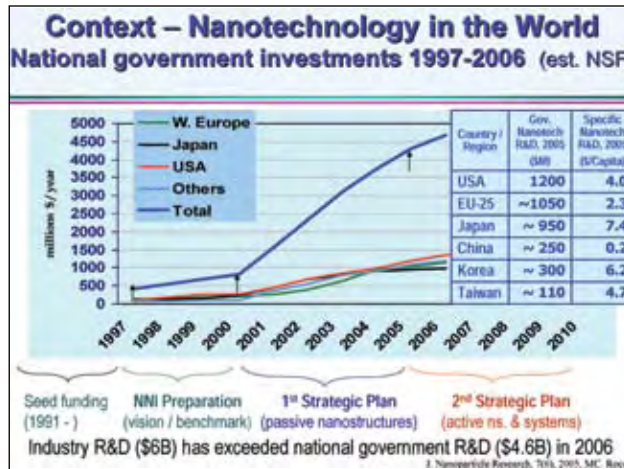
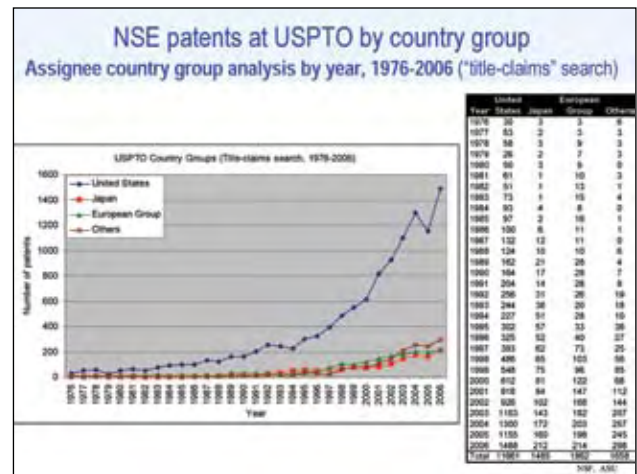
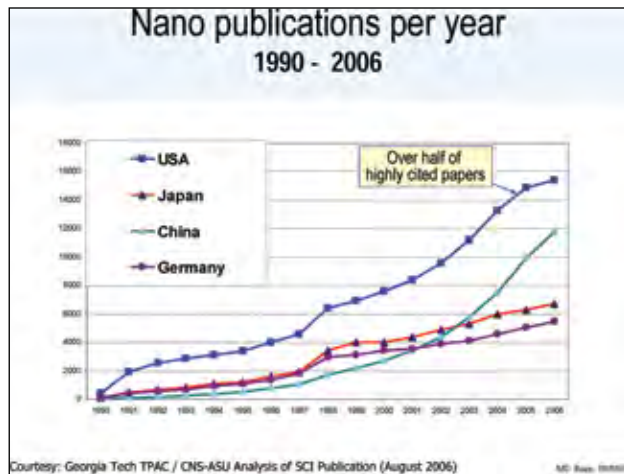
New R&D challenges

Example 1st generation – platform for passive nanostructures

Nanotechnology Platform
 NanoTubes and NanoRods
 NanoParticles
 NanoCeramics
 NanoStructured Metal Systems
 Hybrid Materials

Water
 Energy
 Healthcare
 Aircraft Engines

Nanotechnology at General Electric



NATIONAL NANOTECHNOLOGY INITIATIVE

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/yr)

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
 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 topics

NATIONAL NANOTECHNOLOGY INITIATIVE

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

2005 NCMS Survey on nanotechnology in manufacturing industry (594 companies)

Commercialization timelines indicate many new nanoproducts introductions in 2007-2011, and the high level of expectation in long-term

Reference: National Center for Manufacturing Systems, 2006

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
- Multi-scale, multi-phenomena modeling and simulation
- Novel nano-architectures
- 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 self-assembly

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, ..

Nano House

Dr. Mike Roco

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**

MC Roco, 09/07/07

Reasons for Nano-House

(CSIRO website)

- **Energy Efficiency**
- **Sustainability**
- **Quality of life**
- **Mass Customization**



MC Roco, 09/07/07

From BBC website, March 2007

SOME POTENTIAL USES OF NANOTECHNOLOGIES



- * 1 - Organic Light Emitting Diodes (OLEDs) for displays
- * 2 - Photovoltaic film that converts light into electricity
- * 3 - Scratch-proof coated windows that clean themselves with UV
- * 4 - Fabrics coated to resist stains and control temperature
- * 5 - Intelligent clothing measures pulse and respiration
- * 6 - Bucky-tube frame is light but very strong
- * 7 - Hip-joint made from biocompatible materials
- * 8 - Nano-particle paint to prevent corrosion
- * 9 - Thermo-chromic glass to regulate light
- * 10 - Magnetic layers for compact data memory
- * 11 - Carbon nanotube fuel cells to power electronics and vehicles
- * 12 - Nano-engineered cochlear implant

MC Roco, 09/07/07

Workshop on Nano-modification of Cementitious 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)

MC Roco, 09/07/07

Examples of active NSF awards (September 2007)

Award Number	Title (searched by keywords www.nsf.gov/nano : "nano and cement")	NSF Organi.	Principal Investigator
408427	Sensing Intrinsic Nano-Microstructural Characteristics of Hardening Concrete with High-Frequency Transverse Waves	CMM	Shah, Surendra
409114	Precast Concrete Coupling Beams for RC Walls	CMM	Kurama, Yuhya
510854	Multi-Scale Kinetics-Based Model for Predicting Mechanical Property Development of Concrete Containing Supplementary Cementitious Materials	CMM	Hansen, Will
355253	Effect of Inclusions on Material Performance- Investigation Through Micro-Continuum, Discontinuum and Nano-Indentation Approaches	CMM	Ehrlich, Herbert
629927	Unified Approach for Multiscale Characterization, Modeling, and Simulation for Stone-based Infrastructure Materials	CMM	Wang, Lintong
637297	SITR Phase I: Demonstration of Enhanced Corrosion Resistance using a Nano-composite Thermal Barrier Coating	IIP	Cutron, 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	CMM	Li, Victor
700524	Dielectric & Mech. Spectra Assisted Multi-Scale Study of Early Stage Concrete	CMM	Yu, Xiong

MC Roco, 09/07/07

Examples of active NSF awards (September 2007)

Award Number	Title (searched by keywords www.nsf.gov/nano : "nano and concrete")	NSF Organization	Principal Investigator
510854	Multi-Scale Kinetics-Based Model for Predicting Mechanical Property Development of Concrete Containing Supplementary Cementitious Materials	CMM	Hansen, Will
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, Lintong
652869	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	CMM	Yu, Xiong

MC Roco, 09/07/07

Eight Nanoscale Science and Engineering networks with national outreach

- Network for Computational Nanotechnology (2002-) 12,000 users/ 2006
- National Nanotechnology Infrastructure Network (2003-) 4,000 users/ 2006
- Nanotechnology Center Learning and Teaching (2004-) 1 million students/ 5yr
- Center for Nanotechnology Informal Science Education (2005-) 100 sites/ 5yr
- Network for Nanotechnology in Society (2005-) Involve academia, public, industry
- National Nanomanufacturing Network (2006-) 4 NSETs, DOD centers, and NIST
- NSEC Network (2001-) 16 research & education centers
- MRSEC Network (2001-) 6 new research & education centers since 2000

NSF National Nanotechnology Initiative (NNI)

Search for NSF awards by keywords (Go to the "Full text search", and complete the box with your keywords) Examples of keywords are: "nanotechnology" and "nanoparticle"

NSF awards releases on nanotechnology research since January 2004

NSF awards releases on nanotechnology research from 2003 to 2003

SOLICITATIONS AND OPPORTUNITIES 04 19 2004

NSF Announcement 03-342: Nanotechnology, Science, and Engineering Education Center

NSF Announcement 04-040: Nanoscale Science and Engineering (NSE)

NSF Announcement 04-041: Nanoscale Science and Engineering (NSE)

Joint EPA-NSF-NIEHS solicitation for research in Environmental and Human Health Effects of Manufactured Nanomaterials

Five ways nanotechnology will change business

1. Competitive advantage by improved products now
2. Create S&T nanotech platforms for revolutionary new products (over 50% of new chemical/ electronic/ pharmaceutical/ advanced materials products by 2015)
3. Opportunities for innovation: Convergence with biomedical, electronics, cognition, others
4. New organization and business models - "horizontal" information, S&T clusters, distributed production
5. 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

Nanocem - European Efforts

Vagn Johansen

NANOCEM
European Efforts

Vagn Johansen
Industry Workshop on Nano Technology for Cement and Concrete
September 5, 2007, Arlington, VA

Industry Workshop on Nano Technology for Cement and Concrete, September 4, 2007

European Technology Platform, ETP

European Technology Platforms (ETPs) have been set up in a number of areas where Europe's competitiveness, economic growth and welfare depend on important research and technological progress in the medium to long term. They bring together stakeholders, under **industrial leadership**, to define and implement a Strategic Research Agenda (SRA) The ETPs have contributed to the definition of the themes of the **FP7 Cooperation programme**, in particular in research areas of special industrial relevance. The implementation of the SRA will be supported by the Cooperation programme.

Industry Workshop on Nano Technology for Cement and Concrete, September 4, 2007

European Construction Technology Platform

Strategic Research Agenda
for the European Construction Sector
Implementation Action Plan

Industry Workshop on Nano Technology for Cement and Concrete, September 4, 2007

One example

A project group led by the **Aalborg Portland Group's** Research and Development Centre and also participation from INANO in Arhus and Aalborg universities, as well as Denmark's and Greenland's Geological Survey (GEUS), have been awarded EURO 1.3 million (\$1.75 million) to develop the cement of the future based on nanotechnology.

FUTURECEM, as the project is known, has a combined budget of EURO 2.6 million (\$3.6 million) and runs over three years. The purpose is to utilise nanotechnology to develop new types of cement and additives to concrete. The new products are to be created from Danish raw materials.

Press Release (Sep. 2006) The Green Advanced Technology Foundation awards EURO 1.3 m. for developing the cement of the Future. [Press Release](#)

Industry Workshop on Nano Technology for Cement and Concrete, September 4, 2007

NANOCEM
An Industrial Academic Partnership
for **Fundamental Research**
on Cementitious Materials

Industry Workshop on Nano Technology for Cement and Concrete, September 4, 2007

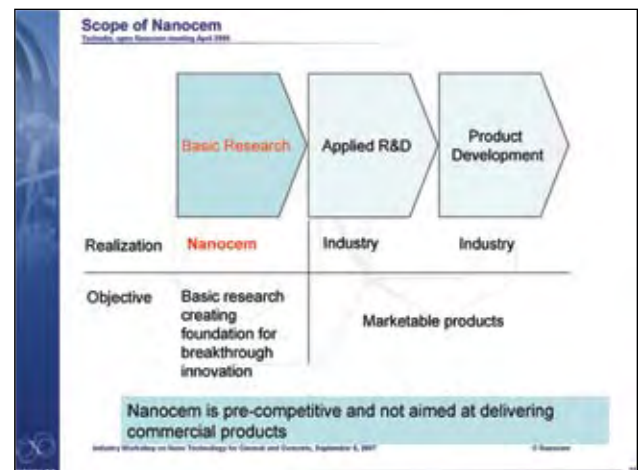
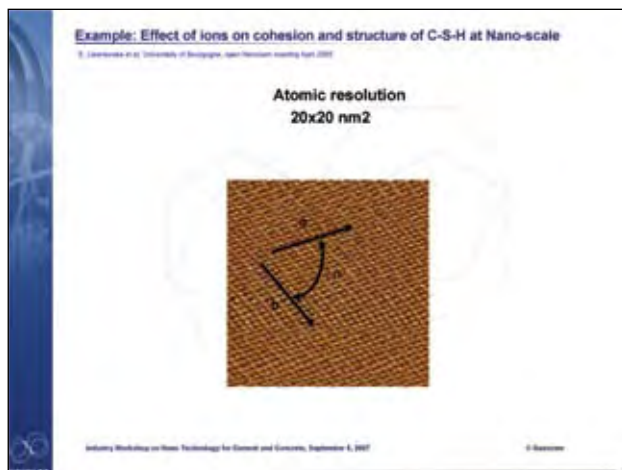
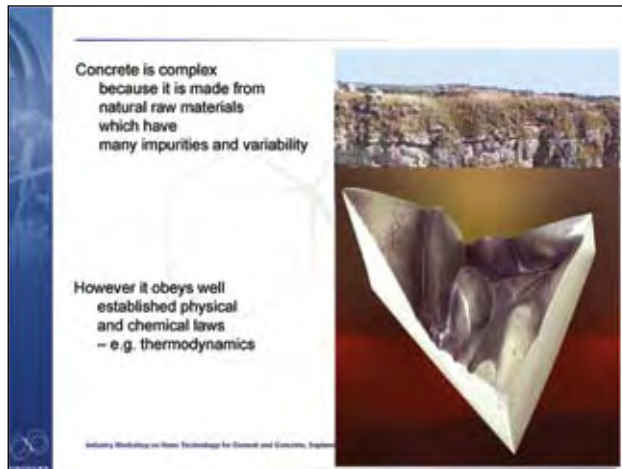
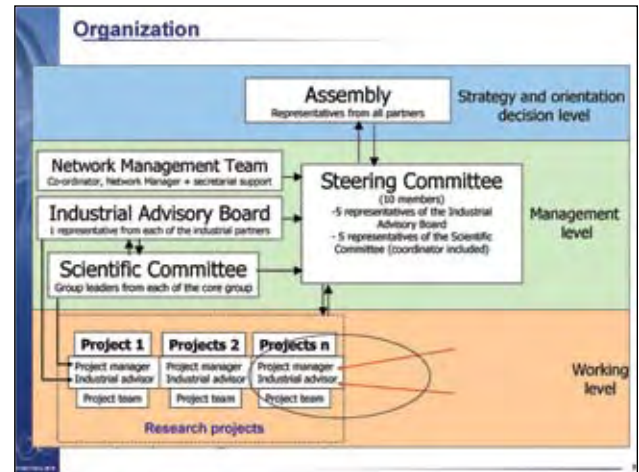
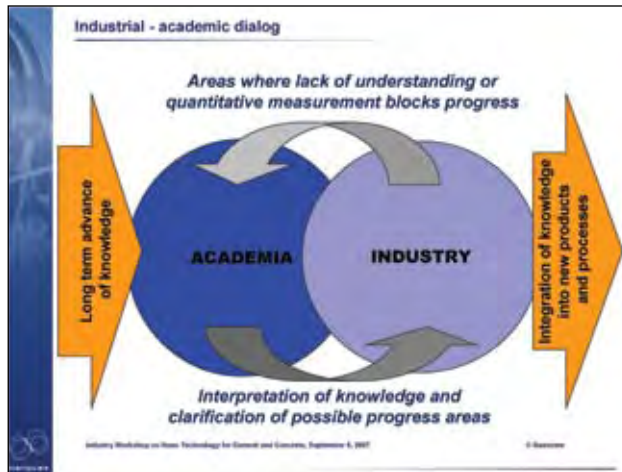
23 Academic partners
Scientific expertise
self financed research projects

14 Industrial partners
Practical expertise
€€€€€€€€

nanoCEM

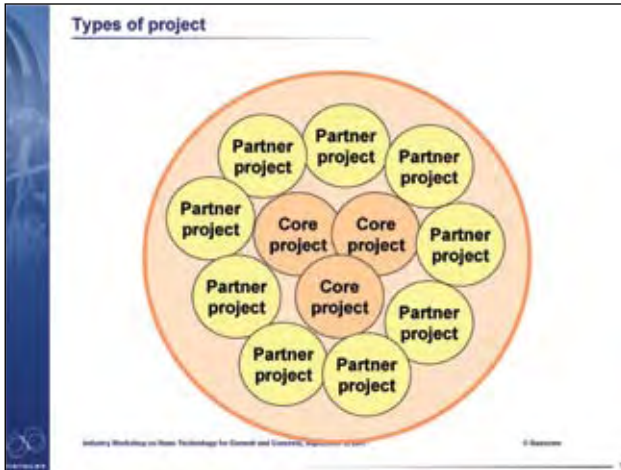
Nanocem - European Efforts

Vagn Johansen



Nanocem - European Efforts

Vagn Johansen



Presently there are 4 Core Projects and 23 Partner projects under way.

In addition a EURO 3.2 million (\$4.3 million) EU funded project under the Marie Curie Programme has started March 2006. This consists of 15 PhD and Post Doctoral projects each involving several Nanocem partners and all linked to the Thematic Areas.

Industry Workshop on Nano-Technology for Cement and Concrete, September 6, 2007

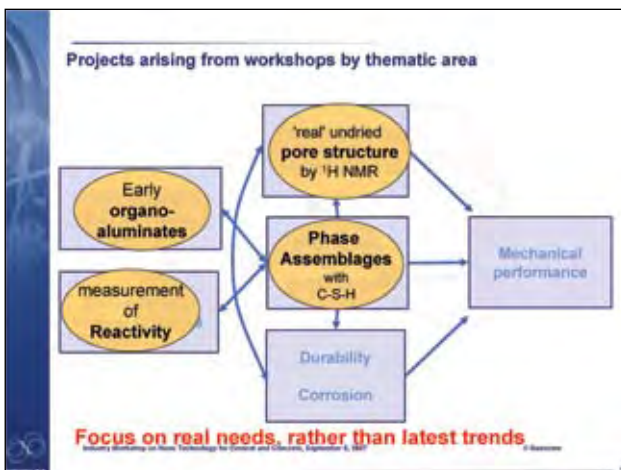
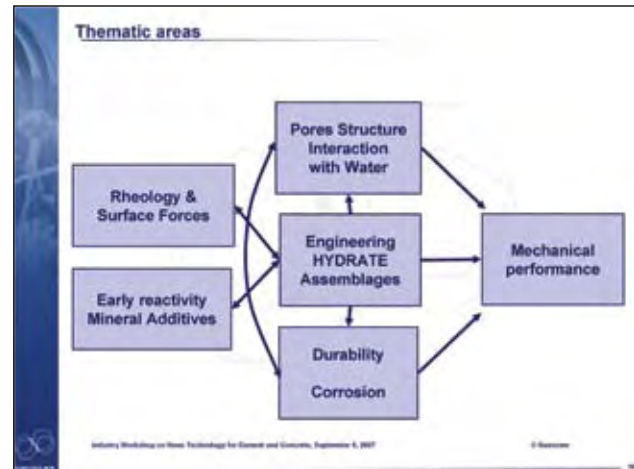
Core projects

Core projects aim to bridge the gaps between the independent research of the different academic partners.

They typically fund 1-2 PhD students working across 2-4 partner institutions

The first core projects were chosen after a series of workshops organised by thematic area:

Industry Workshop on Nano-Technology for Cement and Concrete, September 6, 2007



Core Project 1

UNIVERSITY OF ABERDEEN EMPA

Prof Fred Glasser Dr Barbara Lothenbach
PhD student Thomas Matschei

New approaches to quantification of cement hydration

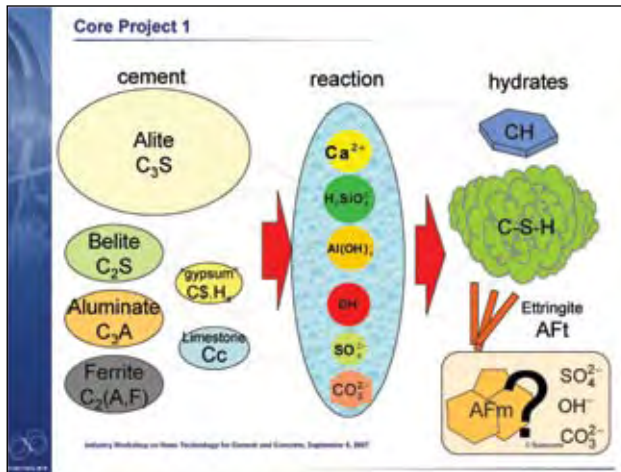
- development of a **generic approach** - based on thermodynamics - to predict the qualitative and quantitative phase development of hydrated cements with user-specified compositions
- **Reduction of experimental work** by simulation of complex reactions (formulation of focussed experiments to validate calculations)
- provide toolkit to **focus and improve research&development**

Stimulation of knowledge transfer by calculation of selected examples relevant to industry.

Industry Workshop on Nano-Technology for Cement and Concrete, September 6, 2007

Nanocem - European Efforts

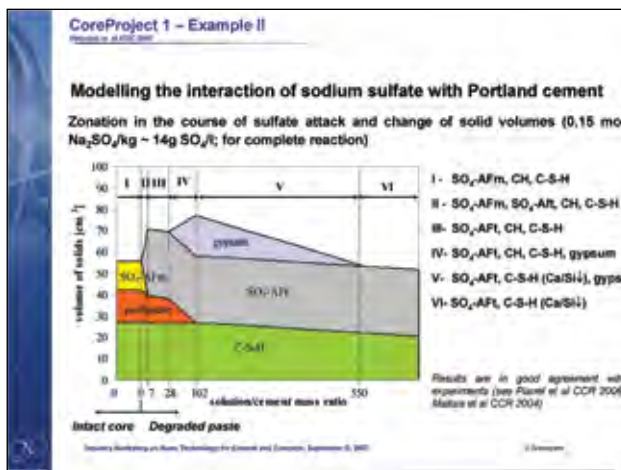
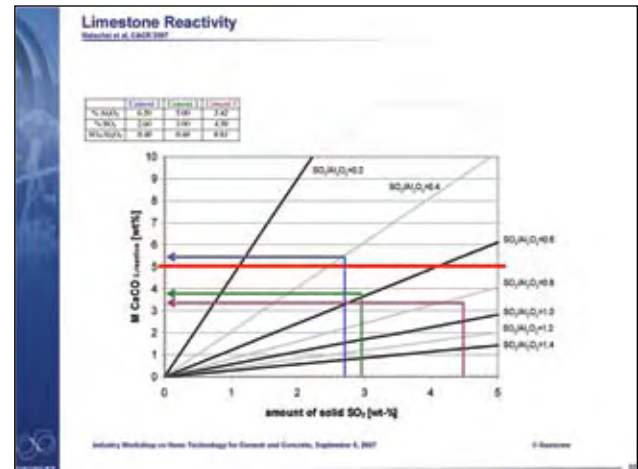
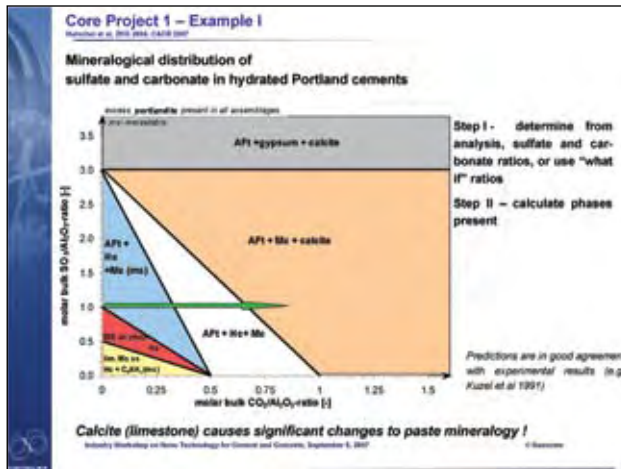
Vagn Johansen



Core Project 1

Development of a self consistent database

- A self-consistent database for cement hydration was developed. Literature data were critically assessed and new experiments completed. The database contains entries for the main hydrate phases of commercial Portland and blended cements, e.g., AFm, AFt, hydrogarnet and C-S-H.
- It was found that except for the sulfate and hydroxide the several AFm phases do not form solid solutions. Thus cements may contain several coexisting AFm phases, depending on anion balances
- Data were completed and allow the user to do calculations in the range 1 to 99°C.
- The database was successfully applied to case studies, e.g. to predict the role of carbonate in cement hydration



Core Project 1

Achievements of Core Project 1

Knowledge transfer based on thermodynamic calculations:

- Determination of the distribution of sulfate and carbonate in hydrated Portland cement and prediction of coexisting phases as a function of cement composition. Systematic investigations to the role of calcite (limestone) in cement hydration (Matschei et al ZKG 2006 and CCR 2007)
- Calculations of the interaction of sodium sulfate with Portland cement
- Prediction of phase assemblages of Portland cement paste undergoing carbonation
- Potential for application to a wide range of problems including identification of kinetic restraints/mechanisms

Approach continued under Marie Curie RTN

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Publications from Core project 1

- 1) Matschei T., Glasser, F.P.: The influence of limestone on cement hydration. *Zement, Kalk, Gips*, 2006, 59, No 12, 78-86
- 2) Matschei, T.; Lothenbach B.; Glasser, F.P.: The AFm-phase in Portland cement. *Cement and Concrete Research*, 2007, 37, 118-131
- 3) Matschei, T.; Lothenbach B.; Glasser, F.P.: The role of calcium carbonate in cement hydration. *Cement and Concrete Research*, 2007, 37, 551-558
- 4) Matschei, T., Skapa, R.; Lothenbach, B.; Glasser, F.P.: The distribution of sulfate in hydrated Portland cement paste. *Proceedings of the 12th Intern. Congress on the Chemistry of Cements, Montreal, 2007*
- 5) Matschei, T., Glasser, F.P.: Interactions between Portland cement and carbon dioxide. *Proceedings of the 12th ICCO, Montreal, 2007*

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Core Project 2



Prof Jean-Pierre Korb **Prof Peter McDonald**
Dr Jonathan Mitchell

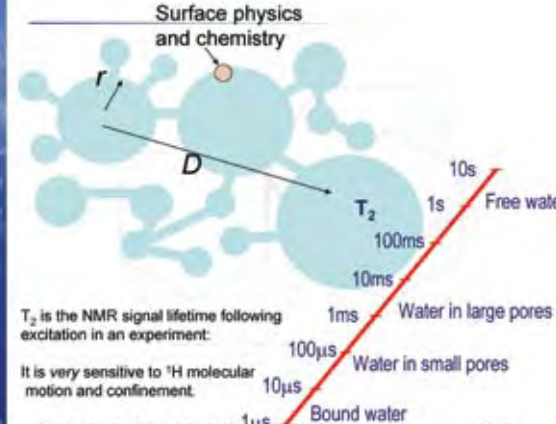
PhD student Luc Montelliet

Magnetic Resonance analysis of water-cement pore interactions in cement paste

- MR probes protons in water molecules and so investigates pores in **undried cement paste**

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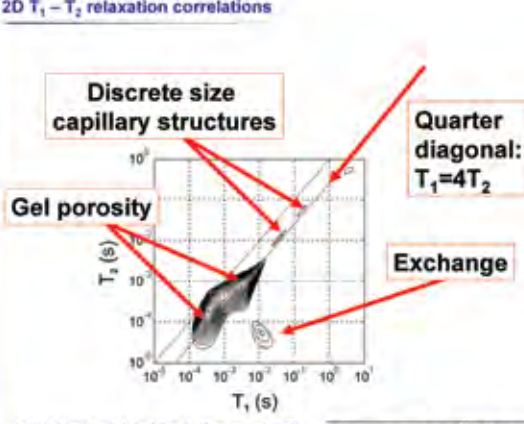
Surface physics and chemistry



T_2 is the NMR signal lifetime following excitation in an experiment:
It is very sensitive to ^1H molecular motion and confinement.

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2D $T_1 - T_2$ relaxation correlations



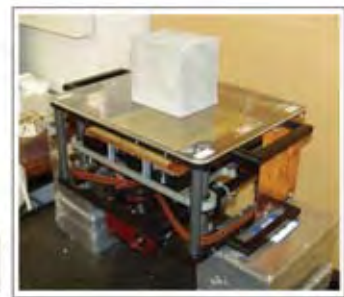
Discrete size capillary structures

Quarter diagonal: $T_1 = 4T_2$

Exchange

McDonald et al., Phys Rev E (2008)


Portable (in-situ) MRI



Proto-type surface GARField

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In-situ MRI



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Nanocem - European Efforts

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Core Project 2

Achievements of Core Project 2

- New methodology for MR experiments with T_1 - T_2 correlations allows quantification of protons in different pore populations and study of the exchange between these populations
- Technique is very sensitive to changes in processing:
 - Temperature of curing
 - Available water
 - Pre-hydration
- Discrete pore structure – New information related to ‘mesostructure’ of C-S-H
- Prototype of portable equipment (UNIS, partner project)

Approach continued under Marie Curie RTN


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Publications from Core Project 2

- i. McDonald P.J, Korb J.P, Mitchell J, Montelhet L, "Surface relaxation and chemical exchange in hydrating cement pastes: A two-dimensional NMR relaxation study" *Phys Rev E* 72 art. no. 011409 (2005)
- ii. L. Montelhet, J.-P. Korb, J. Mitchell, and P. J. McDonald "A NMR T2-store-T2 2-dimensional correlation relaxation study of cement pastes" *Phys Rev E* 74 art. no. 061404 (2006)
- iii. J.-P. Korb, P.J. McDonald, L. Montelhet, A.G. Kalinichev and R.J. Kirkpatrick, "Comparison of proton field-cycling relaxometry and molecular dynamics simulations for proton-water surface dynamics in cement-based materials." *Cement and Concrete Research*, 37, 348-350, (2007)
- iv. J.-P. Korb, L. Montelhet, P.J. McDonald and J. Mitchell "Microstructure And Texture Of Hydrated Cement-Based Materials: A Proton Field-Cycling Relaxometry Approach" *Cement and Concrete Research*, 37, 295-302, (2007)
- v. P. J. McDonald, J. Mitchell, M. Mulheron, P. S. Aptaker, J.-P. Korb, and L. Montelhet "2D Correlation Relaxometry Experiments of Cement Pastes Performed Using A New One-Sided NMR Magnet" *Cement and Concrete Research*, 37, 303-309, (2007)
- vi. P.J. McDonald, P.S. Aptaker, J. Mitchell, and M. Mulheron "A Unilateral NMR Magnet for Sub-Structure Analysis in the Built Environment: The Surface GARFIELD" *J. Magn. Reson.* 188, 1-11, (2007)
- vii. P.J. McDonald, J. Mitchell, M. Mulheron, L. Montelhet, J.P. Korb "2D Correlation Relaxation Studies of Cement Pastes" submitted to *Magn. Reson. Imag.* (Proceedings of Magnetic Resonance in Porous Media 8, Bologna, 2006)

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Core Project 3



Dr Jean-Baptiste d'Espinose **Dr André Nonat** **Dr Robert Flatt**
Dr Angelique Vichot

Prof Henri van Damme

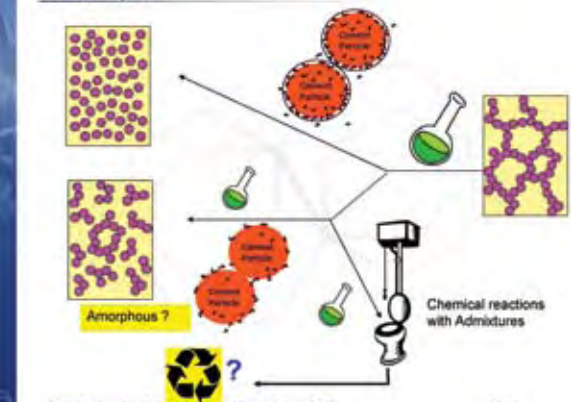
PhD student Claire Lenain

Organo Aluminate Interactions

- Super plasticizers are widely used to improve workability of concrete and facilitate reduction of water to cement ratio (HPCs)
- interactions between these organic and the aluminates in cement can lead to cement-admixture "incompatibility"

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Consumption



Amorphous ?

Chemical reactions with Admixtures

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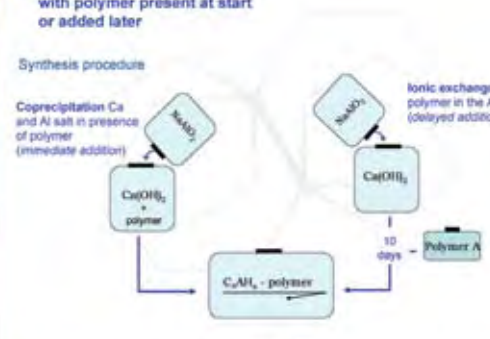
General methodology

Preparation of organo aluminate with polymer present at start or added later

Synthesis procedure

Coprecipitation Ca and Al salt in presence of polymer (immediate addition)

Ionic exchange of OH by polymer in the AFm phase (delayed addition)



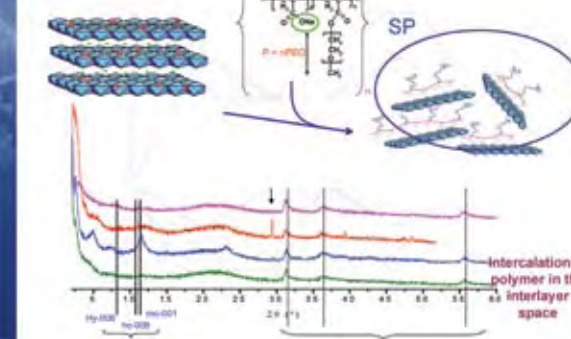
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Results

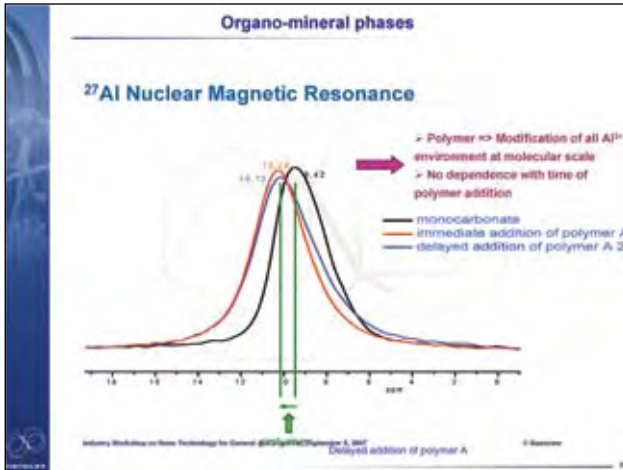
$[Ca_3(AlO)_4]_x$ (AFm):
no positively charged layers

SP

Intercalation of polymer in the interlayer space



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Next steps

Further studies to determine the conformation of the polymers in the AFM phases

Interaction of organo-aluminate phases with sulfate ion in solution

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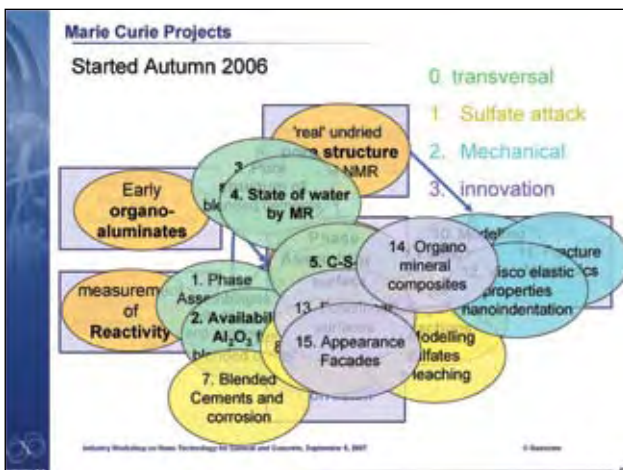
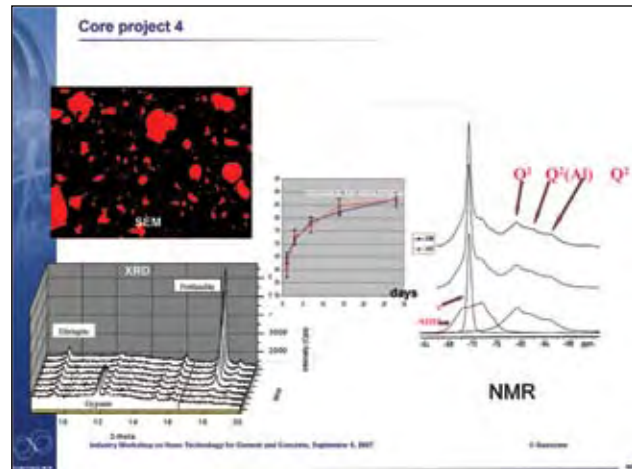
Core Project 4

Prof Karen Scrivener **Dr Jørgen Skibsted**
Dr Mette Geiker
 PhD students Vanessa Kocaba
 Soren Poulsen

Independent measurement of degree of reaction of SCMs and clinker in blended cements

- Supplementary cementitious materials (SCMs) such as slag, fly ash and silica fume are increasingly important as substitutes for clinker to reduce environmental impact
- in order to support the use of increased levels of substitution an accurate method for the measurement of the reactivity of these phases in blended materials is needed
- comprehensive information on the hydrates formed, to compare with the thermodynamic predictions of CP1 will also be provided

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On going workshop process

For example

- Meso-structure of C-S-H: EPFL 16,17 April
- Alkali activated systems
- Prehydration
- Atomic/Molecular scale modeling: November
- Expansive forces in cementitious systems
- Kinetics

INTEGRATION
 INTO WEB BASED
 KNOWLEDGE
 FRAMEWORK

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Nanocem - European Efforts

Vagn Johansen



The Future of Concrete

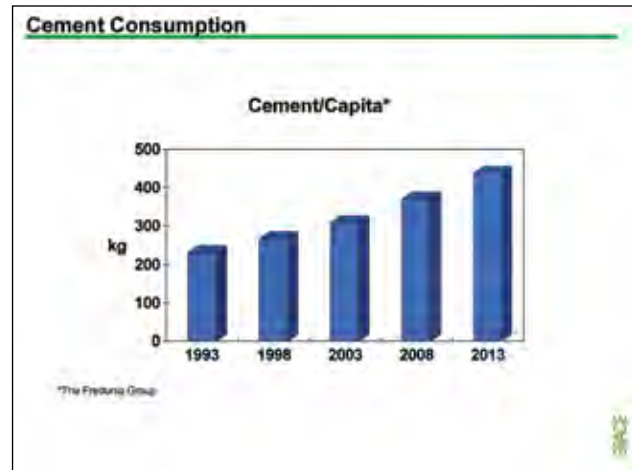
Dr. Felek Jachimowicz

Grace Construction Products

The Future of Concrete

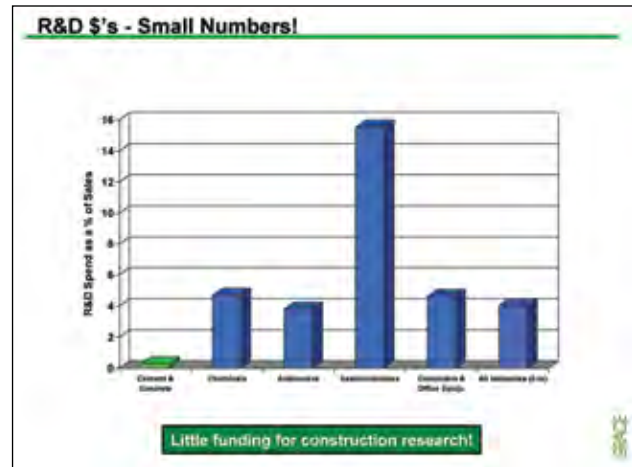
Workshop on Nanotechnology
for
Cement & Concrete

Felek Jachimowicz
Grace Performance Chemicals



More Big Numbers

- WW Cement production 2005: 2.3B MT (Gt)
- WW Concrete production: 10B M
- US 114 cement plants: 96.5MM MT
- US 6,650 Ready Mix plants
- US Concrete industry 220,000 employees



Concrete - Material of Choice for Construction

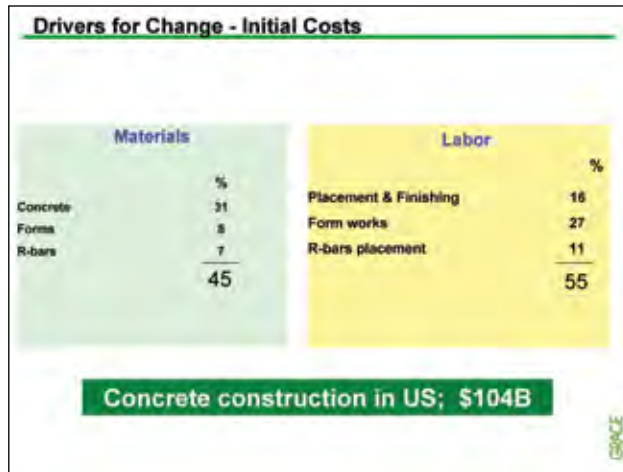
<p>Advantage</p> <ul style="list-style-type: none"> • Availability • Affordability • Unrestricted geometries • Durability • Environmental friendliness 	<p>Opportunities</p> <ul style="list-style-type: none"> • Cost • High Labor • Density (Weight!) • Low ductility, weak in tension (Brittle!) • Durability (Cracking!) • Environmental load (CO₂)
--	---

Drivers for Change

- Initial costs**
 - Materials (Cement, Aggregates, Water)
 - Labor & Time of construction
 - Energy (cement)
- Total cost of ownership - Durability**
 - Repair, restoration, renovation
 - Maintenance
- Environmental load - Environmental pressures and regulations**
 - CO₂ reduction
 - Declining quality of raw materials
 - Cement
 - Aggregates

The Future of Concrete

Dr. Felek Jachimowicz

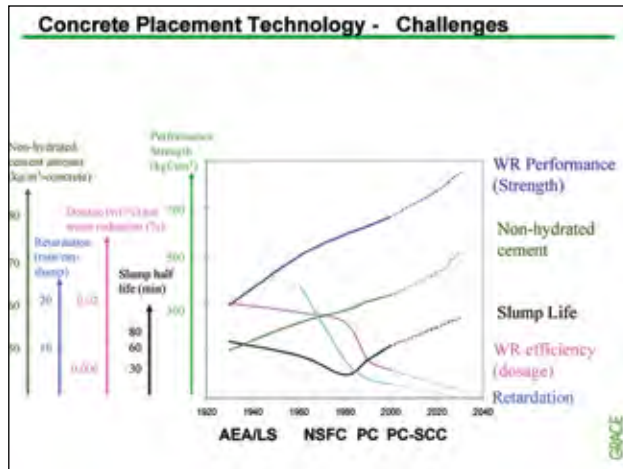


Labor - Challenges

Concrete flow properties (simplify placing and finishing operations)

Curing/Finishing (reduce labor and improve quality (durability and appearance) of concrete after casting/placement)

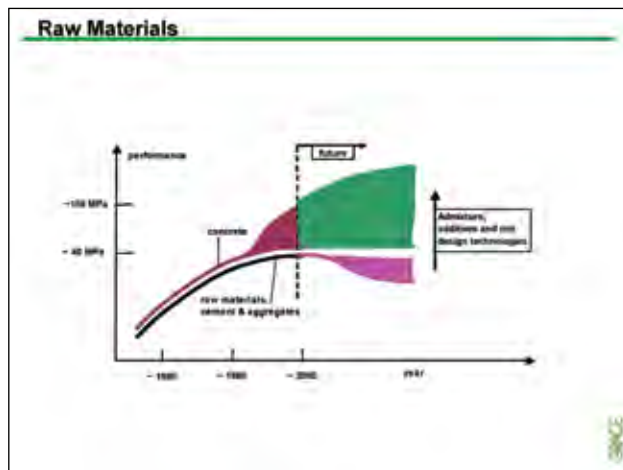
Reinforcing steel (tough concrete - saving on rebar labor, simplifying placing and reduce environmental load (steel))



Raw Materials

Enabling the use of challenging raw materials for normal and high performance concrete

- **Cement:** blended cement
- **Aggregates:** fines, marginal aggregates
- **Water:** water management (recycled water)



Cement - Challenges Energy and CO₂

Use of secondary fuels

- Six-fold increase in the last ten years

Increased use of SCM's (CO₂!!!)

- EU 11%, AP 34%, Russia 55%, NA 2% - to stay at 0 level of CO₂ emission increase

Limestone blended cements (6-35%)

The Future of Concrete

Dr. Felek Jachimowicz

Cement – CO₂!!!

Possible Solutions:

- Clinkers with less CO₂ emissions**
 - BCASF (belite, calcium sulfoaluminat and calcium aluminoferrite)
 - Emits 25% less CO₂ than OPC
 - Raw materials readily available everywhere
- CO₂ sequestration**
 - Economical

Aggregates - Challenges

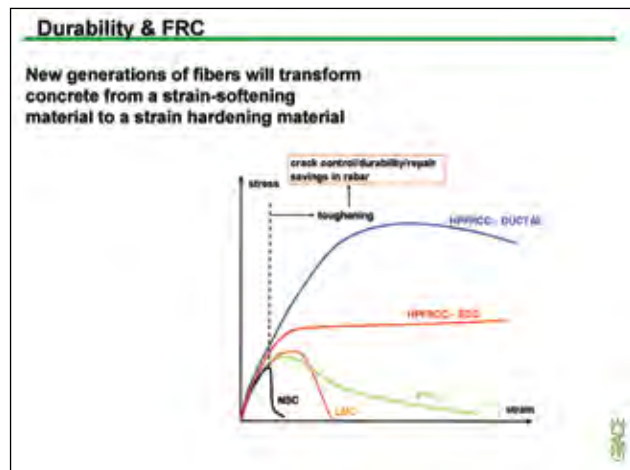
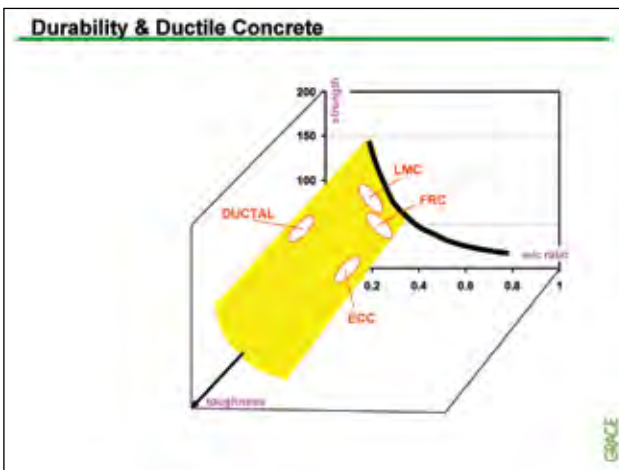
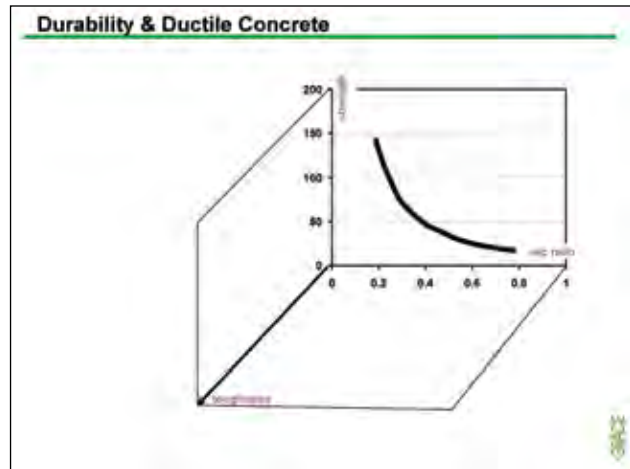
Declining availability of quality aggregates
-growing problem around the world-

Development of technologies to enable the use of marginal (clay, fines) aggregates

Total Cost of Ownership - Durability

Problem	Solution strategies
Brittleness - cracking	Improve ductility
Dimensional stability	Reduce shrinkage <ul style="list-style-type: none"> Improve curing (self-curing)
Permeability	Reduce permeability <ul style="list-style-type: none"> Integral waterproofing QC of raw materials Self repair/sealing Admixtures
Estimating life-expectancy	Self monitoring

Water transport: Root-Cause of the concrete durability problem



The Future of Concrete

Dr. Felek Jachimowicz

Durability & FRC

Building code will adapt advanced modeling tools to design with ductile concrete

- Seismic improvement
- Reduction of conventional reinforcement
- Thinner sections
- Crack control and prevention
- Durability

Engineering Modeling Tools

Output of design tools with input for reduced shrinkage and strain softening*
(steel-reinforced, average-creep, w/c 0.38 concrete)

*Calculation w/ FEMASSE

Curing & Durability

Proper curing improves all properties of concrete!

- Physical properties of the top layer (10mm)
 - Strength
 - Permeability
 - Abrasion resistance
 - Freeze/thaw resistance
- Cosmetics
 - Bug holes
 - Texture

Curing

In US **less than 25%** of concrete is cured according to standards

Lack of standard methods to verify curing adequacy
Labor intensive, time consuming

Curing in the field is critically important to the durability of concrete

Curing - Directions To Go

Address:

- Evaporation – environmental conditions
- Self-desiccation – low w/c concretes
- Labor intensive process delaying construction cycle
- Performance standards for curing in the field

Concrete & Esthetics

Dramatic improvement in the esthetic appeal of concrete

- Self cleaning concrete TiO_2 (2010 Concrete)
- Transparent concrete (2010 Concrete)
- Image printing (2000)

The Future of Concrete

Dr. Felek Jachimowicz

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 on-demand
- 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 attacks
- Specialty: (blast resistant, conductive...)

Nano & Concrete

Understanding of cement chemistry and concrete microstructures

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

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 cement-based materials !!!*

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

The Future of Concrete

Dr. Felek Jachimowicz

What Can Science Do?

Understanding of cement chemistry at the molecular level

Understanding of microstructure at the nano level

- Dynamic (minutes to days)
- After major hydration is over

Predictive models

- Rational concrete mix designs
- Durability

Non-destructive testing methodologies

What Can Technology Do?

Reduce CO₂ load

- Increase the SCM in concrete - less clinker/m³
- Alternative cementing materials

Technologies for robust SCC

Automated QC (sensors) methodologies

Increase durability – reduce propensity for cracking

- Corrosion
- Ductility
- Permeability

What Can We Do?

Elevate the image of cement based materials!!!

Nanoscience of Highway Construction Materials

Dr. Richard Livingston

Type of Admixture	Standard Specifications	Desired Effect
Air-entraining admixture (AEA)	ASTM C 260 and C 233 (AASHTO M 154 and T 157)	To stabilize microscopic bubbles in concrete, which can provide freeze-thaw resistance and improve resistance to deicer salt scaling.
Water reducing admixture (WRA)	ASTM C 494 (AASHTO M 194)	Reduce the water content by 5 to 10%, while maintaining slump characteristics.
Mid-range water reducer (MRWR)	ASTM C 494 (AASHTO M 194)	Reduce the water content by 6% to 12%, while maintaining slump and avoiding retardation.
High-range water reducer (HRWR) (also called superplasticizer)	ASTM C 494 (AASHTO M 194), ASTM C 1017	Reduce the water content by 12% to 30%, while maintaining slump.
Retarding admixture	ASTM C 494 (AASHTO M 194)	To decrease the rate of hydration of cement.
Accelerating admixture	ASTM C 494 (AASHTO M 194)	To increase the rate of hydration of cement.
Shrinkage-reducing admixtures		Reduce drying shrinkage (and related cracking) in concrete.
ASR-inhibiting admixtures		Reduce or eliminate deleterious expansion due to alkali-silica reaction.
Corrosion inhibitors	ASTM C 1582	Minimize steel reinforcement corrosion.

3. CEMMET-Workshop "Cement Research at Large-scale Facilities"

jointly organized with:
 Swiss Light Source (SLS) and Swiss Neutron Source (SNS)

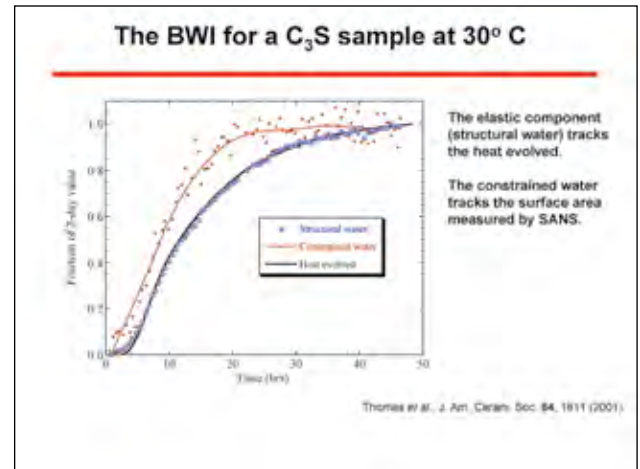
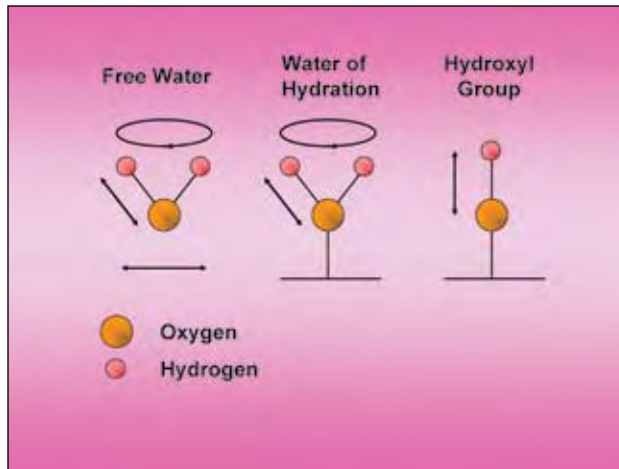
September 10, 2007
 Paul Scherrer Institute, 5232 Villigen PSI

Online registration (P4-Registration)
 Download Program and Registration Form (P5)

Please see online registration if possible!

Workshop theme

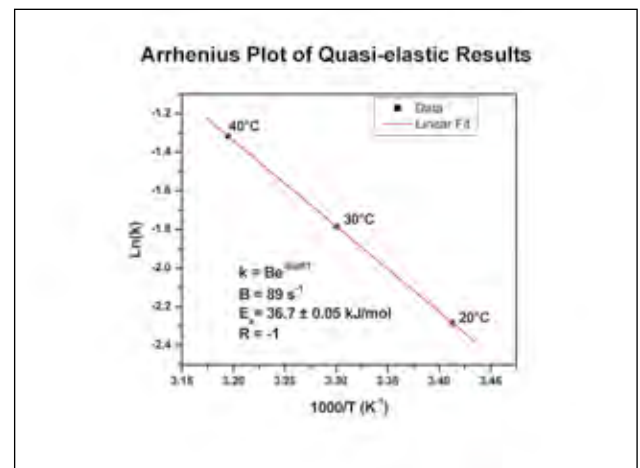
CEMMET.ch, Switzerland has several industrial and university research groups working on the physical and chemical properties of cement and concrete. Workshops on porosity and on the interactions of cement with organics have been organized in the frame of the CEMMET. In collaboration with PSI's Swiss Light Source (SLS) and Swiss Neutron Source (SNS) we are now hosting a 3rd workshop. Focusing – as its title indicates – on cement research at large-scale facilities. The goal is to step out the decreasing role played by operation light studies and neutron sources in cement research, with special relevance to structural and process-oriented investigations.

Nucleation and Growth model

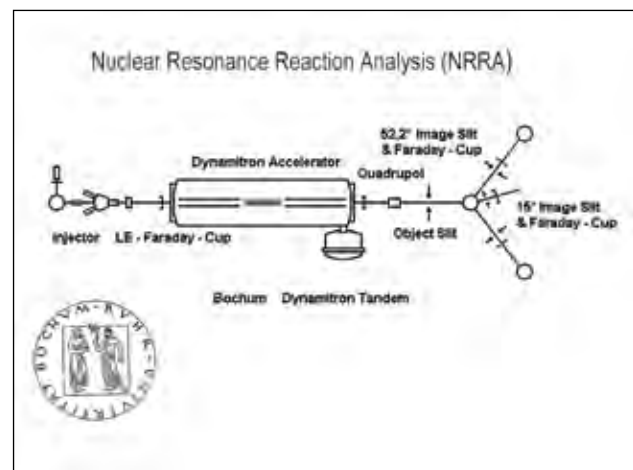
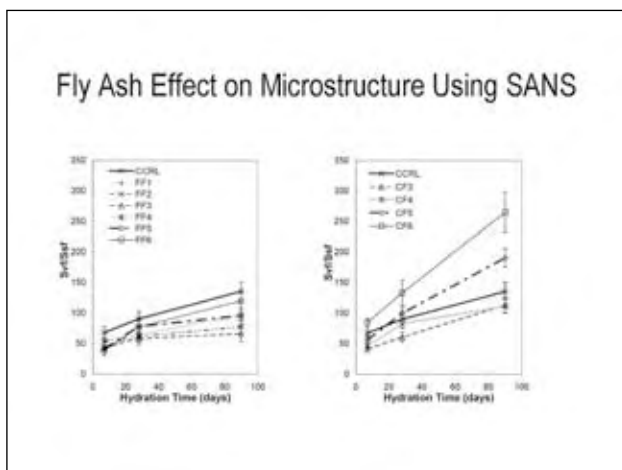
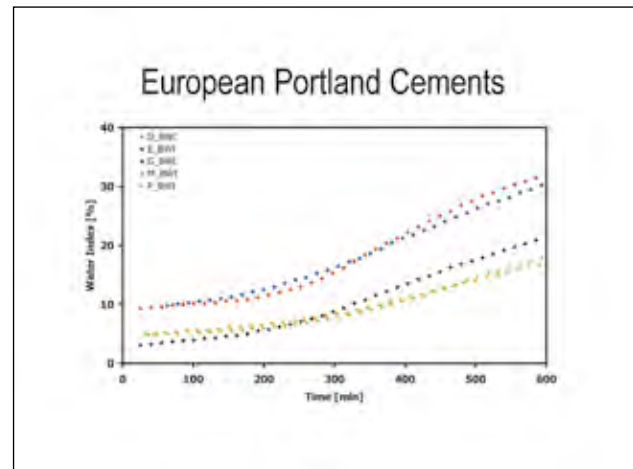
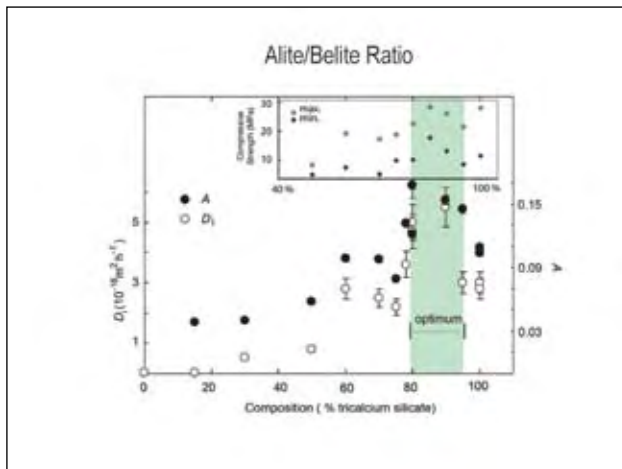
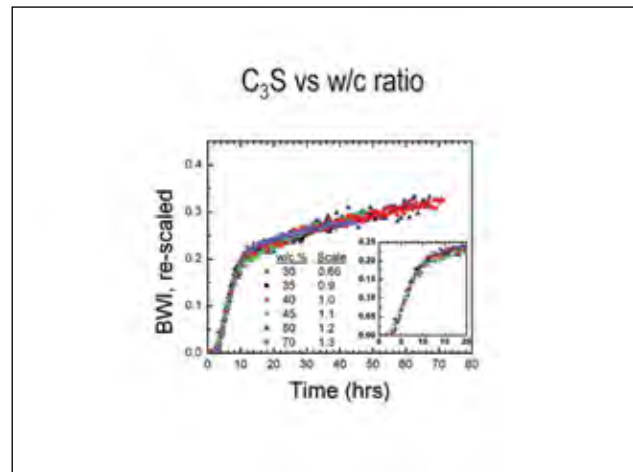
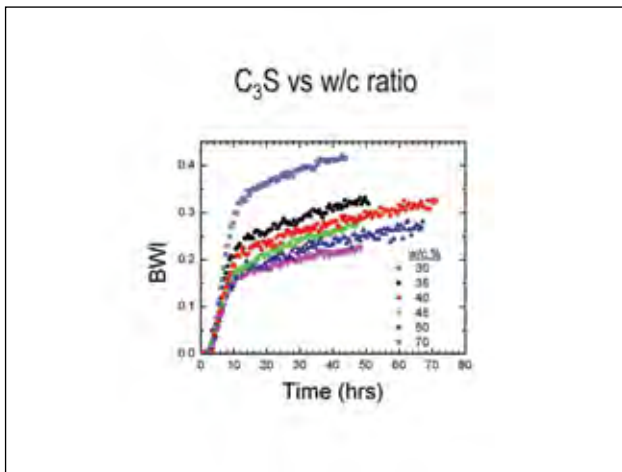
$$\beta(t) = \beta(t_o) + A \left(1 - \exp \left\{ - [k(t - t_o)]^m \right\} \right)$$

$\beta(t)$ = boundwater fraction
 t_o = induction time
 A = asymptotic volume fraction
 k = rate constant
 m = dimensionality



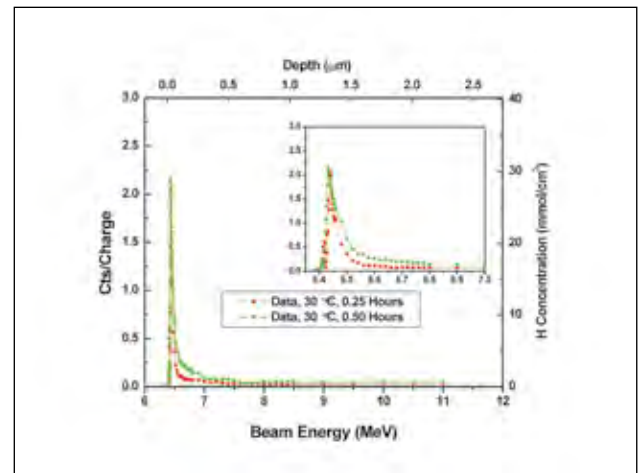
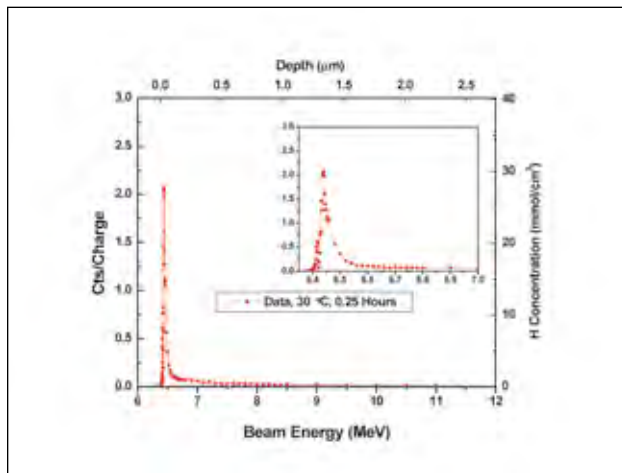
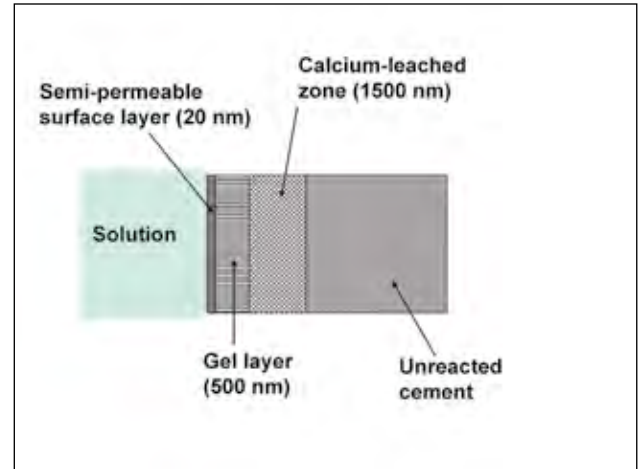
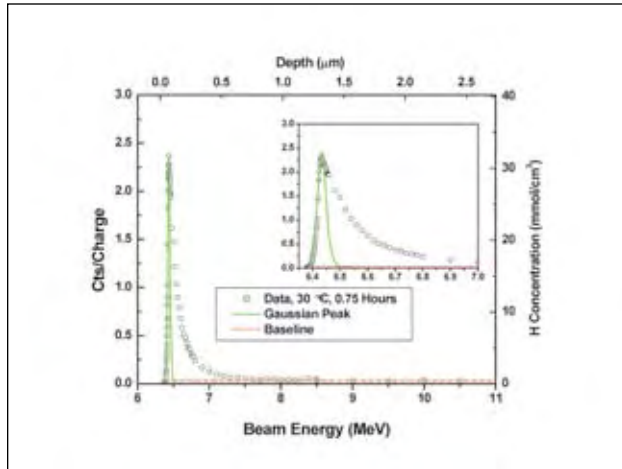
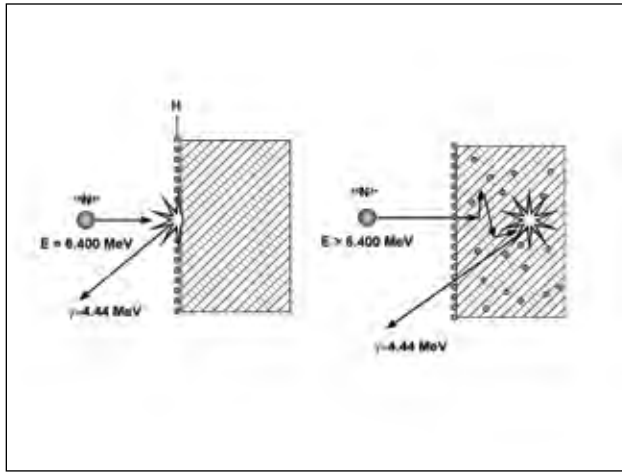
Nanoscience of Highway Construction Materials

Dr. Richard Livingston



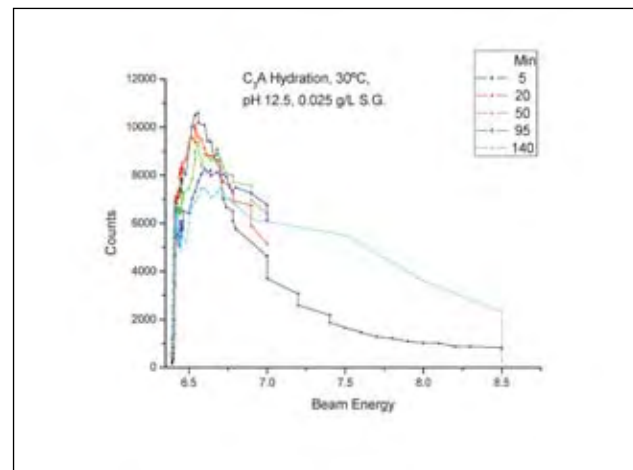
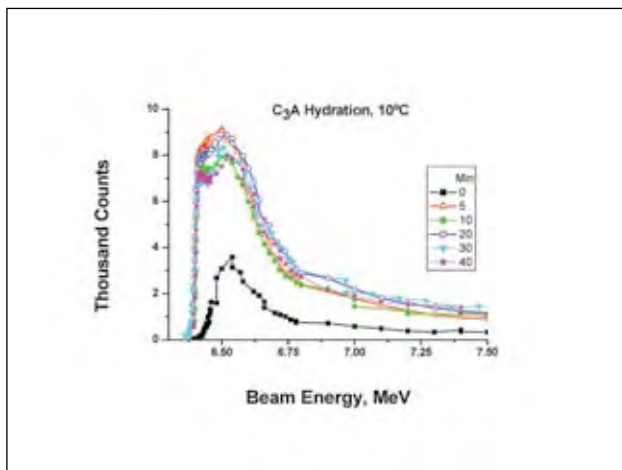
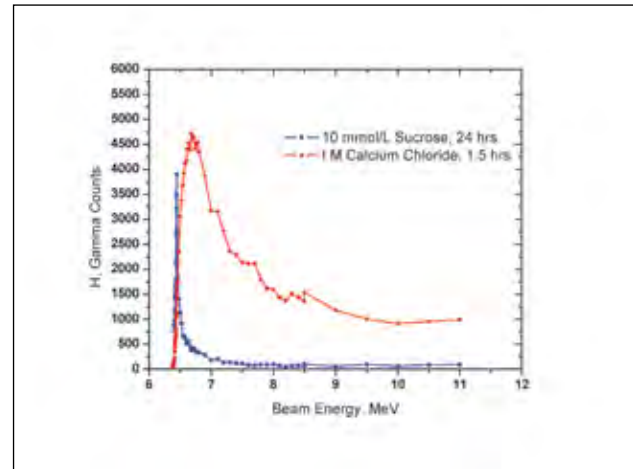
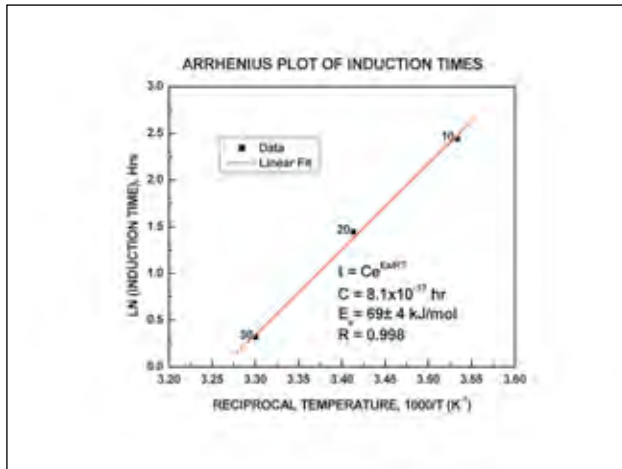
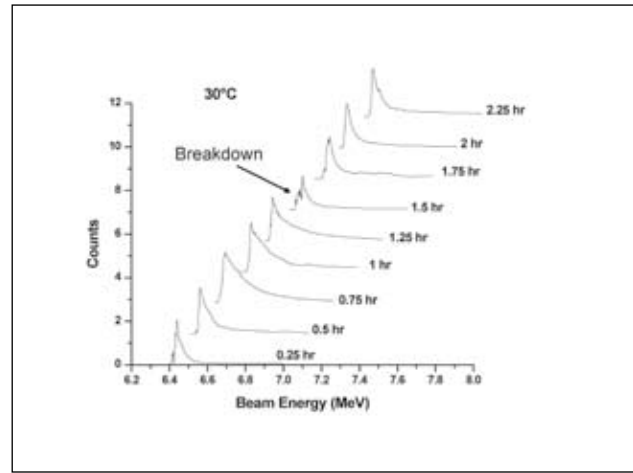
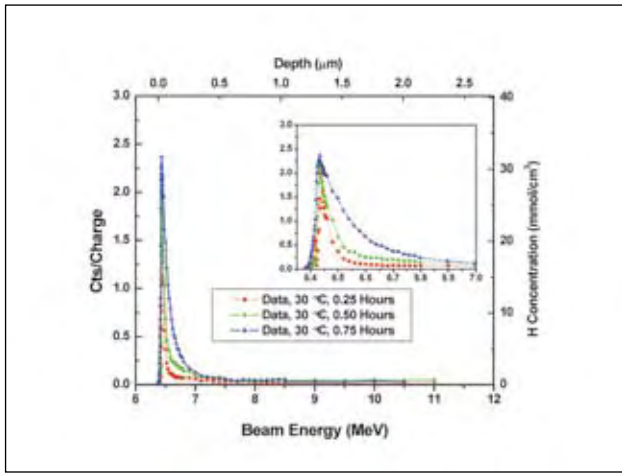
Nanoscience of Highway Construction Materials

Dr. Richard Livingston



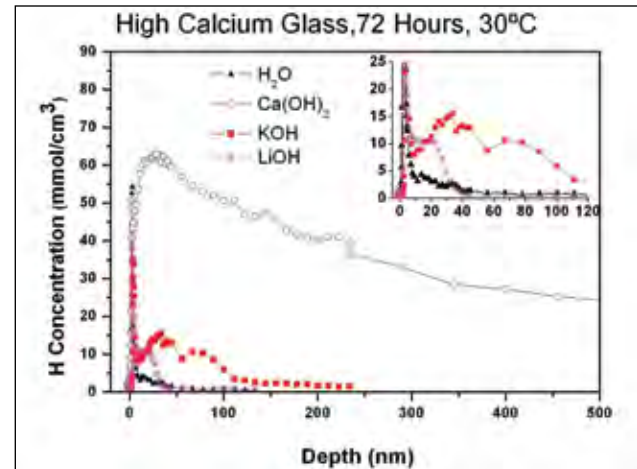
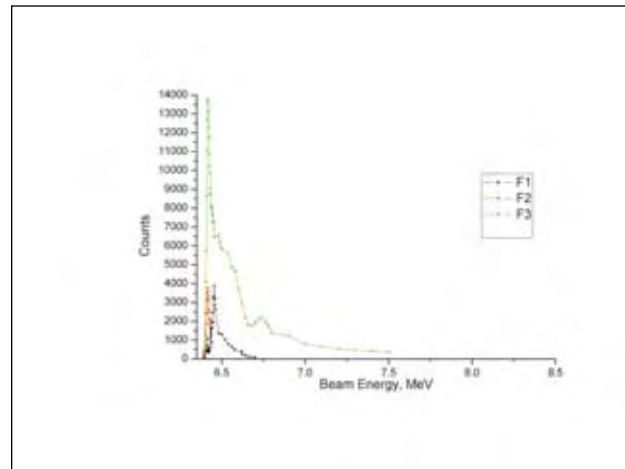
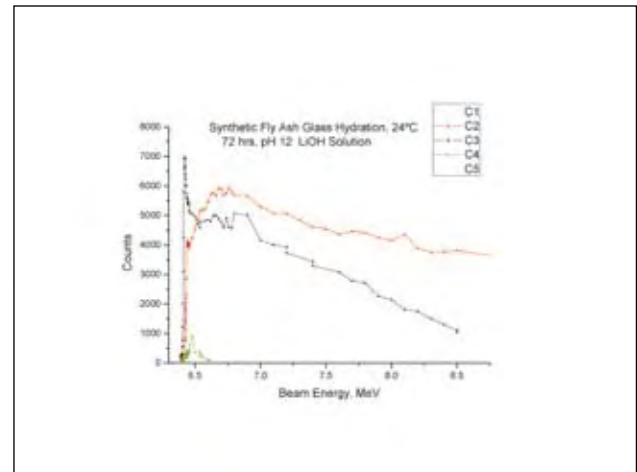
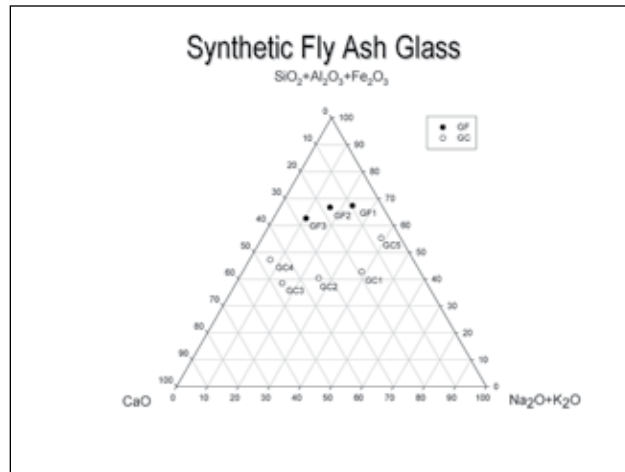
Nanoscience of Highway Construction Materials

Dr. Richard Livingston

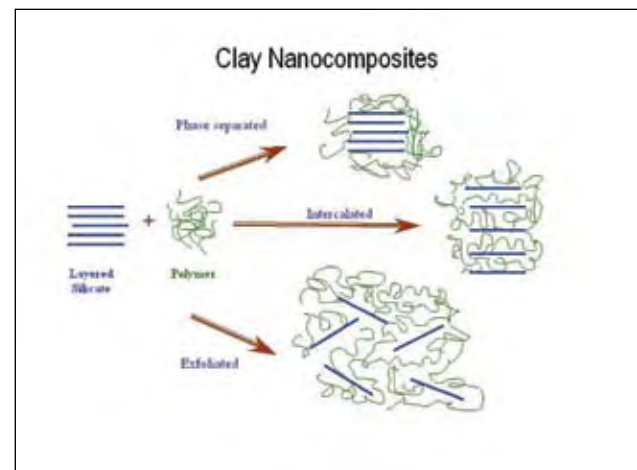


Nanoscience of Highway Construction Materials

Dr. Richard Livingston



- ## Nanoparticles
- Nanosilica
 - $Ca(OH)_2$
 - $CaCO_3$
 - TiO_2
 - Carbon nanotubes
 - Nanoclays

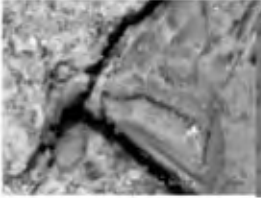


Nanoscience of Highway Construction Materials

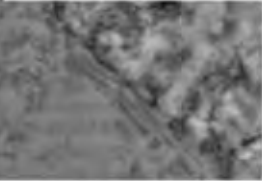
Dr. Richard Livingston

Optimized Microstructure – Concrete Interfacial Transition Zone (ITZ)

Normal Concrete ITZ at 2500X Magnification



Nanomodified Concrete ITZ (2% Clay/2 % Polymer at 3500X Magnification)





Posted on: Monday, August 13, 2007

Hawaii company seeking new patent

By Paul Hill
Honolulu, Sept. 10

Honolulu-based Ozeant Laboratories Inc. is looking to patent a nanotechnology concrete mix that creates stronger material for use in buildings, bridges and roads.

Concrete worldwide has cracking or chips in large parts or called surface spalls that concern its ability to protect structures from the weather, which are thousands of times heavier than a brick. It is not highly resistant. That means that they could be used to create a kind of concrete system called concrete that could be used in about cracking and weaknesses in concrete.

Honolulu says the firm is in the process of patenting technology, including high speed and technical features such as flow to create a consistent nanotechnology manufacturing process. The Ozeant claims it has solved a key problem — how to incorporate such the top materials into a fully self-healing mix in concrete. The company is looking to patent a process in which nanomaterials are incorporated in a liquid environment that is added to concrete to create a self-healing concrete.

Ozeant has applied for a \$100,000 federal research and development grant to develop the technology in coordination with state and county transportation officials. Initially, the nanotechnology would be used for durability and strength. "However, Ozeant hopes the technology will revolutionize the way the concrete longevity of concrete is measured, though the application could take years to develop."



Paul Hill is a reporter for Honolulu Advertiser. He has a degree in the news journalism program.

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Self-Healing Approaches

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

1st International Conference on Self Healing Materials

18-20 April 2007, Noordwijk, The Netherlands

CONFERENCE OBJECTIVE

Although the phenomenon of Self Healing has been recognized in materials throughout history, especially with regards to biological systems, it was only recently that the property of Self Healing was seriously considered as a desirable function for man-made materials. Beginning with the first successful incorporation of self healing functionality in a (man-made) epoxy-system via micro-encapsulation at the University of Illinois, research groups throughout the world have started to explore concepts and materials systems that impart self-healing properties for a variety of applications. Now that the field is gaining momentum, and the first glimpses of a newly emerging scientific community becomes visible, it is time to gather and benefit from the insights gathered thus far in this intriguing new field.

The broad and interdisciplinary environment towards which this field is developing gives an outstanding opportunity for truly multidisciplinary inspiration and collaboration. This expansive scope is well reflected by the topics that are selected as the focal points of this First International Conference on Self Healing Materials:

- Asphaltic materials
- Bio-inspired technical materials
- Cementitious materials
- Composites and hybrids
- Metals
- Paints and other coatings
- Structural polymers
- Biological systems
- Theoretical models related to Self Healing
- Characterisation of Self Healing behaviour

http://www.selfhealingmaterials.nl/index_eng.htm

Other Nanomaterials

- Asphalt
- Steel
- Coatings

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



Nanoscience of Highway Construction Materials

Dr. Richard Livingston

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

New functionalities for the building industry:

some examples related to photocatalytic technology

Workshop on Nanotechnology for cement and concrete

Washington, September 5, 2007



Nanotechnology : the impressive engineering art



Introduction



Nanotechnology : a new wording part of an historical trend toward smaller objects design and characterization

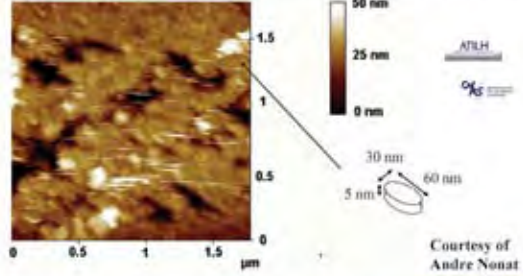
- Protein (critical conformation – nano size)
- Metallic clusters supported on alumina wafer for petroleum cracking (nano size related electronic band structure).
- Building industry field :
 - Limestone in cement (nano size nucleation effect)
 - Silica gel slurry as a mineral addition (nano reactivity)
 - latex (nanoparticle size)
 - polycarboxylate (nano size design)

Introduction




Nanotechnology : a new wording part of an historical trend toward smaller objects design and characterization

➢ CSH grown on C3S, Scanning tunneling microscopy (STM)



Courtesy of Andre Nonat

Introduction



Nanotechnology : a new wording part of an historical trend toward smaller objects characterization and design

➢ Paint pigment: TiO_2 micro particles with nano thick silica coating

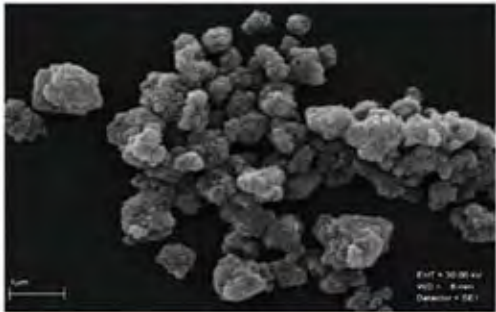


Published by Andrew Lambert
Photography Science Library


Introduction



TiO_2 microparticles made with nanocrystals



Introduction



6. New Functionalities for the Building Industry

Dr. Laurent Bonafous

Anti-fog and self-cleaning surface properties due to super hydrophilic glass



Photocatalysis - properties

bactericide tile's surfaces



Photocatalysis - properties

Self cleaning PVC fabric



Photocatalysis - properties

Dives en Misericordia Church: self cleaning concrete



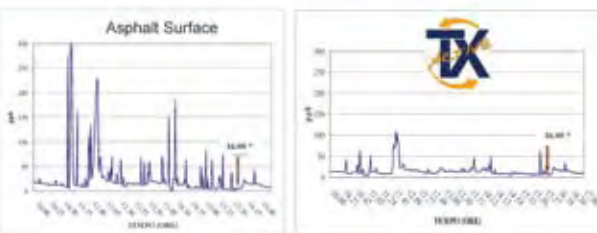
Photocatalysis - properties

Depolluting, self-locking paving blocks



Photocatalysis - properties

Depolluting Self-locking paving blocks: detailed results



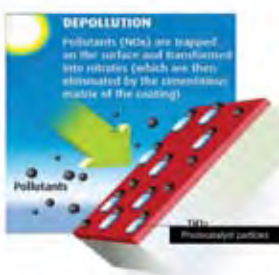
➤ NOx abatement rate, calculated on the basis of average results recorded was found to be 45%.

Photocatalysis - properties

6. New Functionalities for the Building Industry

Dr. Laurent Bonafous

The Principle of Photocatalysis



DEPOLLUTION
Pollutants (NOx) are trapped on the surface and transformed into nitrates (which are then eliminated by the permeation matrix of the coating).

- Pollutants (and stains) are destroyed through **molecular adsorption** and **oxidative** reaction processes
- Ultimate products : CO₂, H₂O, NO₃⁻, SO₄²⁻, O₂, Cl⁻, ...
- Catalyst remains indefinitely

Photocatalysis - properties

Stains and Pollutants Destruction

Published claims of some chemicals oxidized by photo-catalysis

Inorganic Compounds: NOx; SOx; CO; NH ₃ ; H ₂ S	Pesticides: Triadimefon, Pirimicarb, Asulam, Diazinon, MPMC and Atrazine
Organic Compounds: Alcohol, Acids, Alkene, and Aromatic Compounds (phenol, toluene...)	Micro Organisms: Bacteria, Fungus, and Viruses
Chlorinated Organic Compounds: Chloro Alkans, Dioxins, Chloro Benzene and Chloro Phenol	Some PM

Photocatalysis - properties

Precasted concrete panels with a face mix

- **Project:** Air France Headquarters Roissy - Charles de Gaulle International Airport – Paris, France
- **Owner:** Air France
- **Architects:** Denis Vallode and Jean Pistré



Photocatalysis - Applications

RMC covered with active stucco

- **Project:** Ciments du Maroc Headquarters – Casablanca, Morocco
- **Owner:** Ciments du Maroc
- **Architect:** Rachid Andaloussi



Photocatalysis - Applications

Inorganic paint for restauration

Church in Cittanova, Italy



Photocatalysis - Applications

Photocatalytic concrete pavers



Photocatalysis - Applications

6. New Functionalities for the Building Industry

Dr. Laurent Bonafous

Photocatalytic sound barriers



The image shows two views of a photocatalytic sound barrier. On the left is a close-up of the barrier's corrugated surface. On the right is a wider view of the barrier installed along a road, with a utility pole and a cloudy sky in the background.

Photocatalysis - Applications

Porpora Street Tunnel – Milan, Italy



The image shows the interior of the Porpora Street Tunnel. The main view is a long, brightly lit tunnel with a polished floor. Two smaller inset images show workers performing maintenance or cleaning on the tunnel walls and floor.

Photocatalysis - Applications

Photocatalytic concrete roof tiles



The image shows a residential building with a roof made of photocatalytic concrete tiles. The building is surrounded by a well-maintained lawn, palm trees, and a swimming pool, with a clear blue sky and ocean in the background.

Photocatalysis - Applications

Benefits to using photocatalytic technology include:

- 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

Workshop on Nanotechnology for Cement & Concrete
FDIC, Arlington, VA
September 5, 2007

The Nano-Engineering of UHPC & Structures

Vic Perry⁽¹⁾
Bruce Blair⁽¹⁾
Franz-Josef Ulm⁽²⁾

LAFARGE¹ MIT Department of Civil & Environmental Engineering²

What do Concrete and Oranges have in common?

LAFARGE MIT Department of Civil & Environmental Engineering

The Challenge of Consumption

World Portland Cement Consumption

Metric Tons (millions)

Year

1900 1910 1920 1930 1940 1950 1960 1970 1980 1990 2000 2010

World production of concrete
World production of steel
US Apparent Consumption of Steel
US Apparent Consumption of Cement

Ortiz-Vila, S. and Schreyer, J., "Global Environmental Impacts Due to Concrete and Steel," Structural Engineering International, 14:5, Zurich, Int. Assoc. of Bridge and Structural Engineers, August 2004, 158-200.

LAFARGE MIT Department of Civil & Environmental Engineering

SUSTAINABILITY

Definition/ VALUE	Characteristics	Mechanical Properties
<ul style="list-style-type: none"> Use Less Higher functionality Last Longer Lower Maintenance Less 'Loss of Use' 	<ul style="list-style-type: none"> Higher Strengths Improved ductility Improved durability Improved recyclability 	<ul style="list-style-type: none"> Compressive strength Flexural strength Shear strength Ductility/toughness Impermeability F/T Abrasion E-Modulus

LAFARGE MIT Department of Civil & Environmental Engineering

Progress on the Concrete Front

1900 1980 1990 2000 2010

Macro
Micro

Log-Length Scale

Breakthrough in Research

Ordinary Concrete
High Performance Concrete (HPC)
Ultra High Performance Concrete (UHPC)
'C'-Crete?

LAFARGE MIT Department of Civil & Environmental Engineering

The Indentation Test

Instrumented indentation Test

Force P applied

Vertical indenter

leaf spring
displacement gauge & actuator
leaf spring

Depth h measured

Accuracy: 0.1 nm = 10⁻¹⁰ m

LAFARGE MIT Department of Civil & Environmental Engineering

7. The Nano-Engineering of UHPC & Structures

Vic Perry

This is not an Egyptian Pyramid, nor...

- But the nano-mechanical signature of concrete

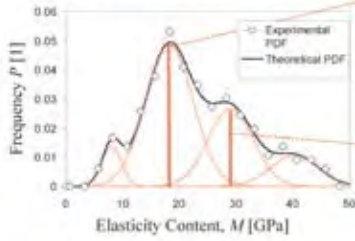


100 nm




A Genomic Code of cementitious materials?

- Ordinary Cement Paste: w/c = 0.5



Nano-mechanical Signature of concrete

Comastromas, G., and Llin, F.-J., "The effect of two types of C-S-H on the elasticity of cement based materials. Results from nanoindentation and micromechanical modeling," *Cement and Concrete Research* 34 (2004) 67-80.



Ordinary Concrete

- 1900–1985 Industrialization/Standardization

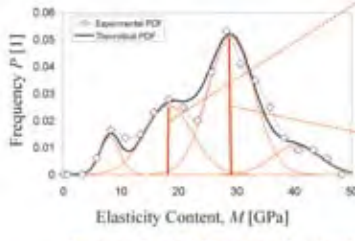


© Murray, H. (2004). *Structural Architecture*.




A Genomic Code of cementitious materials?

- High performance concrete (w/c = 0.4)



Nano-mechanical Signature of concrete

Comastromas, G., and Llin, F.-J., "The effect of two types of C-S-H on the elasticity of cement based materials. Results from nanoindentation and micromechanical modeling," *Cement and Concrete Research* 34 (2004) 67-80.



High Performance Concrete

- 1985-95 Re-discover Diversity





Filling the Voids



The Nano-Granular Nature of C-S-H*

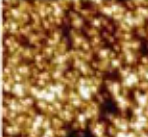

- HD C-S-H
- LD C-S-H

Spherical Limit Packing
Density = 0.74
No. of contact = 12/ sphere





100 nm

Random Packing Limit = 0.64
No. of contact (mean) = 6/spar sphere

© Comastromas, G., Llin, F.-J., (2007). The nanogranular nature of C-S-H. *ACI* January 2007
Picture Credit: *Architectural*, 2004, Novar 2004

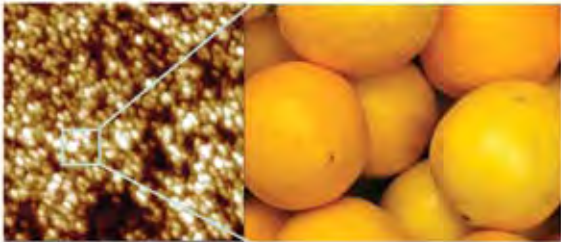


7. The Nano-Engineering of UHPC & Structures

Vic Perry


The Nano-Granular Nature of C-S-H*

- What concrete and Oranges have in Common?

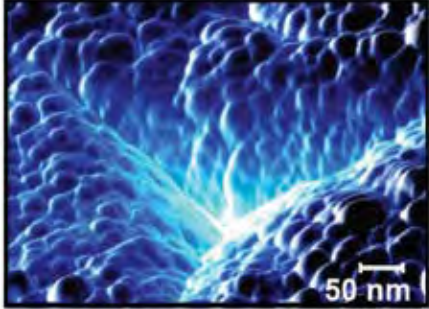


AFM - Image: C-S-H Nanostructure From NIRM, (2004)

(*) Constantinou, G., Uin, F.-J. (2007). The nanostructure nature of C-S-H. JMS, January 2007



The Nano-Granular Nature of Bone*



(*) Tu, K., Uin, F.-J., Gao, C. (2006). Nanoscale origin of the strength of bone". *Nano Letters*.



The True Challenge of Sustainable Development

Economic Growth – Social Progress – Minimizing Ecological Footprint

How to translate scientific progress into day-to-day engineering applications

For the benefit of society, while minimizing the Ecological Footprint

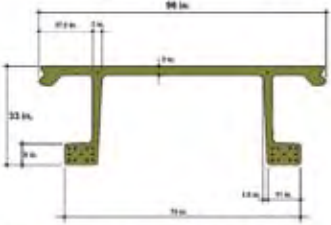


Nano Engineering of Concrete




UHPC Bridge for US Highways

- Prototype Development with MIT, Lafarge and FHWA:
 - Project: "Bridge of the Future"



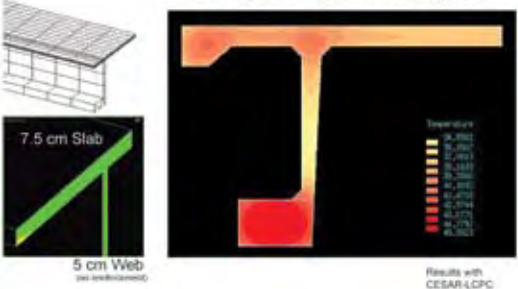
- Max L/H – 35
- Weight Reduction 30%
- Durability (Low maintenance)
- Rapid Construction (circulation)
- Construction: Prestress Services, Kentucky
- Material: DUCTAL®

To replace & reduce structurally deficient and functionally obsolete bridges (~ 160,000)




UHPC Design

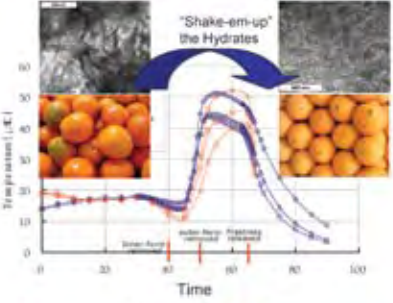
Monitoring the Temperature during Hydration




Results with CESAR-LCPC



Nano Engineer the Performance



"Shake-em-up" the Hydrates



7. The Nano-Engineering of UHPC & Structures

Vic Perry

Prototype Development

- Failure as designed
- Tested in May 2005 by FHWA (Turner-Fairbank, Virginia)

**From Nano-to-Structures:
Nano Engineering of Concrete**

1st Implementation Iowa 2007/08




Impact on Architectural Design

- Shell Structure Revival

Shawnessy LRT Station
Calgary, AB

Architect: Erzo Vicenzino
(CPV Group of Architects and Engineers Ltd.)

Contractor: Walter Construction Ltd.

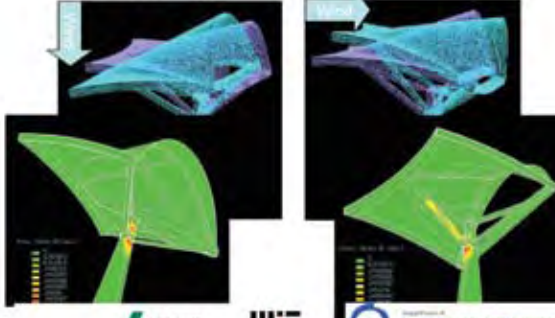

Engineering Design: Strudes, Montreal

Design Verification: MIT




UHPC Shell Structure Revival

- With Software from Space Shuttle Design

SHAWNESSY Light Rail Transit Station

Calgary, Alberta






8. Roadmap for Research

Dr. Bjorn Birgisson

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 Maintain 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 \$26.7 billion for fiscal 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 pavements.
 - 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.

8. Roadmap for Research

Dr. Bjorn Birgisson

The NINE GRAND CHALLENGES in the Original National Nanotechnology Initiative Plan

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

Initial Efforts Modification of Concrete

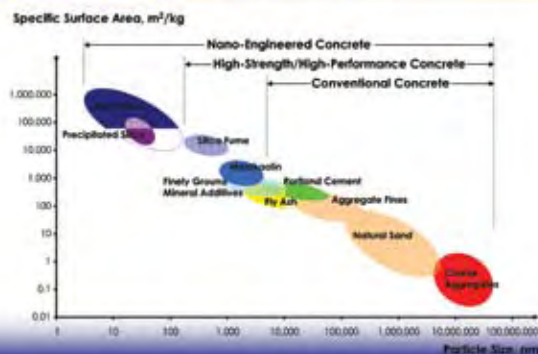
Why concrete?

The most heavily used construction material in the world

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

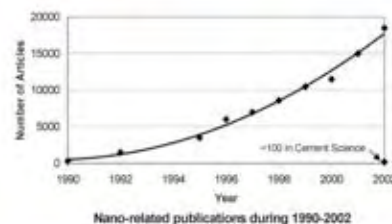
The basic building blocks of concrete are nanosize (C-S-H crystals are about 5 nm long)
 – Lends itself to nanomodification and “bottom-up” engineering

PARTICLE SIZE SCALE RELATED TO CONCRETE



Nanotechnology in Cement Science

Understanding and manipulation of materials on the nanoscale from 0.1 nm to 100 nm.



RILEM TC 197 – NCM, Application of Nanotechnology in Constructive, State-of-the-Art Report 2001

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
 - RILEM
 - 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)

8. Roadmap for Research

Dr. Bjorn Birgisson

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

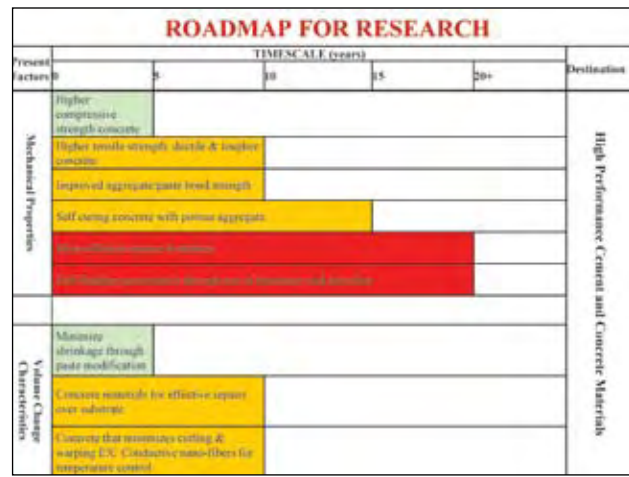
- High Performance Cement and Concrete Materials as measured by their:
 - mechanical,
 - durability, and
 - shrinkage properties.
- Sustainable and Safe Concrete Materials and Structures through:
 - engineering concrete for different adverse environments,
 - reducing energy consumption during cement 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 technologies.

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.

8. Roadmap for Research

Dr. Bjorn Birgisson



- ### Collaborative Approach to Research
- Establish a TRB Task Force on Nanotechnology-Based Concrete Materials
 - Establish a consortium for research in Nanomodification of cementitious Materials to:
 - Develop and maintain a research roadmap,
 - Generate knowledge in a more efficient way, and
 - Provide means for comprehensive communications of research findings.
 - Apply systematic, coordinated, and collaborative approach to research.
 - The research has to be both properties and product driven and cost effective.
 - Establish benchmarks to measure success.

8. Roadmap for Research

Dr. Bjorn Birgisson

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 CO₂, the cement industry is under considerable pressure to reduce the amount of CO₂ 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 systems. 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 heterogeneous 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 CO₂ 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 CO₂ 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, ready-mix 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.

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) <ul style="list-style-type: none">• 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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