Innovative High Performance Thermal Building Insulation Materials - Todays State-of-the-Art and Beyond Tomorrow

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Invited lecture based on the following article:

In addition, results from the following article has been added:

\textit{Building Enclosure Science & Technology (BEST 3 - 2012), Atlanta, Georgia, U.S.A., 2-4 April, 2012.}
Why is Thermal Insulation Important?  
- What Measures Amounts the Most?

Global GHG abatement cost curve beyond business-as-usual – 2030

Thermal Background

- Thermal Conductivity Contributions

\[ \lambda_{\text{tot}} = \lambda_{\text{solid}} + \lambda_{\text{gas}} + \lambda_{\text{rad}} + \lambda_{\text{conv}} + \lambda_{\text{coupling}} + \lambda_{\text{leak}} \]

- \( \lambda_{\text{tot}} \): total overall thermal conductivity
- \( \lambda_{\text{solid}} \): solid state thermal conductivity
- \( \lambda_{\text{gas}} \): gas thermal conductivity
- \( \lambda_{\text{rad}} \): radiation thermal conductivity
- \( \lambda_{\text{conv}} \): convection thermal conductivity
- \( \lambda_{\text{coupling}} \): thermal conductivity term accounting for second order effects between the various thermal conductivities
- \( \lambda_{\text{leak}} \): leakage thermal conductivity
Traditional Thermal Insulation of Today

- **Mineral Wool**
  - Glass wool (fibre glass)
  - Rock wool
  - 30-40 mW/(mK)

- **Expanded Polystyrene (EPS)**
  - 30-40 mW/(mK)

- ** Extruded Polystyrene (XPS)**
  - 30-40 mW/(mK)

- **Cellulose**
  - 40-50 mW/(mK)

- **Cork**
  - 40-50 mW/(mK)

- **Polyurethane (PUR)**
  - Toxic gases (e.g. HCN) released during fire
  - 20-30 mW/(mK)
State-of-the-Art Thermal Insulation of Today
- What is Out There?

- Vacuum Insulation Panels (VIP)
  "An evacuated foil-encapsulated open porous material as a high performance thermal insulating material"
  - Core (silica, open porous, vacuum)
  - Foil (envelope) - 4 - 8 - 20 mW/(mK)

- Gas-Filled Panels (GFP) - 40 mW/(mK)

- Aerogels - 13 mW/(mK)

- Phase Change Materials (PCM)
  - Solid State ↔ Liquid
  - Heat Storage and Release

- Beyond State-of-the-Art High Performance Thermal Insulation Materials?
Major Disadvantages of VIPs

- Thermal bridges at panel edges
- Expensive at the moment, but calculations show that VIPs may be cost-effective even today
- Ageing effects - Air and moisture penetration
  - 4 mW/(mK) fresh
  - 8 mW/(mK) 25 years
  - 20 mW/(mK) perforated
- Vulnerable towards penetration, e.g. nails
  - 20 mW/(mK)
- Can not be cut or adapted at building site
- Possible improvements?

- Vacuum Core
- Air and Moisture Tight Envelope
VIPs – The Thermal Insulation of Today?

- VIPs - Despite large disadvantages - A large leap forward
- Thermal conductivities 5 to 10 times lower than traditional insulation
  - 4 mW/(mK) fresh
  - 8 mW/(mK) 25 years
  - 20 mW/(mK) perforated
- Wall and roof thicknesses up to 50 cm as with traditional insulation are not desired
  - Require new construction techniques and skills
  - Transport of thick building elements leads to increased costs
- Building restrictions during retrofitting of existing buildings
  - Lawful authorities
  - Practical Restrictions
- High living area market value per m² ⇒ Reduced wall thickness ⇒ Large area savings ⇒ Higher value of the real estate
- VIPs - The best solution today and in the near future?
- Beyond VIPs?
Potential Cost Savings by Applying VIPs

VIP Profit

Market Value Living Area (EUR/m² living area)

VIP Profit (EUR/100 m² living area)

-25 000 -20 000 -15 000 -10 000 -5 000 0 5 000 10 000 15 000 20 000 25 000

0 1 000 2 000 3 000 4 000 5 000


Assumed example values
- Building of 10 m x 10 m
- Interior floor to ceiling height of 2.5 m
- 20 cm wall thickness reduction
- VIP costs 6 cm: 200 EUR/m²
- Mineral wool costs 35 cm: 20 EUR/m²

\[ l \times w \times h = 10 \text{ m} \times 10 \text{ m} \times 2.5 \text{ m} \]
## Requirements of the Thermal Insulation of Tomorrow

<table>
<thead>
<tr>
<th>Property</th>
<th>Requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity – pristine</td>
<td>&lt; 4 mW/(mK)</td>
</tr>
<tr>
<td>Thermal conductivity – after 100 years</td>
<td>&lt; 5 mW/(mK)</td>
</tr>
<tr>
<td>Thermal conductivity – after modest perforation</td>
<td>&lt; 4 mW/(mK)</td>
</tr>
<tr>
<td>Perforation vulnerability</td>
<td>not to be influenced significantly</td>
</tr>
<tr>
<td>Possible to cut for adaption at building site</td>
<td>yes</td>
</tr>
<tr>
<td>Mechanical strength (e.g. compression and tensile)</td>
<td>may vary</td>
</tr>
<tr>
<td>Fire protection</td>
<td>may vary, depends on other protection</td>
</tr>
<tr>
<td>Fume emission during fire</td>
<td>any toxic gases to be identified</td>
</tr>
<tr>
<td>Climate ageing durability</td>
<td>resistant</td>
</tr>
<tr>
<td>Freezing/thawing cycles</td>
<td>resistant</td>
</tr>
<tr>
<td>Water</td>
<td>resistant</td>
</tr>
<tr>
<td>Dynamic thermal insulation</td>
<td>desirable as an ultimate goal</td>
</tr>
<tr>
<td>Costs vs. other thermal insulation materials</td>
<td>competitive</td>
</tr>
<tr>
<td>Environmental impact (including energy and material use in production, emission of polluting agents and recycling issues)</td>
<td>low negative impact</td>
</tr>
</tbody>
</table>
Properties of Concrete
– A Construction Material

- Thermal Conductivity

- Concrete
  - 150 – 2500 mW/(mK)

- Traditional Thermal Insulation
  - 36 mW/(mK)

- Vacuum Insulation Panels (VIPs)
  - 4 mW/(mK)

Possible to decrease the thermal conductivity of concrete?
## Properties of Concrete

### Some key properties of concrete (example values)

<table>
<thead>
<tr>
<th>Property</th>
<th>With Rebars</th>
<th>Without Rebars</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass density (kg/dm³)</td>
<td>2.4</td>
<td>2.2</td>
</tr>
<tr>
<td>Thermal conductivity (mW/mK)</td>
<td>2500</td>
<td>1700</td>
</tr>
<tr>
<td>Specific heat capacity (J/(kgK))</td>
<td>840</td>
<td>880</td>
</tr>
<tr>
<td>Linear thermal expansion coefficient (10⁻⁶/K)</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>Compressive strength (MPa)</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Tensile strength (MPa) a</td>
<td>500 b</td>
<td>3</td>
</tr>
<tr>
<td>Fire resistance</td>
<td>&gt; 2 h</td>
<td>&gt; 2 h</td>
</tr>
<tr>
<td>Environmental impact (incl. energy and material use in production, emission of polluting agents and recycling issues)</td>
<td>large CO₂ emissions</td>
<td>large CO₂ emissions</td>
</tr>
</tbody>
</table>

a As a comparison, note that carbon nanotubes have been manufactured with tensile strengths as high as 63 000 MPa and have a theoretical limit at 300 000 MPa. b Rebars.
The cement industry produces 5% of the global man-made CO₂ emissions of which:

- 50% from the chemical process
  - e.g.: $3\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{Ca}_3\text{SiO}_5 + 3\text{CO}_2$
  - $2\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{Ca}_2\text{SiO}_4 + 2\text{CO}_2$

- 40% from burning fossil fuels
  - e.g. coal and oil

- 10% split between electricity and transport uses

And let us not forget the corrosion issues with reinforced concrete…
Beyond Traditional Thermal Insulation?

"I think you should be more explicit here in step two"
Beyond VIPs – How May It Be Achieved?

"I think you should be more...

VIP

Air

Moisture

VIM

Open Pore Structure

Closed Pore Structure

NIM
Nano Technology

Nanotechnology:
Technology for controlling matter of dimensions between 0.1 nm - 100 nm.

For comparison:
- Solar radiation: 300 nm - 3000 nm
- Atomic diameters:
  - Hydrogen: 0.16 nm
  - Carbon: 0.18 nm
  - Gold: 0.36 nm
- Molecular length:
  - Stearic Acid: 2.48 nm

Nanotechnology:
Technology for controlling matter at an atomic and molecular scale.
Nano Technology and Thermal Insulation

Nano Particles

Nano Pores

0.1 nm - 100 nm
How Good are You at Guessing?

The A4 Paper Folding

- Fold an A4 paper 100 times.
- Press out all air between the paper sheets.
- Put the paper pile on the table in front of you.
- Guess how far above the table does the paper pile reach?
Beyond VIPs – How May It Be Achieved?

Introducing New Concepts as

- Advanced Insulation Materials (AIM):
  - Vacuum Insulation Materials (VIM)
  - Gas Insulation Materials (GIM)
  - Nano Insulation Materials (NIM)
  - Dynamic Insulation Materials (DIM)

Vacuum Insulation Material (VIM)

VIM - A basically homogeneous material with a closed small pore structure filled with vacuum with an overall thermal conductivity of less than 4 mW/(mK) in the pristine condition.
Gas Insulation Material (GIM)

... and analogously with VIM we may define GIM as follows:

GIM - A basically homogeneous material with a closed small pore structure filled with a low-conductance gas with an overall thermal conductivity of less than 4 mW/(mK) in the pristine condition.
Nano Insulation Material (NIM)

NIM - A basically homogeneous material with a closed or open small nano pore structure with an overall thermal conductivity of less than 4 mW/(mK) in the pristine condition.
The Knudsen Effect – Nano Pores

Gas Thermal Conductivity $\lambda_{\text{gas}}$

$$
\lambda_{\text{gas}} = \frac{\lambda_{\text{gas},0}}{1 + 2\beta \text{Kn}} = \frac{\lambda_{\text{gas},0}}{1 + \frac{\sqrt{2\beta k_B T}}{\frac{\pi d^2 p\delta}{2\pi d^2 p\delta}}}
$$

where

$$
\text{Kn} = \frac{\sigma_{\text{mean}}}{\delta} = \frac{k_B T}{\sqrt{2\pi d^2 p\delta}}
$$

$\lambda_{\text{gas}}$ = gas thermal conductivity in the pores (W/(mK))
$\lambda_{\text{gas},0}$ = gas thermal conductivity in the pores at STP (standard temperature and pressure) (W/(mK))
$\beta$ = coefficient characterizing the molecule-wall collision energy transfer efficiency (between 1.5 - 2.0)
$\text{Kn} = \frac{\sigma_{\text{mean}}}{\delta} = \frac{k_B T}{\sqrt{2\pi d^2 p\delta}}$ = the Knudsen number
$k_B$ = Boltzmann’s constant $\approx 1.38 \cdot 10^{-23}$ J/K
$T$ = temperature (K)
$d$ = gas molecule collision diameter (m)
$p$ = gas pressure in pores (Pa)
$\delta$ = characteristic pore diameter (m)
$\sigma_{\text{mean}}$ = mean free path of gas molecules (m)
Gas Thermal Conductivity

Conductivity vs. Pore Diameter

Various Pore Gases

100 000 Pa
300 K

Characteristics:
- Air
- Argon
- Krypton
- Xenon
- 4 mW/(mK)

Gas Thermal Conductivity (mW/(mK))

Characteristic Pore Diameter

10 mm 1 mm 100 μm 10 μm 1 μm 100 nm 10 nm 1 nm
Gas Thermal Conductivity

Conductivity vs. Pore Pressure

Various Pore Gases

- Air
- Argon
- Krypton
- Xenon
- 4 mW/(mK)

Pore Pressure (Pa)

Gas Thermal Conductivity (mW/(mK))

10 mm
300 K
Gas Thermal Conductivity

![3D graph showing the relationship between gas thermal conductivity (mW/(mK)), pore diameter (nm), and pore pressure (Pa). The graph uses a color scale to represent different pressure levels (0, 5, 10, 15, 20, 25, 30 Pa).]
Gas Thermal Conductivity

- **Air**
- **Argon**
- **Krypton**
- **Xenon**

The graphs depict the relationship between gas thermal conductivity (mW/(m·K)) and pore diameter (nm) at different pore pressures (Pa). Each gas (Air, Argon, Krypton, Xenon) shows distinct patterns in how these variables interact.

**Key Observations:***
- **Air** has a moderate thermal conductivity with a peak around a pore diameter of 10^6 nm and a pore pressure of 10^5 Pa.
- **Argon** shows a similar trend but with slightly lower values.
- **Krypton** exhibits higher thermal conductivities, particularly at higher pore pressures.
- **Xenon** has the highest thermal conductivities, with a significant peak at 10^6 nm and 10^5 Pa.

These findings can be crucial for understanding the thermal insulation properties of materials with varying pore structures and pressures in applications like ZEB (Zero Energy Buildings).
Nano Pores – Thermal Radiation

- Knudsen effect ⇒ $\sigma_{\text{mean}} > \delta$ ⇒ low gas thermal conductivity $\lambda_{\text{gas}}$
- What about the thermal radiation in the pores?
- ”Classical” – from Stefan-Boltzmann’s law (Linear $\lambda_{\text{rad}}$ vs. $\delta$ relationship):

$$\lambda_{\text{rad}} = \frac{\pi^2 k_B^4 \delta}{60\hbar^3 c^2} \left( \frac{2}{\varepsilon} - 1 \right) \frac{(T_i^4 - T_e^4)}{(T_i - T_e)}$$

- Pore diameter $\delta$ small ⇒ low thermal radiation conductivity $\lambda_{\text{rad}}$
- But what happens when $\xi_{\text{ir}} > \delta$? (IR wavelength > pore diameter)
- $\xi_{\text{ir}} > \delta$ ⇒ high thermal radiation conductivity $\lambda_{\text{rad}}$?
- Tunneling of evanescent waves
- Indications that the large thermal radiation is only centered around a specific wavelength (or a few) ⇒
- The total thermal radiation integrated over all wavelengths is not that large (?)
- Currently looking into these matters…

$\lambda_{\text{rad}}$ = radiation thermal conductivity in the pores (W/(mK))
$\sigma = \pi^2 k_B^4/(60\hbar^3 c^2)$ = Stefan-Boltzmann’s constant $\approx 5.67 \cdot 10^{-8}$ W/(m²K⁴)
$k_B$ = Boltzmann’s constant $\approx 1.38 \cdot 10^{-23}$ J/K
$\hbar$ = $h/(2\pi) \approx 1.05 \cdot 10^{-34}$ Js = reduced Planck’s constant ($h$ = Planck’s constant)
$c = \text{velocity of light} \approx 3.00 \cdot 10^8$ m/s
$\delta = \text{pore diameter (m)}$
$\varepsilon = \text{emissivity of inner pore walls (assumed all identical)}$
$T_i = \text{interior (indoor) temperature (K)}$
$T_e = \text{exterior (outdoor) temperature (K)}$
$\xi_{\text{ir}} = \text{infrared radiation wavelength (m)}$
Thermal Radiation in Nano Pores

Stefan-Boltzmann’s Law

Total Radiation Heat Flux $J_{\text{rad, tot}}$

$$J_{\text{rad, tot}} = \frac{\sigma}{n\left(\begin{array}{c}
\frac{2}{\varepsilon} - 1
\end{array}\right)} \left(T_i^4 - T_e^4\right)$$

Radiation Thermal Conductivity $\lambda_{\text{rad}}$

$$\lambda_{\text{rad}} = \frac{\sigma \delta}{\left(\begin{array}{c}
\frac{2}{\varepsilon} - 1
\end{array}\right)} \frac{(T_i^4 - T_e^4)}{(T_i - T_e)} = \frac{\pi^2 k_B^4 \delta}{60 \hbar^3 c^2 \left(\begin{array}{c}
\frac{2}{\varepsilon} - 1
\end{array}\right)} \frac{(T_i^4 - T_e^4)}{(T_i - T_e)}$$

$\lambda_{\text{rad}}$ is found by applying the approximation $(T_{k-1} - T_k) = (T_i - T_e)/n$

$\lambda_{\text{rad}} = \text{radiation thermal conductivity in the pores (W/(mK))}$

$\sigma = \pi^2 k_B^4/(60 \hbar^3 c^5)$ = Stefan-Boltzmann’s constant $\approx 5.67 \cdot 10^{-8}$ W/(m²K⁴)

$k_B$ = Boltzmann’s constant $\approx 1.38 \cdot 10^{-23}$ J/K

$h = \hbar/(2\pi) \approx 1.05 \cdot 10^{-34}$ Js = reduced Planck’s constant ($h = \text{Planck’s constant}$)

$c = \text{velocity of light} \approx 3.00 \cdot 10^8$ m/s

$\delta = \text{pore diameter (m)}$

$\varepsilon = \text{emissivity of inner pore walls (assumed all identical)}$

$T_i = \text{interior (indoor) temperature (K)}$

$T_e = \text{exterior (outdoor) temperature (K)}$

$J_{\text{rad, tot}} = \text{total radiation heat flux (W/m²)}$

$n = \text{number of pores along a given horizontal line in the material}$
Radiation Thermal Conductivity

Conductivity vs. Pore Diameter

- Emissivity
  - Increasing Emissivity

- Indoor 20°C
- Outdoor 0°C

Characteristic Pore Diameter (mm)

Radiation Thermal Conductivity (mW/(mK))
First Experimental Attempts towards NIMs: *Hollow Nanospheres*

Three Main Preparation Methods:

(which we have tried... more exist...)

1. **Membrane Foaming:** Use a membrane to prepare foam with nanoscale bubbles, followed by hydrolysis and condensation of a precursor within bubble walls to make a solid structure.

2. **Internal Gas Release:** Controlled decomposition or evaporation of a component to form nanobubbles in a liquid system, followed by formation of a solid shell at the bubble perimeter.

3. **Templating:** Formation of a nanoscale liquid or solid structure, followed by reactions to form a solid shell at the perimeter. Finally, the core is removed to make a hollow sphere.
Membrane Foaming

Silica sol stir foamed at 1000 (left) and 2500 (right) mPas

Gas capsules by membrane emulsification. J. Yang et al. SINTEF.
Foam Formation

Requirement for nanosized bubbles:
Controlled pressure to avoid continuous gas stream.
\( \Delta \rho \): Density difference between gas and liquid, should be large.
\( r_{\text{cap}} \): Pore radius, should be small.
\( \sigma_l \): Surface tension of liquid, should be small.
\( \theta \): Contact angle, should be large.

Foam walls should be thin and stable:
\( \eta \): Liquid viscosity, should be low.
\( \sigma_l \): Surface tension of liquid, should be small.
Stability: Requires surfactant bialayers.
Membrane Foaming – Attempted the Following:

Rapid Hydrolysis and Condensation:

\[ \text{Ti(OR)}_4 + \text{H}_2\text{O} \leftrightarrow (\text{RO})_3\text{-Ti-OH} + \text{ROH} \]

\[ (\text{RO})_3\text{-Ti-OH} + \text{HO-Ti-(RO)}_3 \leftrightarrow (\text{RO})_3\text{-Ti-O-Ti-(RO)}_3 + \text{H}_2\text{O} \]

\[ (\text{RO})_3\text{-Ti-OR} + \text{HO-Ti-(RO)}_3 \leftrightarrow (\text{RO})_3\text{-Ti-O-Ti-(RO)}_3 + \text{ROH} \]

Should proceed upon exposure to \( \text{H}_2\text{O} + \text{CO}_2 \)

to form a gel shell around bubbles

Not successful

- Reaction too slow; bubbles broke (with smoke).
- No suitable surfactant systems found to stabilize alcohol-based foams!
Internal Gas Release

Would Require:

• Simultaneous formation of gas bubbles throughout reaction system.
• Narrow bubble size distribution.
• Very homogeneous system temperature.
• Rapid shell formation (before Ostwald ripening process).
• Extremely reactive chemicals, requiring strict humidity control.

• Very demanding experimental conditions, work terminated.
Template-Assisted Systems

Schematic diagram of the formation mechanism of hollow silica spheres, from (Wan and Yu 2008)
Stöber Method for Synthesis of Hollow SiO$_2$ Nanoparticles (ex.)

- Polyacrylic acid (PAA, MW ≈ 5000)
- Ammonium hydroxide (25 wt%)
- 100% ethanol
- Tetraethoxysilane (TEOS)
- Ion exchanged destilled water

0.27 g PAA

Dissolve

4.5 ml NH$_4$OH

Mix in 50 ml conical flask (magnetic stirring)

90 ml 100% EtOH

0.45 ml TEOS

1 h interval

0.45 ml TEOS

1 h interval

0.45 ml TEOS

1 h interval

0.45 ml TEOS

1 h interval

0.45 ml TEOS

1 h interval

2.25 ml TEOS in total

Precipitation after 10 h

Colloid to be washed with dest. Water in centrifuge and dried at RT.
Same Chemical Reaction as for Aerogel Production:

**Hydrolysis**

\[
R'-\text{Si-OR} + \text{H-OH} \rightleftharpoons R'-\text{Si-OH} + \text{ROH}
\]

**Condensation**

\[
R'-\text{Si-OH} + \text{HO-Si-R'} \rightleftharpoons R'-\text{Si-O-Si-R'} + \text{H}_2\text{O}
\]

\[
R'-\text{Si-OR} + \text{HO-Si-R'} \rightleftharpoons R'Si-O-Si-R' + \text{ROH}
\]
First Attempts to Make the NIMs

- wish us good luck...!

SEM Photos

FIB burning... confirming the nanospheres are hollow...

... are we getting the first glimpse at the Holy Grail here...?
Achieved particle size:

90 – 400 nm, most: ~ 200 nm

Next:
- Control droplet size
  - Stirring rate
  - Membrane emulsification
  - Ultrasonic treatment
- Control shell thickness
- Drying to obtain powder
- Surface modification: hydrophobic
- Sintering to make NIMs
Further Ahead

- Vary particle morphology
  - Hollow SiO$_2$ particles
  - Mesoporous SiO$_2$ particles
  - Hollow particles with mesoporous shells

- Particle synthesis – Optimization
  - Particle size
  - Bulk mesoporosity
  - Shell thickness
  - Shell mesoporosity
ZEB-1SK (60 mg PAA, 2 ml NH₄OH (28%), 20 ml EtOH)

Preparation of Silica Capsules

1. ZEB-1SK-A:
   - 5x100μl TEOS
   - 1h in between
   - Partly precipitation
   - Washed with water
   - Single capsules difficult to sediment in EtOH

2. ZEB-1SK-B:
   - 5x50μl TEOS
   - 0.5h in between
   - Less precipitation
   - EtOH evaporated first
   - Washed with water
   - Capsules sediment a bit better w/o EtOH

<table>
<thead>
<tr>
<th>Sample</th>
<th>d₂ [nm]</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZEB-1SK</td>
<td>38.2</td>
<td>0.11</td>
</tr>
<tr>
<td>ZEB-1SK-A</td>
<td>155.5</td>
<td>0.16</td>
</tr>
<tr>
<td>ZEB-1SK-B</td>
<td>144.5</td>
<td>0.18</td>
</tr>
</tbody>
</table>
ZEB-6SK (60 mg PAA, 2 ml NH₄OH (14%), 20 ml EtOH)

Preparation of Silica Capsules

- Slight precipitation
- Washed with water
- Single capsules difficult to sediment in EtOH

- No precipitation
- EtOH evaporated first
- Washed with water
- Capsules sediment a bit better w/o EtOH

<table>
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<tr>
<th>Sample</th>
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<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZEB-6SK</td>
<td>41.2</td>
<td>0.12</td>
</tr>
<tr>
<td>ZEB-6SK-A</td>
<td>89.9</td>
<td>0.12</td>
</tr>
<tr>
<td>ZEB-6SK-B</td>
<td>61.6</td>
<td>0.08</td>
</tr>
</tbody>
</table>
ZEB-13SK (300 mg PAA, 10 ml NH₄OH (14%), 100 ml EtOH)

Preparation of Silica Capsules

ZEB-13SK

5x500 µl TEOS
0.5h in between

- No precipitation

ZEB-13SK-A

- EtOH evaporated

ZEB-13SK-A1

ZEB-13SK-A2

- Tempered at 550°C
- Washed with water

ZEB-13SK-A3

<table>
<thead>
<tr>
<th>Sample</th>
<th>d₂ [nm]</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZEB-13SK</td>
<td>36.1</td>
<td>0.10</td>
</tr>
<tr>
<td>ZEB-13SK-A</td>
<td>67.1</td>
<td>0.10</td>
</tr>
</tbody>
</table>
Different amount of silicon

ZEB-1SK-A
5x100µl TEOS
1h in between
2ml NH₄OH (28%)
Size: 50-60 nm
Cavity: 20-25 nm
Wall: 30-35 nm

ZEB-1SK-B
5x50µl TEOS
0.5h in between
2ml NH₄OH (28%)
Size: 40-45 nm
Cavity: 20-25 nm
Wall: 20-25 nm

TEM Photos
Different amount of NH$_4$OH

ZEB-1SK-A  
5x100µl TEOS  
1h in between  
2ml NH$_4$OH (28%)  
Size: 50-60 nm  
Cavity: 20-25 nm  
Wall: 30-35 nm

ZEB-6SK-A  
5x100µl TEOS  
1h in between  
2ml NH$_4$OH (14%)  
Size: 40-45 nm  
Cavity: 18-22 nm  
Wall: 20-25 nm

TEM Photos
Sizes of the hollow silica nanospheres range from 50 to 250 nm; while the thickness is fairly uniform, about 10 nm, which can be tuned by varying the silica source materials.
Sizes of the hollow silica nanospheres are fairly uniform, about 300 nm in diameter; the thickness of the shell is about 20 nm, which can be tuned by varying the etching time.
The Path Ahead

- At the moment following various paths to make hollow nanospheres
- First thermal conductivity measurements on the powder ... no optimization yet...
  - ~37 mW/(mK)... some indications that this value is really
  - ~20 mW/(mK) (?) ... to be checked... we intend to go further down yes...
- ... then to piece the nanospheres together to form a bulk insulation material...
- Other paths...?
Dynamic Insulation Material (DIM)

- Thermal conductivity control may be achieved by:
  - Inner pore gas content or concentration including the mean free path of the gas molecules and the gas-surface interaction
  - The emissivity of the inner surfaces of the pores
  - The solid state thermal conductivity of the lattice

- What is really solid state thermal conductivity? Two models:
  - Phonon thermal conductivity - atom lattice vibrations
  - Free electron thermal conductivity

- What kind of physical model could describe and explain thermal conductivity?

- Could it be possible to dynamically change the thermal conductivity from very low to very high, i.e. making a DIM?
Dynamic Insulation Material (DIM)

- Dynamic Vacuum
- Dynamic Emissivity of Inner Pore Surfaces
- Dynamic Solid Core Thermal Conductivity
  - Is it possible?
  - Fundamental understanding of the thermal conductance?
- Other?

Learning from Electrochromic Materials?:

\[ \lambda_p = \left(\frac{2\pi c}{q_e}\right)\left(\frac{m_e\varepsilon_0}{n_e}\right)^{1/2} \]

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Inspiration and Ideas

Could other fields of science and technology inspire and give ideas about how to be able to make DIMs, e.g. from the fields?:

- Electrochromic Materials
- Quantum Mechanics
- Electrical Superconductivity
- Other?
Aerogels – Approaching the NIMs

- Aerogels – At the moment the closest commercial approach to NIMs
- 12 – 14 mW/(mK)

- Aspen Aerogels
  - Spaceloft
- Cabot Aerogel
  - Nanogel

- Production costs still high
- Relatively high compression strength
- Very fragile due to very low tensile strength
- Tensile strength may be increased by incorporation of a carbon fibre matrix
- May be produced as either opaque, translucent or transparent materials

Thus enabling a wide range of possible building applications
**Thinner Concrete Buildings with NIMs**

- Mineral Wool or Polystyrene
  - 36 mW/(mK)
  - 40 cm traditional thermal insulation retrofitting

- NIM
  - 3.6 mW/(mK)
  - 4 cm NIM thermal insulation retrofitting

- A vast reduction – factor 10 – of the thermal insulation layer and thereby the total building envelope thickness.
Concrete with NIMs

Concrete with NIM Indoor and Outdoor
- Retrofitting

NIM in the Midst of Concrete

NIM Mixed in the Concrete

NIM and Concrete Mixture

... or going beyond these...?
To Envision Beyond Concrete?

- In the community of concrete it might be compared to using profane language in the church and close to blasphemy to suggest that maybe the answer is not concrete after all… 😝

- Concrete:
  - High thermal conductivity.
  - Total thickness of the building envelope will often become unnecessary large (passive house, zero energy building or zero emission building).
  - Large CO₂ emissions connected to the production of cement.
  - Prone to cracking induced by corrosion of the reinforcement steel.
  - Easy accessible and workable, low cost and local production.
  - High fire resistance.

- Is it possible to envision a building and infrastructure industry without an extensive usage of concrete?
Emphasis on Functional Requirements

- Not the building material itself which is important.
- Property or functional requirements are crucial.
- Possible to invent and manufacture a material with the essential structural or construction properties of concrete intact or better, but with substantially lower thermal conductivity?
- Beneficial with a much lower negative environmental impact than concrete with respect to CO₂ emissions.
- Envisioned with or without reinforcement or rebars.
NanoCon – Introducing a New Material

Making a New Material: NanoCon

NanoCon – Introducing a New Material

- NanoCon
- Basically a homogeneous material
- Closed or open small nano pore structure
- Overall thermal conductivity < 4 mW/(mK) (or another low value to be determined)
- Exhibits the crucial construction properties that are as good as or better than concrete.
  - Utilize carbon nanotubes (CNT)? Tensile strengths of 63 GPa (measured) and 300 GPa (theoretical). (Steel rebars 500 MPa and concrete 3 MPa.)

Essentially, NanoCon is a NIM with construction properties matching or surpassing those of concrete.
Materials and Solutions Not Yet Thought Of?

- The more we know the more we know we don’t know…!
  - … and the more we want to know…!
  - … and that’s the whole fun of it…!
- Think thoughts not yet thought of…!
Conclusions

- The Thermal Insulation Materials of Beyond Tomorrow?
- Theoretical concepts established – Others?
- Nano Insulation Materials (NIM)
- Dynamic Insulation Materials (DIM)
- NanoCon
- Others?
- First experimental attempts towards NIMs
Sorry folks…
… we simply couldn’t resist
the following slides…(!)


… though… with Concrete and NanoCon it might take several years…(!)
Sunset...

R.I.P.
VIP
IVIS
2009
?
Sunrise...
and the Phoenix rises again...!
Sunset...

R.I.P.
CONCRETE
COIN
2010
?
Sunrise...
and the Phoenix rises again...!
Sunrise...
and the Phoenix rises again...!