

Fabrice ROSSIGNOL



UMR CNRS 7315

**Couplage cryo-MEB, microscopie confocale  
et simulations de Dynamique Brownienne**  
*Mise en forme de céramiques (nanostructurées)*



**GN-MEBA**

7 Juin 2013

## *162 personnes, dont 82 permanents*



[thierry.chartier@unilim.fr](mailto:thierry.chartier@unilim.fr)

48 professeurs et maîtres de conférences  
14 chercheurs CNRS  
20 ingénieurs et techniciens  
80 doctorants - post-doctorants - CDD

## **La vocation**

*« la compréhension et la maîtrise des procédés d'élaboration, appliqués aux céramiques et aux traitements de surface, en vue de la réalisation d'objets possédant les propriétés recherchées »*

# PERIMETRE DU SPCTS

**1 Laboratoire commun**



**1 Laboratoire correspondant**



**Appui à 2 Centres de Transferts labellisés CRT**



Un des 2 laboratoires de l'Institut des Procédés Appliqués  
aux Matériaux (IPAM = SPCTS + GEMH)

Membre du pôle de compétitivité « Céramique »

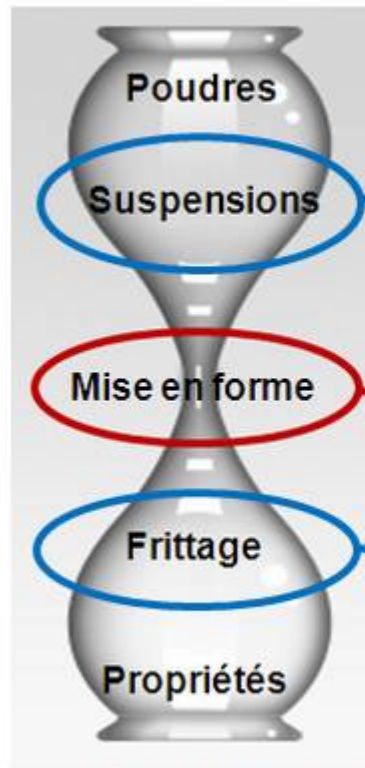
Appartenant au PRES Limousin Poitou-Charentes

**LabEx  $\Sigma$ -Lim (SPCTS-XLIM)**

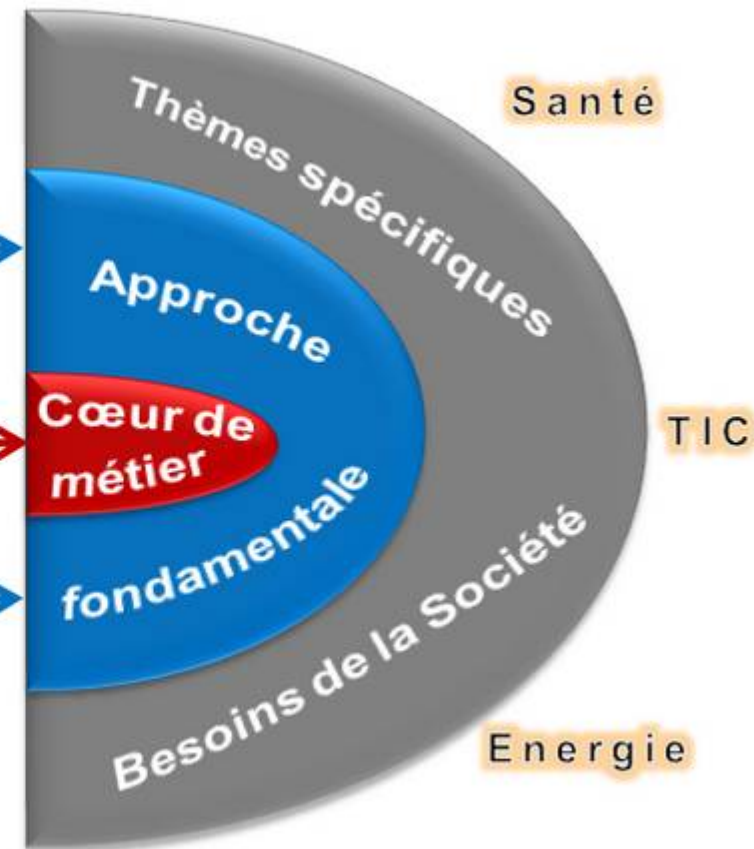
« Des matériaux et composants céramiques spécifiques aux  
systèmes communicants intégrés, sécurisés, intelligents »

# EQUIPE PROCÉDES CERAMIQUES

## Approche intégrée procédés

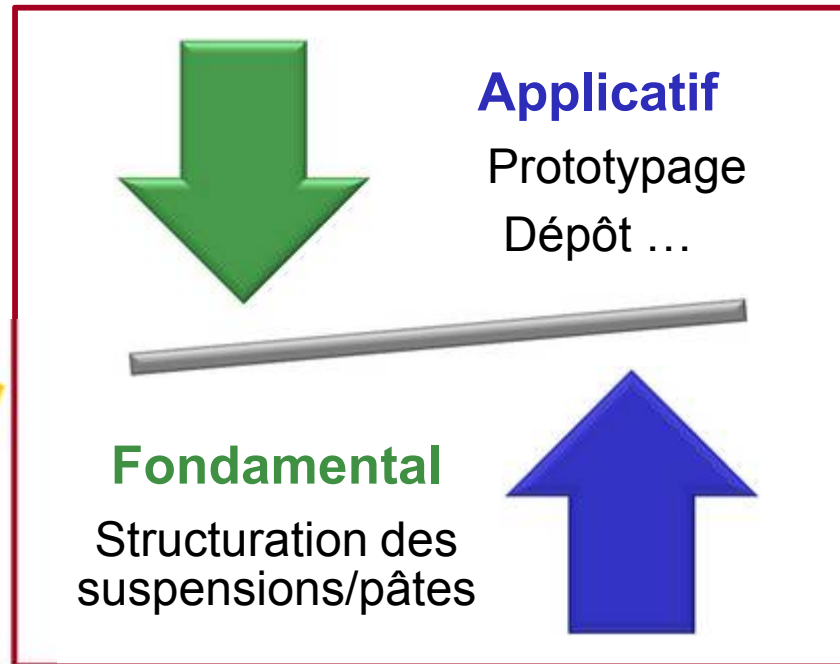
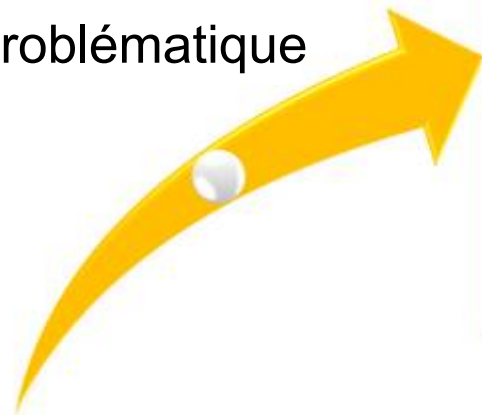


Aller au-delà de l'échelle labo.  
(Valorisation industrielle)



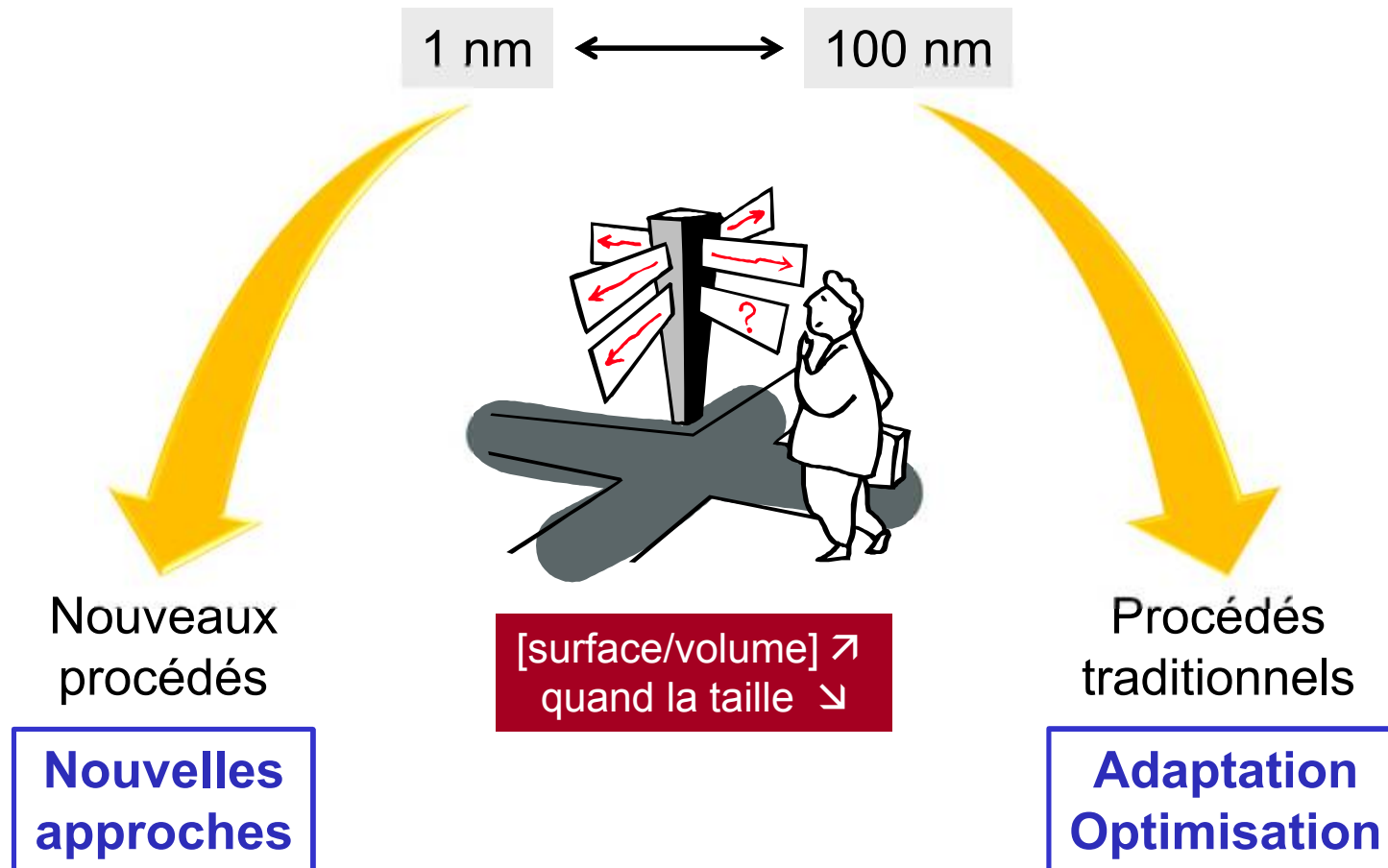
# PLAN DE L'EXPOSE

Problématique

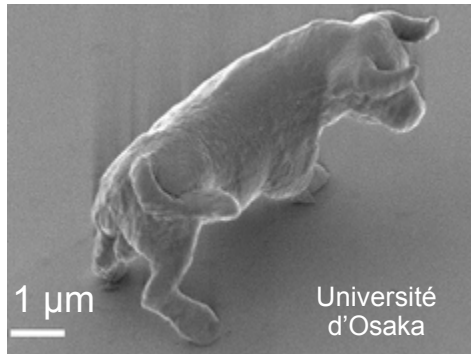


Intérêt du couplage des  
approches *bottom-up* et *top-down*

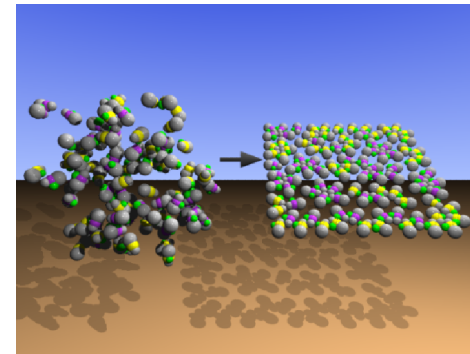
## Spécificité des céramiques nanostructurées



## Les deux approches possibles



Nanofabrication laser



Auto-assemblage moléculaire



Temple d'Abou Simbel

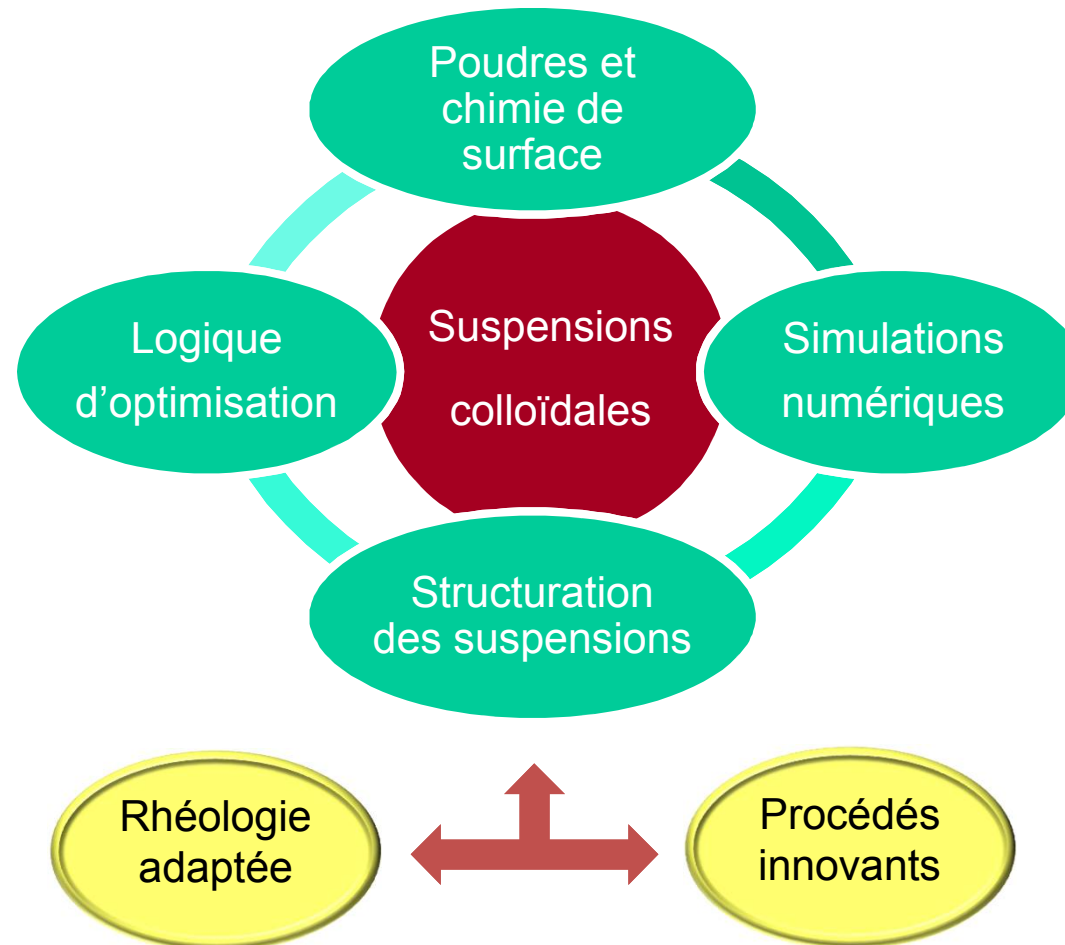
**Top-down**



Briques élémentaires + liant

**Bottom-up**

## Stratégie générale



## Simulations numériques

Arnaud VIDECOQ (MCF ENSCI)

- Simulation de dynamique Brownienne, équation de Langevin :

$$\boxed{m_i \frac{dv_i(t)}{dt}} = \boxed{-\zeta_i v_i(t)} + \boxed{\Gamma_i(t)} + \boxed{\sum_j F_{ij} \{r_{ij}(t)\}}$$

↓

**Inertie**

$m_i$ - masse des particules  
 $v_i$ - vitesse des particules

↓

**Friction (Stokes)**

$\eta$ - viscosité du solvant  
 $a_i$ - rayon des particules  
 $\zeta = 6\Pi\eta a_i$

↓

**Forces aléatoires**

↓

**Forces d'interaction  
interparticulaire  
(DLVO theory)**

## Théorie DLVO

$$U_{ij}^{DLVO} = U_{ij}^{\text{van der Waals}} + U_{ij}^{\text{electrostatic}}$$

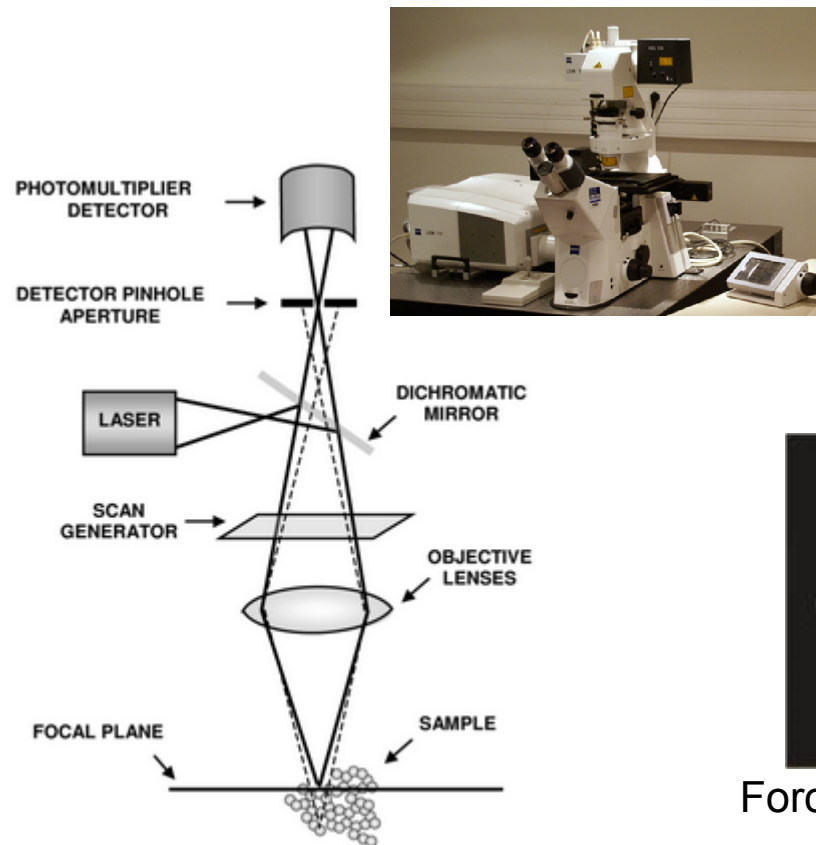
$$U_{ij}^{\text{vdW}}(r_{ij}) = -\frac{A_{ij}}{6} \left[ \frac{2a_i a_j}{r_{ij}^2 - (a_i + a_j)^2} + \frac{2a_i a_j}{r_{ij}^2 - (a_i - a_j)^2} + \ln \left( \frac{r_{ij}^2 - (a_i + a_j)^2}{r_{ij}^2 - (a_i - a_j)^2} \right) \right]$$

$$U_{ij}^{\text{el}}(r_{ij}) = \pi \varepsilon \frac{a_i a_j}{a_i + a_j} (\psi_i^2 + \psi_j^2)^2 \left[ \frac{2\psi_i \psi_j}{\psi_i^2 + \psi_j^2} + \ln \left( \frac{1 + e^{-\kappa h_{ij}}}{1 - e^{-\kappa h_{ij}}} \right) + \ln \left( 1 + e^{-2\kappa h_{ij}} \right) \right]$$

$r_{ij}$  – distance entre particules  
 $A_{ij}$  – constante de Hamaker  
 $a_i, a_j$  – rayons des particules

$\varepsilon$  – constante diélectrique du solvant  
 $\psi_i, \psi_j$  – potentiels de surface des particules  
 $\kappa$  – inverse de la longueur de Debye

## Les outils analytiques



**Microscopie confocale**



Forces colloïdales

**AFM**



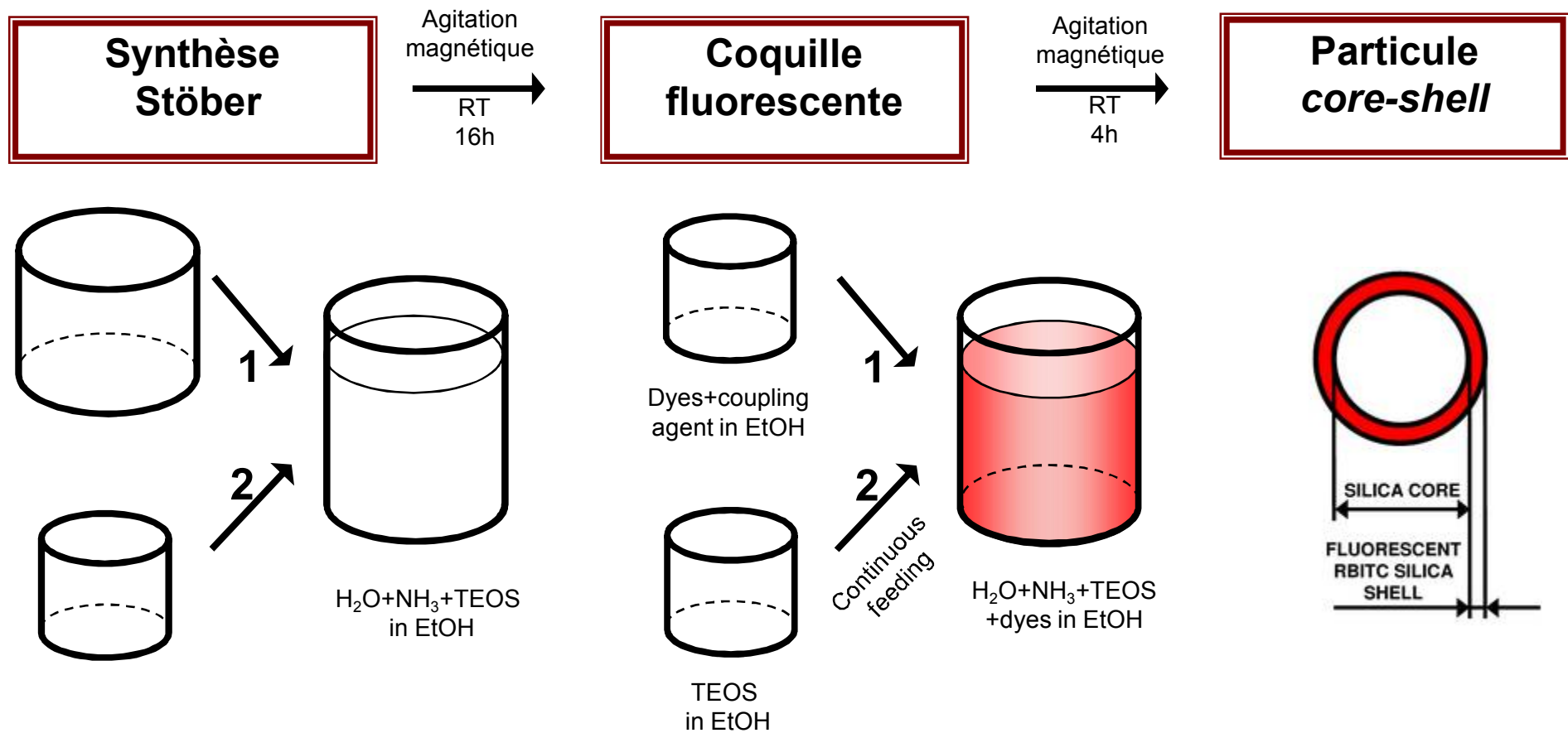
Congélation haute pression



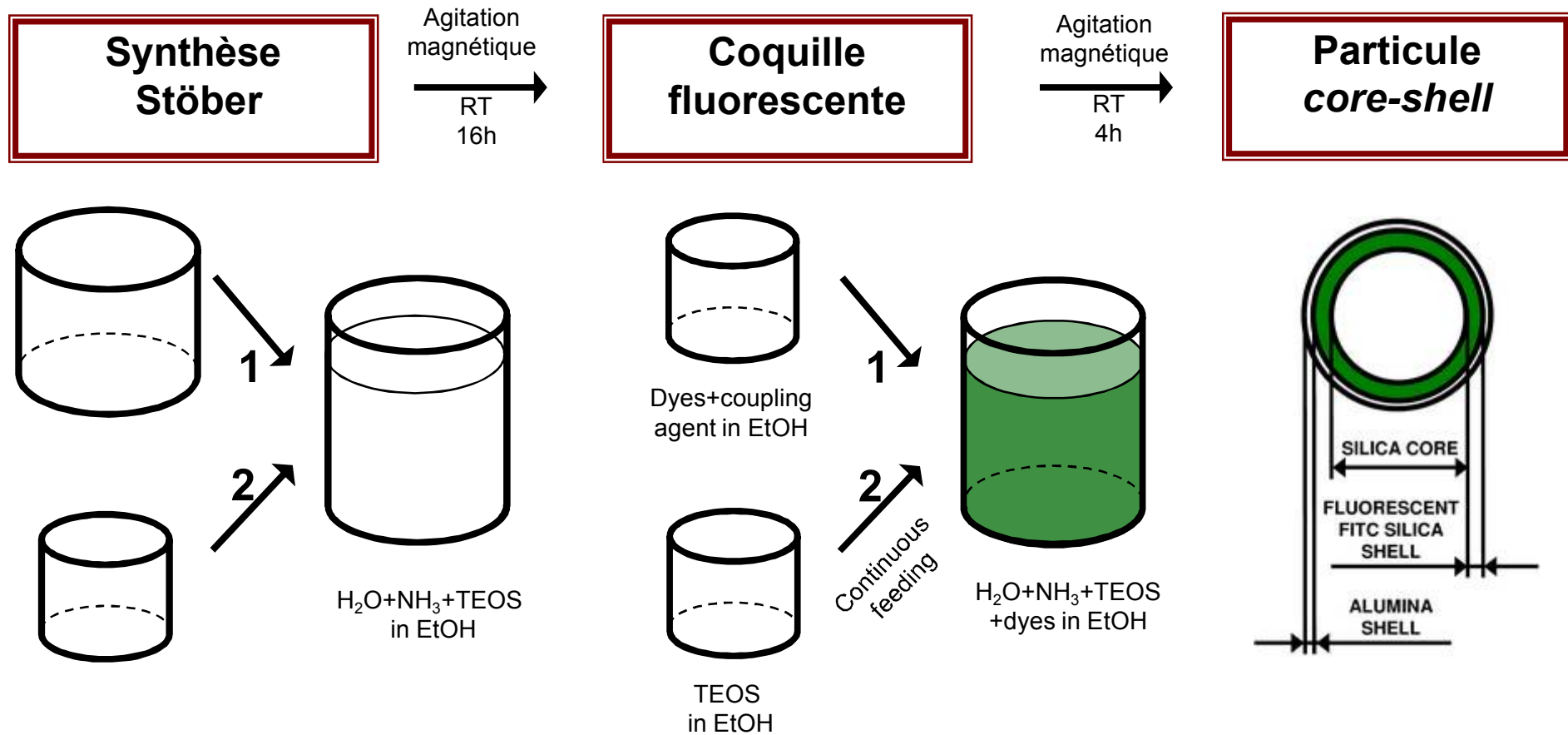
Cryo-transfert MEB

**Cryo-MEB**

## Particules de silice marquées à la rhodamine

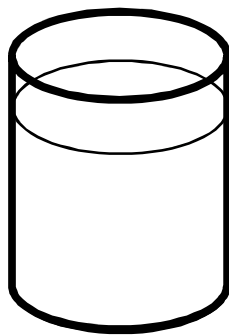
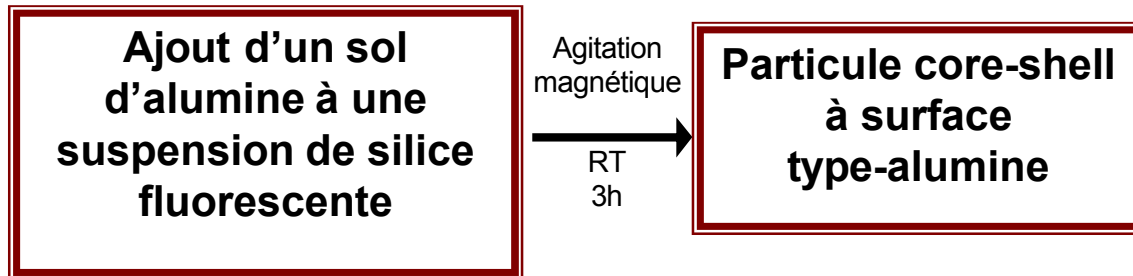


## Particules de silice marquées à la fluorescéine

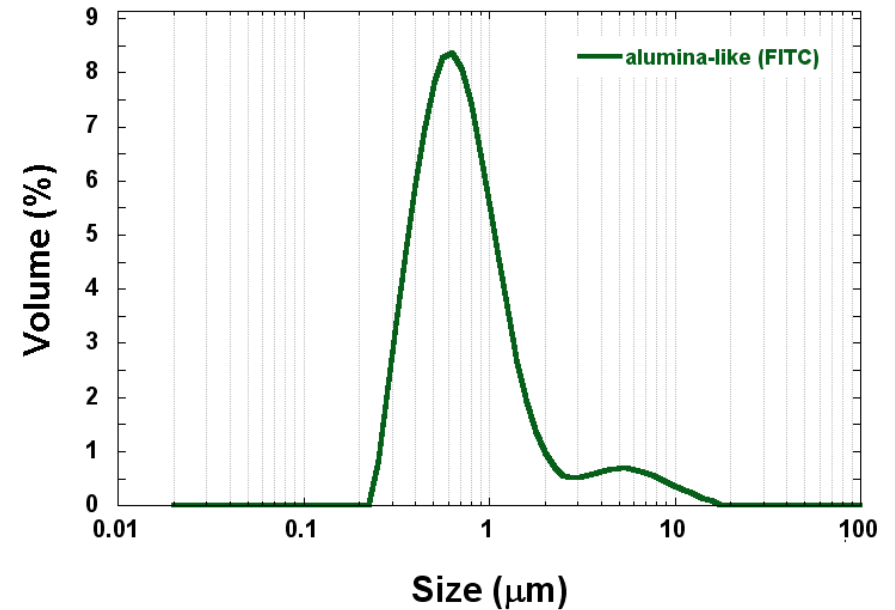
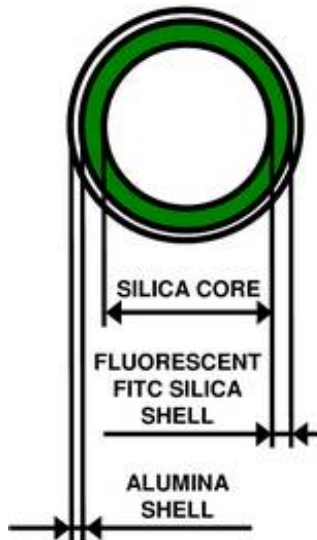


# SUSPENSIONS

## Adaptation de la chimie de surface

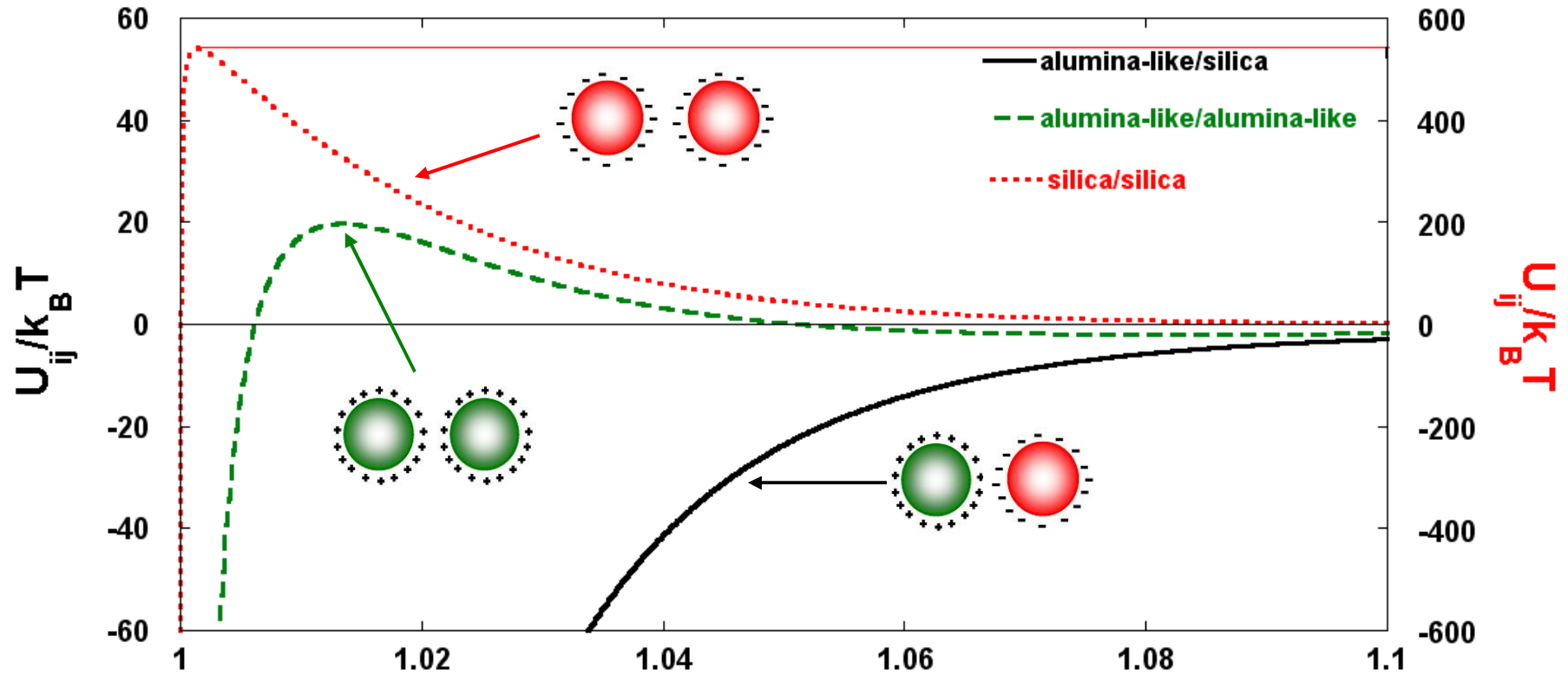


$H_2O + SiO_2 / FITC$   
 $+ Al_2O_3$   
pH 6.5



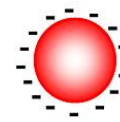
[5] Materials Research Bulletin 43, 714–722, (2008)

## Potentiel d'interaction



**ALUMINA-LIKE PARTICLES**

$\zeta_1 = 20 \text{ mV}$   
 $A_{11} = 4.76 \times 10^{-20} \text{ J}$

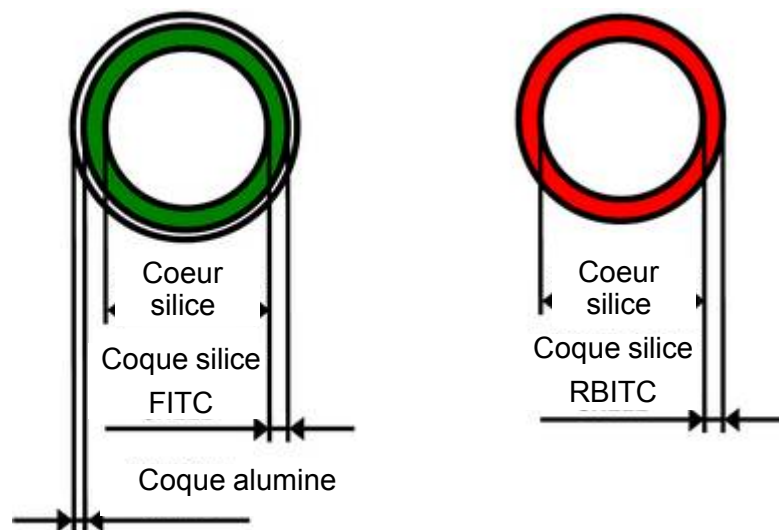
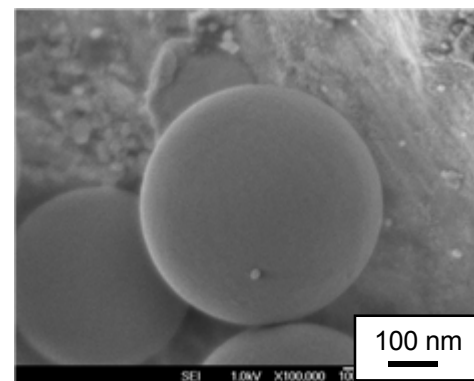
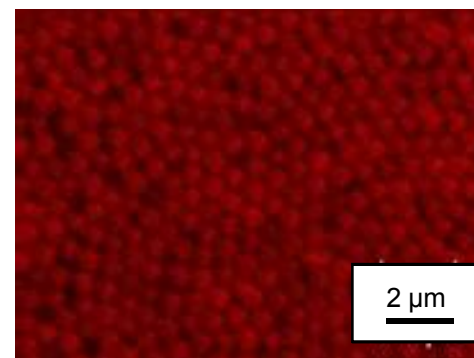
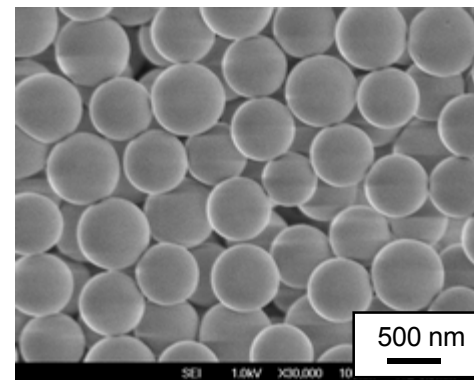
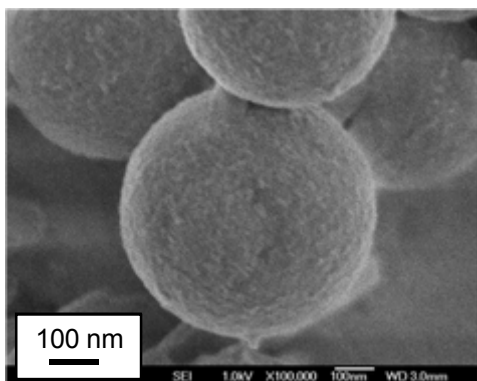
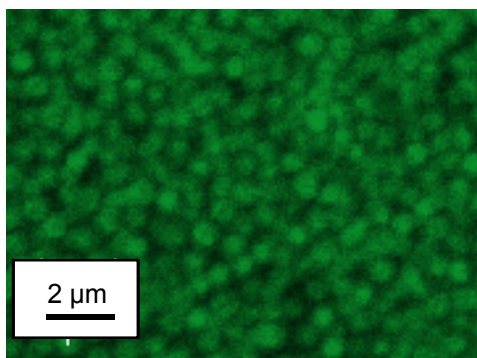
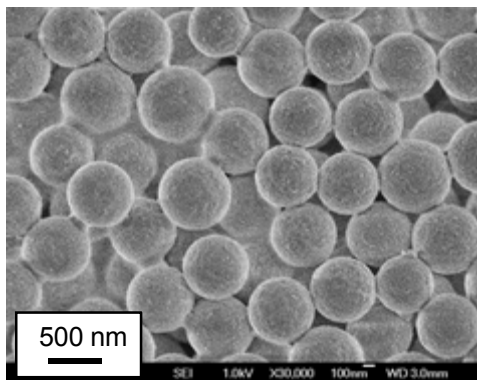


**SILICA PARTICLES**

$\zeta_2 = -52 \text{ mV}$   
 $A_{22} = 4.60 \times 10^{-21} \text{ J}$

# SUSPENSIONS

## Les particules modèles



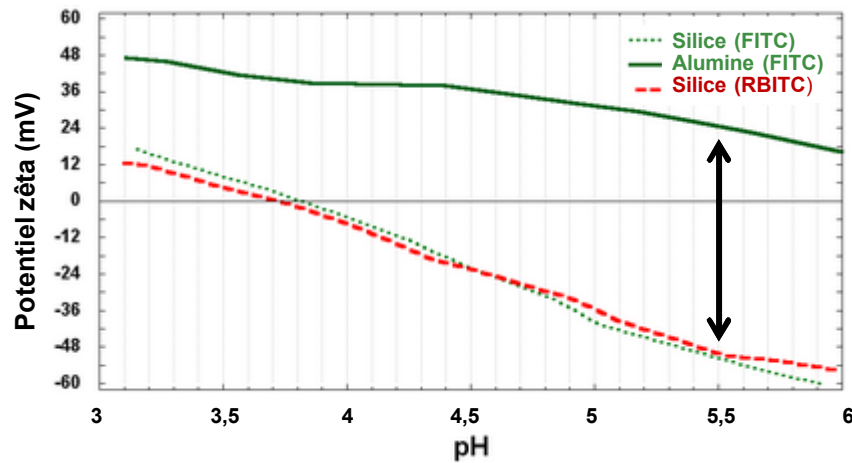
$d_{1(50)} = 620 \text{ nm}$   
 $\rho_1 = (2.45 \pm 0.02) \text{ g/cm}^3$   
 $\zeta_1 = (20 \pm 2) \text{ mV}$   
 à pH 5,5

**Type-alumine**

$d_{2(50)} = 585 \text{ nm}$   
 $\rho_2 = (2.23 \pm 0.02) \text{ g/cm}^3$   
 $\zeta_2 = -(52 \pm 2) \text{ mV}$   
 à pH 5,5

**Type-silice**

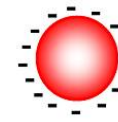
## Hétéro-agglomération de suspensions modèles



**Alumine (FITC)**

$$\zeta_1 = 20 \text{ mV}$$

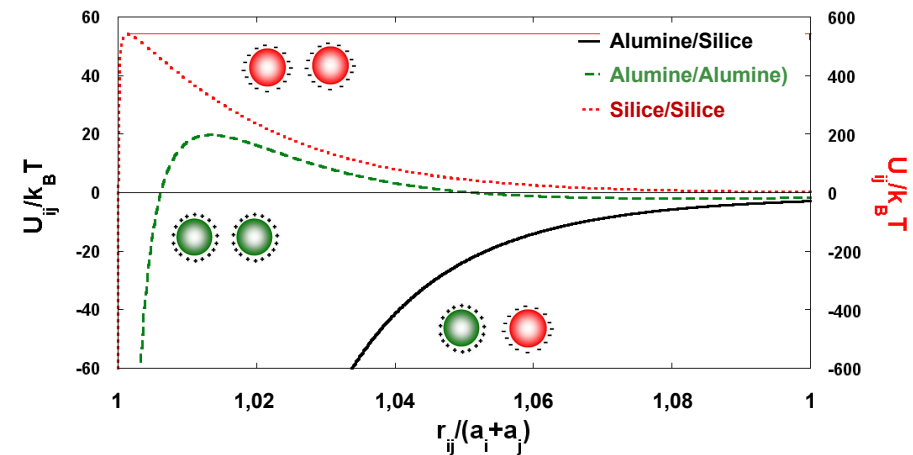
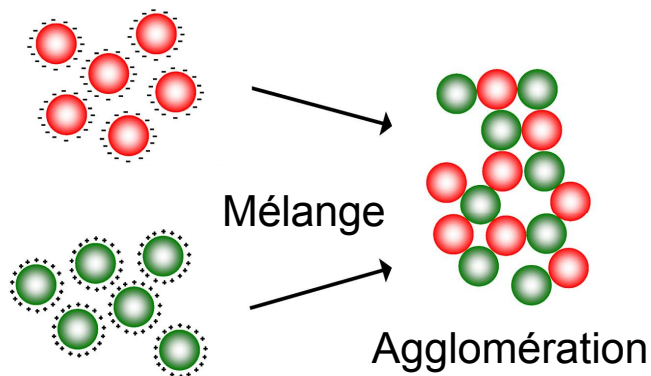
$$A_{11} = 4,76 \times 10^{-20} \text{ J}$$



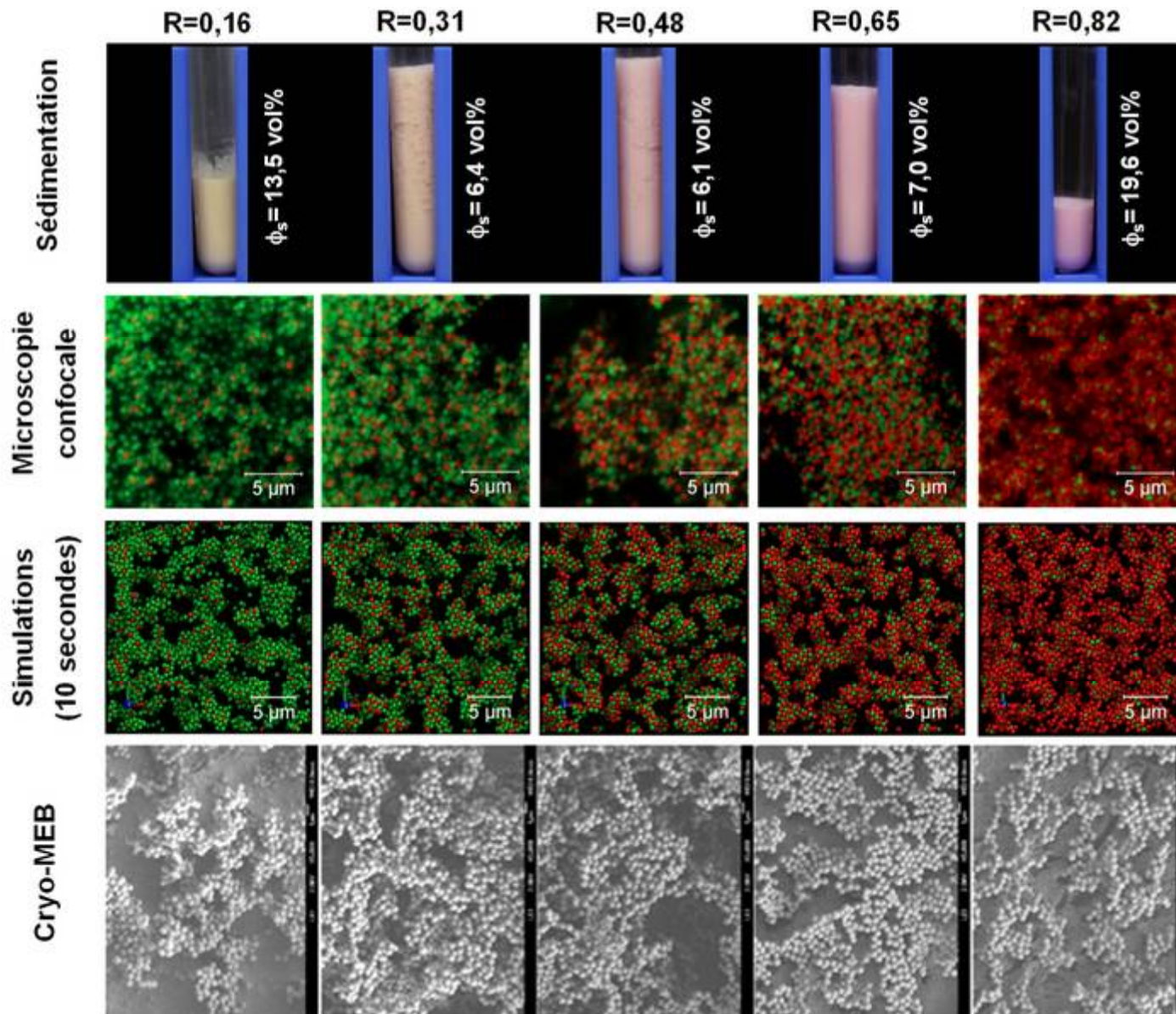
**Silice (RBITC)**

$$\zeta_2 = -52 \text{ mV}$$

$$A_{22} = 4,60 \times 10^{-21} \text{ J}$$

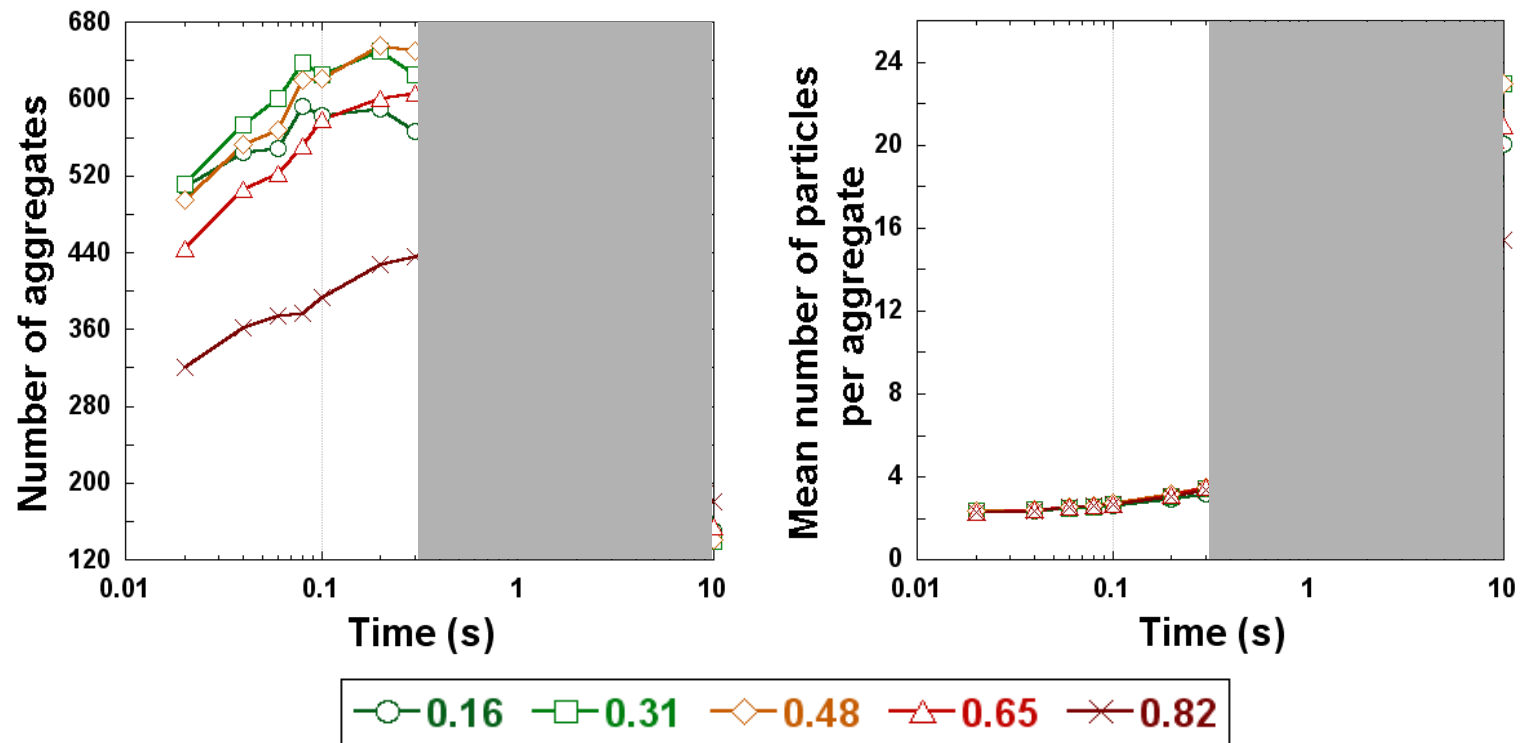


# SUSPENSIONS



$$R = \frac{m_{silice}}{m_{silice} + m_{alumine}}$$

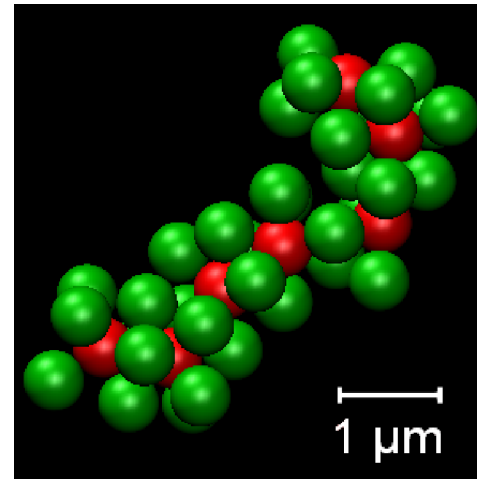
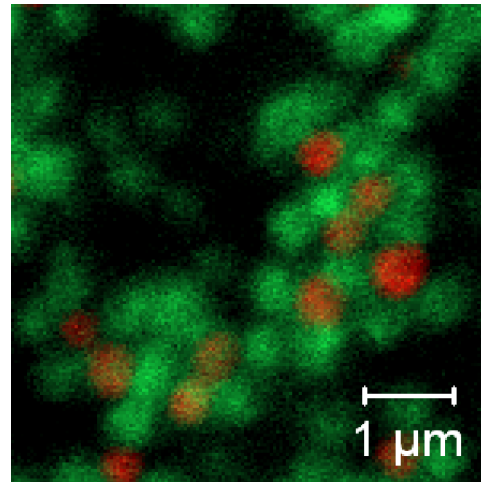
## Cinétiques d'agrégation



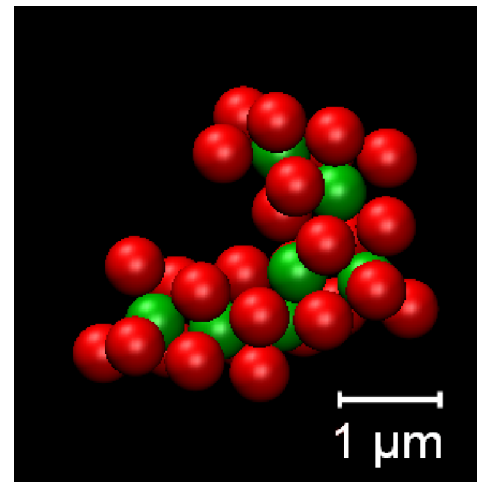
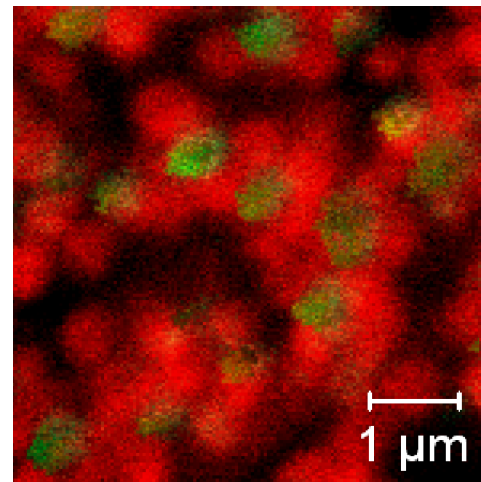
# SUSPENSIONS

## Comparaison simulations/expériences

R=0,16

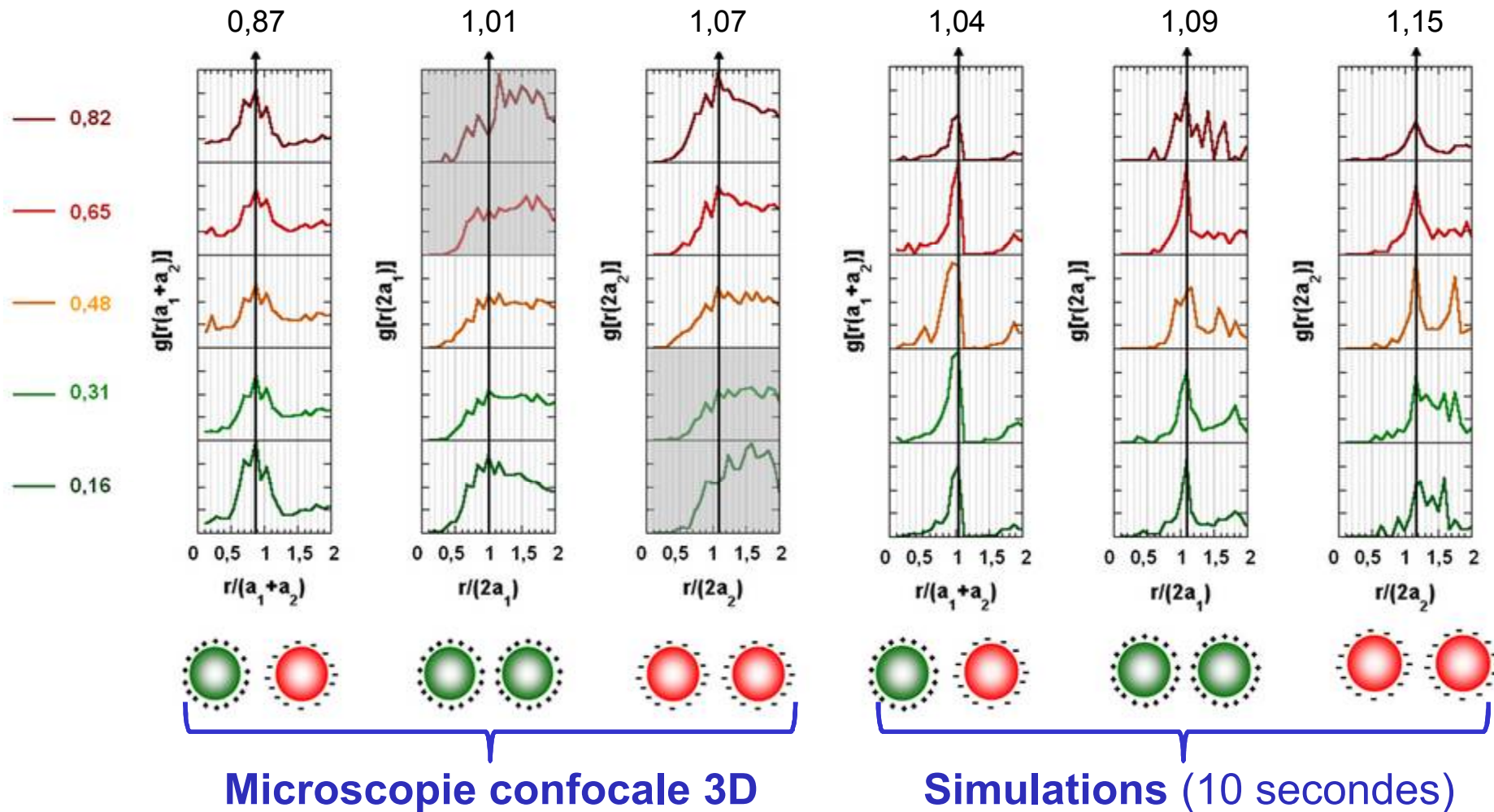


R=0,82

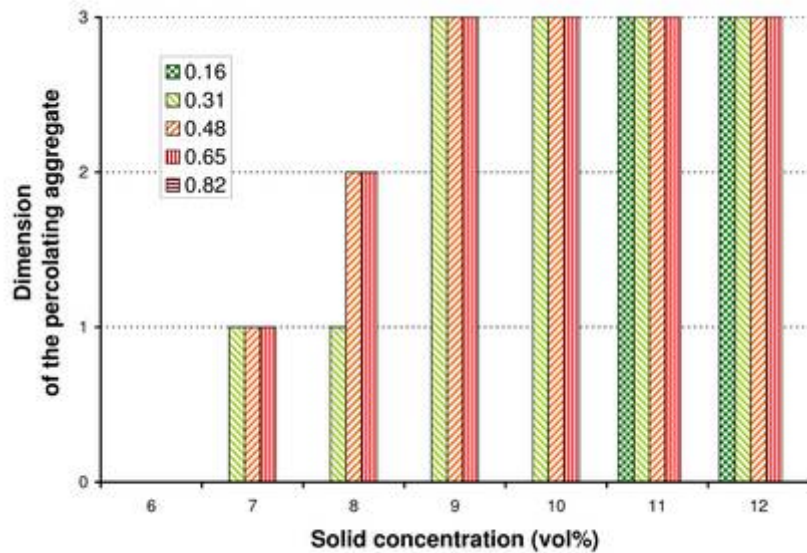
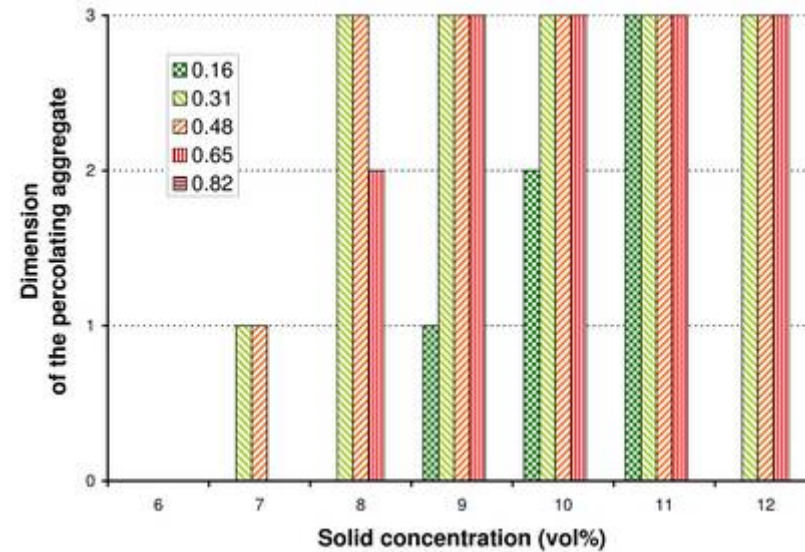
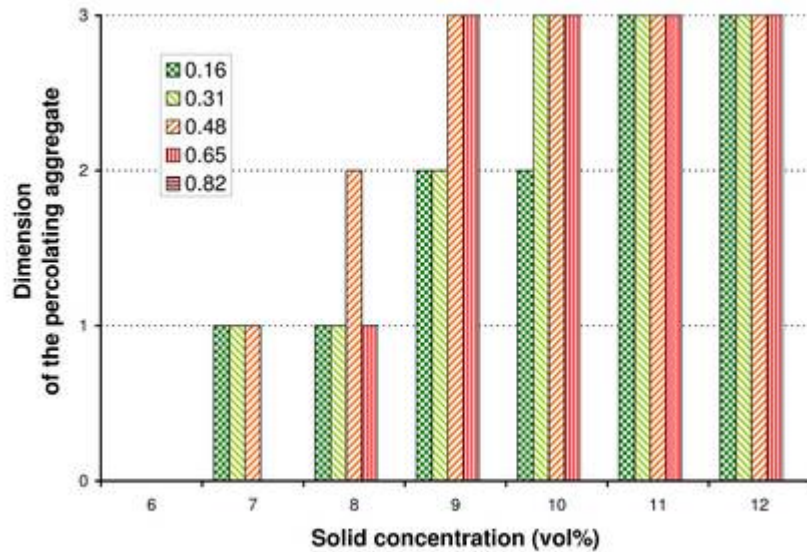


## Au-delà de l'accord qualitatif

Fonctions de distribution radiale



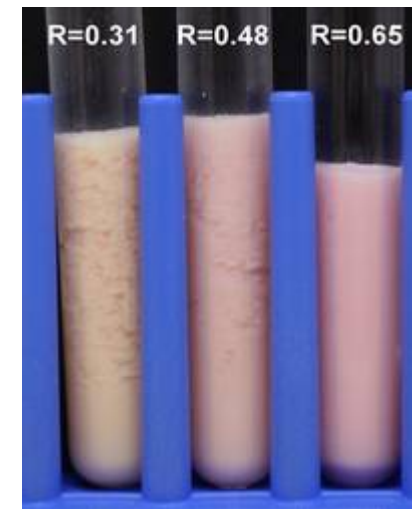
## Percolation des agrégats



$$R = 0.31 \rightarrow \phi_s = 6.4\%$$

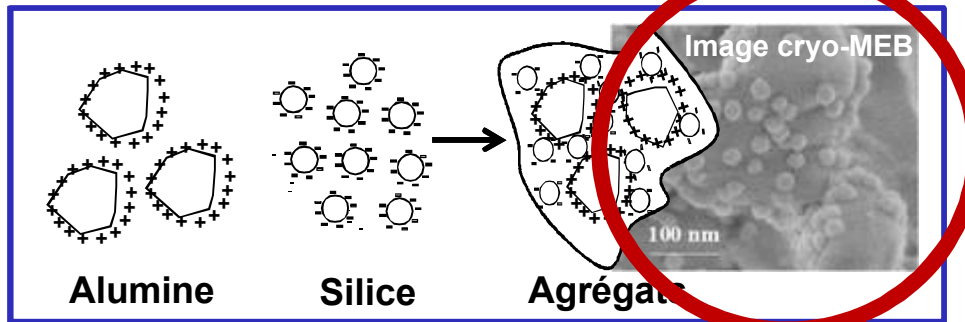
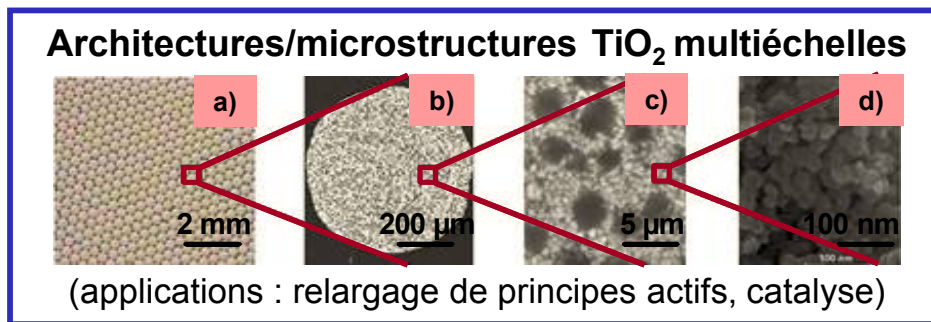
$$R = 0.48 \rightarrow \phi_s = 6.1\%$$

$$R = 0.65 \rightarrow \phi_s = 7.0\%$$

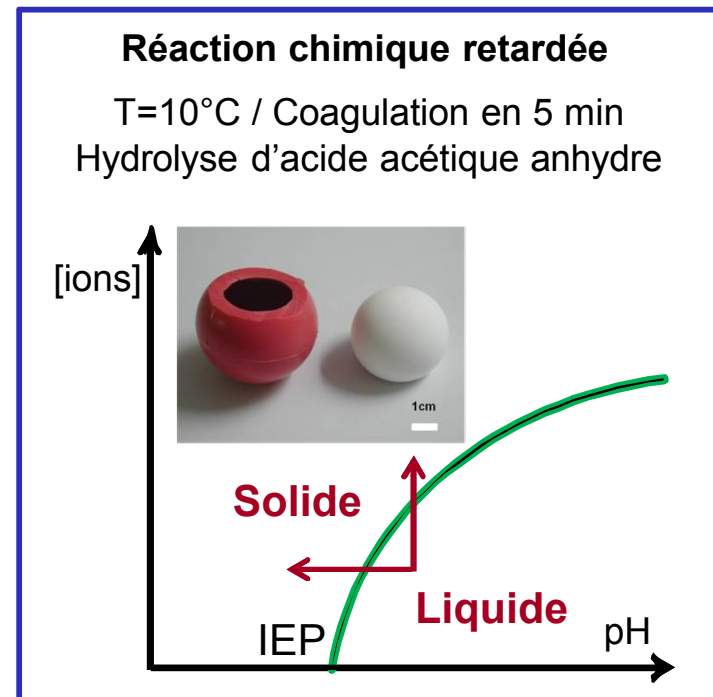


## Applications : procédés de mise en forme innovants

Couplage *bottom-up* et *top-down*



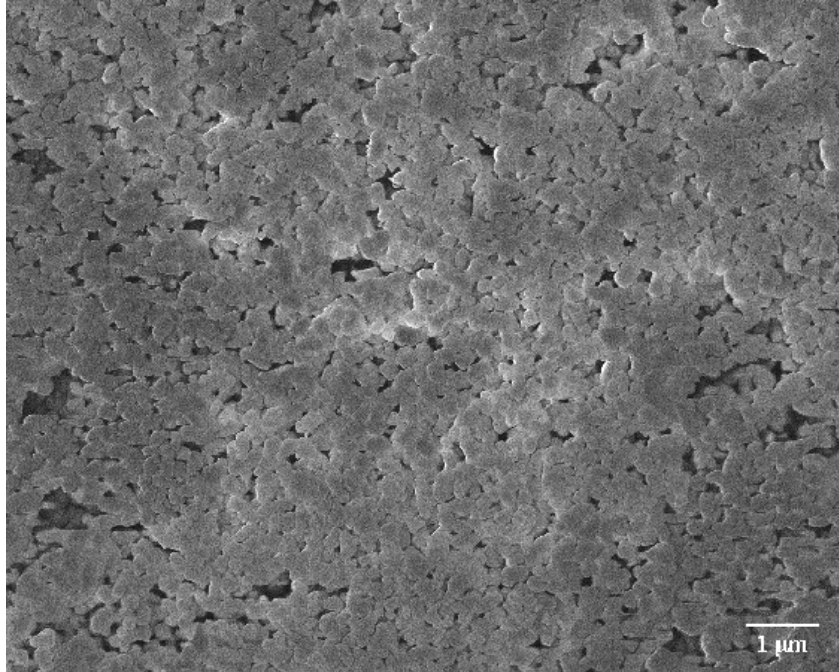
**Granulation en voie liquide**



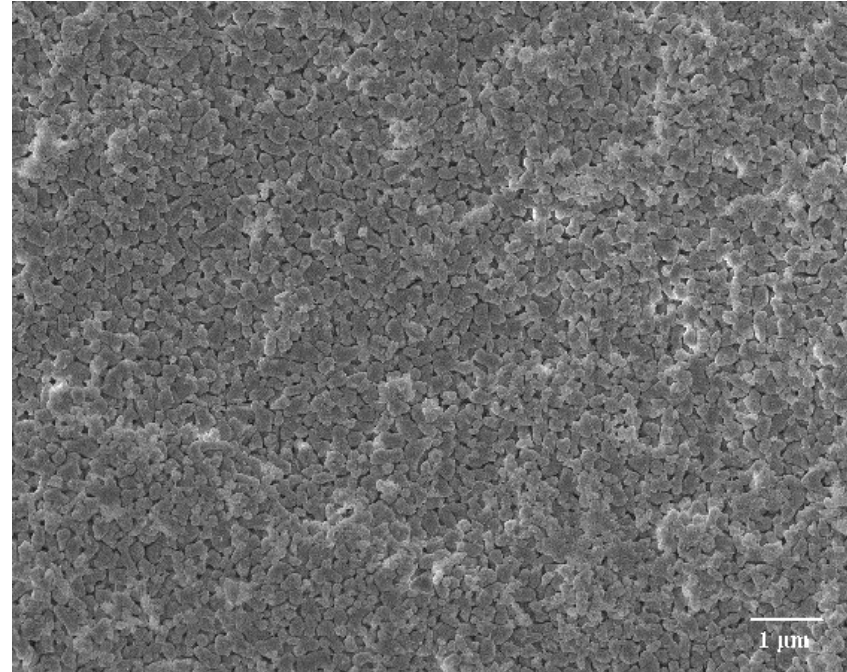
**Coulage-coagulation**

Cécile PAGNOUX (PR ENSCI)

# SUSPENSIONS



[Tiron] < optimum

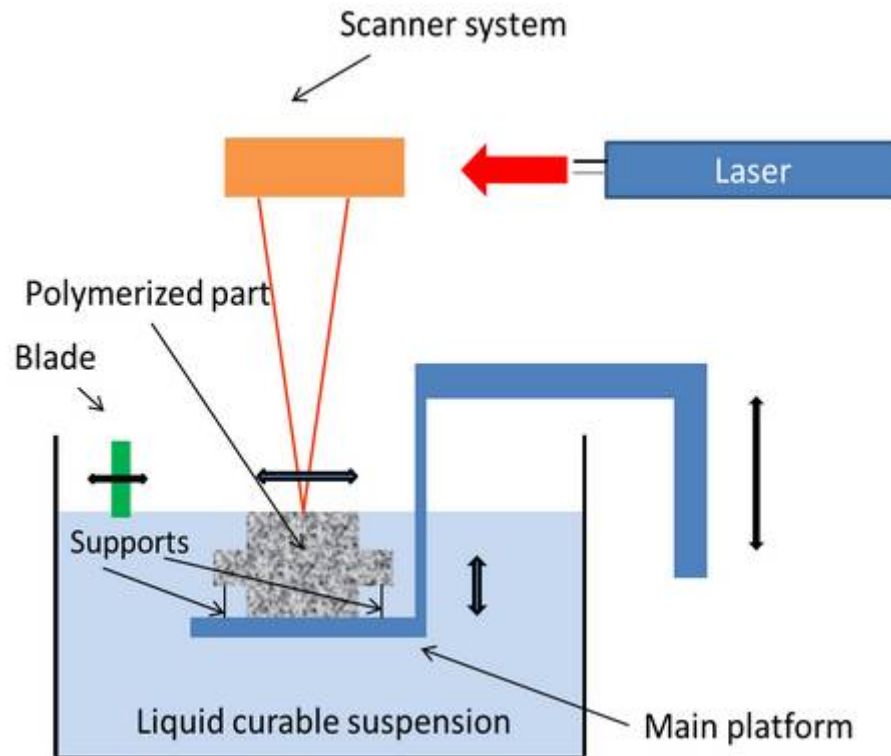


Optimum [Tiron]  $\sim 10^{-6} \text{ mol.m}^{-2}$

**Images cryo-MEB – 57,5 vol.%  $\text{Al}_2\text{O}_3$  ( $\phi$ :300nm) suspensions**

## Stéréolithographie

Thierry CHARTIER (DR CNRS)



Production en couches successives

Epaisseur de couche : 25 – 150  $\mu\text{m}$   
Vitesse de fabrication : 100 couches/heure  
Précision >1 %, sections > 10  $\text{cm}^2$  possible

## Stéréolithographie

Thierry CHARTIER (DR CNRS)

### Transfert

Collaboration : XLIM

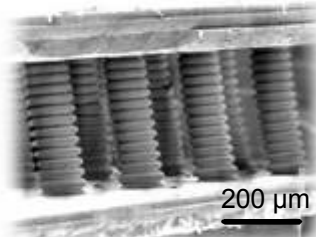


Résonateur diélectrique

CTTC

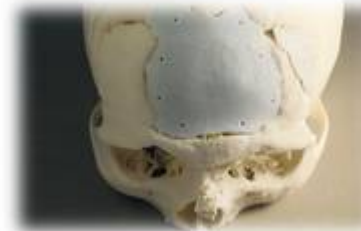


Antenne à bande photonique interdite



### Valorisation

Collaboration : CHU Limoges



Implant en HAP

3DCERAM  
Advanced Ceramics



Chirurgien : joel.brie@chu-limoges.fr



(\*) Journal du CNRS n°207 (avril 2007)  
Sciences et Avenir n°736 (juin 2008)

# PROTOTYPAGE RAPIDE



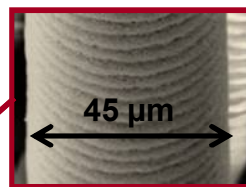
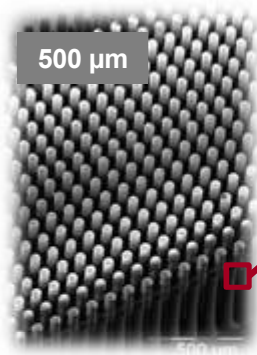
## Impression jet d'encre

Martine LEJEUNE (PR ENSCI)



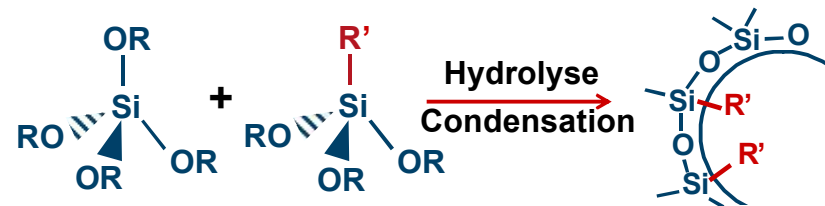
## Suspensions colloïdales

## Sols de précurseurs polymériques

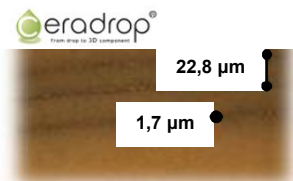
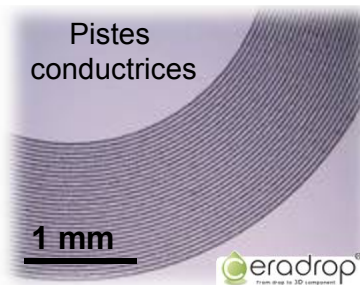


Plots PZT

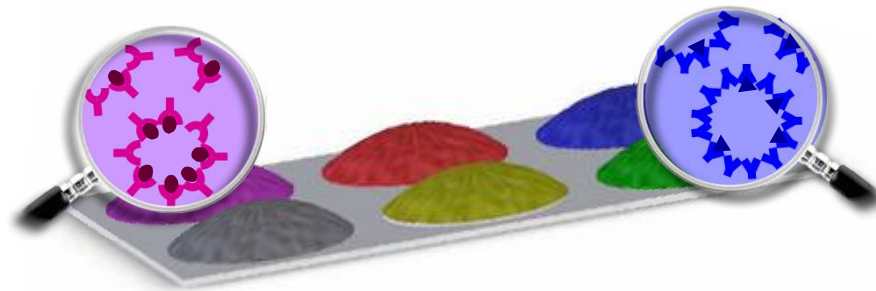
(Sonde d'échographie)



Silice mésoporeuse fonctionnalisée *one pot*



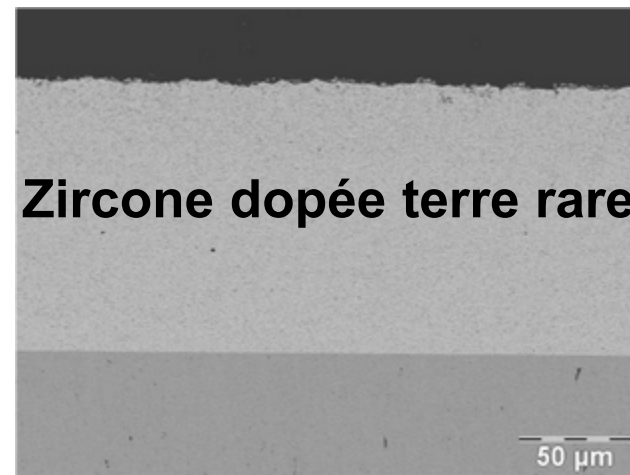
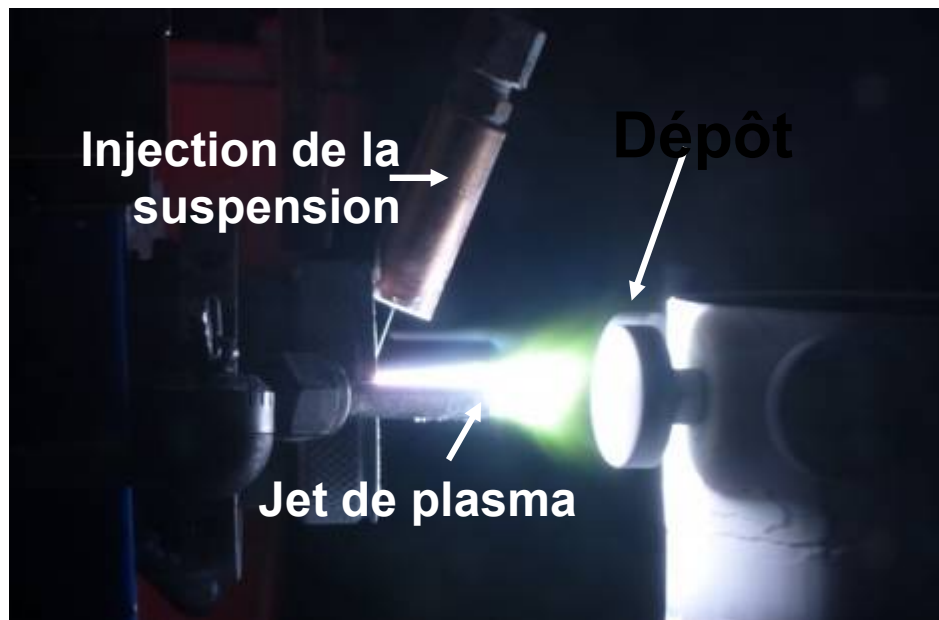
Condensateurs multicouches



## Barrières thermiques finement structurées par projection plasma de suspensions

Application: propulsion spatiale (Ariane 5)

*Alain DENOIRJEAN (DR CNRS)*



Température de service: 1100°C

Porosité: 15%

Conductivité thermique < 1 W/m.K

Taux de déposition > 10 μm/min

# REMERCIEMENTS

## Collègues



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Stéréolithographie

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M. Cerbelaud  
O. De Los Cobos  
B. Fousseret  
A.L. Pénard  
M. Piechowiak  
A. Pringuet  
W. Zhang

## Thésard(e)s

...



X. Cattoën  
M. Wong Chi Man



M. Granier  
J-O. Durand



## IJP

F. Ribot  
C. Boissière  
C. Sanchez



## STEREO-



## ADM

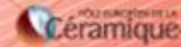
## CTTC



Agence Nationale de la Recherche  
**ANR**

# 13<sup>th</sup> International Conference of the **European Ceramic Society**

23 - 27 June 2013  
Ester Technopole - Limoges, France





**Merci**

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