NanoEngineering Green Concrete

or

C-Crete: From Atoms to Concrete Structures

April 15, 2010

Franz-Josef Ulm
Massachusetts Institute of Technology
What is at Stake?

- Large-Scale Infrastructure Renewal: New Deal – Will it be Green?
- Sustainable Centennial Project
  - Economical-Durable
  - Social Impact
  - Environmental Impact
- Transformational Projects for the United States and Far Beyond
Worldwide Consumption of Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Million tons*</th>
<th>Embodied Energy**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>2,750</td>
<td>32.5 x 10⁹ GJ***</td>
</tr>
<tr>
<td>Concrete</td>
<td>25,000</td>
<td></td>
</tr>
<tr>
<td>Timber</td>
<td>3,200</td>
<td>26.5 x 10⁹ GJ***</td>
</tr>
<tr>
<td>Ecological capacity of the Earth:</td>
<td>2,500</td>
<td></td>
</tr>
<tr>
<td>Timber for construction:</td>
<td>&lt; 1,000</td>
<td></td>
</tr>
<tr>
<td>All metals:</td>
<td>1,350</td>
<td></td>
</tr>
<tr>
<td>Steel:</td>
<td>1,000</td>
<td></td>
</tr>
<tr>
<td>Steel for construction:</td>
<td>&lt; 400</td>
<td></td>
</tr>
<tr>
<td>Paper and cardboard:</td>
<td>300</td>
<td></td>
</tr>
<tr>
<td>Plastics:</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>Aluminium:</td>
<td>32</td>
<td></td>
</tr>
</tbody>
</table>

(*) Data from P. Acker – 2007/08
(**) Based on data from Chaturvedi (2004)
(***) Sum equivalent to more than 1,000 Nuclear Power Plants, 3,000 Hoover Dams.

1 Ton CO₂ = 1 Ton of Cement = 8 Tons of concrete = Equivalent $85 Anticipated Damage (Stern Report, 2006, UK)
Scales of Concrete Innovation

Classical: Top – Down (Empirical)

- Ordinary Concrete
- High Performance Concrete (HPC)
- Ultra High Performance Concrete (UHPC)

Picture Credit: Macro: NIST-webpage
Micro: Jennings, 2004; Nano: Richardson, 2004
Target 2050

- Adapted from DOE Cement Workshop (SF, Sept 29-30, 2009)

Clean Heating (solar, wind, etc.)
Carbon Capture & Sequestration
Etc.

Cement & Concrete Technology
Innovation

Greenhouse Gas Emissions

2011(*)
EPA 25 KT

2005 2050

83%

(*) NYTimes
Sep 30, 2009
CShub@MIT: R&D Platforms

Concrete Sciences
Scientific breakthroughs towards reducing the CO2 footprint of Cement & Concrete

Building Technology
The CO2 Mileage of Pavement and Buildings
- Material Flow
- Life Cycle Analysis

Econometrics
Impact on economy, job creation:
- System Dynamics
- Input - Output

Effect of policy (e.g. Carbon Tax)
Why Is Strength Important?

• “Green” Concrete Through Higher Strength

Columns
Beams

CO2 Reduction scales with $L^3$ (volume), while structural strength scales with Section $S$ (columns) and $S^{1.5}$ (beams).

- Reduction in Size of Columns and Beams
- CO2 Reduction (Strength Design):
  - $1/x$ for columns and perfect shells
  - $x^{2/3}$ for beams
- CO2 Reduction (LEFM)
  - $1/x$ for columns
  - $x^{-4/5}$ (notched) beams
Dream: Bottom-Up Approach

- **Start with Electrons – Atoms**
  - Challenge: C-S-H Structure not known
  - First Principle Calculations: Determine Molecular Properties

- **MicroPoroMechanics: From molecular properties to Porous MicroStructure**
  - Challenge: MicroStructure still not well known
  - Functional Properties: Creep, Shrinkage,…

- **Multiscale Approaches:**
  - Go all the way up to structures…
A Consistent Molecular Model of C-S-H: The DNA of Concrete?

Concrete Science Platform@MIT
MIT – “Liquid Stone Team”

Sidney Yip (NSE/MSE)
- Multiscale materials modeling & simulation
- Stress-corrosion cracking in oxides

Franz-Josef Ulm (CEE)
- Nanoindentation
- Upscaling Methods

Roland Pellenq (CEE-CNRS)
- Computational Materials Science
- Nanoporous Materials

Markus J. Buehler (CEE)
- Potentials with chemical reactivity
- Molecular dynamics of organic molecules

Nicola Marzari (MSE)
- Electronic-structure modeling of complex materials
- Structure, dynamics, spectroscopic properties

Krystyn J. Van Vliet (MSE)
- Nanoscale mechanical experiments
- kMC simulations of stress-assisted diffusion

Bilge Yildiz (NSE)

Jeff Grossman (MSE)
- Design, synthesis and assembly of novel nanoscale materials based on quantum simulations
The DNA of Concrete?

- green = inter-layer Ca
- grey = intra-layer Ca
- blue = oxygen
- white = hydrogen

\[(\text{CaO})_{1.65}(\text{SiO}_2)(\text{H}_2\text{O})_{1.75}\]

Pellenq et al. (2009) PNAS
Nano-Design Principles

• Chemistry is key: C/S ~ 1.7

J. Vanzo (2009), Wavelength Dispersive Spectroscopy

- Phase 1: C-S-H
- Phase 2: C-S-H + ???
- Phase 3: Belite/C-S-H
- Phase 4: CH/C-S-H
- Phase 5: Alite/C-S-H

CONCRETE: April 15, 2010
Scale of WDS ~ 1-2 microns

[same scale as Nanoindentation]

Translate Chemistry into Molecular Structure: NMR Signature

- **Tobermorite**
  - Infinite Silicate Chains
  - NMR: $Q_2=100\%$
  - Max $C/S \sim 1.0$

- **Real C-S-H**
  - Cut infinite silica chains, to create silicate monomers ($Q_0 \sim 13\%$)
  - Silicate Chain Chunks ($Q_1 \sim 67\%$)
  - Infinite Silicate Chains ($Q_2 \sim 20\%$)
  - $C/S \sim 1.65$

Pellenq et al. (2009), In Review
Water Content Predicted by GCMC

- \( H_{\text{dry}} = 11.3 \) Å
- Density (dry) \( \rho = 2.12 \) g/cc
- Hydration (GCMC, \( \mu = \text{liq} \)):
  - \( 99 \text{ H}_2\text{O} : \text{density} \ 2.56 \) g/cc (exp. 2.6 g/cc)
- Relaxation of the hydrated structure \( H = 11.9 \) Å, \( \rho = 2.48 \) g/cc,

Defective Layers have Cavities that can accommodate water molecules
A consistent C-S-H model

- important features
  - disordered layers due to defective silica chains
  - intra-layer cavities accommodate water molecules

Sim. : \([\text{CaO}]_{1.65}\text{[SiO}_2\text{]}\text{[H}_2\text{O}]_{1.75}\)

Exp. : \([\text{CaO}]_{1.70}\text{[SiO}_2\text{]}\text{[H}_2\text{O}]_{1.80}\)
Elasticity from MD-Simulations

- Elastic Properties

\[
C_{ijkl} = \frac{\partial^2 E}{\partial \varepsilon_{ij} \partial \varepsilon_{kl}} = \begin{bmatrix}
93.5 & 45.4 & 26.1 & 0.58 & -0.05 & 3.46 \\
94.9 & 30.01 & -4.60 & 1.79 & -3.00 \\
68.5 & -4.32 & -2.72 & -0.57 \\
19.2 & 0.33 & 1.82 \\
16.1 & -0.40 \\
31.2 & 
\end{bmatrix}
\]

Voigt – Reuss – Hill Average

\[
k_s = 49 \text{ GPa} \quad m_s = 65 \text{ GPa} \\
g_s = 23 \text{ GPa} \quad \nu_s = 0.30
\]
Probing the Ultimate Strength

Shear stress $\tau_{xz}$, GPa vs. Shear strain $\gamma_{xz}$

- "Dry" CSH
- "Wet" CSH

Pellenq et al. (2009) In Review

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Computational Design of C-S-H

Nanoindentation modulus for C-S-H samples

Nanoindentation modulus for Tobermorite samples

3D zeolitic materials

2D layered materials

3D glassy materials

11A Tobermorite

14A Tobermorite

\[
1/ [\text{Ca/Si}]
\]

[Dr. Pellenq et al. 2010, In preparation]
From Atoms to MicroStructure

Applied MicroPorom Mechanics

Georgios Constantinides, Matthieu Vandamme,
Chris Bobko, Benjamin Gathier, Sophie Cariou,
Alberto Ortega, Luca Sorelli, Franz-Josef Ulm
Nanoindentation as a Tool to Probe C-S-H Microstructure

Depth Resolution ~ 0.1 nm
Load Resolution ~ 10 nN

(**) AFM picture: Courtesy C. Bobko
Measurement and Interpretation

- What is measured?
- ...and what is extracted?
  - Hardness
  \[ H = \frac{P}{A} = c \times R(\varphi, \alpha, \frac{c}{E} \to 0) \]
  - Elasticity (Indentation Modulus)
  \[ M = c \frac{\text{slope}}{\sqrt{A}} \]
  - \( A \) = Contact Surface

Continuum Model – Homogeneous Material

10,000 \( \mu N \) ~ 1 gram

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Indentation in Porous Materials

- Continuum Analysis

![Diagram showing indentation analysis](image)

**Strength**

\[
\frac{H}{c_s} = \frac{P}{c_s A_c} = \Pi(\alpha_s, \eta, \eta_0)
\]

**Elasticity**

\[
\frac{M}{m_s} = c \frac{\text{Slope}}{m_s \sqrt{A_c}} = \Pi(\nu_s, \eta, \eta_0)
\]
Porous C-S-H at $\mu$-scale

MIT-CSH structure (C/S = 1.65, fully hydrated, H = 11.9 Å)

From a bottom-up fully predictive strategy, CSH is a granular material
Does (C-S-H) Particle Shape Matter? - MicroPoroMechanically?

- Bone (Ultrastructure)
- Shales (C_{11})
- Shales (C_{33})
- CSH (LD + HD)

Ulm & Jennings, CCR, 2007

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Packing Density $\eta$

Ulm & Jennings, CCR, 2007
Percolation Threshold

- Effect of particle shape

---

Percolation threshold, $\eta_0$ [1]

Particle aspect ratio, $X^s$ [1]

- Buchalter & Bradley (1994)
- Coelho et al. (1997)
- Sherwood (1997)
- Onoda & Liniger (1990)
- Self-consistent scheme, (variable alignment, $k$)
- Sanahuja et al. (2007) (self-consistent scheme, random orientation)
The Nano-Granular Nature of Shale*

• Compacted Clays from 3 km depth


Atomic Force Microscopy Image of Shale (normal to bedding) by Chris Bobko, MIT, Now at NCSU
The Nano-Granular Nature of Bone*

Why Strength Matters?

- Green Concrete Through Higher Strength

- Reduction in Size of Columns and Beams
- CO2 Reduction
  - $1/x$ for columns
  - $1/x^{0.66}$ for beams

- HPC: $\frac{1}{2} - \frac{1}{3}$
- UHPC: $1/7 - 1/10$ (if produced with same amount of cement)

CO2 Emission scales with $L^3$ (volume), while structural strength scales with Section $S$ (columns) and $S^{1.5}$ (Beams).
Statistical Indentation Analysis

- **Indentation Arrays**

Example: w/c=0.3

- 20 x 20 
  - 3 μm Nano-Indentation Grid
- Micro-Indent

![Graph with coordinates and grid]


What makes the Difference?

Probing the Nanoscale of Concrete

- Ordinary Concrete

Ordinary Concrete

The romance of modernism wrought in concrete*

7-10 Times the Strength

- **Ultra-High Performance Concrete**

![Graph showing packing density and w/c ratio](image)

- LD-C-S-H: Low Density (~15%), 10%
- HD-C-S-H: High Density (~85%), 55%
- UHD-C-S-H: Ultra-High Density (~85%), 35%

Ultra-High Performance Concrete

Seoul Peace Bridge by Rudy Ricciotti (architect)
Built by Bouygues in DUCTAL® by Lafarge.
Photo: Jae-Seong E
CSH is granular, but ain’t Oranges

- Thanks to Computational Materials Science: Correlation - Intensity
- Pierre Levitz (CNRS, Polytechnique); Roland Pellenq (CNRS-MIT)

• CSH a granular, but poly-disperse material

[Allen et al, Nature Mat. 2007]

[Morales, Mol. Sim., 2009]
How to Monitor the C-S-H Packing: e.g. Effect of w/c ratio

- Material Phases

- C-S-H Morphology Phases

Vandamme & Ulm, *CCR*, 2010
How to Monitor the C-S-H Packing: e.g. Effect of HT

- **Material Phases**

- **C-S-H Morphology Phases**
  - C-S-H Solid
  - Gel Porosity

- **Water-to-Cement (mass) Ratio**

![Graph showing material phases and C-S-H morphology phases](image)
Sensing Microstructure from Nanoindentation

- w/c = 0.2
- w/c = 0.3

HD C-S-H  
LD C-S-H  
UHD C(-S-)H  
Clinker

10 μm

Vandamme & Ulm, *CCR*, 2010
In Situ Mapping of...

- **WDS Results**

- **Microstructure**

  $\text{w}_{\text{c}} = 0.2$ WDS Topography 980 Probes, 3 micron grid

  M. Bentivegna (2010)
Nano-Chemo-Mechanical Mapping

- Grid

- WDS
  \( w/c = 2 \) WDS Topography 380 Probes, 3 micron grid

- NI
  2 Nanicer indentation Topography 400 Probes (300 successful), 3 micron grid

- If Water Starved, Only CH/C-S-H Composite; leading to a dominating Ultra-High Density Phase.

- CH may well be a seed for C-S-H formation (to be confirmed).

See also: Chen et al., JACS, 2010

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And what’s about concrete creep?

NanoEngineering of Functional Properties

Matthieu Vandamme, Franz-Josef Ulm
Creep Testing

- Macroscopic Creep Tests

- Nanoindentation Creep

Scale: $\sim 10^{-1}$m
Time: $\sim 10^3$days

Scale: $\sim 10^{-7}$m
Time: $\sim 10^2$s
What time-dependent properties can we access by indentation?

- An indentation creep test yields the contact creep compliance $L(t)$.

<table>
<thead>
<tr>
<th></th>
<th>Uniaxial Testing</th>
<th>Indentation Testing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic</td>
<td>$E$</td>
<td>$M$</td>
</tr>
<tr>
<td>Relaxation</td>
<td>$E(t)$</td>
<td>$M(t)$</td>
</tr>
<tr>
<td>Creep</td>
<td>$J(t)$</td>
<td>$L(t)$</td>
</tr>
</tbody>
</table>

\[
\frac{dL}{dt} = \frac{2a(t)h(t)}{P_{\text{max}}} 
\]

(*) Vandamme, M., Ulm, F.-J., //SS, 2006
Shahsavari & Ulm, MoMS, 2009
Measure the creep of C-S-H by nanoindentation

- A function of the form \( \Delta h(t) = x_1 \ln(x_2 t + 1) + x_3 t \) fits very well each test.

- \( x_3 \) is not correlated with \( M \) or \( H \). It is due to drift of the apparatus.

- Therefore, the long term creep behavior of C-S-H depends on only one parameter, the contact creep modulus \( C \)

\[
L(t) \sim h \rightarrow \frac{1}{(Ct)}
\]
Creep-Modulus – Packing Density Relations

• Functional Properties

Uniaxial creep Modulus \( \sim \frac{1}{3} \)

Indentation creep Modulus (like Hardness-strength)

\[
\dot{\varepsilon} \sim \frac{1}{\sigma C_t}
\]

Vandamme & Ulm, PNAS, 2009

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2010 Concrete Sustainability Conference 46 © National Ready Mixed Concrete Association
From Functionalized MicroStructure to Structural Performance

Here speaks the Engineer!
Impact: “Bridge of the Future”

• US-FHWA Project

To replace 150,000 bridges (of 450,000)
“Bridge of the Future”

- Prototype Development @ MIT

Max L / H ~ 30
Weight Reduction ~ 30%
Durability (low maintenance)
Rapid Construction (circulation)

- AASHTO III
- AASHTO VI

Span \( L \) [m] vs. Height \( H \) [m]

- \( P = 4.45 \text{ MN} \)
- \( P = 6.68 \text{ MN} \)

Max Load under Ultimate Limit State (ULS)

ULS: 0.83, 0.98, 1.15, 1.35, 1.58

Weight Reduction: 30%
“Bridge of the Future”

- Sponsor: FHWA (Joey Hartmann)
- Design: MIT
- Construction: Prestress Services, Kentucky
- Material: DUCTAL®

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UHPC Design

Monitoring the Temperature during Hydration

7.5 cm Slab
5 cm Web
(no reinforcement)

Results with CESAR-LCPC

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Nano-Engineering Performance

“Shake-em-up” the Hydrates

- But, please, don’t quote me on the Oranges
Conclusion

Join us:

Concrete Sustainability Conference@MIT

August 9-11, 2011
It’s no “C-crete”:
Change in paradigm: Bottom-Up

- Ordinary Concrete
- High Performance Concrete (HPC)
- Ultra High Performance Concrete (UHPC)

“C”-Crete?
Welcome to MIT!
Concrete Sustainability Conference August 9-11, 2011

- “Why would we care about cement? Well cement … is a very important piece of reducing CO₂, and you have to understand the structure”
  
  Susan Hockfield, MIT President, State-of-the-Institute 09/30/2009

- “Putting engineers together with economists, urban planners, architects and industry experts and practitioners on issues related to our built infrastructure will create truly novel opportunities for intervention.”

  Subra Suresh, Dean of School of Engineering, MIT, 10/05/2009
Just a reminder not to quote me on Oranges!