Design radiatif de céramiques poreuses à base de CeO_2 pour la production d'H_2 par thermochimie solaire

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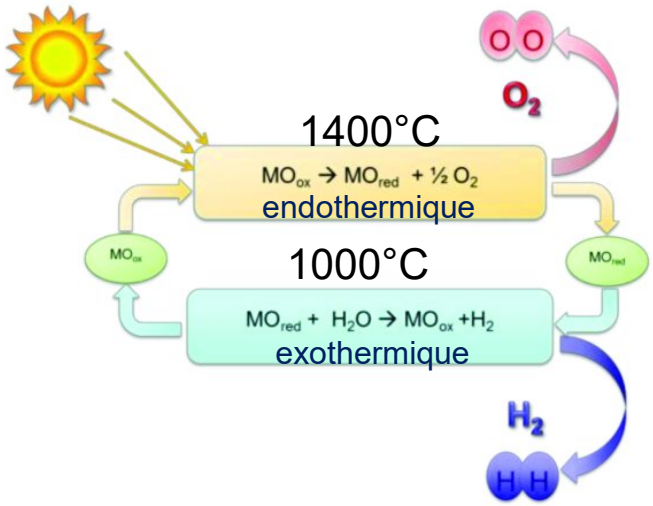
Cycle thermochimique “haute temperature” en 2 étapes

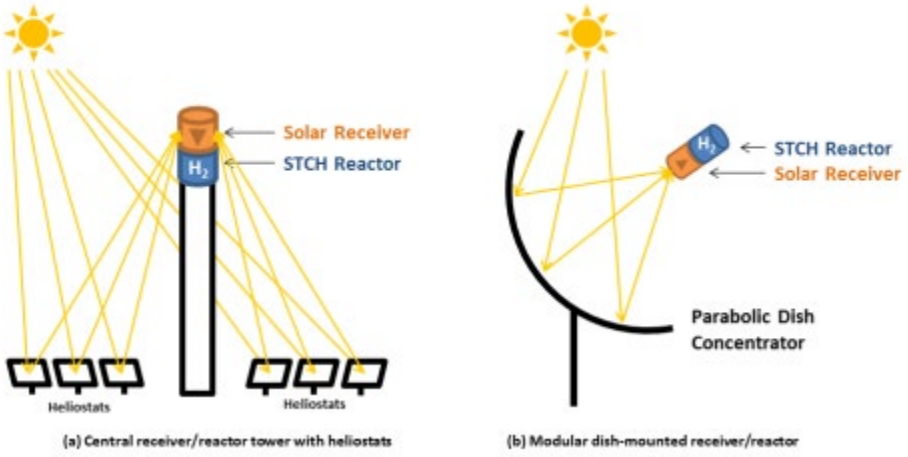
Décomposition thermique de la vapeur d’eau

$H_2O \rightarrow H_2 + 1/2\ O_2$ (T~ 3000°C)

Dissociation thermochimique de la vapeur d’eau



Apport de chaleur



Fort intérêt pour l’oxyde de cérium $CeO_{2-\delta}$:

- Stabilité thermique (T>1400°C)
- Bonne cinétique d’oxydation (~1000°C),
- Bon taux de diffusion de l’oxygène
- Bonne disponibilité d’approvisionnement

Phénomènes physiques complexes :

- Transferts radiatifs couplés
- Ecoulement fluide gazeux (laminaire)
- Réactions chimiques
- Approches modélisations homogénéisés/discrètes

Réacteurs solaires pour la production de H_2

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Technology Readiness Level of Solar Thermochemical Splitting Cycles

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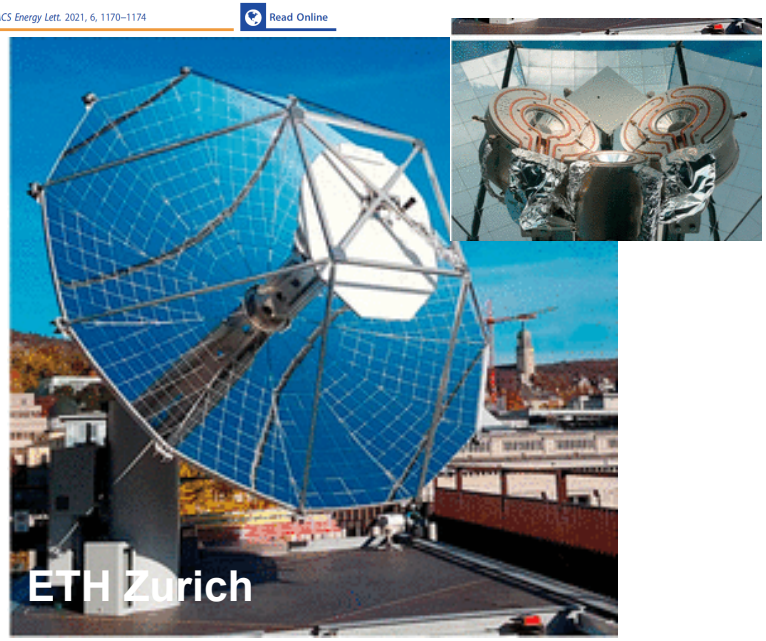
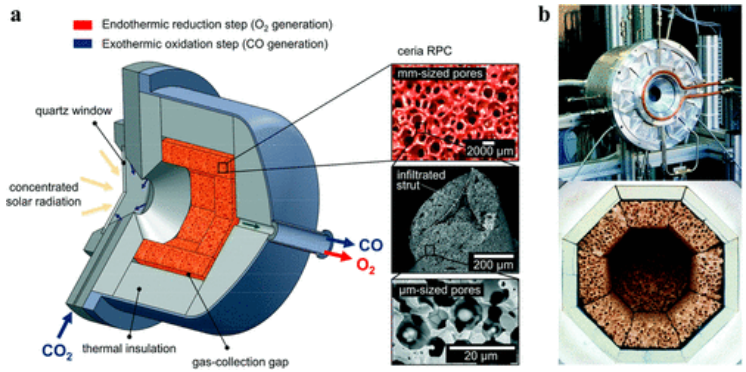
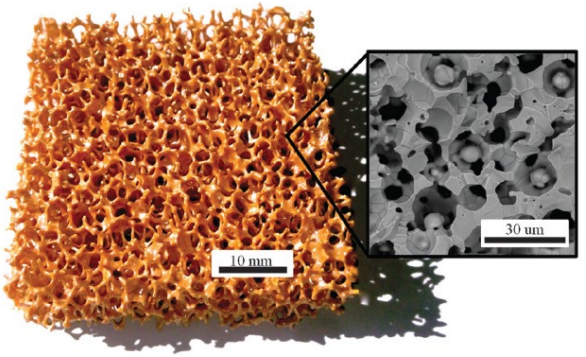




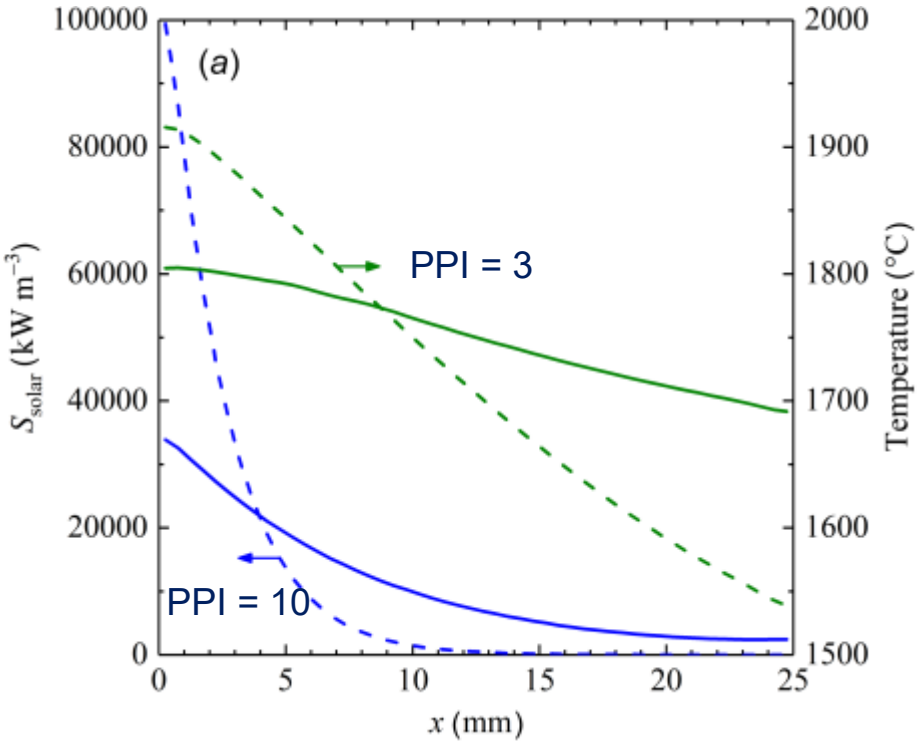


- Réacteur 4 kW / 0.002 m^2
- Concentration : 3000 suns
- Efficacité de conversion solaire-H_2 ~ 5.25 %
- Mise en œuvre d'un second réacteur 50 kW, IMDEA Madrid

Limitations actuelles liées à la géométrie des mousses de CeO_2

- Efficacité de conversion solaire-H_2 ~ 20-25 % pour rentabilité économique
- Manque d'homogénéité de chauffage lors de l'étape de réduction (lié au chauffage sur une face) → chauffage volumique
- Etape d'oxydation requiert sur une surface volumique la plus élevée possible
- Identifier structure poreuse garantissant une bonne productivité d'H_2 par kg de CeO_2

- PPI = 3 → pores = 7 mm→ gradient = 113°C
- PPI = 10→ pores = 2 mm → gradient = 377°C



Heat Transfer Model of a 50 kW Solar Receiver–Reactor for Thermochemical Redox Cycling Using Cerium Dioxide

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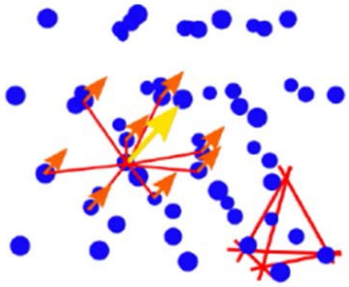
This work reports on the development of a transient heat transfer model of a solar receiver–reactor designed for thermochemical redox cycling by temperature and pressure swing of pure cerium dioxide in the form of a reticulated porous ceramic (RPC). In the first, endothermal step, the cerium dioxide RPC is directly heated with concentrated solar radiation to 1500 °C while under vacuum pressure of less than 10 mbar, thereby releasing oxygen from its crystal lattice. In the subsequent, exothermic step, the reactor is repressurized with carbon dioxide as it cools, and at temperatures below 1000 °C, the partially reduced cerium dioxide is re-oxidized with a flow of carbon dioxide. To analyze the performance of the solar reactor and to gain insight into improved design and operational conditions, a transient heat transfer model of the solar reactor for a solar radiative input power of 50 kW during the reduction step was developed and implemented in ANSYS CFX. The numerical model couples the incoming concentrated solar radiation using Monte Carlo ray tracing, incorporates the reduction chemistry by assuming thermodynamic equilibrium, and accounts for internal radiation heat transfer inside the porous ceria by applying effective heat transfer properties. The model was experimentally validated using data acquired in a high-flux solar simulator (HFSS), where temperature evolution and oxygen production results from model and experiment agreed well. The numerical results indicate the prominent influence of solar radiative input power, where increasing it substantially reduces reduction time of the cerium dioxide structure. Consequently, the model predicts a solar-to-fuel energy conversion efficiency of >6% at a solar radiative power input of 50 kW; efficiency >10% can be obtained provided the RPC macroporosity is substantially increased, and better volumetric absorption and uniform heating is achieved. Managing the ceria surface temperature during reduction to avoid sublimation is a critical design consideration for direct absorption solar receiver–reactors. [DOI: 10.1115/1.4042059]

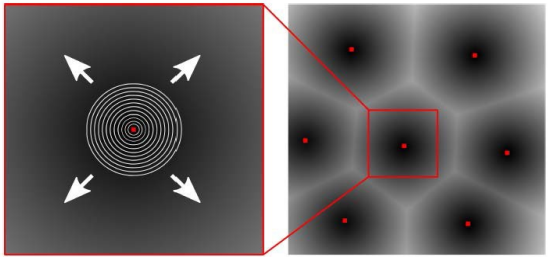
Keywords: solar energy, thermochemical cycles, ceria, reticulated porous ceramic, reactor modeling, design optimization

Génération numérique de structures poreuses (genMat, C++, Qt)

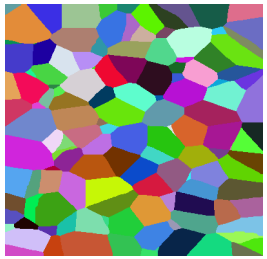
Algorithme



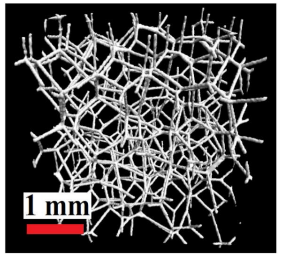
Ensemencement de graines



Algorithme de fast-marching

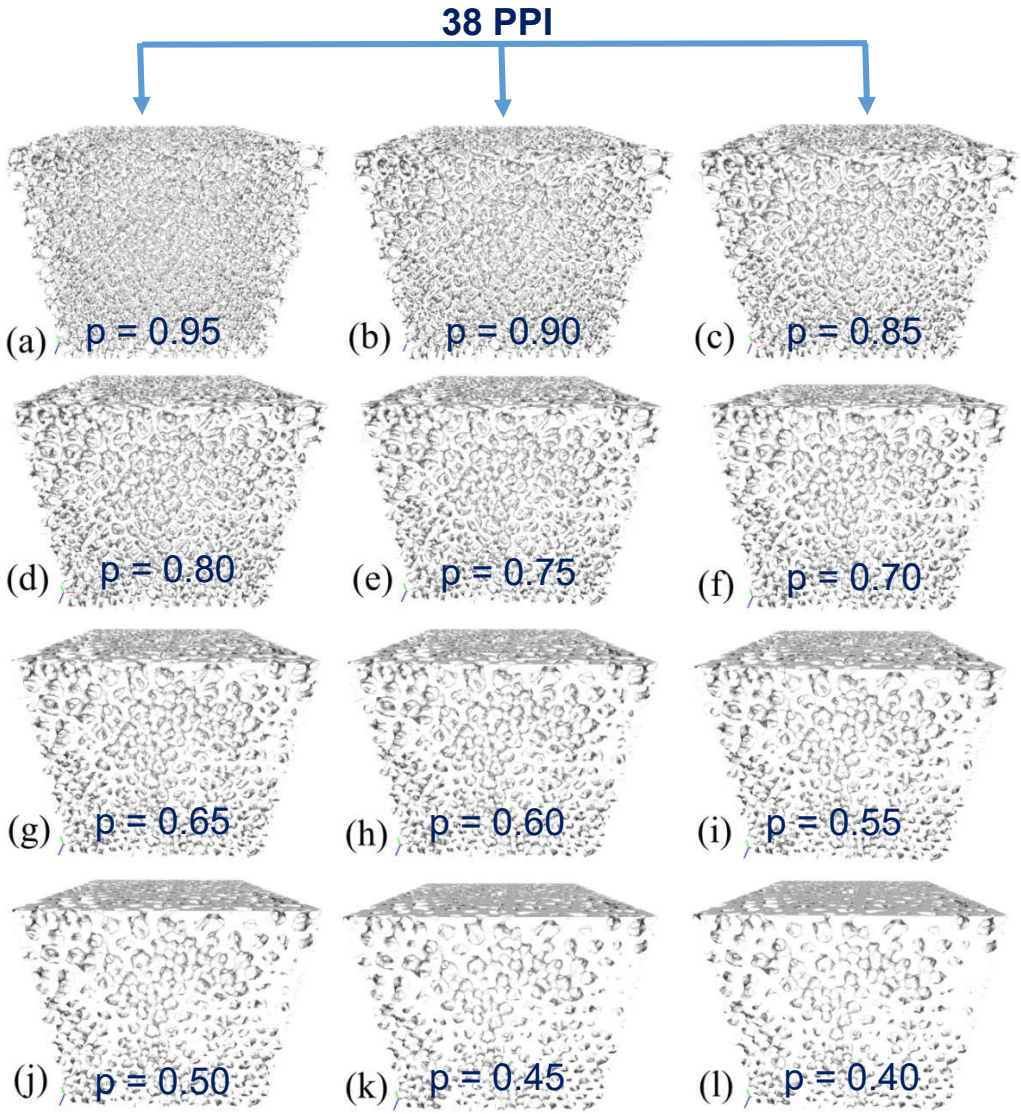


Segmentation



Squelettisation

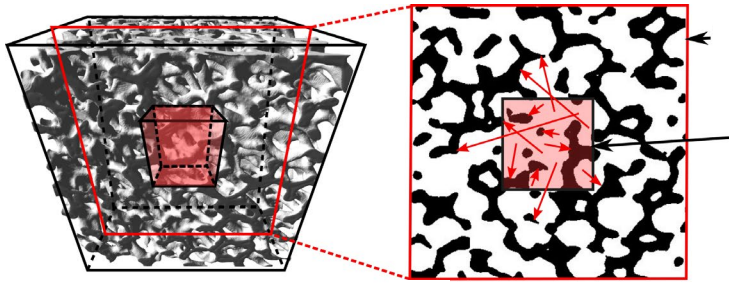
Guévelou et al. , JPM 2015 ; Guévelou et al., IHTC, Kyoto 2015



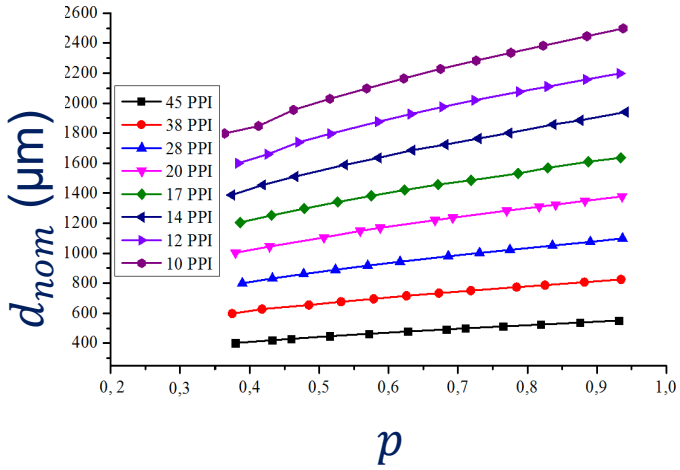
Génération numérique de structures poreuses (genMat, C++, Qt)

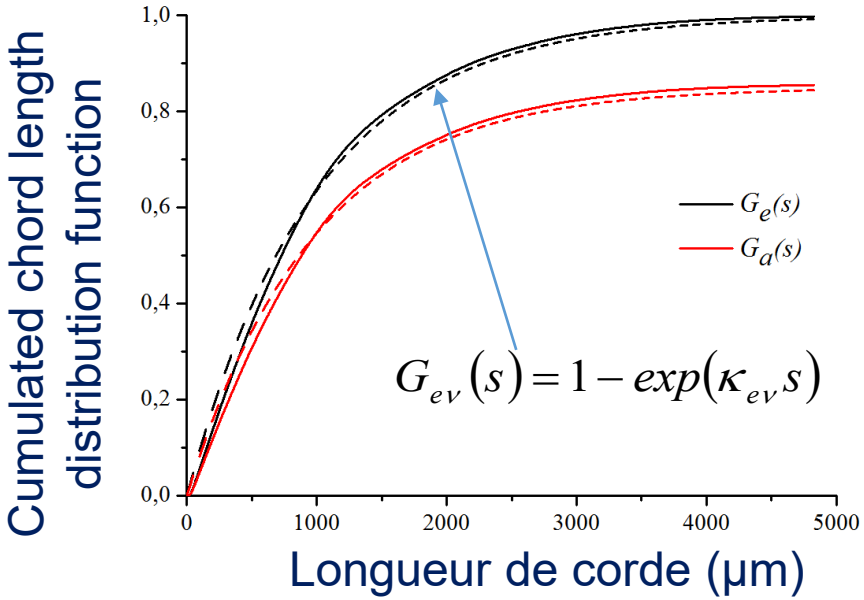
Méthode d'identification statitistique

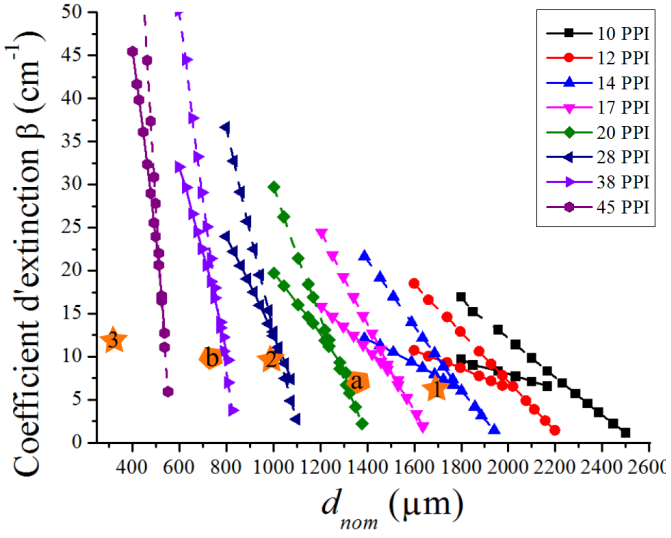
Tancrez et al., IJHMT, 2004, 47, 373–383



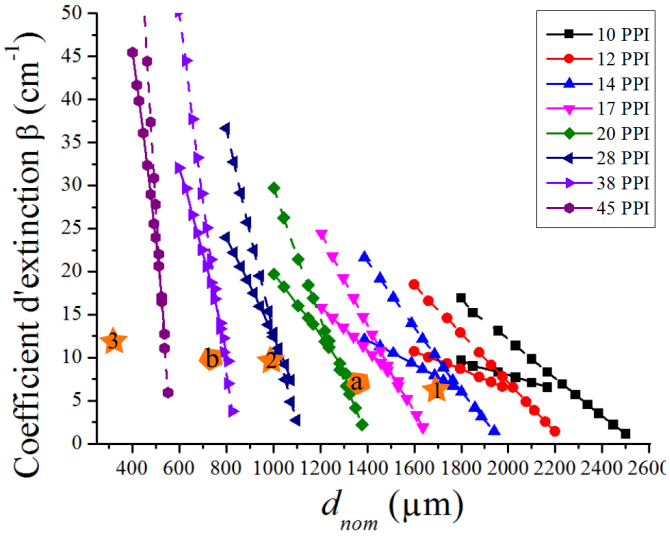
Guévelou et al., JPM, 2015, 18, 1031-1045



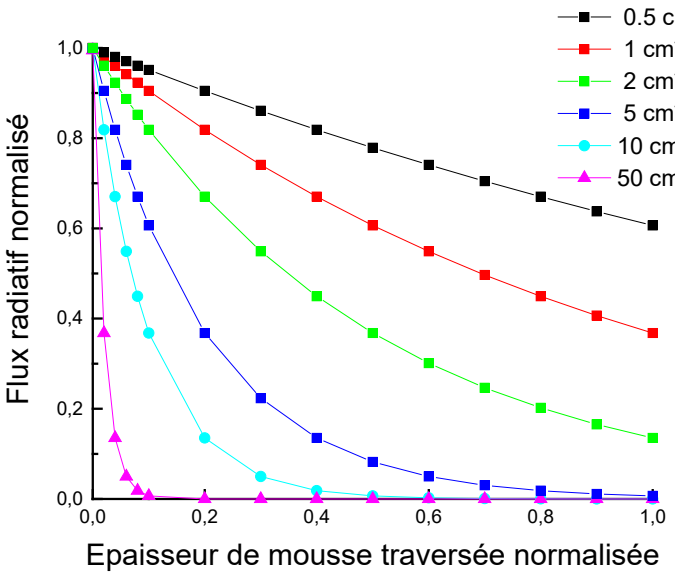




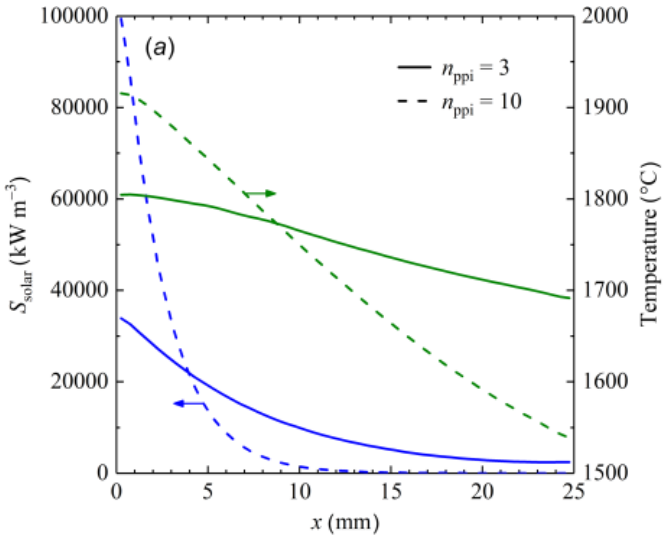
Vers la recherche de matériaux poreux à texture plus inhomogène



$$\kappa_{ev} = 2.45\frac{(1-0.7p)}{d_{nom}}$$

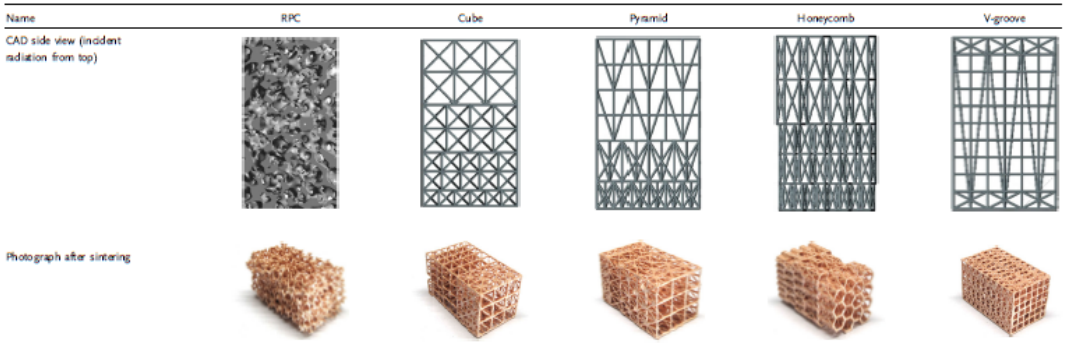


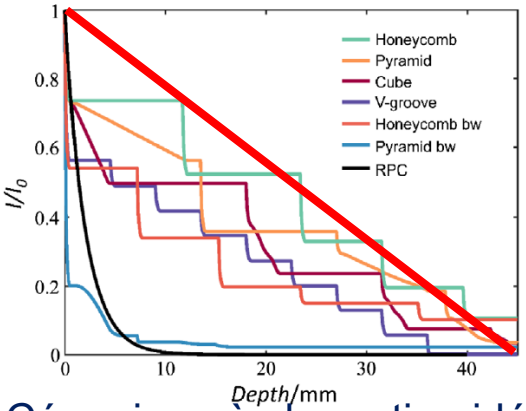
p = 0.9



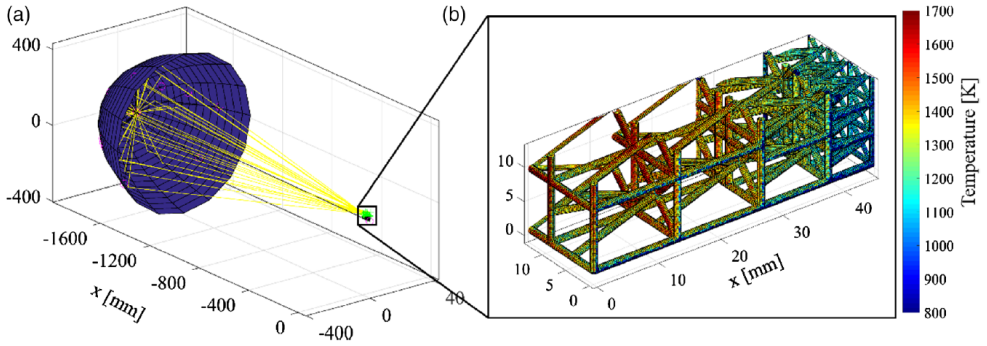
petit PPI ↔ haut d_{nom} ↔ petit coefficient d'extinction

Nouvelles géométries 3D par fabrication additive





Céramique à absorption idéale



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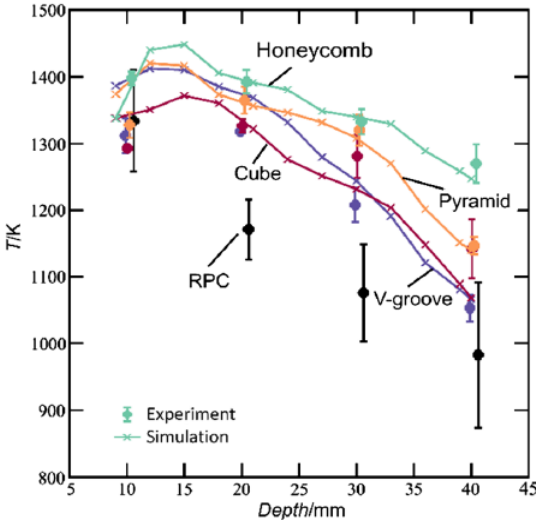
Additive-Manufactured Ordered Porous Structures Made of Ceria for Concentrating Solar Applications

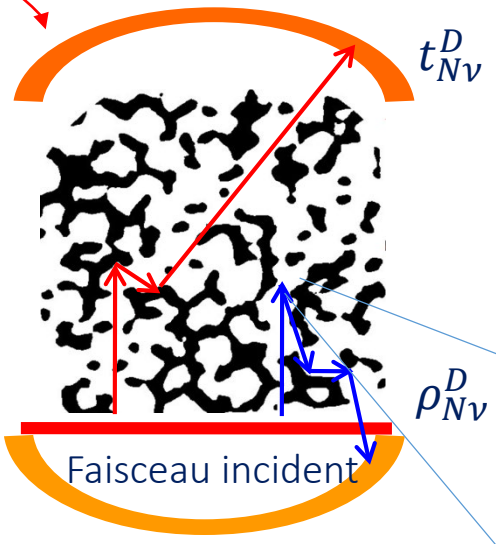
*Marie Hoes, Simon Ackermann, David Theiler, Philipp Furler, and Aldo Steinfeld**



Réduction gradient thermique

Caractérisation de la propagation volumique du rayonnement

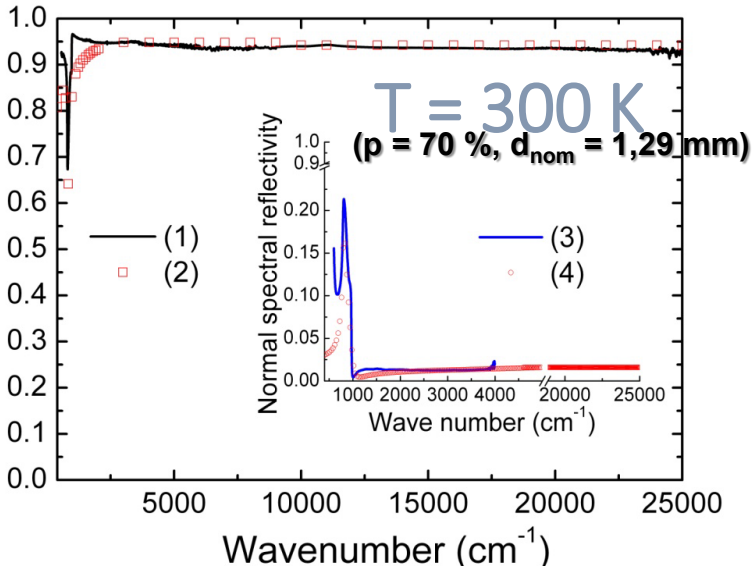
Code de Monte Carlo Lancer de Rayon :
genMat (C++, Qt)



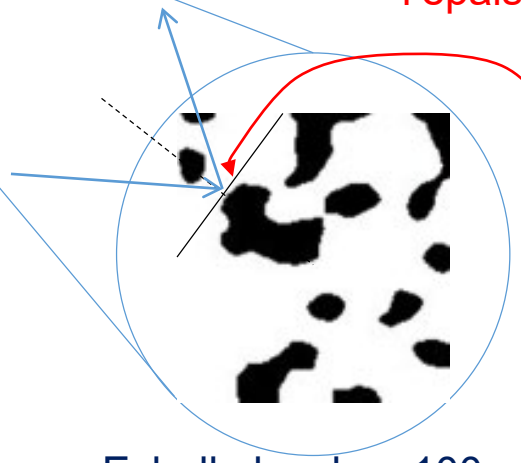
Echelle macroscopique: ~10000 µm

Rousseau et al., JCPS, 2012
Guevelou et al., IJHMT 2016

$\epsilon_{\nu N}$



% énergie absorbée en fonction de l'épaisseur de l'échantillon



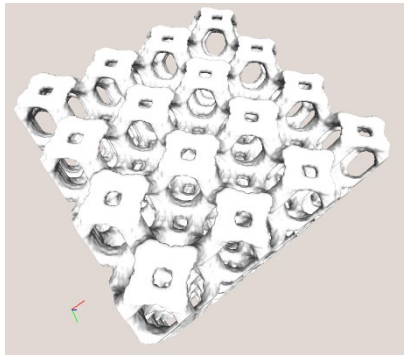
Echelle locale: ~100 µm

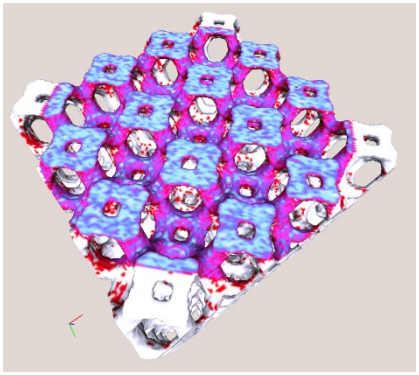
$$\rho_{N\nu} = \left| \frac{\sqrt{\tilde{\varepsilon}_{veff}} - 1}{\sqrt{\tilde{\varepsilon}_{veff}} + 1} \right|^2$$

Comparaison céramiques poreuses cellulaires / céramiques poreuses régulières

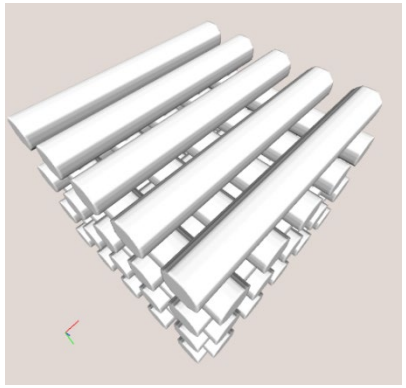
p ~ 80 %, d_{pore} ~ 300 µm, épaisseur = 2.5 mm

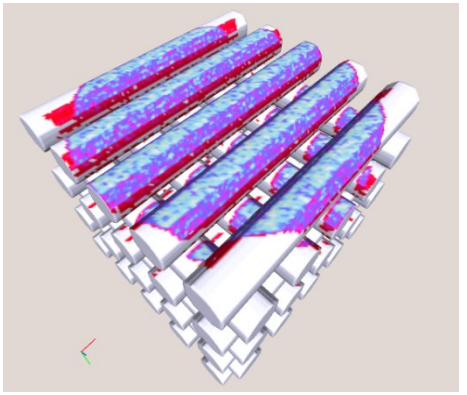
Cellule de Kelvin



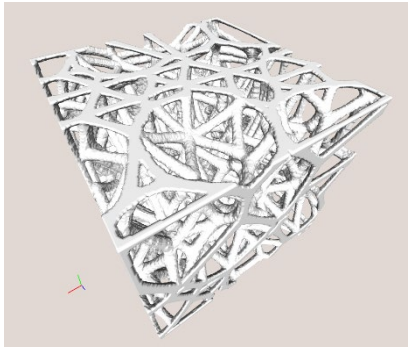


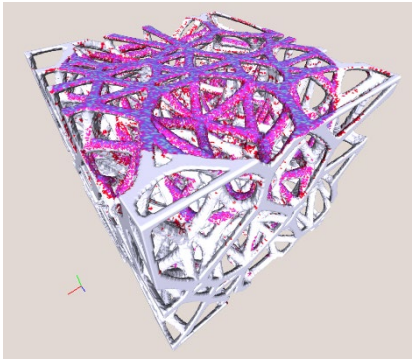
Structure régulière



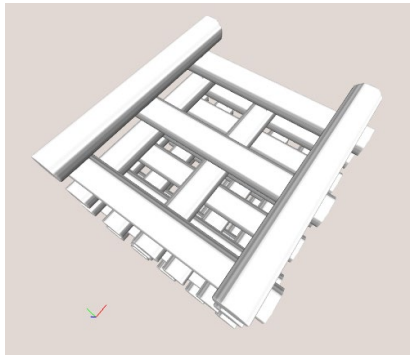


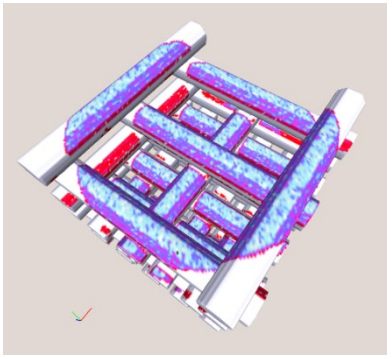
Mousse à pore ouvert



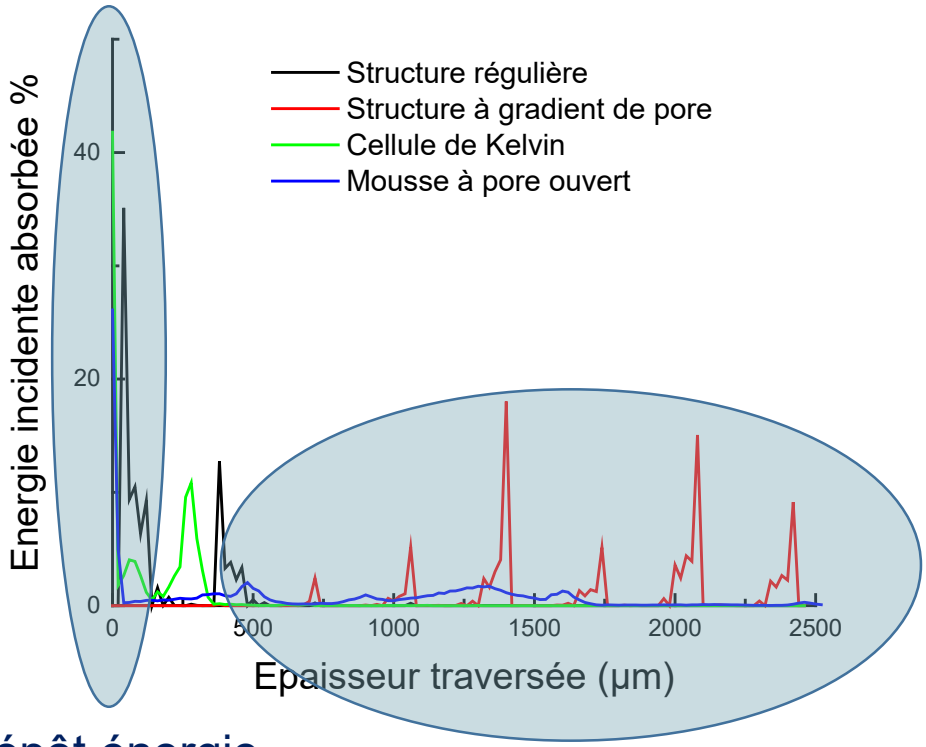


Structure à gradient de porosité



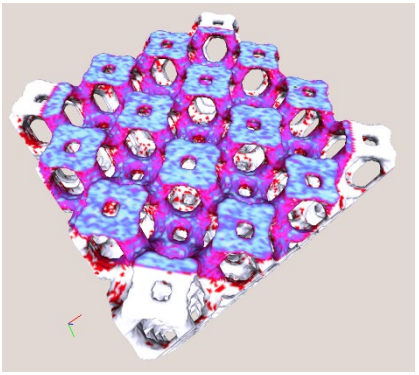


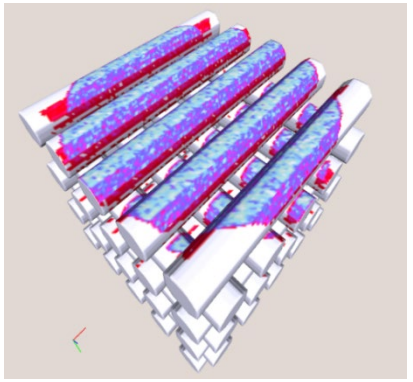
Absorption volumique du rayonnement

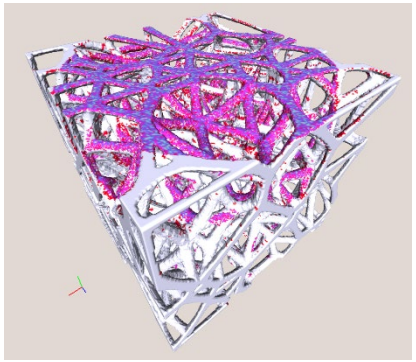


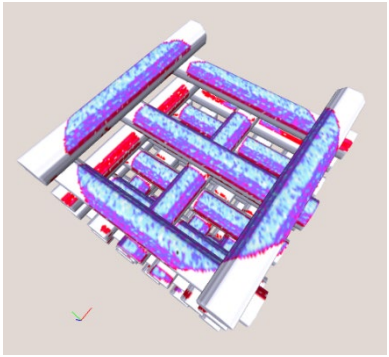
Dépôt énergie pseudo-surface

Dépôt énergie en volume



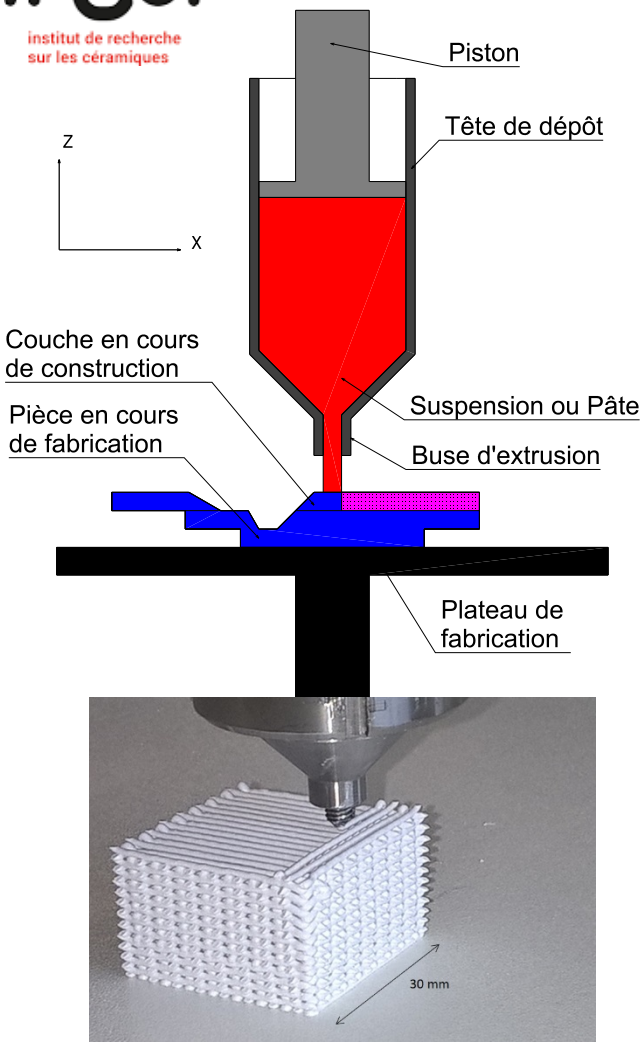




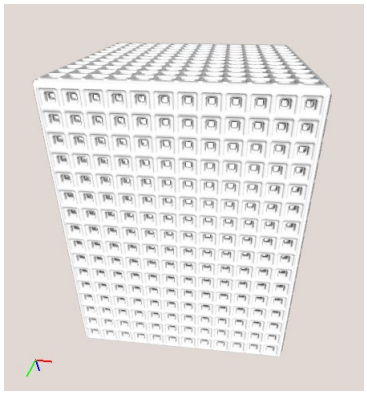


Elaboration de céramiques poreuses de CeO2 par micro-extrusion

institut de recherche sur les céramiques

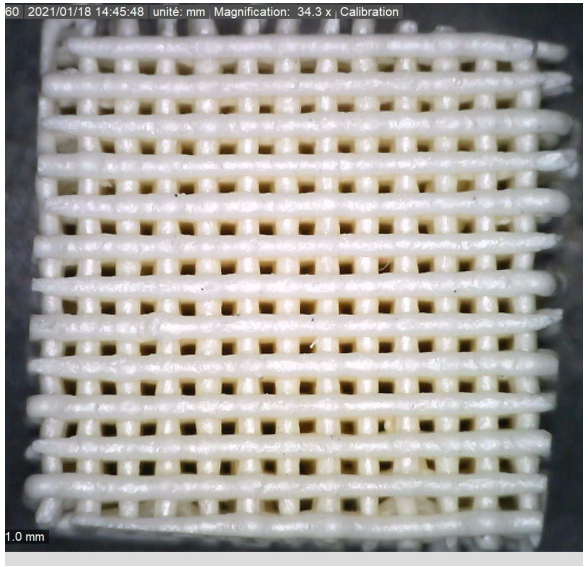


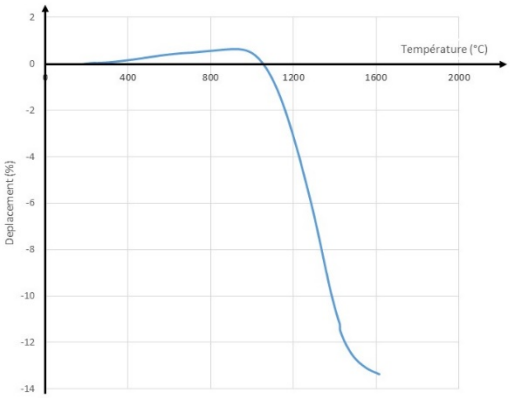
Maillage stl

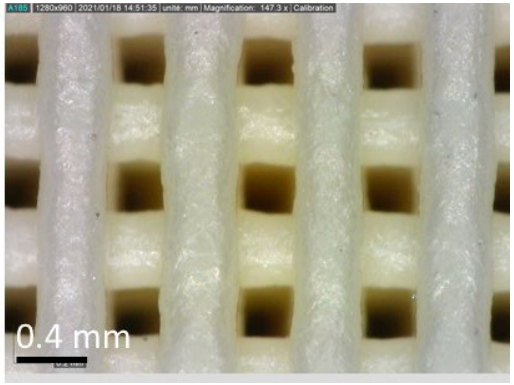


robocasting

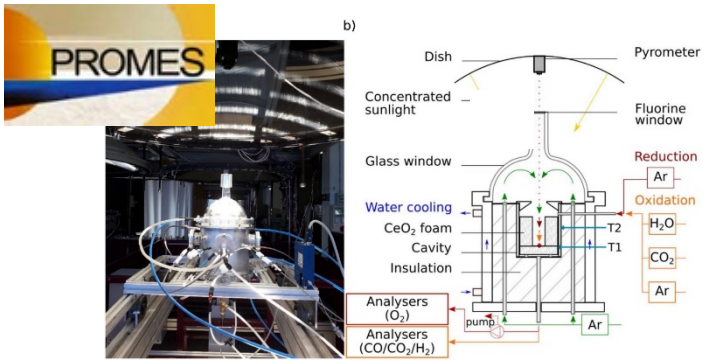
10 mm



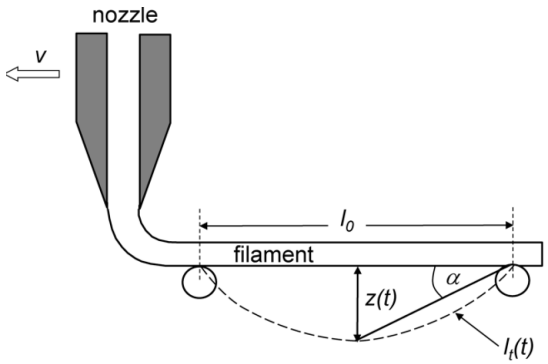


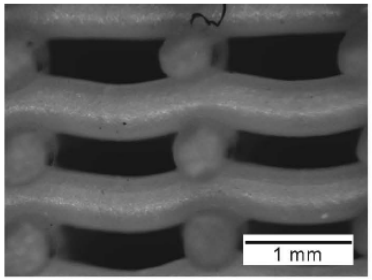


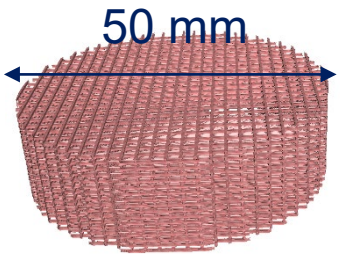
Conception numérique d'une céramique poreuse à gradient de porosit



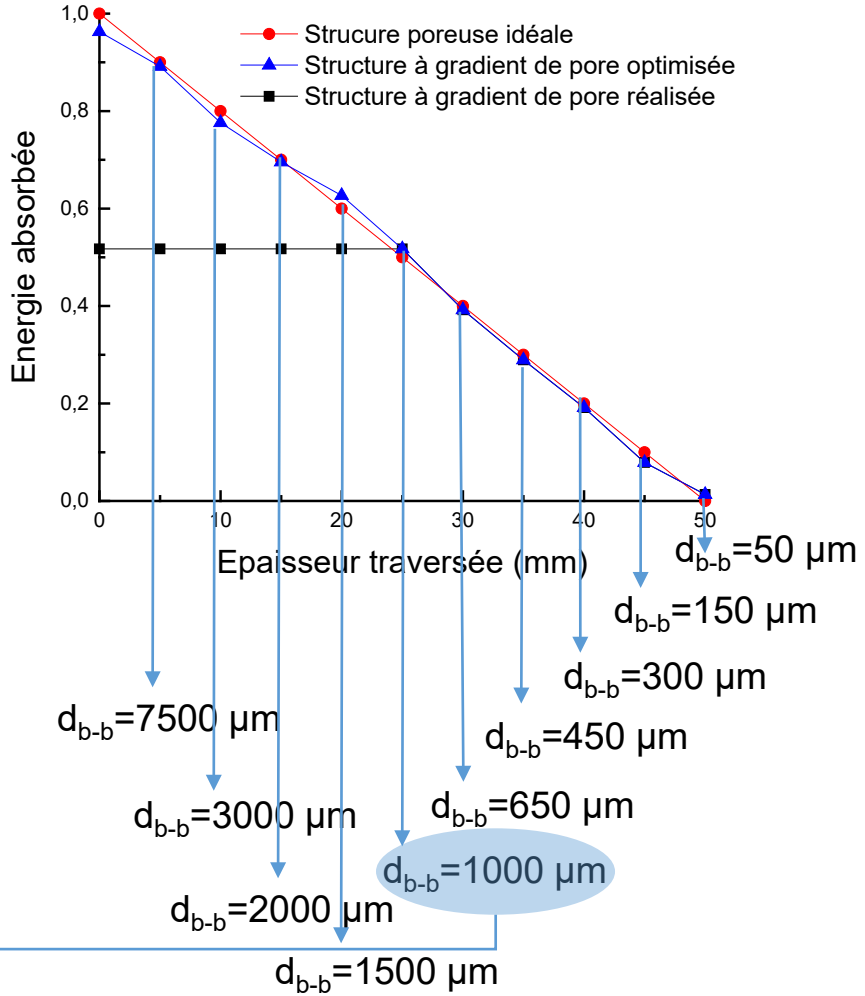
Empilement de 10 blocs poreux à porosité descendante (∅ = 50 mm, épaisseur = 5 mm)







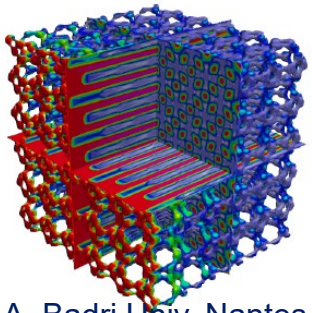
d_b= 380 µm



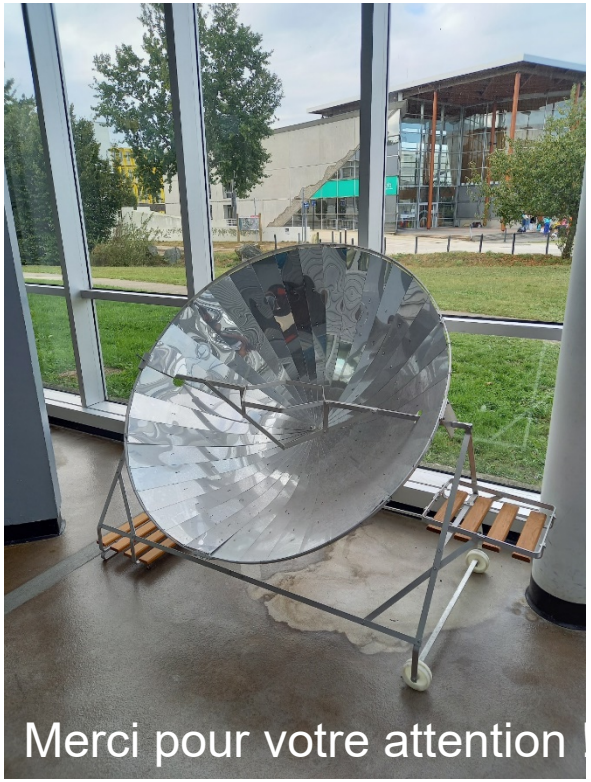
Conclusion et perspectives

- Production d'H_2 vert par thermochimie solaire
- Description statistique de la propagation volumique du rayonnement
- Optimisation de l'absorption volumique du rayonnement solaire → structures de CeO_2 à gradient de porosité
- Design radiatif numérique ↔ procédé de mise en forme ↔ génie des réacteurs solaires : structure poreuse à gradient de porosité

- Tests en réacteur réel au PROMES
- Calcul du champ de température par la méthode des éléments finis (FreeFem++, Y. Favennec, OPTHOCERA NExT) : problème thermo-fluidique avec pris en compte du rayonnement thermique
- Optimisation géométrique des céramiques de CeO_2 en tenant compte des transferts thermiques couplés



Th. A. Badri Univ. Nantes. 2018



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Normal spectral reflectivity of $CeO_{2-\delta}$ ceramics

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Spectral hemispherical reflectivity of nonstoichiometric cerium dioxide

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ABSTRACT

Nonstoichiometric ceria, $CeO_{2-\delta}$, has emerged as a promising redox material for thermoc
splitting H_2O and CO_2 using concentrated solar energy. Knowledge of its radiative properties is
the design of efficient solar reactors. Samples of various nonstoichiometries ($0 \le \delta \le 0.0377$)
pared by thermal reduction in a thermogravimetric analyzer at high temperatures ($T > 1473$ K) a
low oxygen partial pressures ($p_{O2} \le 2.5 \cdot 10^{-4}$ atm). The spectral hemispherical reflectivity was
using a spectroscopic goniometry system in the spectral range 300–2800 nm. A porous ceria sa
interconnected μm-sized pores showed comparable selectivity because of its high optical thick
total hemispherical reflectivity was computed for emission temperatures in the range 900–6
levant to solar reactors.

PROMES

Checked with PROMES : $0<\delta<0.03$

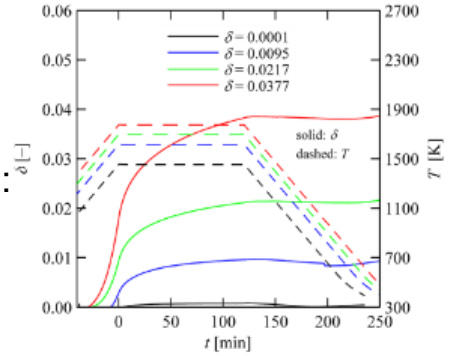

Fig. 2. Nonstoichiometry (solid) and temperature (dashed) of ceria as a function of time during a TGA run.

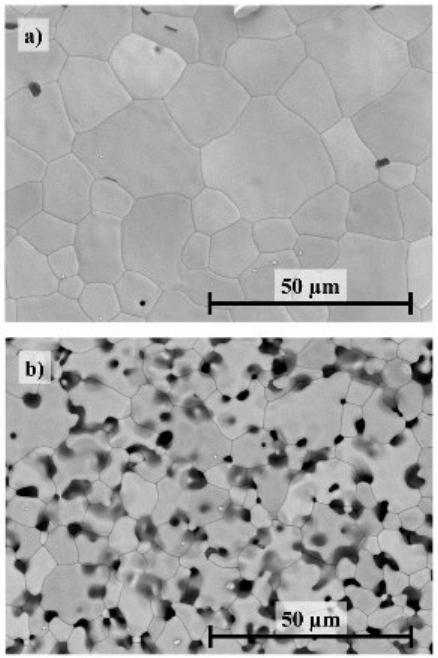

Fig. 3. SEM of the ceria pellets: a) non-porous; and b) porous with 0.26 porosity and 10 μm mean pore diameter.

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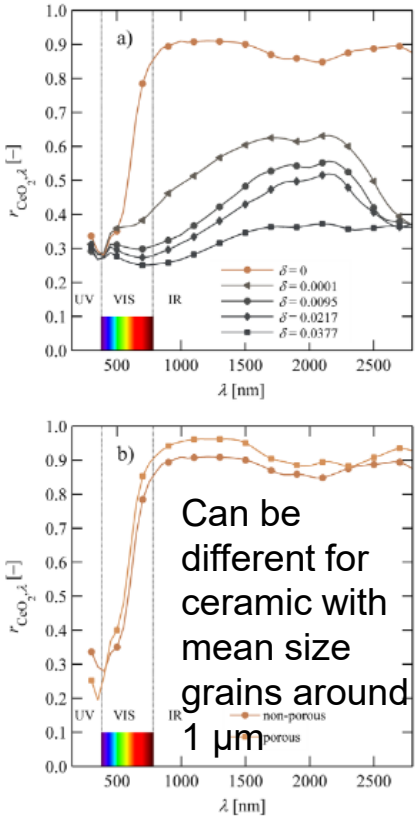

Can be different for ceramic with mean size grains around 1 μm

Fig. 5. Spectral hemispherical reflectivity of sintered polycrystalline ceria pellets as a function of the wavelength for: a) non-porous for various nonstoichiometries; and b) non-porous and porous for $\delta=0$. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)