

# Porosity as a contributor to solutions for sustainable production

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# Outline

- **Introduction**
- **Ceramic membranes**
- **Porous scaffolds for bone regeneration**
- **Ceramic foams as filter or as catalytic support**
- **Conclusion**



# Introduction

## **Sustainable manufacturing must be:**

- more efficient and less energy consuming
- non or less polluting
- resource efficient
- improved components

## **The use of porous materials can be a solution**

- ceramic membranes
- porous orthopedic implants
- ceramic foams as filter or catalytic support

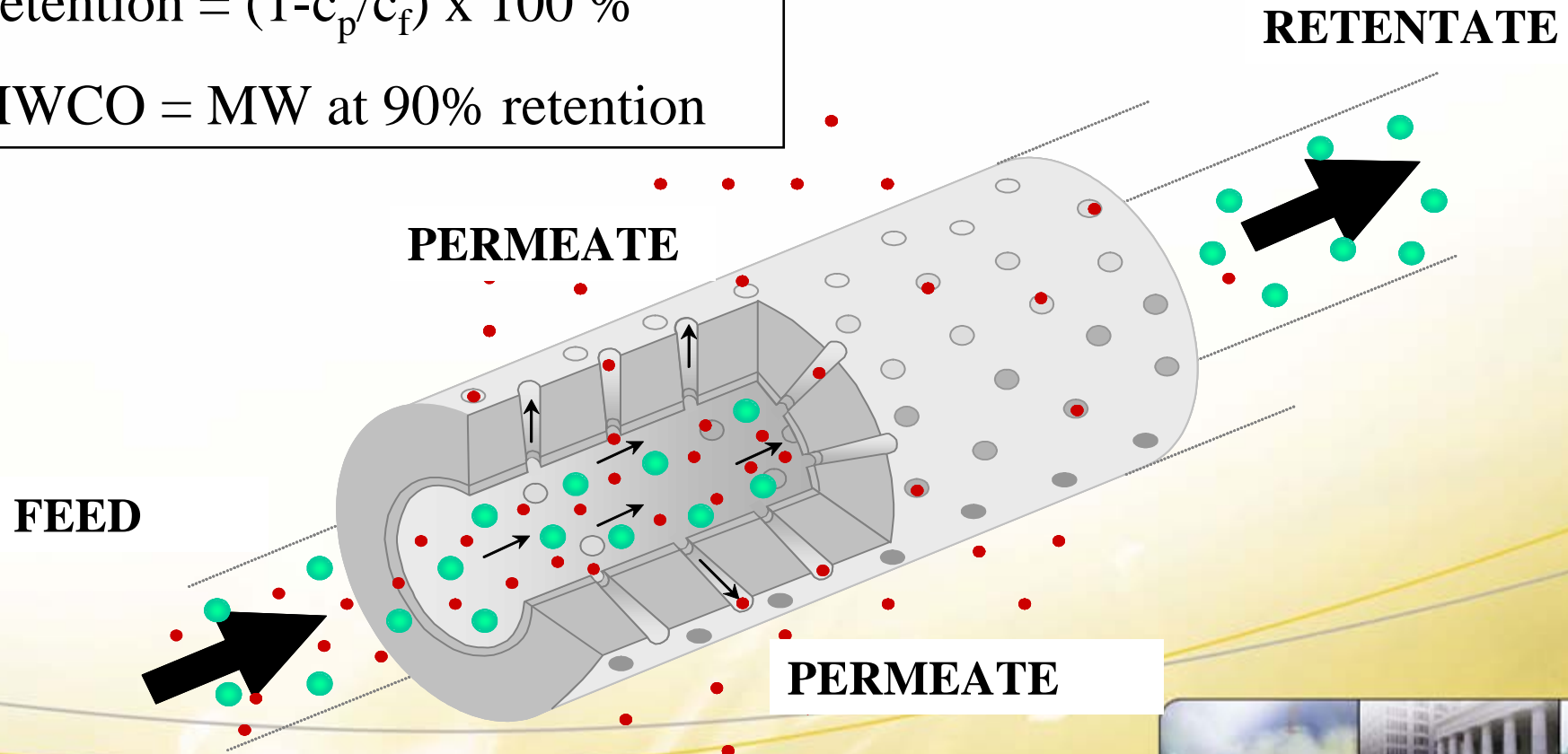


# Membrane filtration

Permeability (l/hm<sup>2</sup>bar)

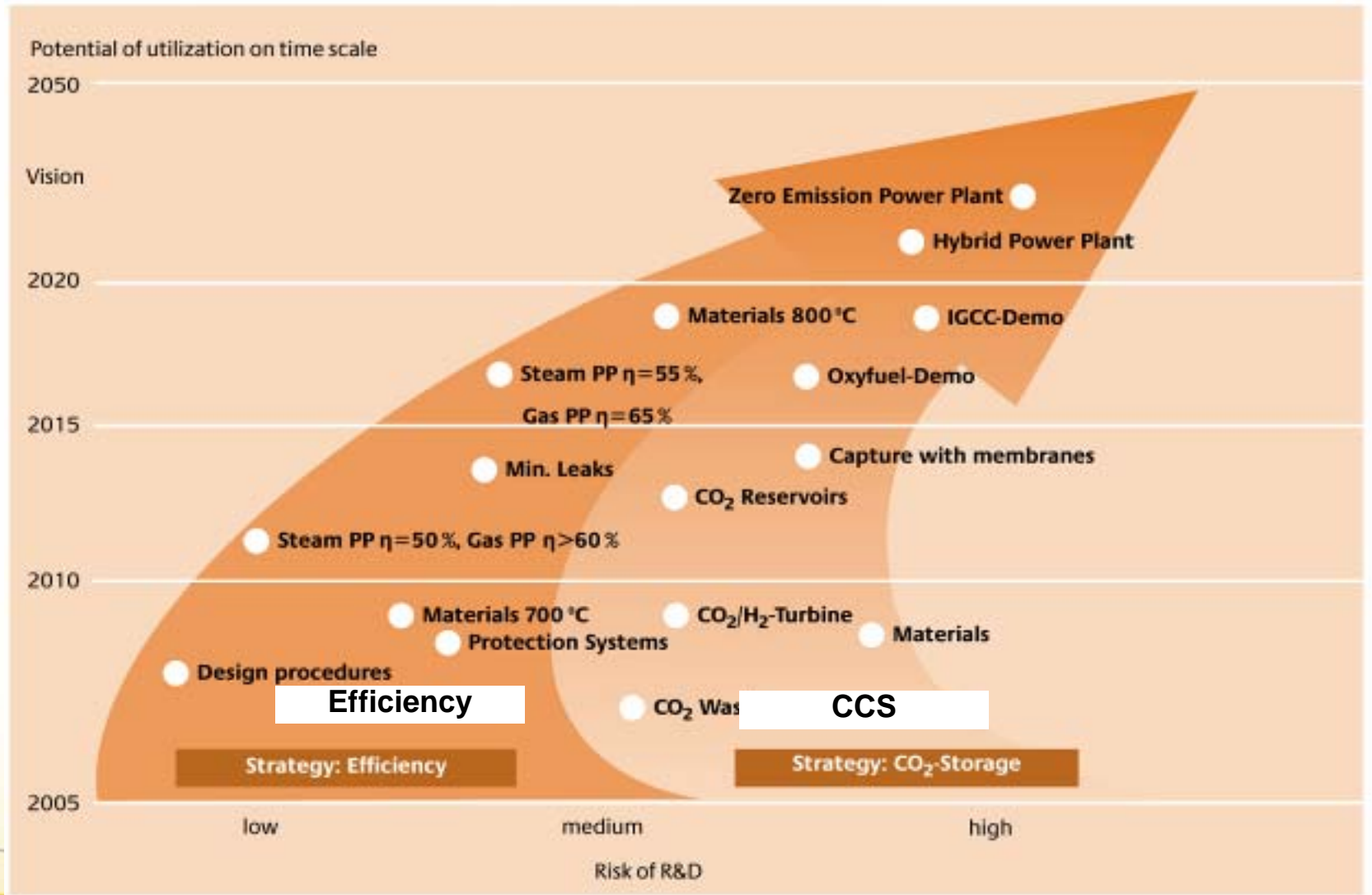
Retention =  $(1 - c_p/c_f) \times 100 \%$

MWCO = MW at 90% retention



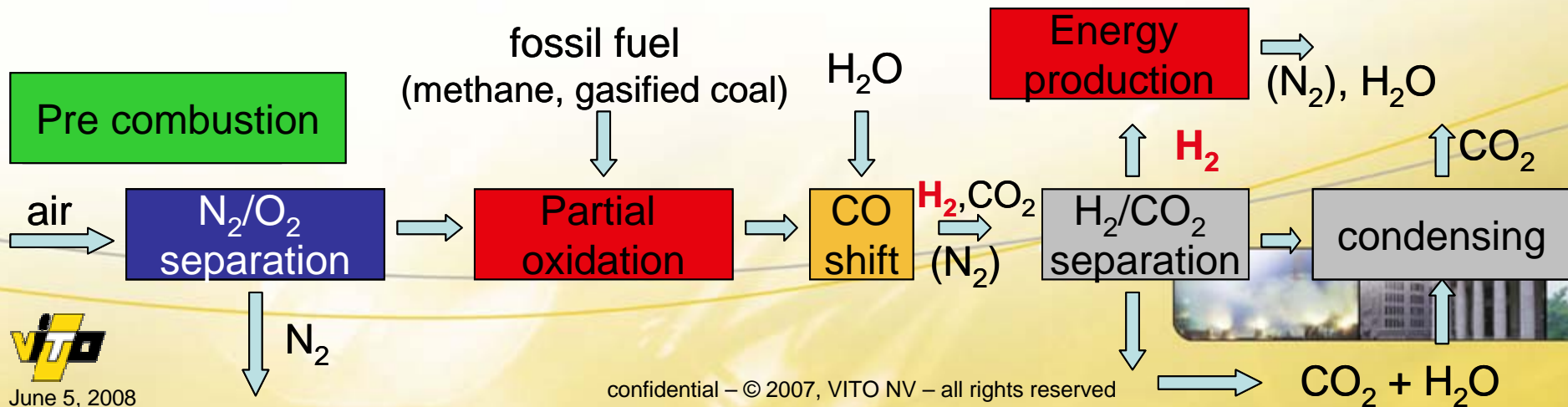
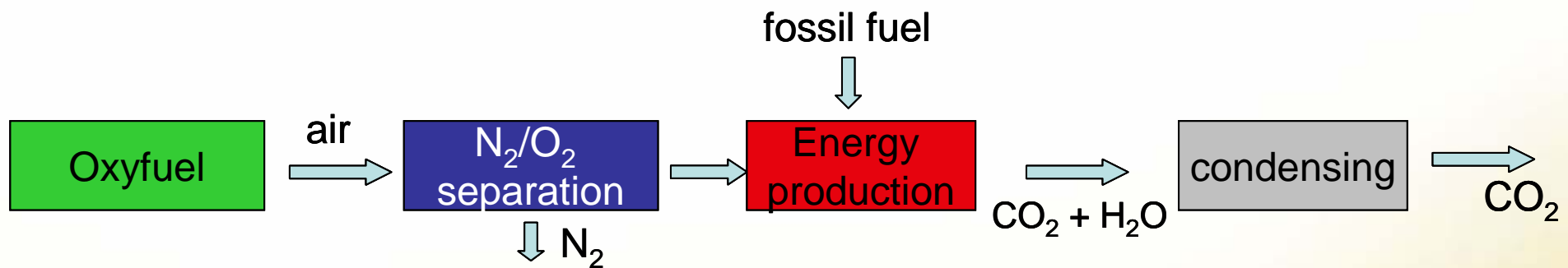
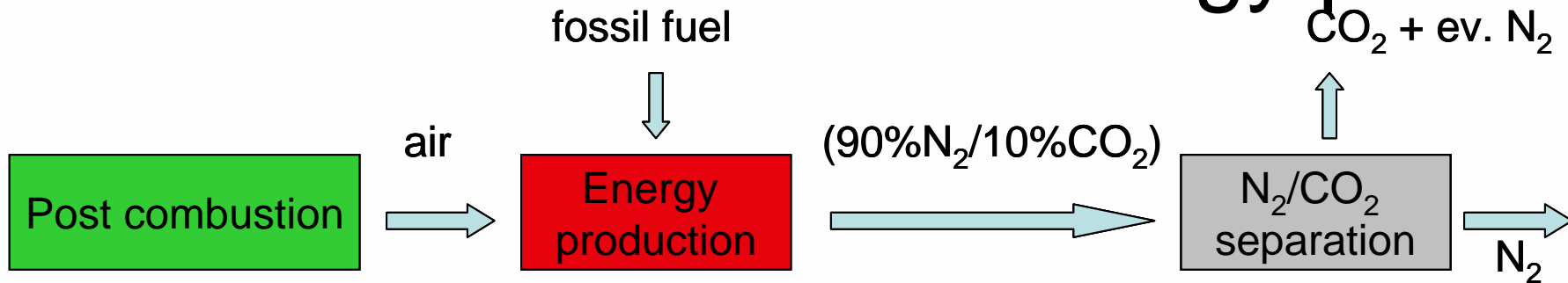
# Approaches to reduction of CO<sub>2</sub> emission

## Direction of research in the field of power plant engineering



Data source : German COORETEC initiative

# Routes for sustainable energy production



June 5, 2008

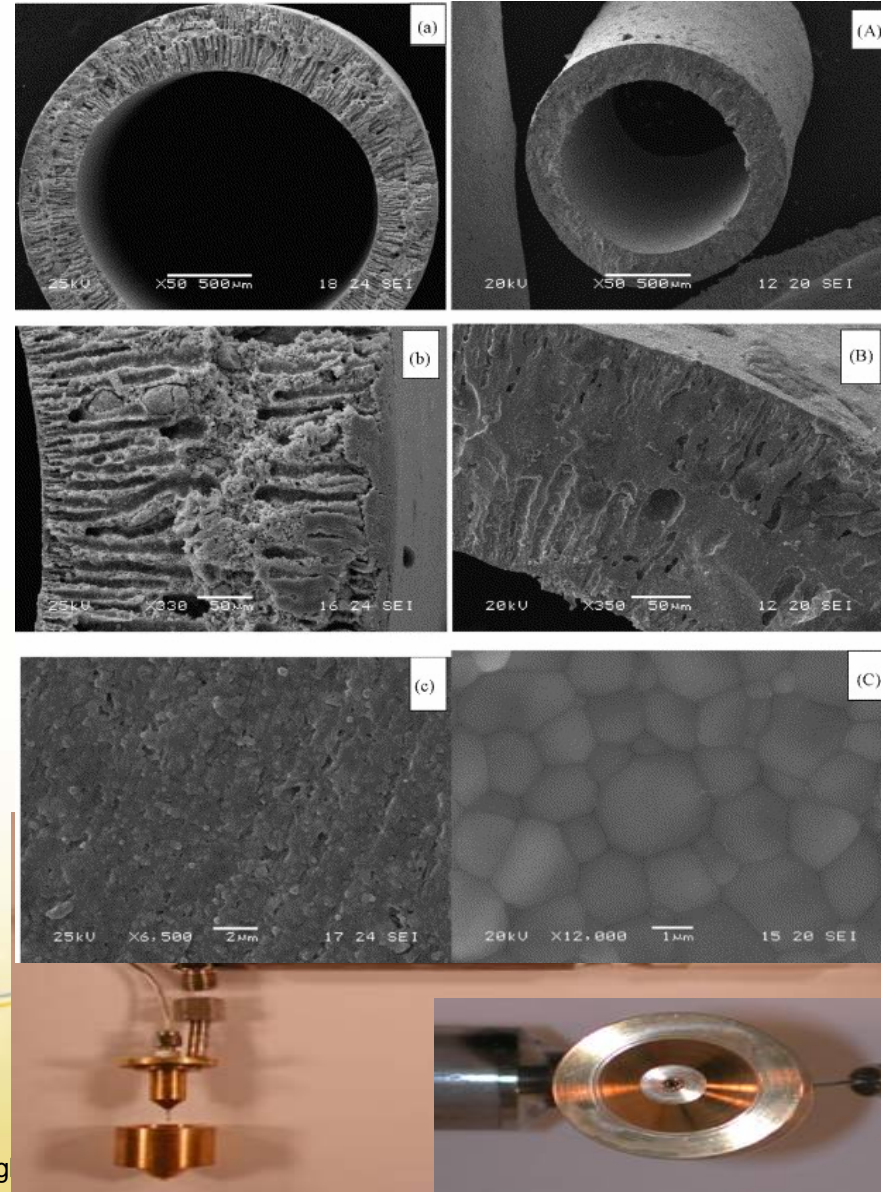
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# Ceramic hollow fibers

- Dens ceramic (proton and oxygen conductors) membranes, hollow fibers
- High surface area to volume ratio of hollow fibers enhance membrane fluxes
- Spinning with phase inversion,
- Bending strength upto 80 MPa

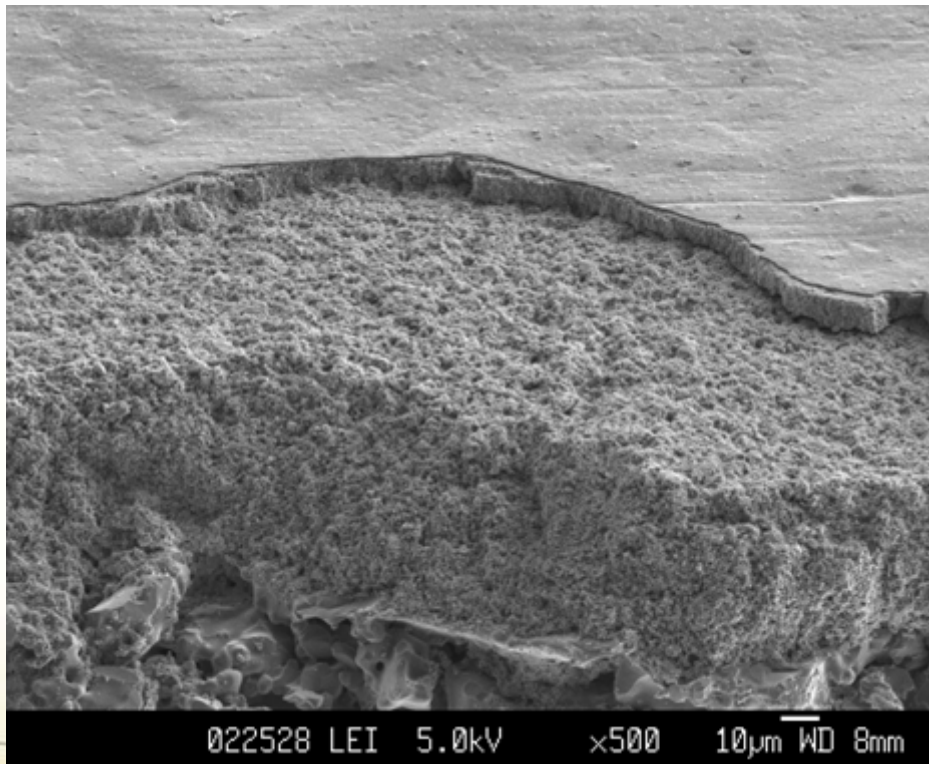
VITO participation in 'MEM-BRAIN'-project (FZJ, Helmholtz-institutes)

J. Luyten, A. Buekenhoudt, et al., Preparation of LaSrCoFeO<sub>3-x</sub> membranes, Ceramic Trans., vol 109.



# Ceramic NF membranes

High flux + retention : multilayer structure



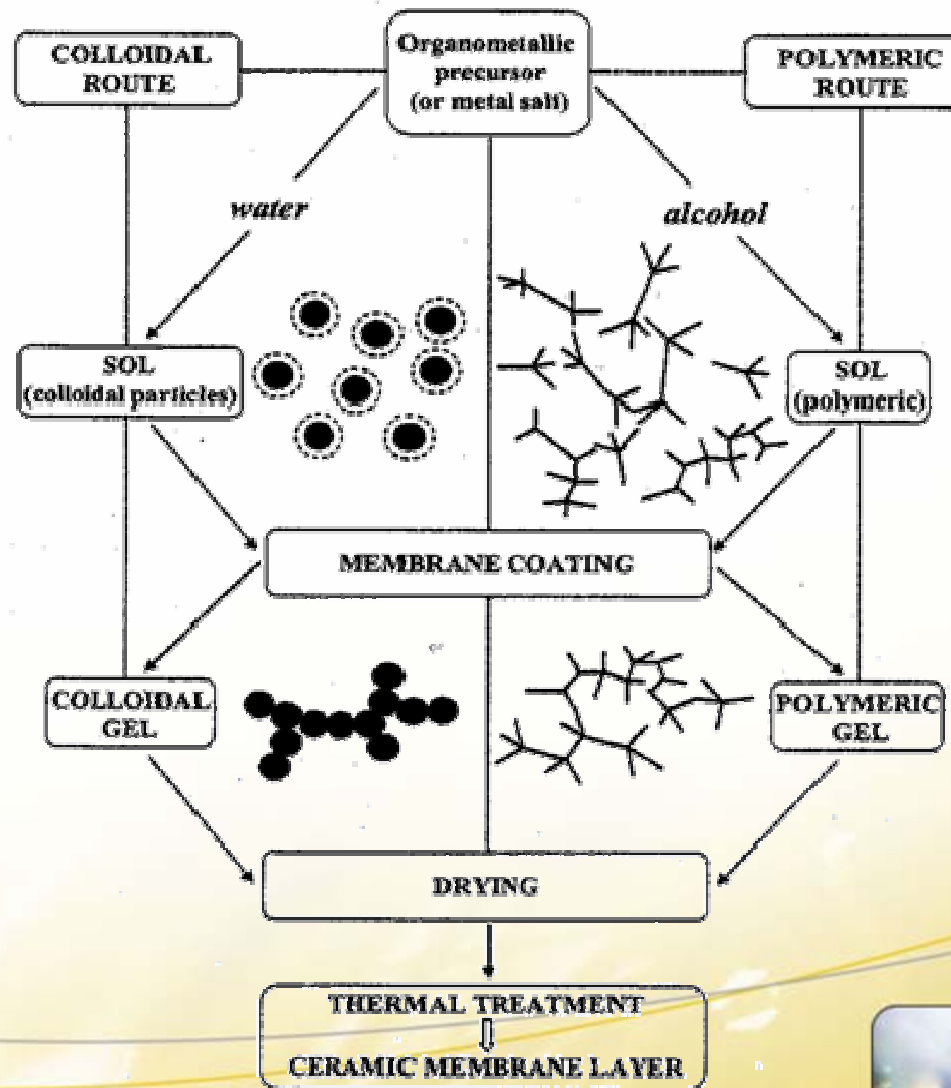
1 or 2 toplayers (NF)  
2 interlayers (UF)

support



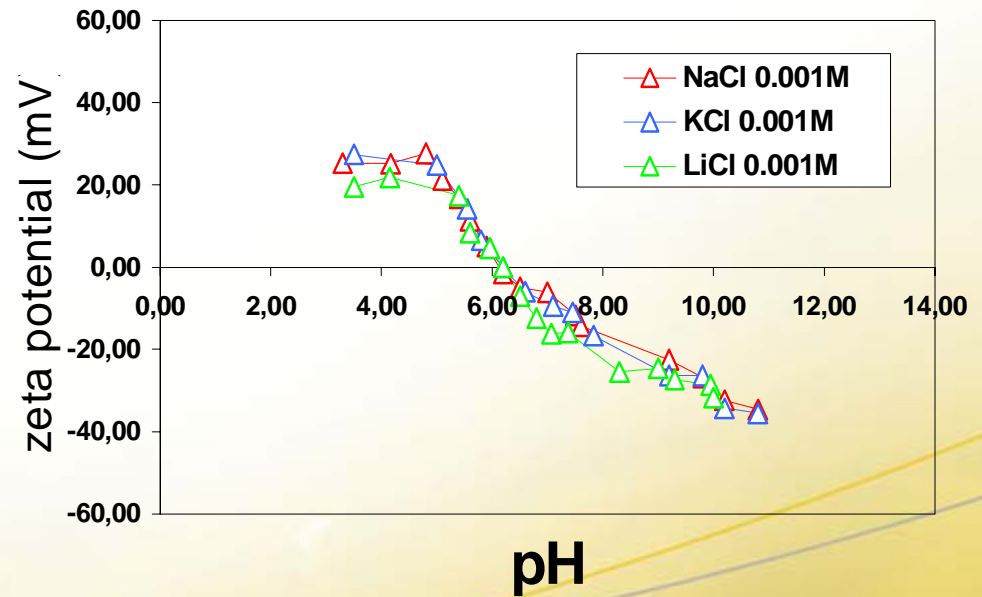
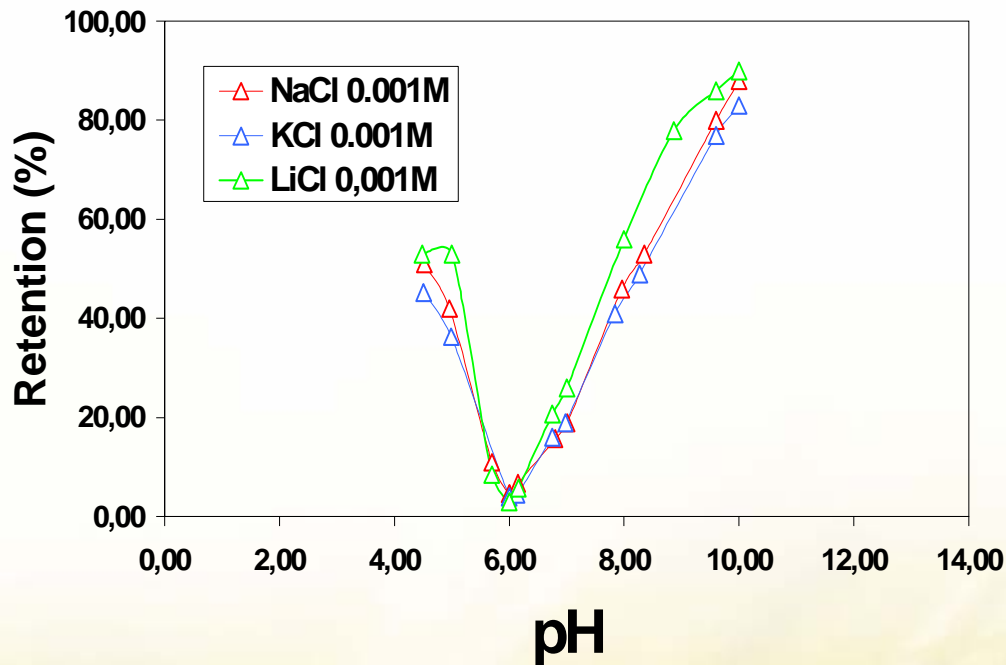


# Sol-gel coating (colloidal, polymeric)



# Separation performance in water

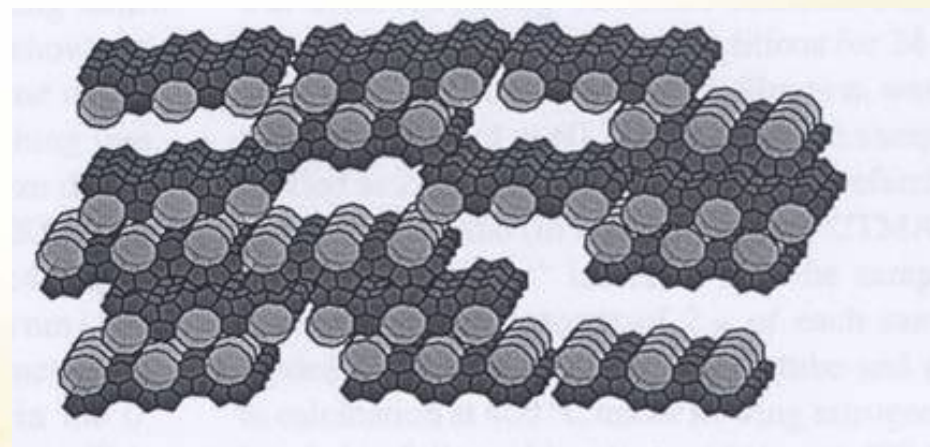
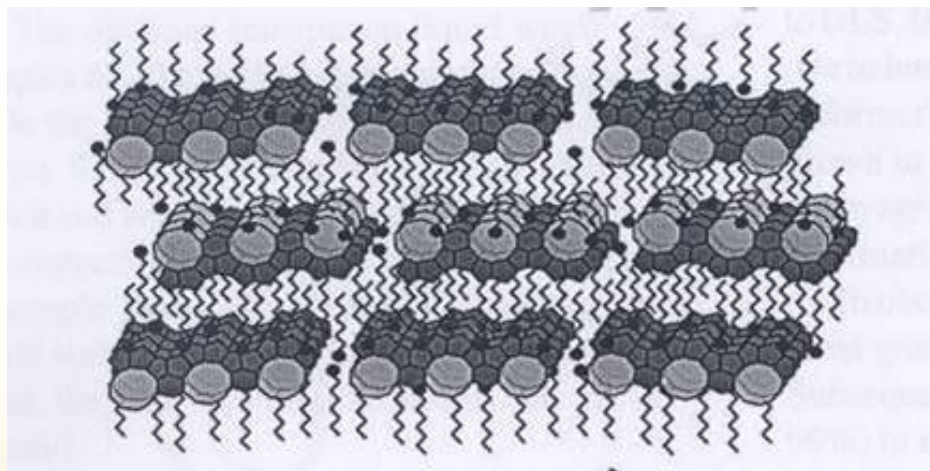
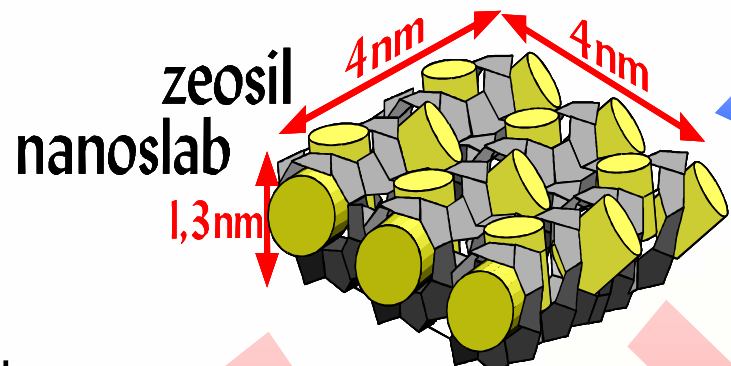
Salt retention : monovalent salts on  $\text{TiO}_2$  NF membrane



# Zeogrid powder

Recently discovered know-how [X] :

- Nanoblocks can be stacked in an ordered way with the use of appropriate surfactants
- Leads to micrometer large grains called zeogrid
- Zeogrid calcined has dual porosity : micropores(0.5nm)+ interblock voids

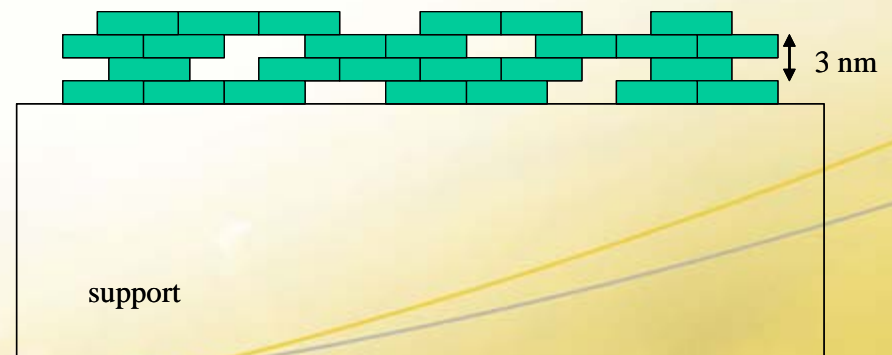


[X] Kremer at al., Adv. Funct. Mater., 12, 286, 2002



# A new generation of zeolite membranes

- Zeogrid on support : dipping in solution of nanoblocks + surfactants
- thin membranes < 100 nm : high flux, crack free, high selectivity
- simpler production than hydrothermal synthesis



# Zeogrid layer on porous support

Supports :

flat and tubular

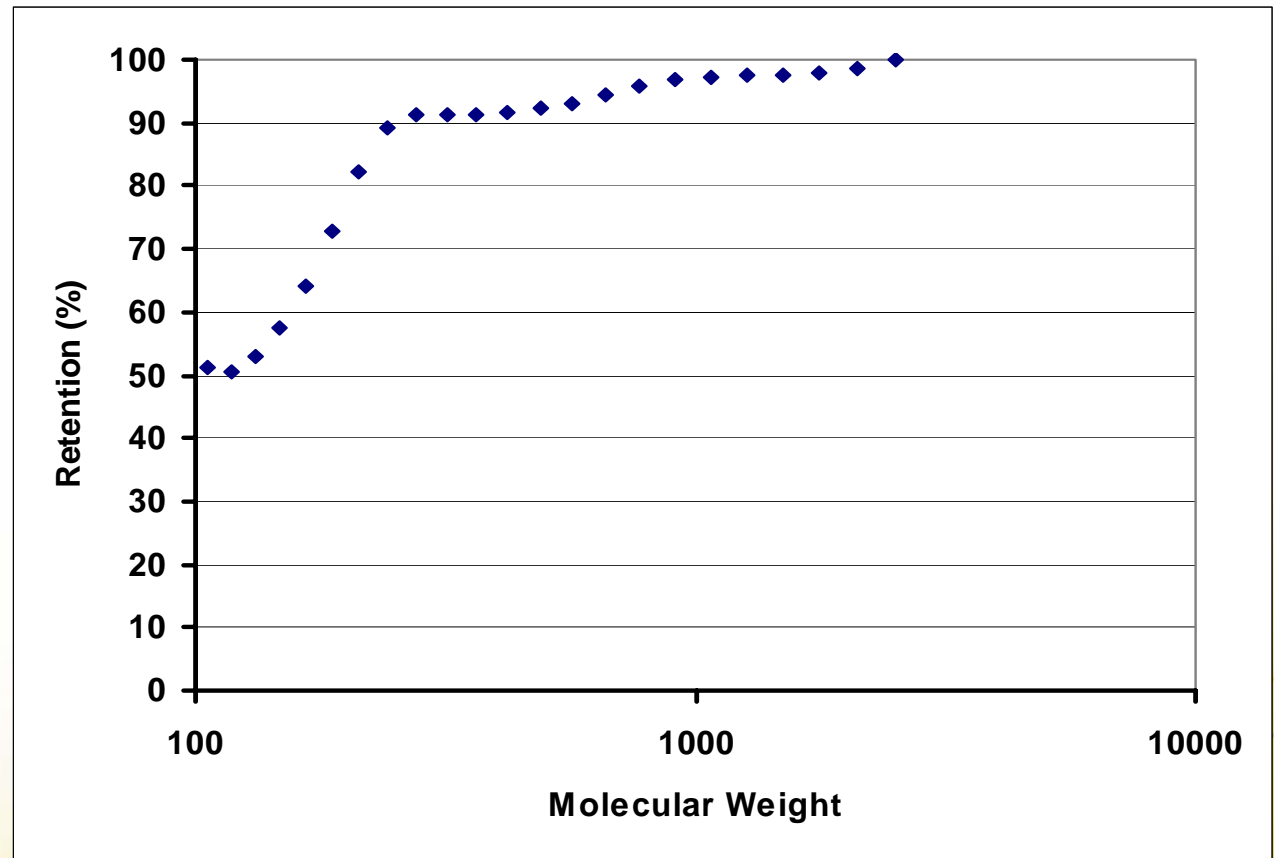
$\alpha$ -Al<sub>2</sub>O<sub>3</sub> (100 nm)

and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub>

(50 nm) + TiO<sub>2</sub> (3nm)

Zeogrid coatings :

with surfactant



# Ceramic Foams

- **Ceramic foams are a cellular material with a broad field of applications:**  
filters for molten metal, dust and soot filters, scaffolds for bone replacement, high temperature isolation,...
- **Application performance is strongly related to cell size, window opening and other structural parameters**
- **Objective is to produce ceramic foams with sufficient strength and controlled micro-macro structure.**
- **We produced ceramic foams by:**
  - A reaction bonded PU replica technique
  - Biogelcasting of foams
  - Hollow beads method
  - Robocasting



# Manufacturing routes

## 1. PU Replica technique

metallic aqueous suspension  
↓  
Infiltration/coating polymeric foam  
↓  
Removing excess

## 2. Bio gel casting

metallic suspension + foaming agent + gelling agents

↓  
Foaming of mixture  
↓  
Moulding  
↓  
Gelation

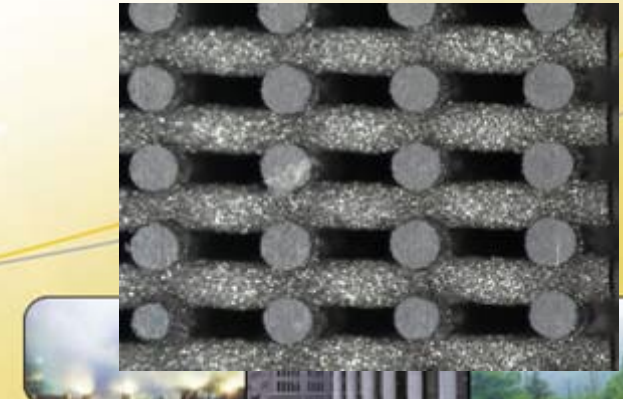
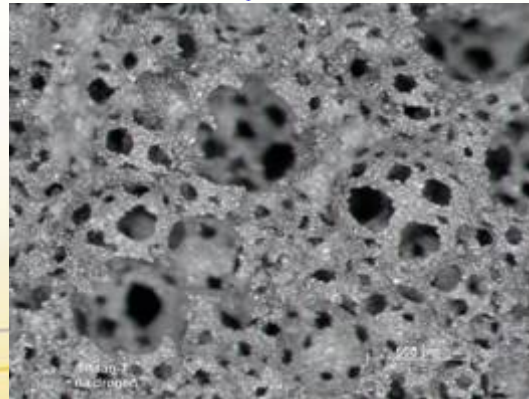
## 3. 3D fiber deposition

Viscous metallic paste  
↓  
Extrude through thin nozzle  
↓  
Computer controlled deposition of fibers

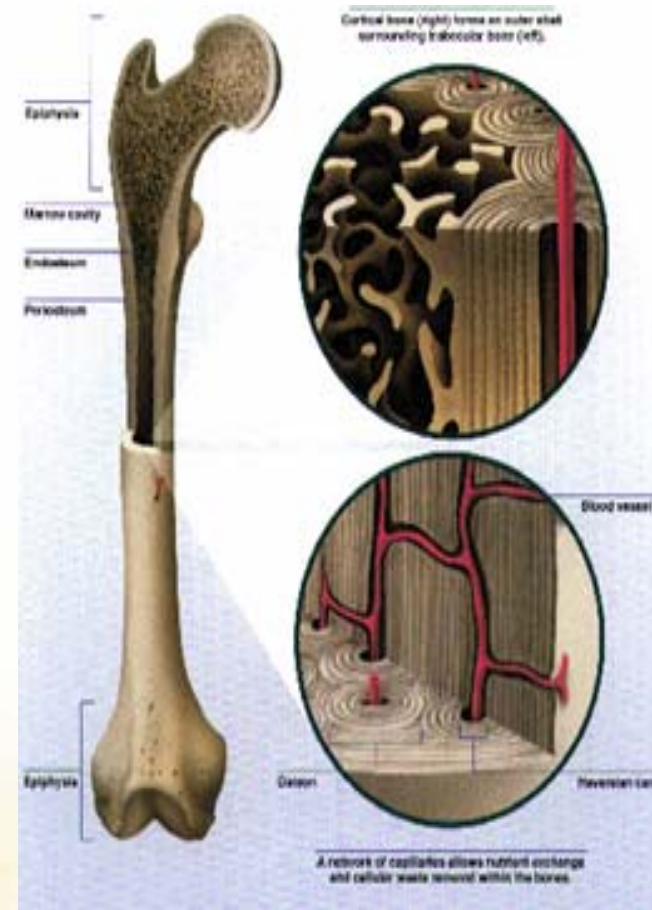
↓  
Drying, calcination

↓  
Sintering

↓  
Porous Metal Structures

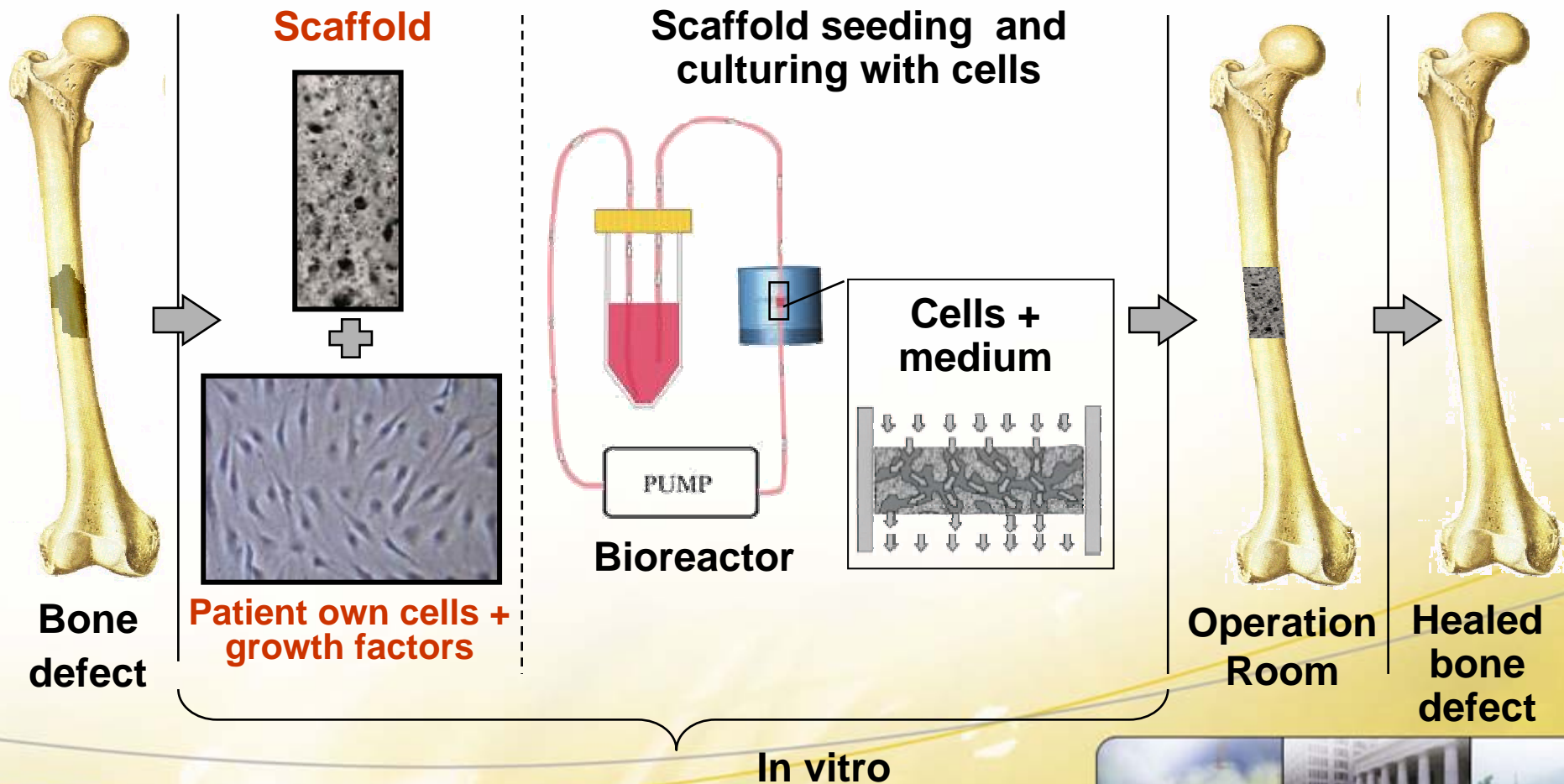


# Quality of Life of elder people



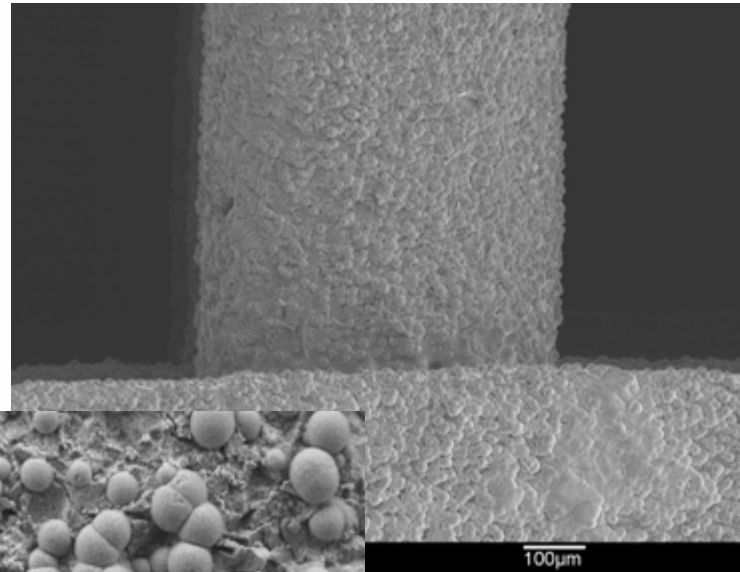
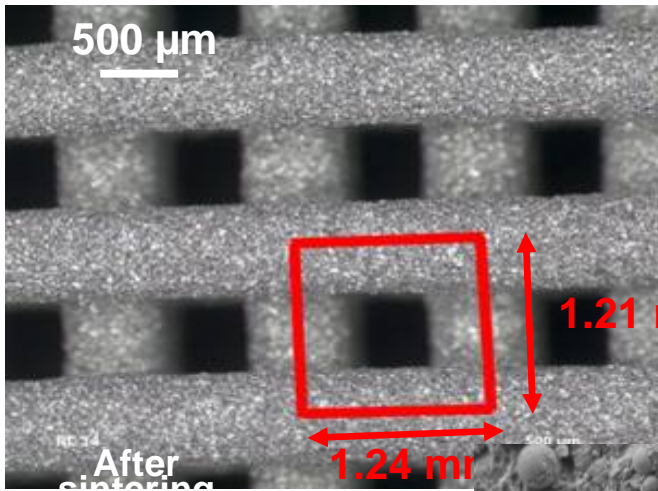


# Tissue Engineering for Bone generation



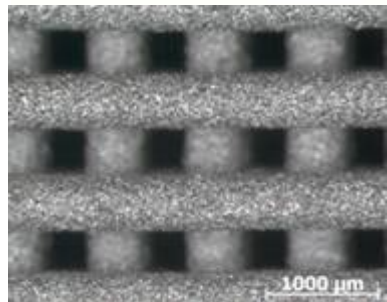
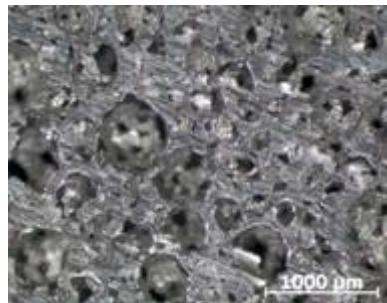
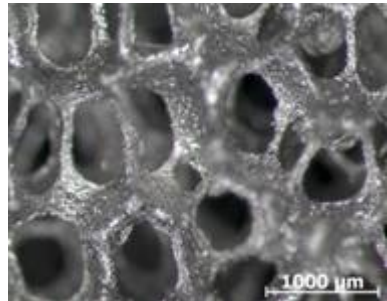
# Orthopedic Implants

## Ti-foams + biomimetic coating



# Drug delivery system

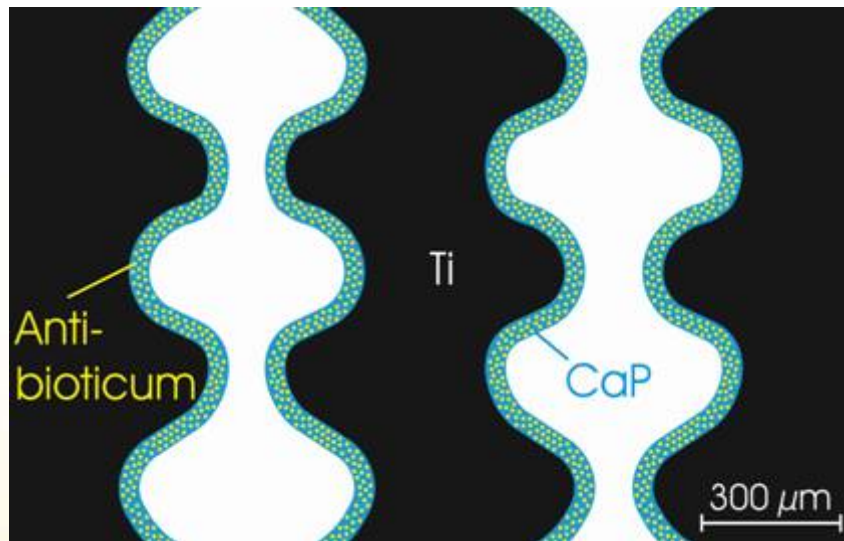
Porous Ti-structures



Local drug delivery system

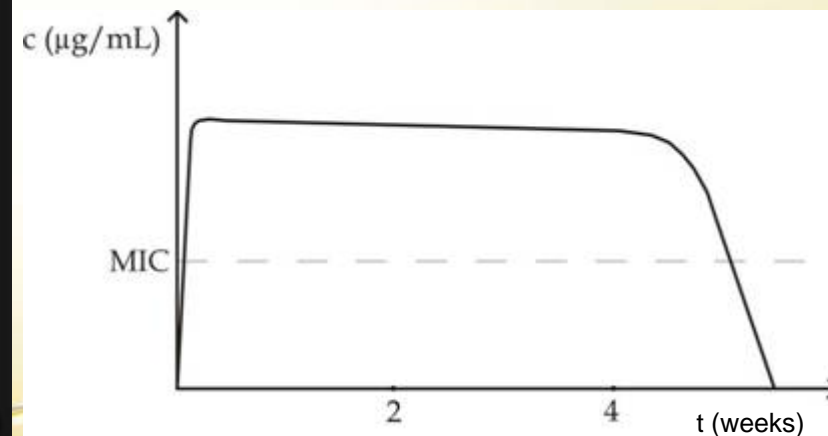
CaP coating

- osteoinductive
- drug delivery matrix



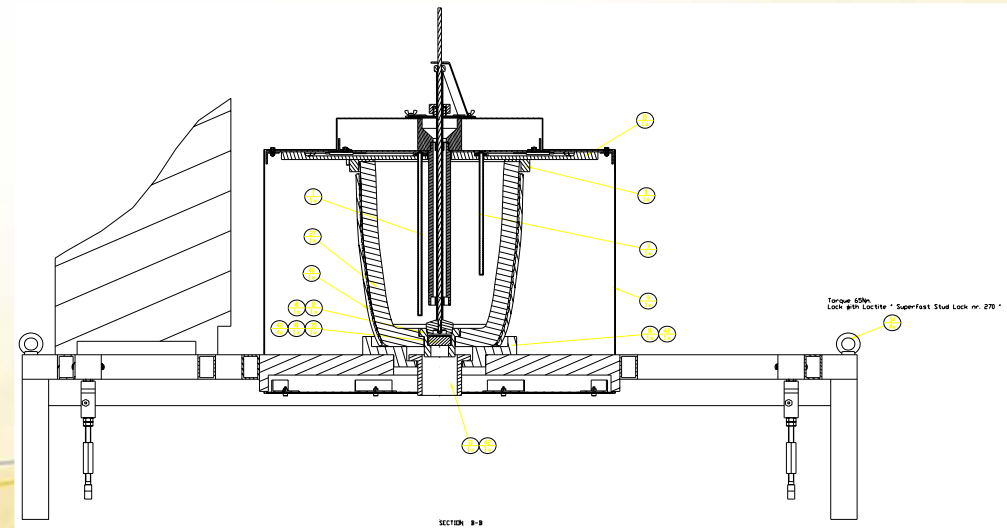
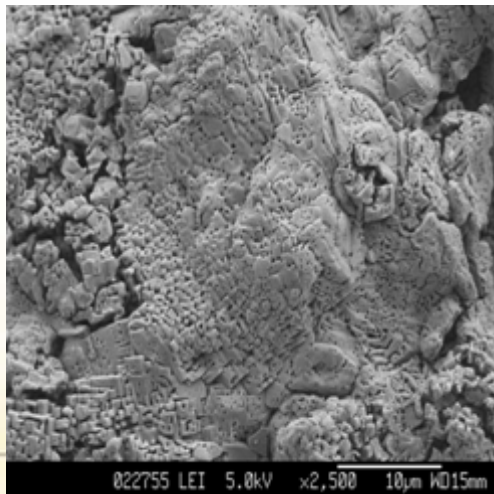
optimal release profile

- initial burst release
- therapeutic concentrations from a few weeks till some months
- sharp release fall at the end



# Filter for Molten Metal

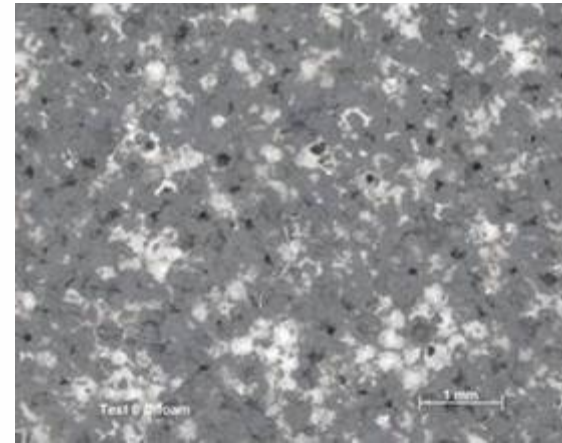
- EU project Al recycling project aiming to remove intermetallic materials from the molten melt
  - RB Mullite replica technique,
  - with a gradient in cell size
  - coated with a salt
- Filter tests



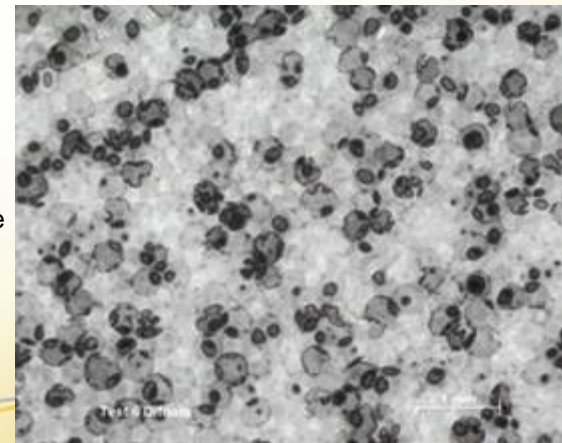
# Soot Filter for diesel cars

- 90% removal of particles with low pressure increase.
- Replica technique on different Pu cell sizes
- Improve strength by using RB-processing
- Can be washcoated

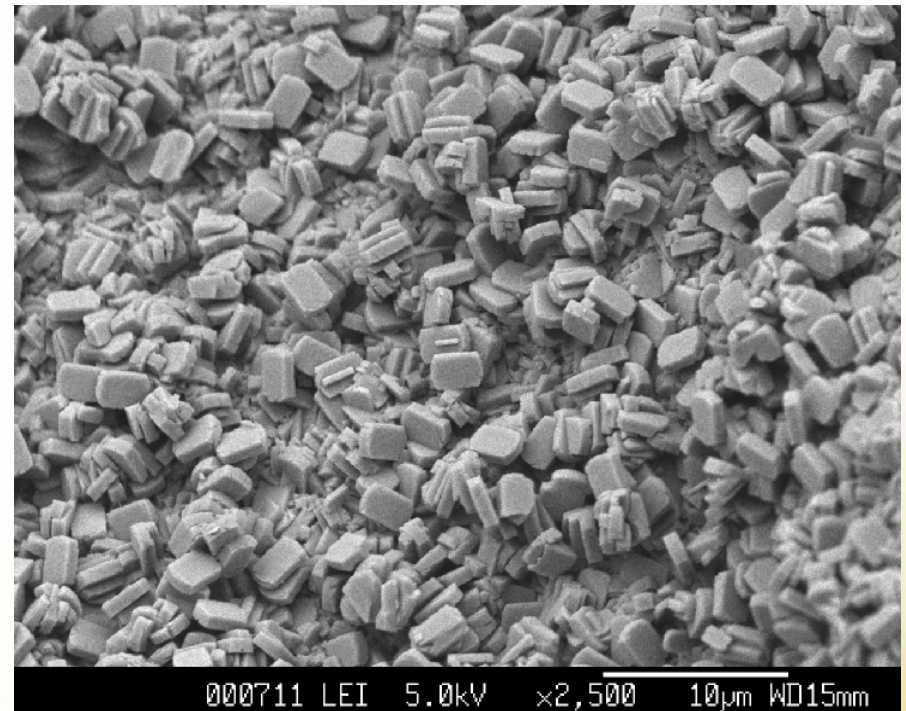
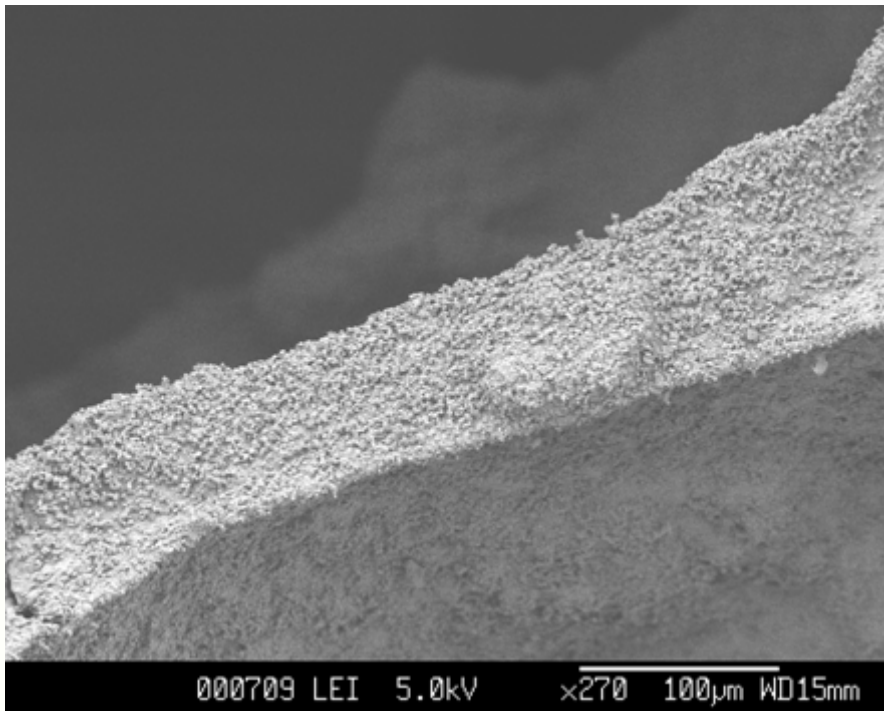
Inlet side



Outlet side



# Zeolites on a Catalytic ceramic foam



# Conclusions

- **Sustainable production is a need**
- **We demonstrate that different kind of porous materials can contribute to such process improvement**
- **Special attention was given to the use of ceramic membranes and to different application with ceramic and metallic foams**





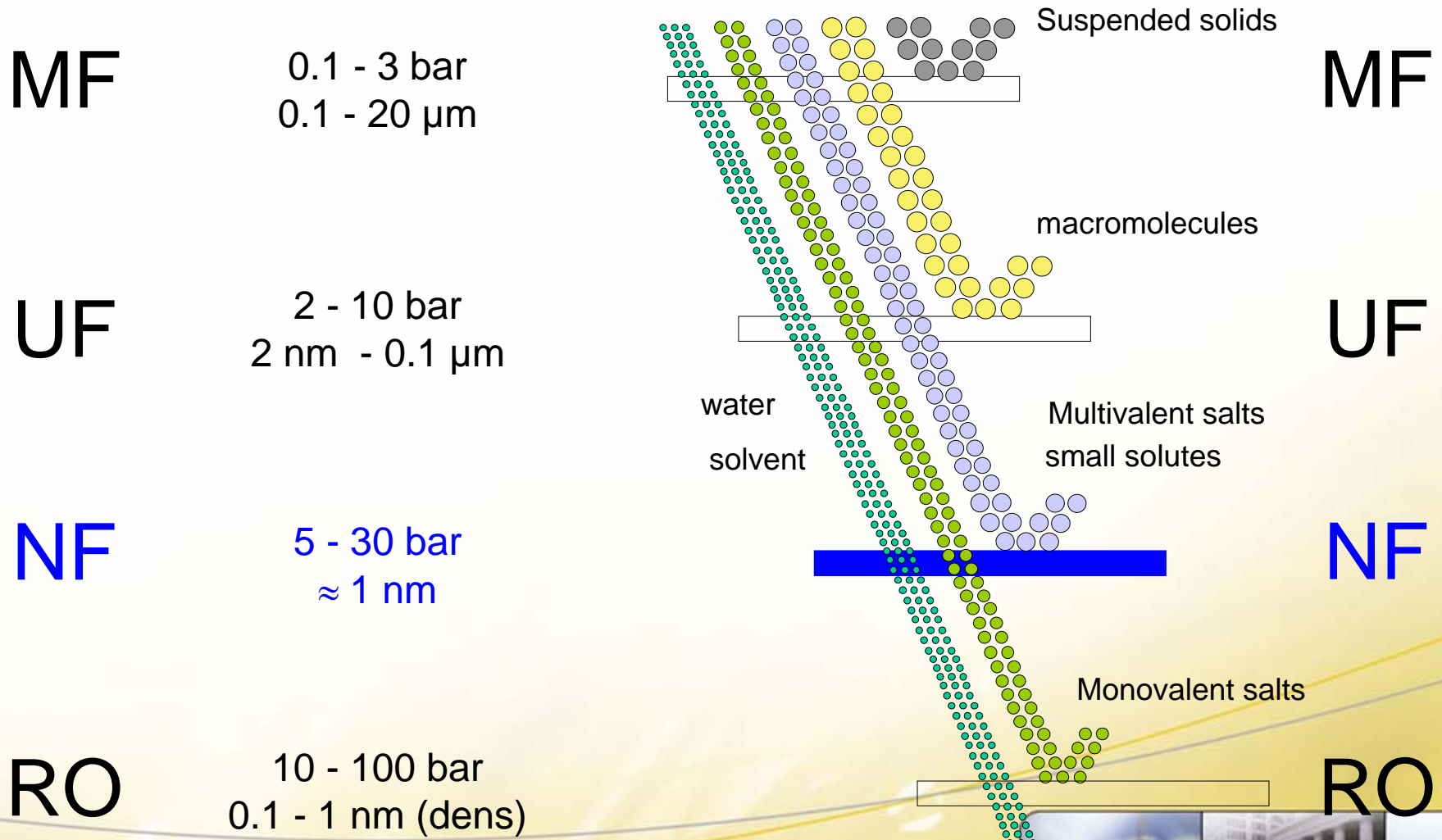
June 5, 2008

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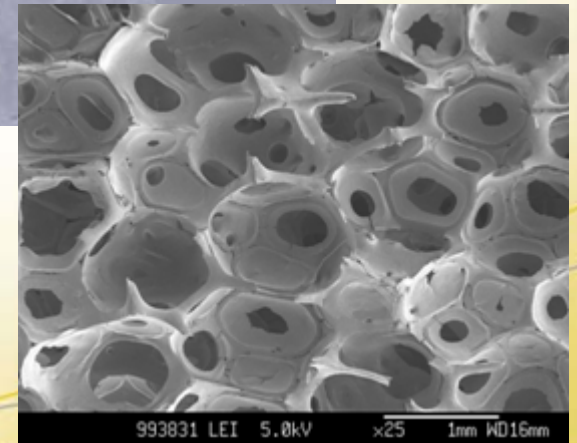
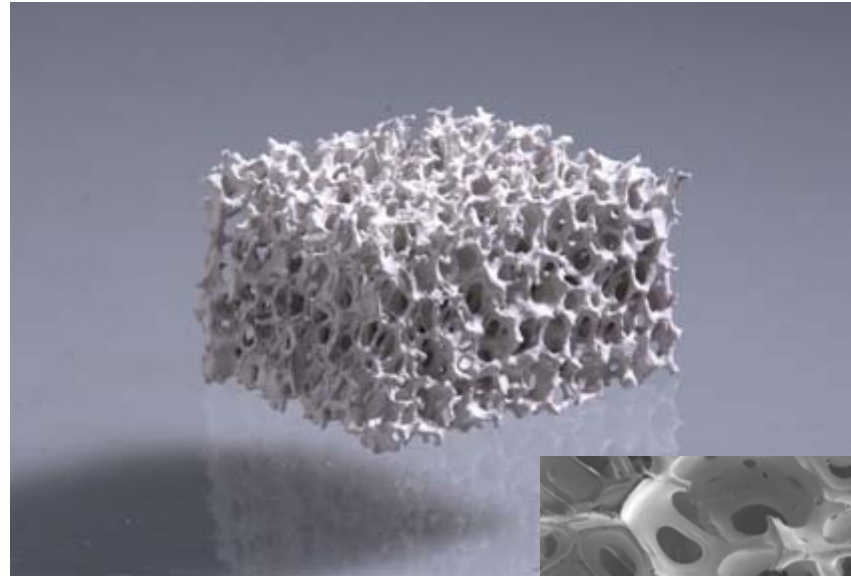


# Different pores : different filtration proces



# Reaction Bonded Modified Replica Technique

- Preparation of the metal/metaloxide mixture
- Preparation of an aqueous slurry ( no gas evolution, rheology)
- Coating of the PU-sponge, squeezing and drying
- Calcination and oxidation
- Sintering



# Gel casting

Ceramic suspension

Foaming agent

Hydrocolloid

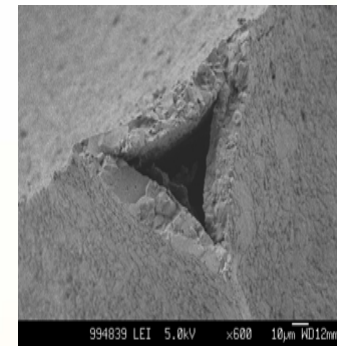
Mixing/foaming

Moulding

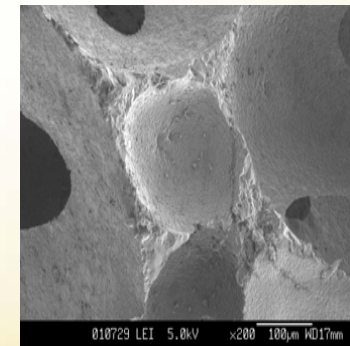
Gelation

Thermal treatments

Ceramic foam structure



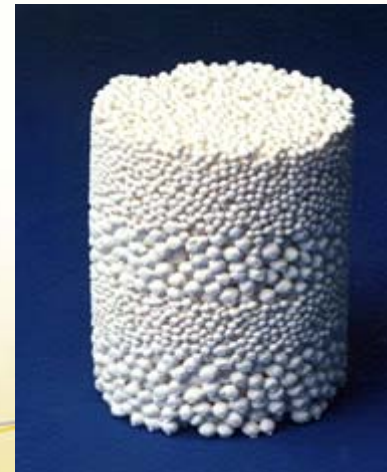
1a)



1b)

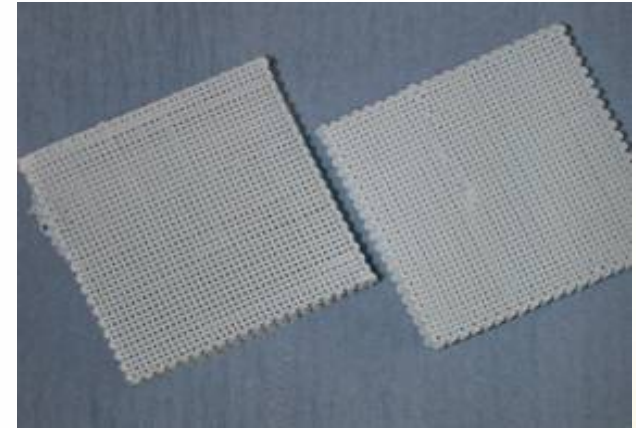
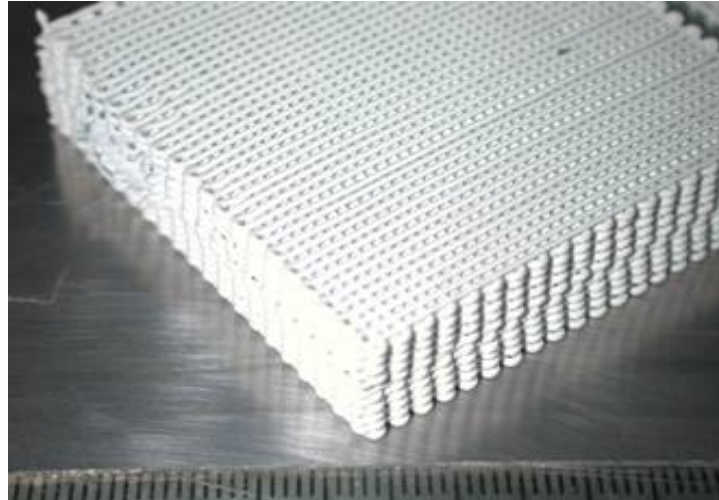
# Hollow beads method

- Preparation of the slurry
- Coating of the sacrificial cores (peas, seeds, styrofoam granules,...)
- Packing of the cores
- Second coating
- Thermal treatments (drying, calcining, sintering)

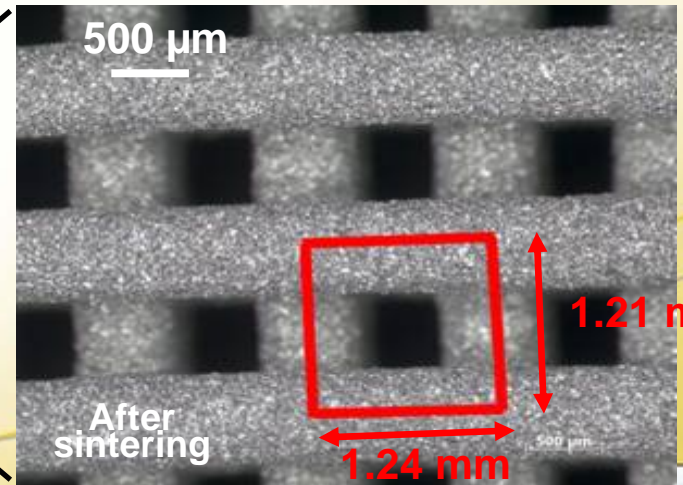
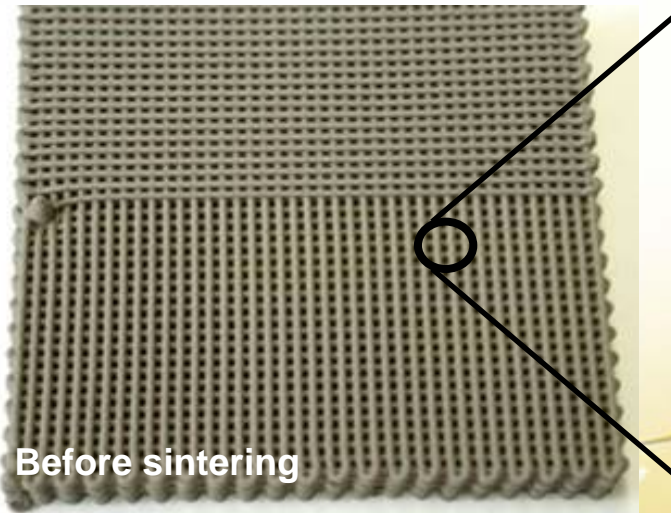
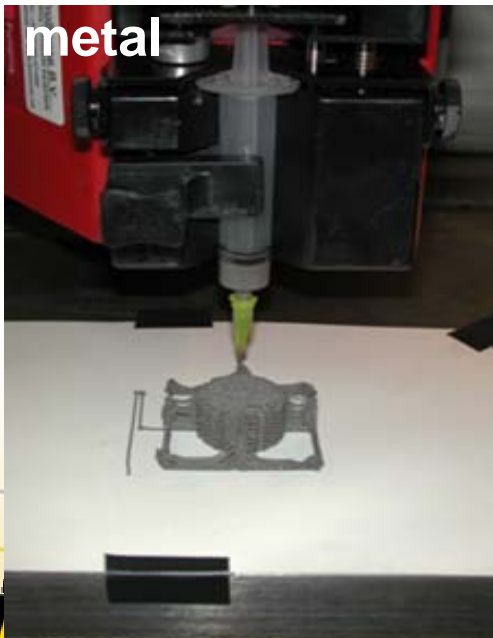


# 3DFD

Hydroxyapatiet



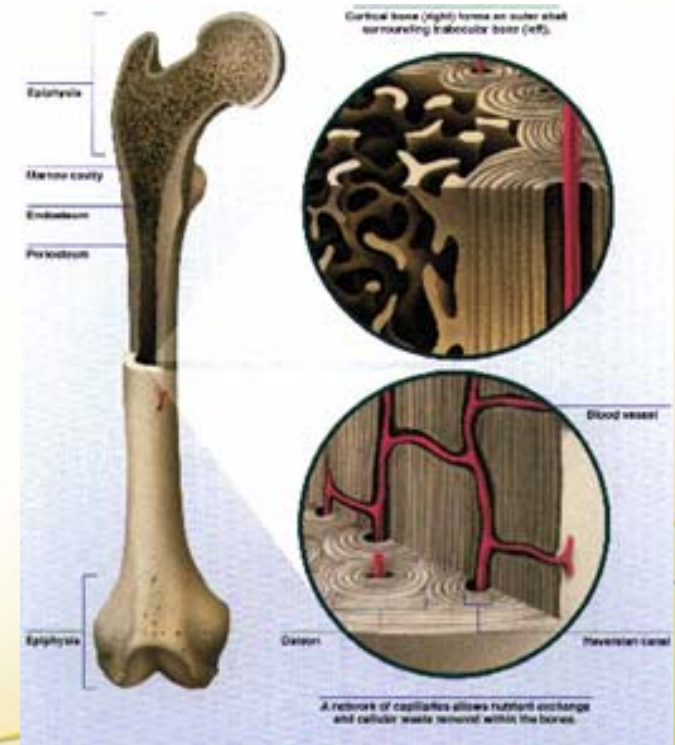
metal



After sintering  
~40-50 %TD  
Pore sizes ~500 x 500 μm

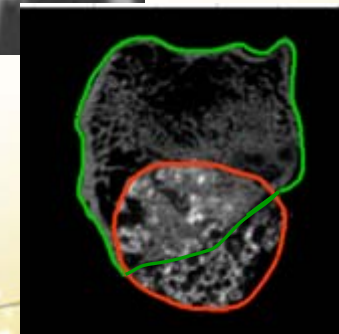
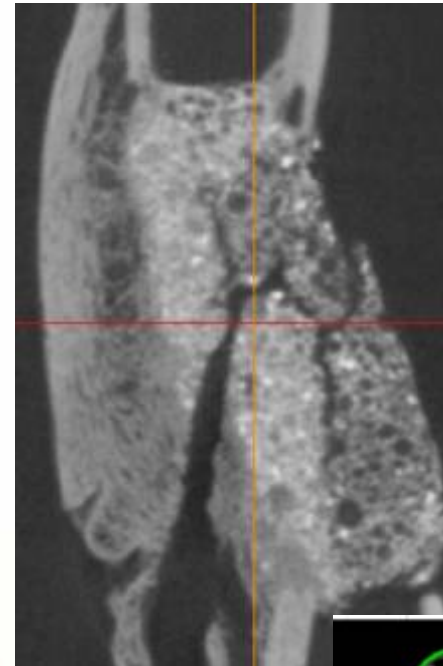
# Bone scaffold requirements

- Biocompatibility: bio-inert or bio-active
  - Bio-inert metals: Ti-6Al-4V, Ti, SS, Ta
  - Bioresorbable ceramics: hydroxyapatite,  $\alpha$ - or  $\beta$ -tri calcium phosphate .
  - Biodegradable polymers: PGA, PLA, PGLA
- Structural parameters:
  - High porosity
  - Open porosity :
    - Allowing osteoprogenitor cell seeding
    - cell attachment/cell migration
    - Mass transport cell nutrition
  - Interconnectivity
  - Specific surface area
- Adequate mechanical behavior

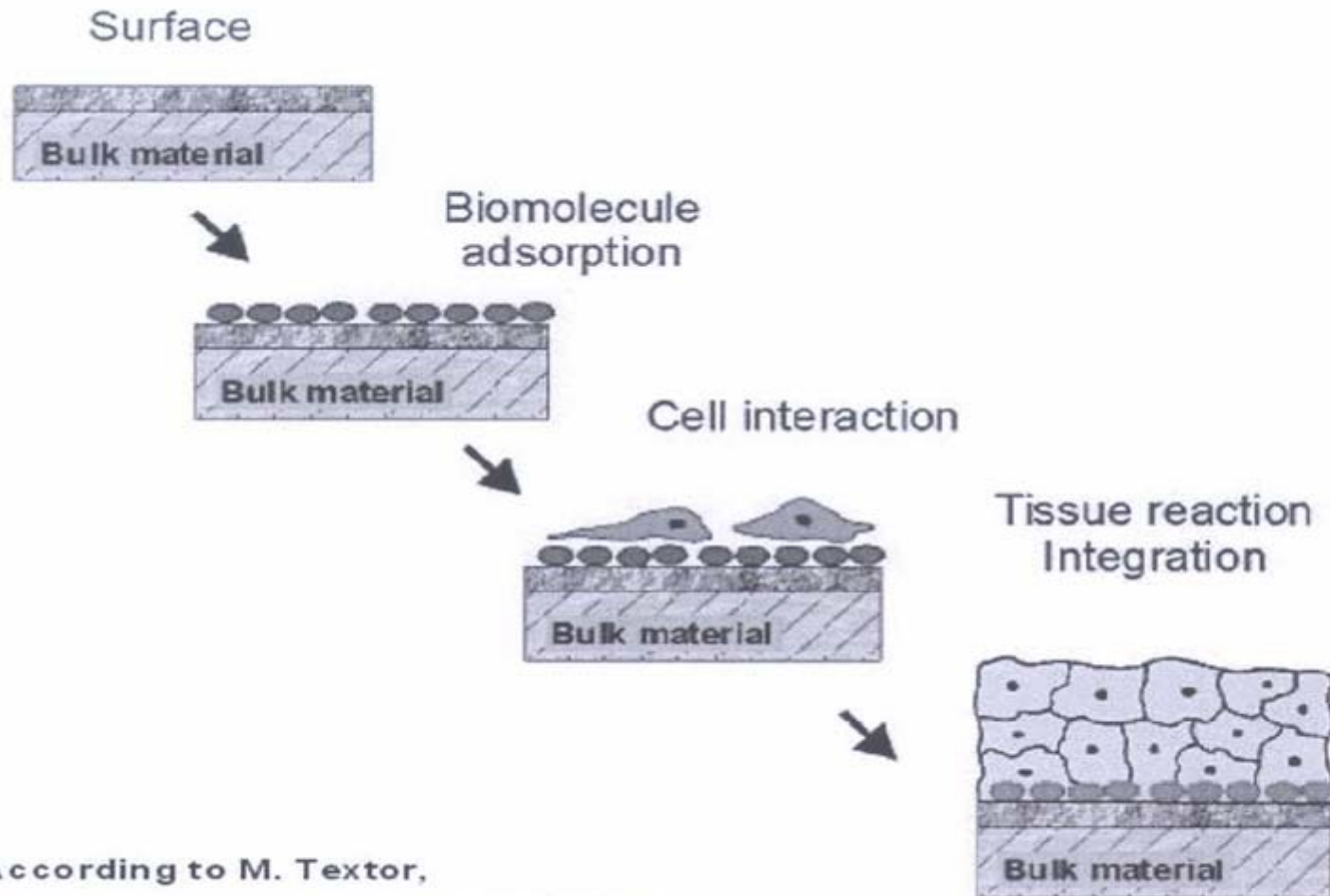


# In vivo behavior

- Nude mice model
  - Ectopic implantation
  - Osteoinduction?
- Rabbit
  - Tibia – large defect
  - Scaffold h=20mm;  $\varnothing$ =6mm



# Steps to tissue integration



According to M. Textor,  
Department of Materials, ETH Zürich