

# **Aerogels - Structure, properties and applications**

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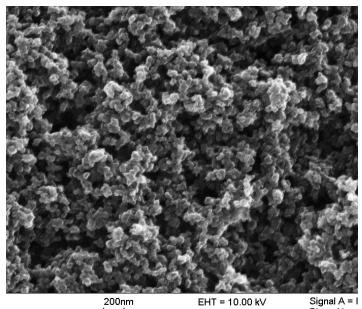
Email: lorenz.ratke@dlr.de

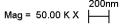
## What are aerogels?

Aerogels are nanostructured, open porous solids made via sol-gel technology

#### Types of aerogels

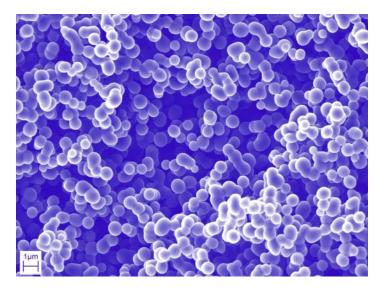
- Oxides (Quarz, Titania, Zirkonia. Mixed oxides)
- Polymers (Resorcin-, Melamin-Formaldehyd)
- Carbon (pyrolysed Polymere)
- cellulose, starch, alginates,...
- And almost everything that can be gelled





WD = 2 mm

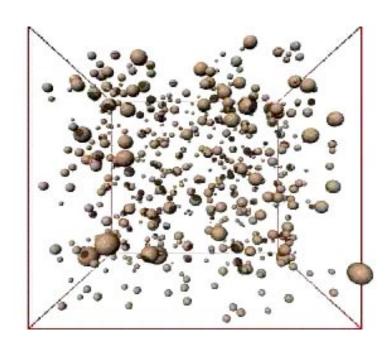
Photo No. =



#### Synthesis of aerogels

- → General technique is "sol-gel processing" meaning
  - Mixing of chemicals (alcoxides, water, alcohol, catalyst)
  - → Gelation (catalyst, temperature, fluid flow)
  - → Drying
  - → Final product

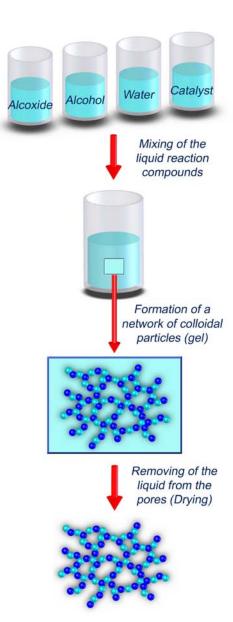




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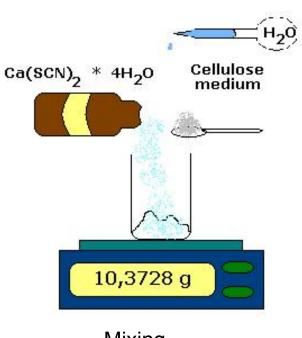




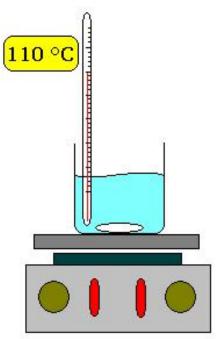
#### Preparation of cellulose aerogels

Dissolution of cellulose in e.g. salt-hydrate melts

- dissolution
- gelation
- regeneration
- aging

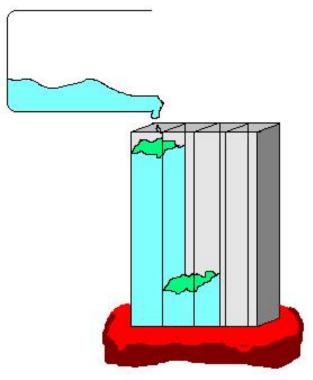


Mixing



Dissolution

Gelation on cooling (80°C) and regeneration





## The wet gel is ready and now?

## **Drying – determines everything\*!**

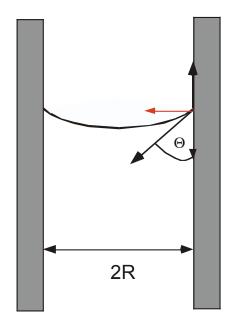
methods: air freeze drying supercritical

# Drying under ambient condition leads to Xerogels

- huge shrinkage
- Destruction of the nanosized pore system
- Fragmentation of the gel body
- → Porosity between 5 and 50 %
- but:

proper drying routine can give perfectly shaped xerogels!

#### capillary forces



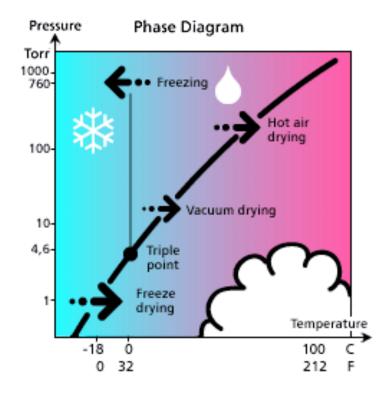
wetting stresses lead to a collapse of the gel network

p ≈ 1/R

## **Drying – determines everything!**

methods: air freeze drying supercritical

- Shock or rapid freezing (after solvent exchange) to minimize freezing effects on the solid gel structure
- Sublimation along the sublimation line by
  - pressure changes and
  - temperature increase

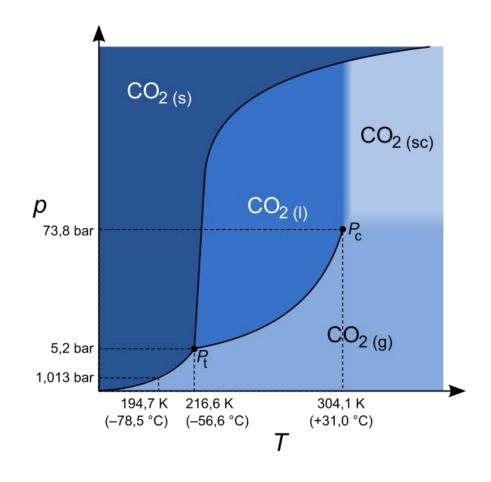


## **Drying – determines everything!**

methods: air freeze drying

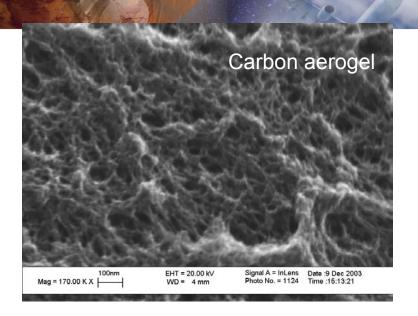
- Solvent exchange gel liquid against CO<sub>2</sub>
- Temperature increase above critical point
- T<sub>c</sub>=31.1°C, 73.8 bar.
- Real process ≈ 40 °C with pressure of ≈ 90 bar
- Slow depressurization

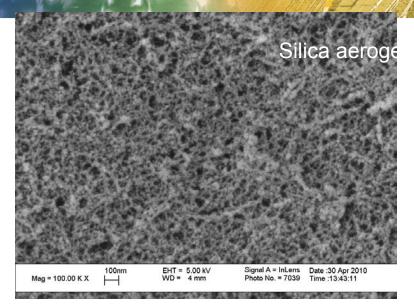
#### supercritical



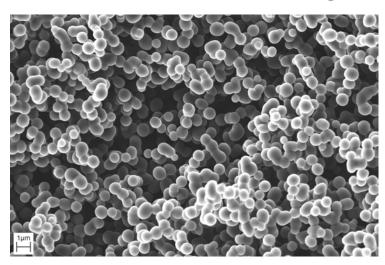


## And the result?



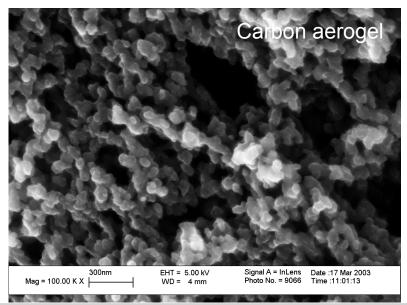


## Answer: almost always a nanostructure



RF-Aerogel (HCl catalysed)





Silica	Aerogel	Silina	^erogel	Silica
Silica	Aerogel Aero	Silica	Ac. gel	Silica
Silica	A rogel	Silica	Aerogt	Silica
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ca	Aerogel	Silica	Aerogel	Silica
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ca	Aerogel	Silica	herogel	Silica A



## **Appearance of some aerogels**



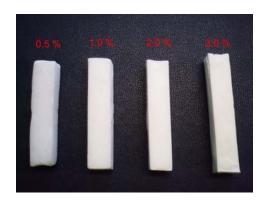




RF-Aerogel

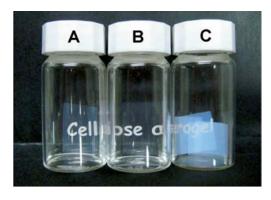


#### Appearance and structure of Cellulose aerogels



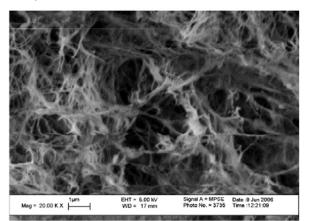
Cellulose-Aerogels are generally opaque and milky with densities of around 5 - 60 kg/m<sup>3</sup>

Structure: nanofelt of microfibrils



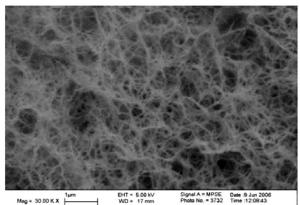
Cai et al, ChemSusChem 2008

0,5 % Cellulose

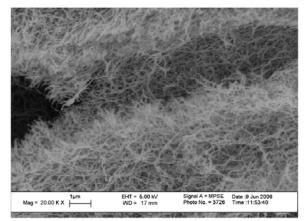


Aerogels with

1,0 % Cellulose



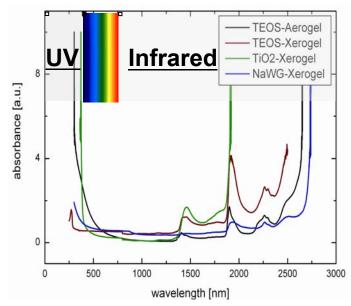
2,0 % Cellulose



## **Properties**

#### **Properties of aerogels**

- Low density high porosity
  - 90 99,9 % porosity
- Large sound absorption low sound velocity
  - damping > 50 dB,  $v_1 \approx 100$  m/s
- Low thermal conductivity
  - 0.005 0.1 W/mK
- Transparent or opaque or can be coloured
  - variable refractive index (1,001 to 2,1)
- No reaction with metallic melts up to 950°C (Silica and some other oxide aerogels)
- Huge internal surface
  - 10 2000 m<sup>2</sup>/g
- Surface can be functionalized
  - Hydrophobic by polymeric residues (-CH<sub>3</sub>)
  - CVD deposition of magnetic layers
- Functionalisation of the gel body
  - Embedding of particles (e.g. dyes, ferroelectrics)
  - Interpenetrating hybrid aerogel networks



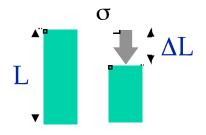




## Mechanical properties of aerogels

#### Young's modulus

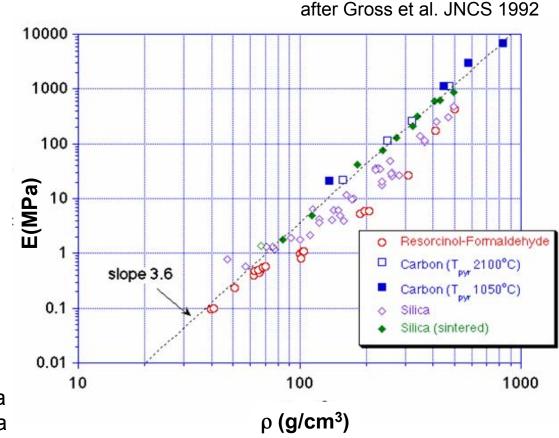
pressure



$$\sigma = \frac{\Delta L}{L_0} \cdot E = \varepsilon \cdot E$$

Fracture strength:

Silica-Aerogels: 20 kPa bis 2 MPa RF-Aerogels: 100 kPa bis 10 MPa



$$\sigma_B \propto \rho^{1.5}$$

$$E \propto \rho^{3.6}$$



## Are there applications?

#### Industrial areas of application

- → thermal insulation
  - home building, vehicles, pipelines, packaging
- electronic components
  - capacitors, humidity sensors, batteries, fuel cell, soft magnets, Geiger counter, IR detector
- foundry technology
  - aerogelic binders, aerogel granules for foundry sands
- architecture
  - illumination, superlight concrete, wall isolation
- → superlight composites
- → non-linear optics (SHG)
- Cosmetics
- → Pharmacy (drug delivery)
- Apparel & sportsware
  - Tennis rackets
  - Security shoes
  - Sport shoes
- → Space
  - Space suits
  - Anti-sloshing in tanks
  - Cryogenic tank insulation



Insulated Bo

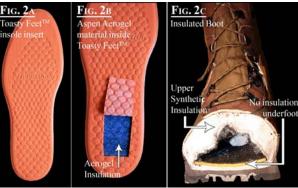


## Industrial areas of application

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  - Security shoes
  - Sport shoes
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  - Space suits
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# **Suppliers? Vendors? Who delivers what?**

#### **Aerogel granulates**

**Company:** Cabot (Frankfurt)

→ Material: water glass

→ Shape: polyhedric 0.5 - 4 mm

→ transparent

→ super hydrophobic

CABOT

price ≈ 2000 € /cbm

dried at ambient conditions

Company: Dow Corning

material: pure quartz

→ super hydrophobic

DOW CORNING

Application in cosmetic products

#### TL - Translucent

Particle Size Range: =	0.5 to 4.0 mm (0.02 to 0.16 in)
Pore Diameter:	≥ 20 nm
Porosity:	> 90%
Bulk Density:	90 to 100 kg/m³ (5.6 - 6.2 lb/ft³)
Surface Chemistry:	Fully Hydrophobic
Thermal Conductivity:	0.018 W/m-K at 25°C
	(0.125 Btu-in/hr-ft2-°F)
Surface Area:	600 to 800 m <sup>2</sup> /g
CAS RN:	102262-30-6



density 40 - 100 kg/cbm Particle size  $5 - 15 \mu m$  Surface area  $600 - 800 m^2/g$  > 90%





## **Aerogel tiles**

company: Airglass (Schweden)

material: Silica (precursor TMOS:Methanol)

→ Hydrophilic

Drying is made supercritically (methanol)



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~		•	•	•

• tiles 10 x 10 x 1 inch ≈ 500 €

• granulate 1 L ≈ 150 €

Density	50 - 200 kg/m³
Refractive index	1.02 - 1.05
Heat transfer coeff.	0.021 W/m°C At 20°C(68°F)
	rising to 0.2 at 300°C(570°F)
Non deforming	up to 750°C(1380°F)
Chemical composition	99.99%SiO2
Standard size today	60 x 60 x 2 cm3 (2 ft x 2 ft x 3/4 inch)
Grain size	10 - 30 nm in diameter

Airglass AB BOX 150 245 22 Staffanstorp SWEDEN

www.airglass.se

TEL: +46 46 255200 FAX: +46 46 25692



## Aerogel pieces & papers

company: MarkeTech (USA)

→ material:

→ Silica (TEOS:Methanol)

RF aerogel pieces and paper

→ Carbon aerogel (pieces and paper)

> hydrophilic

→ shape: small tiles and pieces

→ price:

¬ Random pieces: 100 g ≈ 880 US\$

 $\neg$  Tiles (4x8x0,5") = 1228 US\$





Marketech International Inc. 107B Louisa Street Port Townsend, WA 98368

Tel: 360-379-6707

Toll Free: 877-452-4910

Fax: 360-379-6907 info@mkt-intl.com



Properties	Value
Density	0.1 (0.3 - 0.05) g/cm <sup>3</sup>
Dielectric Constant	1.14 (18 - 40 Ghz)
Surface Area, BET	800 m <sup>2</sup> /g
Percent Solids	0.13 - 15%
Mean Pore Diameter	~20 nm
Primary Particle Diameter	2 - 5 nm
Index of Refraction	1.0 - 1.05
Thermal Tolerance	to 500°C
Poisson's Ratio	0.2
Young's Modulus	10 <sup>6</sup> - 10 <sup>7</sup> Nm <sup>2</sup>
Tensile Strength	16 kPa
Fracture Toughness	~0.8 kPa*m <sup>1/2</sup>
Compressive Modulus	0.3 MPa
Coefficient of Thermal Expansion (CTE)	2 ppm/C° @20 - 80°C
Electrical Resistivity	10 <sup>15</sup> ohm-cm
hermal Conductivity in Air	0.016 W/m/°K
Thermal Conductivity in Vacuum	0.004 W/m/°K
Sound Velocity Through the Medium	100 m/sec
Color	translucent

http://www.mkt-intl.com/index.shtml



## **Aerogel blankets**

company: Aspensystems (USA)

→ material: fibre composite

→ Silica-Aerogel on polymeric fiber felt

→ Silica-Aerogel on glass fibers

→ superhydrophobic





ASPEN AEROGELS, INC. 30 Forbes Road, Building B Northborough, MA 01532 USA

Tel: 1.508.691.1111 Fax: 1.508.691.1200

# aspen aerogels

		ninal kness		ermal luctivity	Der	nsity		um Use erature
Product Name	mm	in	mW/ m-K	Btu-in/ hr-ft <sup>2</sup> -°F	g/cc	lb/ft <sup>3</sup>	°C	°F
Cryogel™ 6000  Data Sheet  MSDS-English	6.0	0.24	13.5	0.094	0.13	8.0	40	100
Spaceloft™ 3251  Data Sheet  MSDS-English	3.0	0.12	14.0	0.097	0.15	9.4	200	390
Spaceloft™ 6251 <u>Data Sheet</u> MSDS-English	6.0	0.24	14.0	0.097	0.15	9.4	200	390
Spaceloft™ 9251  Data Sheet  MSDS-English	9.0	0.36	14.0	0.097	0.15	9.4	200	390
Spaceloft™ 6250 <u>Data Sheet</u> <u>MSDS-English</u>	6.0	0.24	12.5	0.087	0.13	8.0	200	390
Pyrogel® 2250  Data Sheet  MSDS-English  MSDS-French  MSDS-Italian	2.0	0.08	15.5	0.107	0.17	10.7	250	480
Pyrogel® 6250  Data Sheet  MSDS-English  MSDS-French  MSDS-Italian	6.0	0.24	15.5	0.107	0.17	10.7	250	480
Pyrogel <sup>®</sup> 6350  Data Sheet  MSDS-English  MSDS-French  MSDS-Italian	6.0	0.24	15.5	0.107	0.17	10.7	350	660

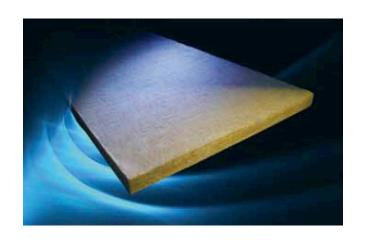
http://www.aerogel.com/



## Aerogel blankets



#### Composite of mineral wool and silica aerogel





Koebel 2007

Brand name: Aerowoλλe®

Thermal conductivity 0.019 W/mK

#### And some other companies

#### Aerogel Composite

- Product: Polymeric (RF) and Carbon aerogels, crushed and compressed into arbitrary shapes
- → http://www.aerogelcomposite.com

PROPERTIES OF CARBON AEROGELS		
Density (g/cm <sup>3</sup> )	0.1 - 0.6	
Surface Area (m²/g)		
Average Pore Size (nm)	4 - 30	
Electrical Conductivity (S/cm)	1 - 10	

#### American Aerogel

- Product: VIPs
- → http://www.americanaerogel.com







#### → Nano High-tech Co, China

Products: everything all others fabricate
 Granular materials, tiles, blankets, hydrophobic, fibre reinforced...



## **Examples of industrial applications**

#### Illuminating systems - diffusers

Basic idea: transparent to translucent aerogel granules scatter light into all directions

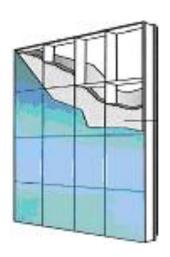
**Technology**: fill hollows plates with aerogel grains.

**Company**: Cabot (brand name: Nanogel) in co-operation with window companies

#### Effects:

a) Diffusive illumination of rooms

b) Thermal insulation







before

after





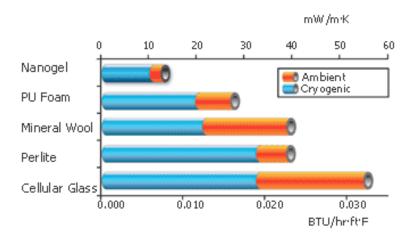
#### Isolation of subsea pipelines

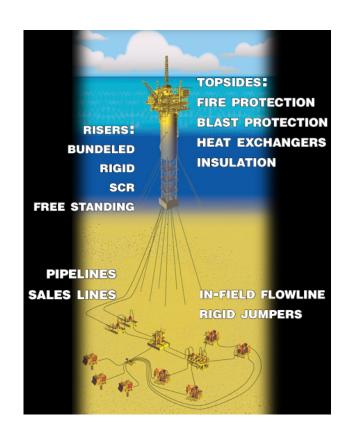
#### Basic idea:

Utilize low thermal conductivity of aerogels

#### Challenges:

- Huge mechanical loads in subsea double walled pipelines (dynamic and static)
- High temperature of the raw oil -> cooling leads to clogging
- High service life







#### **Insulation of Pipelines - solutions**

#### **Vendors:**

- → Cabot
- Aspenssystems

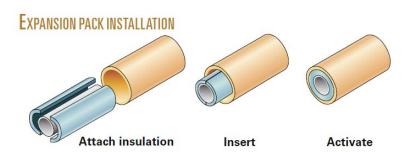


Insert

#### Different technical solutions

Cabot: Compression/Expansion-Pack

Aspen: aerogel blankets



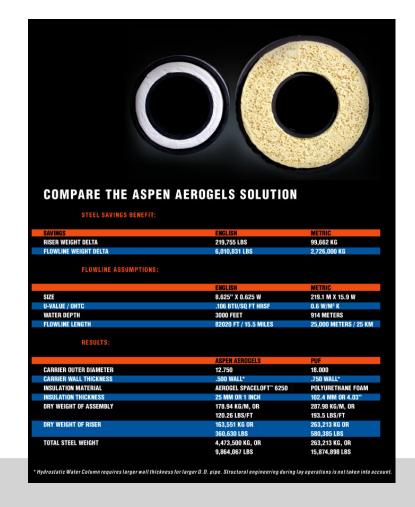
# COMPRESSION PACK INSTALLATION

Sheath, activate

source: Cabot.com

Attach insulation

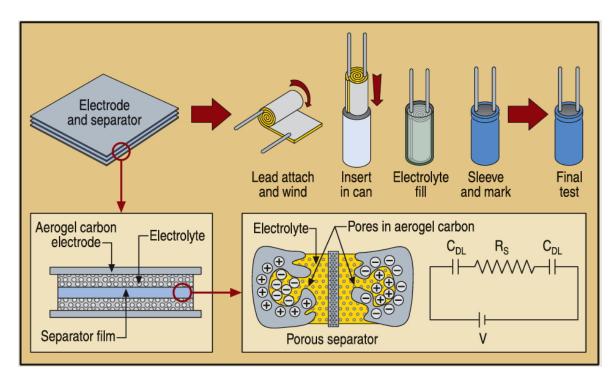




## **Electronic components - capacitors**

Basic idea: use the large internal surface of aerogels capacity is proportional to area!

Material: Carbon aerogels as thin films





Specific values 100 - 300 F/g

Fibre reinforced and CNT additions of aerogels lead to ≈ 750 F/g



#### Home building & insulation - Challenges

- Energy savings by thermal isolation measures
- Regulation of indoor climate
- Light weight material (1-person structural panel)
- → High fire protection class (> F120)
- Utilization of natural construction materials
- No colonization by fungi
- Low cost material

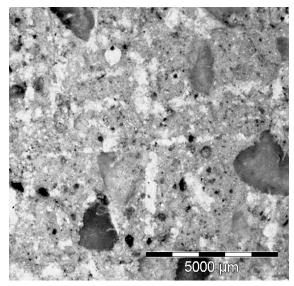


A solution aerogel concrete

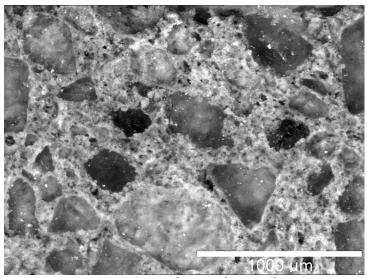


## Aerogel concrete is a

- → composite made from
  - hydrophobic Aerogel granulate and
  - inorganic Binder/Matrix
- binder / matrix materials
  - gypsum or plaster
  - cement or rendering
- → technical challenges
  - Extreme density difference aerogel / matrix
  - Bonding strength aerogelmatrix interface

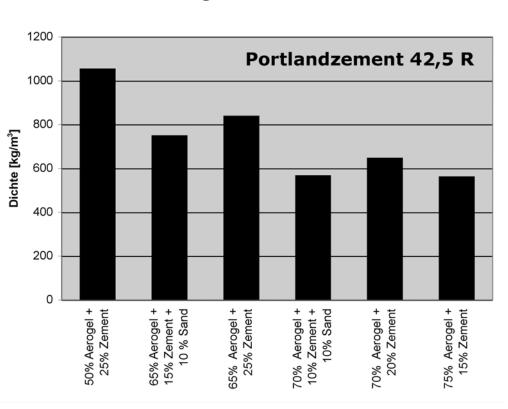


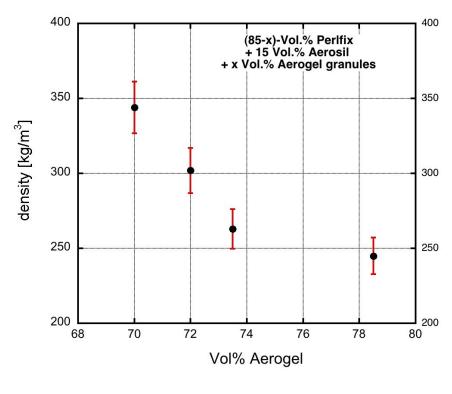
Aerogel granules + Goldband ™



Aerogel granules + cement

#### **Density**





Lowest density with hydrophobic Aerogel granules:

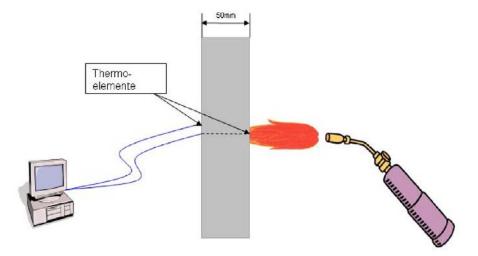
Values between 600 and 1100 kg/m<sup>3</sup>

Lowest density material made by us: Pure building plaster with ≈ 80% aerogel granules at 250 kg/m<sup>3</sup>

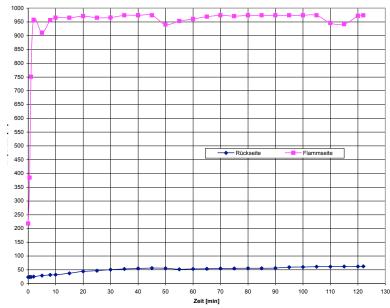


## Fire protection

- → requirement: better than fire class F90
- → Laboratory tests close to DIN-Norm









## Thermal conductivity and U-value



Aerogel content [vol%]	Heat conduction [W/mK]	U-value (25 cm wall thickness)
65% (+10% Sand)	0,16	0,64
70% (+10% Sand)	0,11	0,44
70% (without Sand)	0,13	0,52

construction material	wall thickness	U-value [W/m²K]
massive concrete	25 cm	3,3
common brick	24 cm	1,5
common brick (17,5 cm) plus PUR damping	30 cm	0,32
honeycomb brick	25 cm	0,34 - 0,46
massive wood	20,5 cm	0,5
timber frame construction	25 cm	0,15 - 0,2

# The future of aerogel concrete in the Netherlands?



Built by students of the University Duisburg-Essen

Canoe made form high strength concrete and aerogel to save weight.



#### Other solutions

- → Structural panels:
  - Composite of PU-foams or styrofoams plates with aerogel-infiltarted felts

U-value=0.34

→ Aerogel wrap for storefront



Stadur-Süd



#### Foundry applications

#### Casting of metals in a mould needs a mould material

Mould materials: sands = sand casting

metals = permanent mould casting

ceramics = investment casting

Sand grains must be bonded!

#### Binders used:

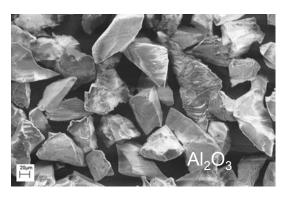
oils, polymers (phenol based, polyurethane, epoxy resins,...) water glass,...

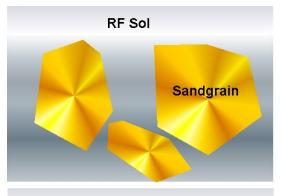
new: binder = RF Aerogel = AeroSand

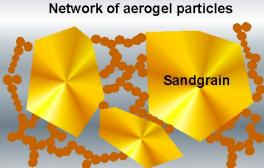
#### **Technology:**

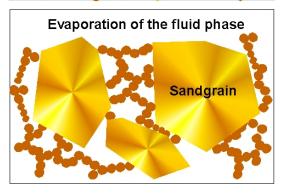
Preparation of RF-sol, mixing with sand, core shooting, ambient drying, ready!











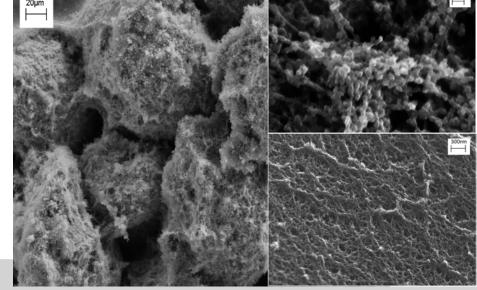
Brück-Ratke Giessereiforschung 56 (2004) 55 - 65 Voss-Ratke Giessereiforschung 57 (2005) 18-25 Reuß-Ratke Giessereiforschung 61 (2009) 24 - 33

#### **AeroSands - real structure**

RR 10µm

RF-Aerogel with corundum sand

Carbon aerogel with Corundum sand

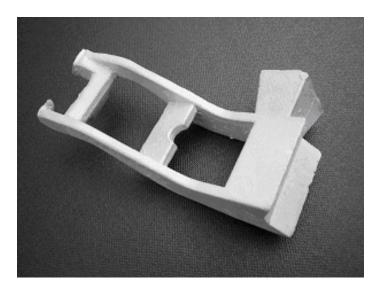


#### **AeroSands - properties**

- → Easy core removal
- → Thermal conductivity 0,3 2 W/Km
- → High strength 100 to 600 N/cm²
- → Smooth surfaces
- → No shrinkage
- → No gas release during casting
- → Insensitive to humidity







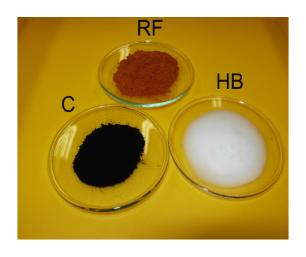
#### Aerogel based additives

#### idea:

Mix aerogel granules with foundry sands to improve the cast piece and work without a facing

#### utilizing:

- Large surface area
- High adsorption capability
- Non-wetting with metals



#### Granulate from

- Silica-Aerogel (sc and ambient dried)
- → RF Aerogel
- Carbon aerogel

#### Particle size:

- → Fits to sand grain size
- > Volume fraction: ≤ 5 Vol.%

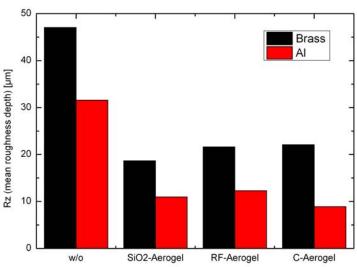
#### → Binder:

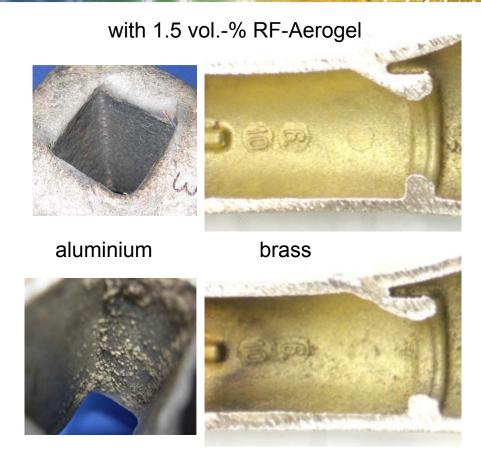
- Whatever is used in a foundry shop
- → RF-aerogel binder



#### **Aero-Additives**







w/o Nano-Additives

Effects of aerogels in brass, aluminium and bronze castings

## **Summary**

Oxide aerogels, polymeric aerogels, mixed aerogels, hybrids, composites with fibers and felts offer a wide variety of applications going far beyond what is explored today and is on the market.

"The global market for aerogels is expected to grow up from \$62 Million in 2006 (700t) to \$951 Million in 2011 (12,679t)." JOM 58 (August 2006) 10-11

