CATALYST CARRIER SYNTHESIS: FROM PRECIPITATION TO IMPREGNATION

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A. DANDEU, M. MINIÈRE, F. SALVATORI, J-M SCHWEITZER, M. SERVEL

CONTEXT

- What is actually done

Catalyst synthesis at lab scale

- Main part of the work is done on the formulation
- No fundamental studies are done on the hydrodynamic/physical-chemistry coupling: mainly empirical approaches based on experiments

Lab's protocol →

Industrial catalyst

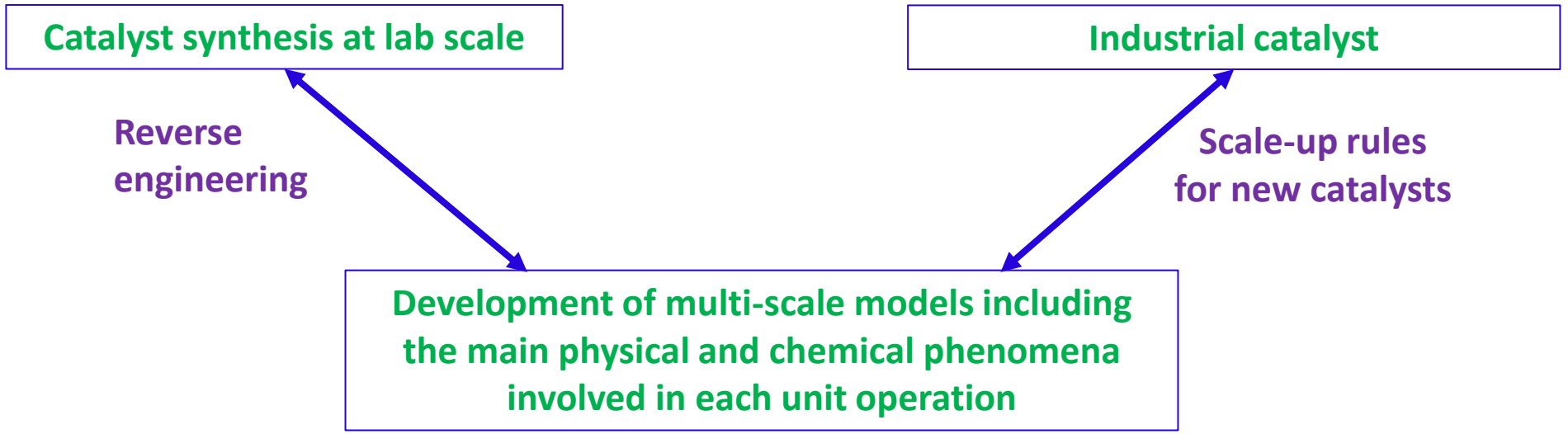
- Lab scale →Industrial scale: done by Axens
- Recipes are adapted to satisfy constraints imposed by each unit operation
- Experimental approach: tools at different scales
- knowhow

- Many innovative catalysts are developed and industrialized using this approach

- Limits of this approach:
  - Knowledge are limited to propose new formulations out of our « standard » ranges
  - Promising product at lab scale which cannot be scaled-up industrially

CONTEXT

- Development of a Chemical Engineering approach



- Creation of a specific team in 2015-2016
- The objective of this team is to interact with different entities involved in the catalyst manufacturing:
  - To improve existing catalyst manufacturing procedures
  - To propose new developments

RESEARCH STRATEGY

HYDROCARBURES RESPONSABLES

Development of Building Blocks (Collaborations, PhD, Post Doc)

- Comprehensive studies at local scale to understand which are the physical and chemical phenomena controlling catalyst textural properties
- Local measurements with specific analytical tools in controlled lab devices
- Identification of scale-up parameters (« descriptors »)
- Model development including those parameters

Make available models for industrial projects to develop innovative catalysts

CATALYST MANUFACTURING CHAIN

HYDROCARBURES RESPONSABLES

1. Boehmite gel synthesis

Raw material
Aluminum sulphate
Sodium aluminate
Water

→ Precipitation → Washing & Filtration → Suspension → Drying atomization →

Boehmite powder

2. Carrier manufacturing

→ Kneading Extrusion → Drying → Calcination →

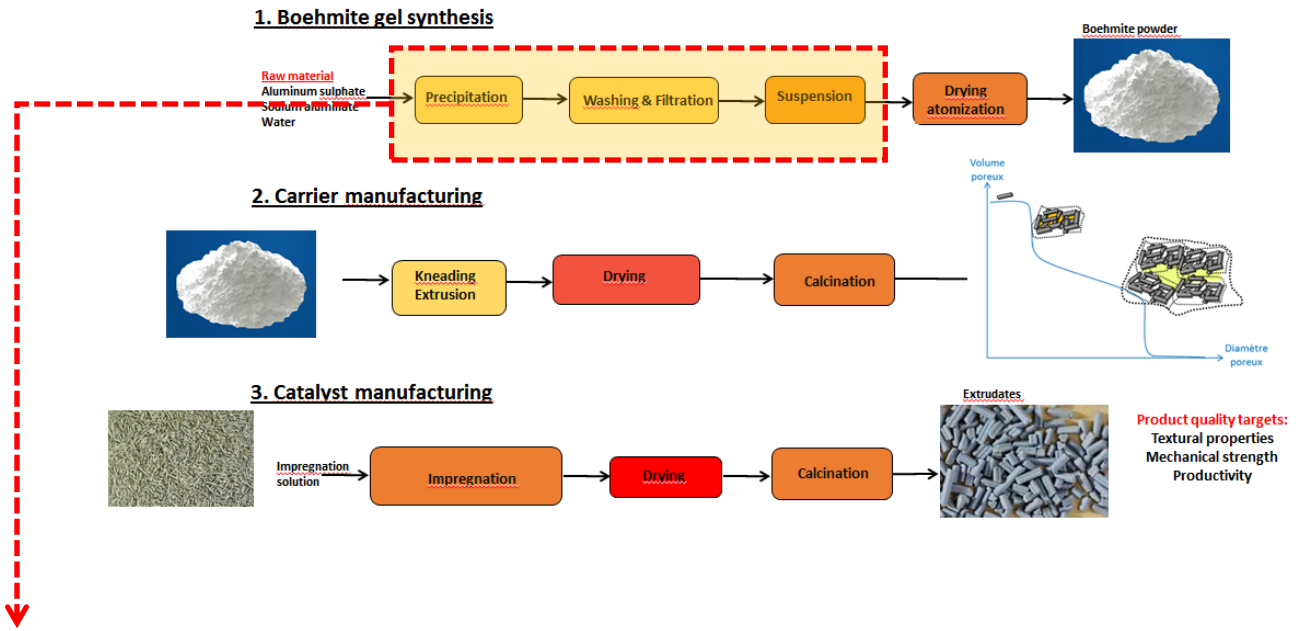
Carrier extrudates

3. Catalyst manufacturing

Impregnation solution → Impregnation → Drying → Calcination →

Extrudates

Product quality targets:
Textural properties
Mechanical strength
Productivity

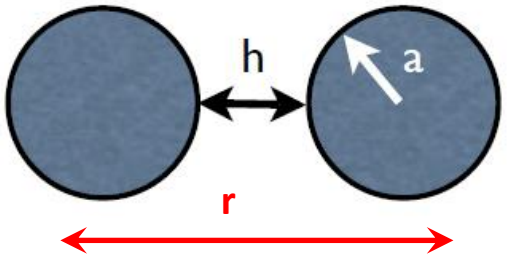


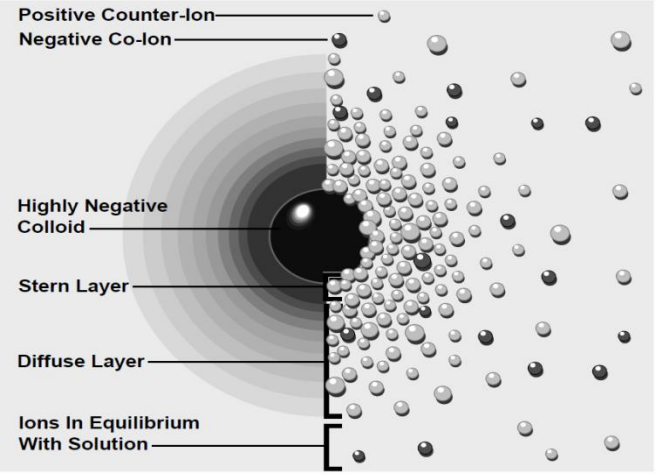
PRECIPITATION - GELATION – PARTICLE SIZE DISTRIBUTION:

FROM DLVO THEORY TO POPULATION BALANCE

DLVO THEORY

B. **D**erjaguin, L. **L**andau, E. **V**erwey and T. **O**verbeek
(1941-1948)





- DLVO modeling: Objective: modeling of the aggregation / breakage phenomena to reproduce the gelation of colloidal suspensions
  - Van de Waals potential

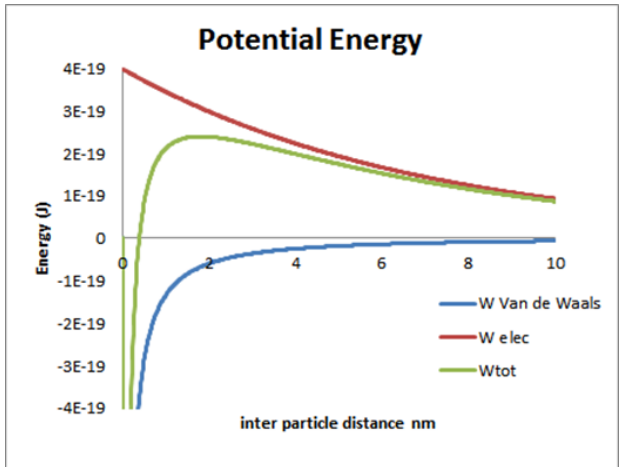
$$W_{vdW} = -\frac{A_H}{6} \cdot \left(\frac{2 \cdot a^2}{r^2 - 4 \cdot a^2} + \frac{2 \cdot a^2}{r^2} + ln\left(\frac{r^2 - 4 \cdot a^2}{r^2} \right) \right)$$

  - Electrical potential depends on
    - Activity coefficient
    - Debye length = f(Ionic strength)

$$W_{elec} = \frac{64 \cdot \pi \cdot k_B \cdot T \cdot n_{ion} \cdot a}{K_{debye}^2} \cdot \gamma_G^2 \cdot e^{-K_{debye} \cdot h}$$

  - Total potential

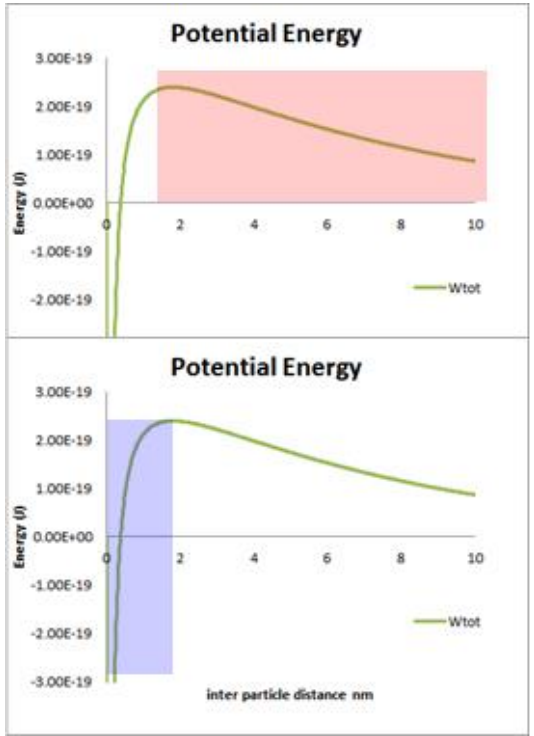
$$W_{tot} = W_{vdW} + W_{elec}$$

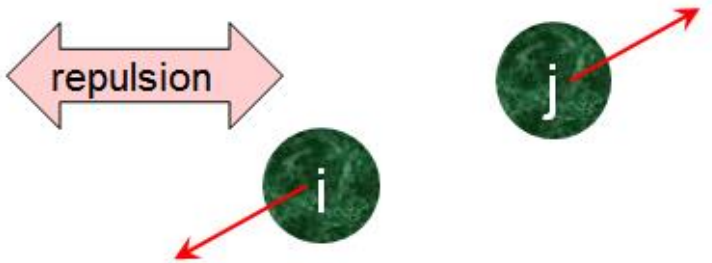


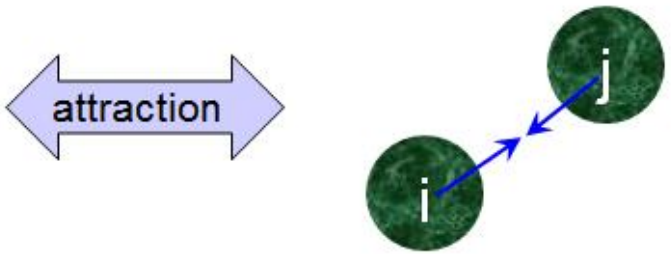
DLVO THEORY

- Interaction forces = potential gradient $\overrightarrow{F_{ij}} = -\vec{\nabla} W_{tot}$

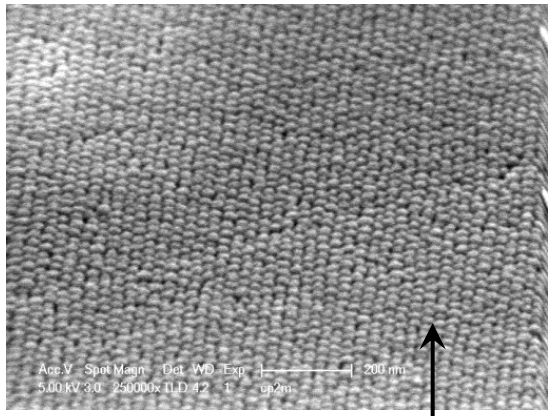
- Momentum balances $m \cdot \overrightarrow{a_i} = \sum_{i \neq j} \overrightarrow{F_{ij}} - 6 \cdot \pi \cdot \eta \cdot a \cdot \vec{v}$







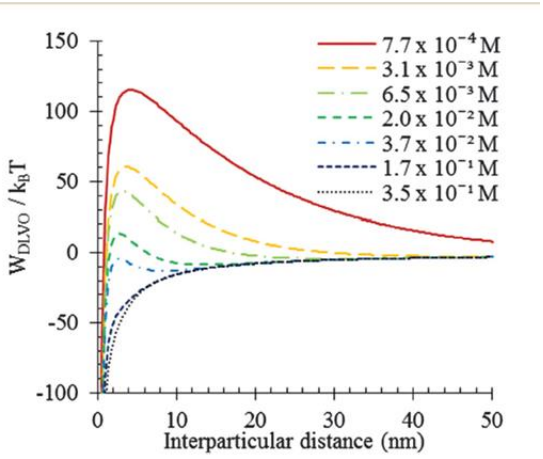
DLVO THEORY FOR DRYING

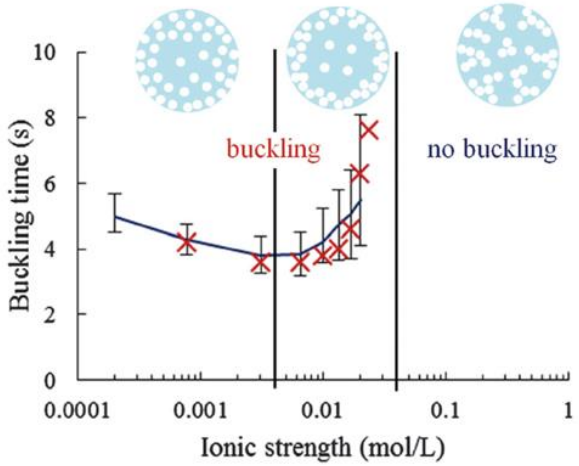


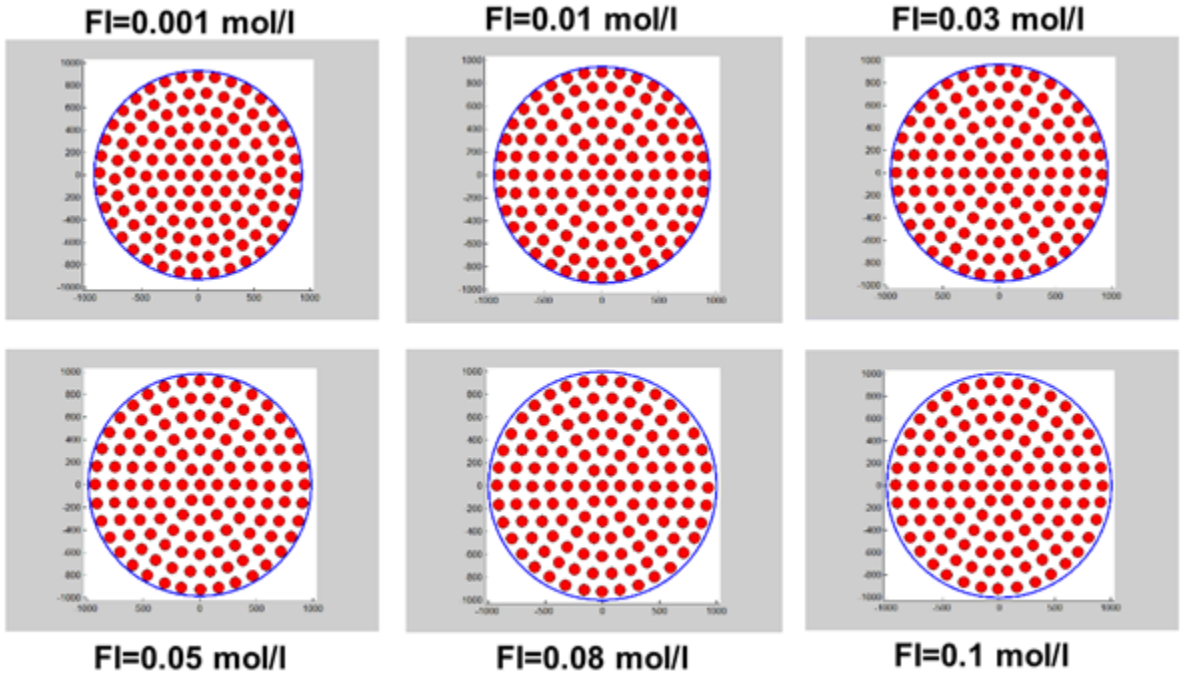
HYDROCARBURES RESPONSABLES

Strong repulsive forces → structured arrangement

- Effect of the ionic strength
  - The energy barrier can be decreased by changing the environment (Ionic environment)



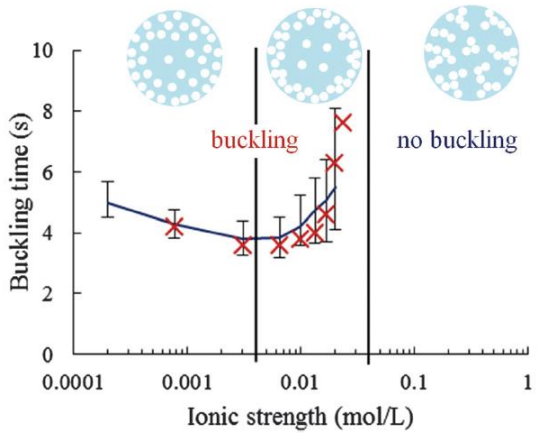




Lintingre, É.; Ducouret, G.; Lequeux, F.; Olanier, L.; Périé, T.; Talini, L. (2015) Controlling the buckling instability of drying droplets of suspensions through colloidal interactions. In : Soft Matter, vol. 11, n° 18, p. 3660–3665

DLVO THEORY FOR DRYING

- Key suspension characteristics
  - Ionic strength
  - Solid holdup
  - Zeta potential
  - Colloid radius



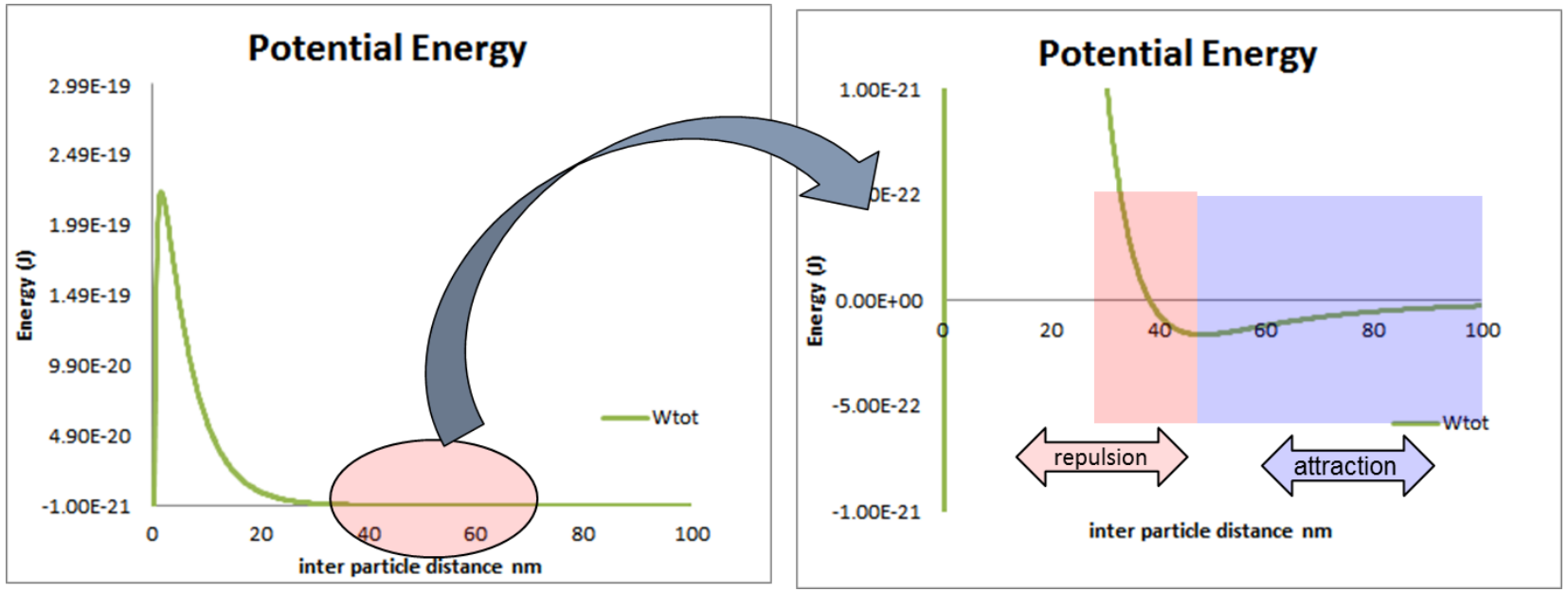
Repulsion ++ ←

- Repulsion controls the particle porosity and/or the mechanical strength
- More repulsion leads to dense particles with a deformation risk

Lintingre, É.; Ducouret, G.; Lequeux, F.; Olanier, L.; Périé, T.; Talini, L. (2015) Controlling the buckling instability of drying droplets of suspensions through colloidal interactions. In : Soft Matter, vol. 11, n° 18, p. 3660–3665

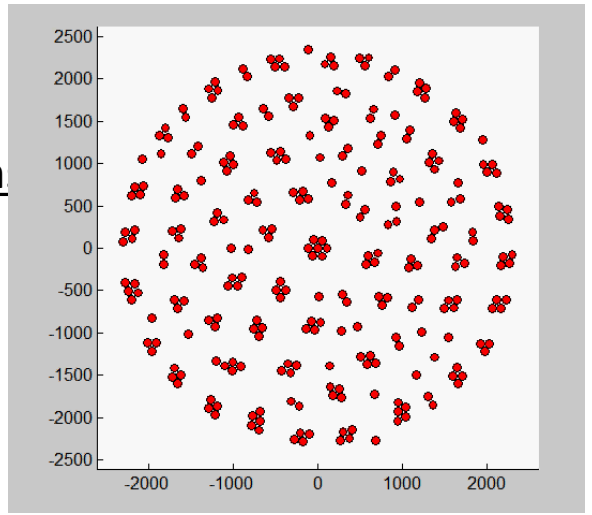
DLVO THEORY: EXTENSION TO AGGREGATION AND GELATION

- Aggregation and Gelation
  - DLVO potential: Secondary minimum
  - Use of DLVO theory for the suspension preparation steps
  - Forces involved: long distance attraction (reversible)
  - Aggregate geometry characterized by a fractal dimension

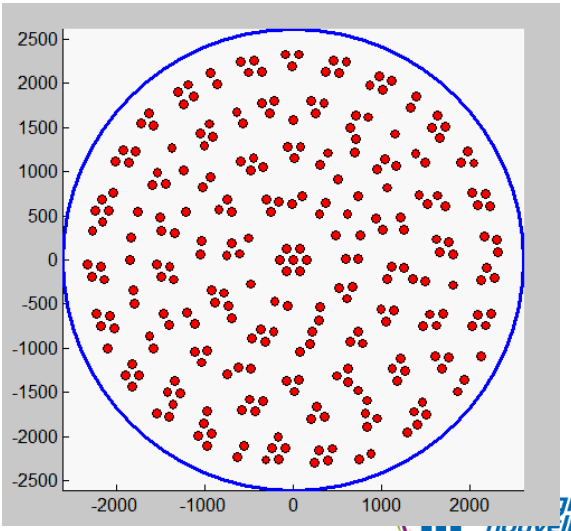


2D simulation

FI=0.03 mol/l



FI=0.003 mol/l



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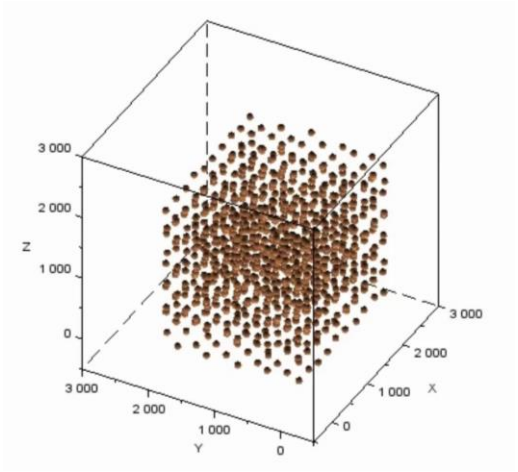
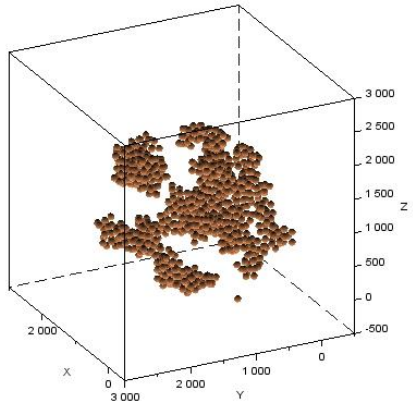
DLVO THEORY: EXTENSION TO AGGREGATION AND GELATION

HYDROCARBURES RESPONSABLES

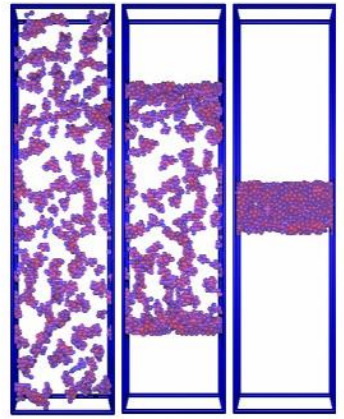




Fractal dimension

- Aggregation and Gelation
  - Use of DLVO theory for the suspension preparation steps
  - 3D simulations with 1000 particles (CPU = 3 weeks)
    - Colloid radius: 50 nm
    - Ionic strength: 0.01 mol/l
    - Solid holdup: 10% vol.
    - Zeta potential: 45 mV
  - Evaluation of the fractal dimension → fundamental parameter for aggregation modeling using population balance

Schäfer, Bastian; Hecht, Martin; Harting, Jens; Nirschl, Hermann (2010) Agglomeration and filtration of colloidal suspensions with DVLO interactions in simulation and experiment. In : Journal of colloid and interface science, vol. 349, n° 1, p. 186–195.



AGGREGATION AND GELATION MODELING

- Models are based on the master population balance equation (PBE)
  - Continuous formalism

$$\frac{\partial f_1(x,\ t)}{\partial t} = \frac{1}{2}\int_0^x a(x-x',\ x')\, f_1(x-x',\ t)\, f_1(x',\ t)\, dx' - f_1(x,\ t) \times \int_0^\infty a(x,\ x')\, f_1(x',\ t)\, dx'.$$

Ramkrishna, Doraiswami (2000) Population balances. Theory and applications to particulate systems in engineering. San Diego, CA : Academic Press.

  - Discrete formalism

$$\frac{\mathrm{d}N_m}{\mathrm{d}t} = \frac{1}{2}\sum_{i,j=1}^{i+j=m} K_{ij}^{\mathrm{A}} N_i N_j - N_m \sum_{i=1}^{\infty} K_{im}^{\mathrm{A}} N_i - K_m^{\mathrm{B}} N_m + \sum_{i=m+1}^{\infty} K_i^{\mathrm{B}} G_{im} N_i$$

aggregation

breakage

Lattuada, Marco; Zaccone, Alessio; Wu, Hua; Morbidelli, Massimo (2016) Population-balance description of shear induced clustering, gelation and suspension viscosity in sheared DLVO colloids. In : Soft Matter, vol. 12, 2016, p. 5313–5324.

K^A: aggregation kernel
K^B: breakage kernel

AGGREGATION AND GELATION MODELING

- Definition of discrete aggregate classes:
  - Based on the fractal dimension

$$n_i = \frac{m_i}{m_p} = k_f \cdot \left(\frac{R_{g,i}}{R_p}\right)^{d_f}$$

Sorensen, C. M. Light Scattering by Fractal Aggregates: A Review. In : Aerosol Science and Technology, vol. 35, n° 2, p. 648–687.

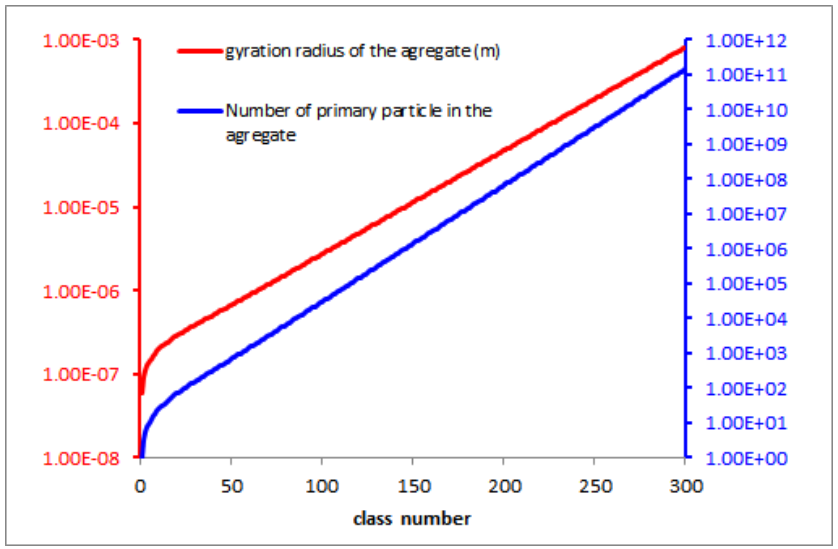
Where n_i is the number of colloids which constitute the i^{th} aggregate

  - The number of colloids which constitute the i^{th} aggregate

$$n_i = n_{i-1} + 1 + (1.08)^i$$

  - The gyration radius

$$R_{g,i} = R_p \cdot \left(\frac{n_i}{k_f}\right)^{1/d_f}$$



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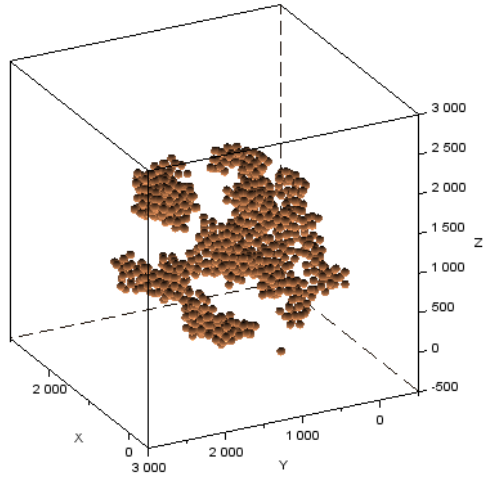
AGGREGATION AND GELATION MODELING

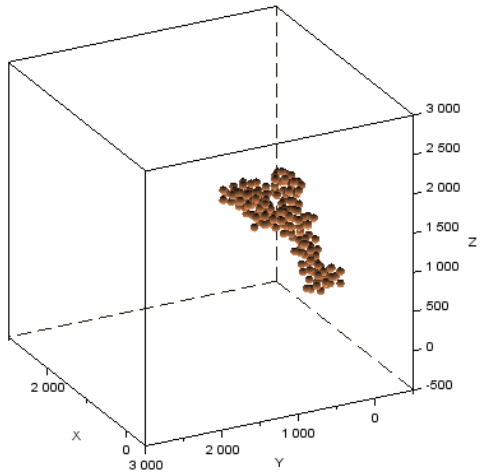
HYDROCARBURES RESPONSABLES

- Fractal dimension: Ionic strength = 0.01 mol/l
  - Calculation on the basis of 3D DLVO aggregation modeling

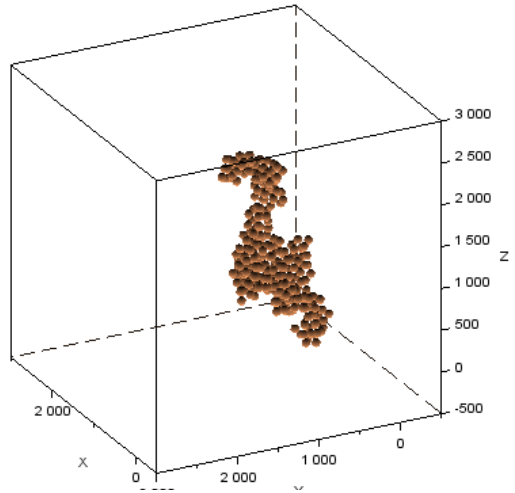
$$d_f = \frac{ln\left(\frac{n_i}{k_f}\right)}{ln\left(\frac{R_{g,i}}{R_p}\right)}$$

cluster number	R_gyr cluster (nm)	Rp (nm)	np_cluster	dim fractal
1	514.32	50	182	2.23
2	676.70	50	305	2.20
3	550.07	50	153	2.10
4	401.45	50	185	2.51
			average	**2.26**

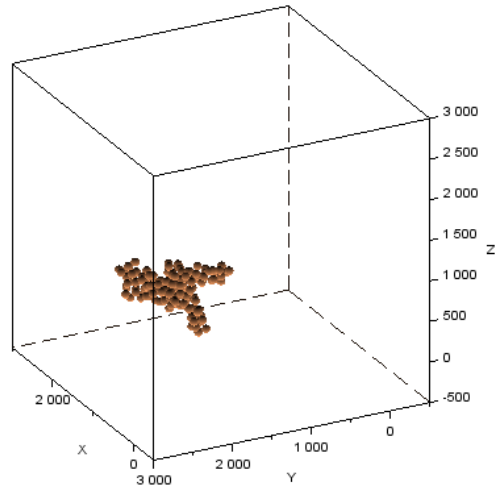




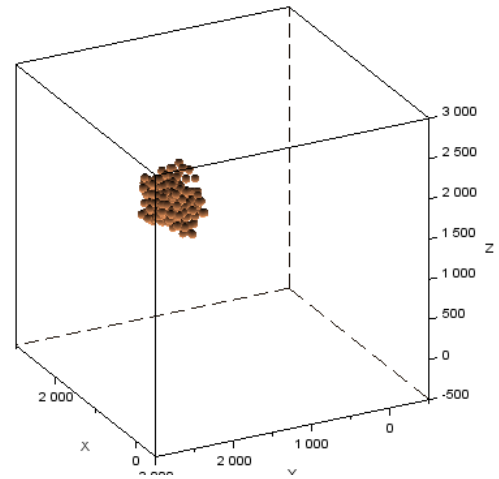
Cluster 1



Cluster 2



Cluster 3



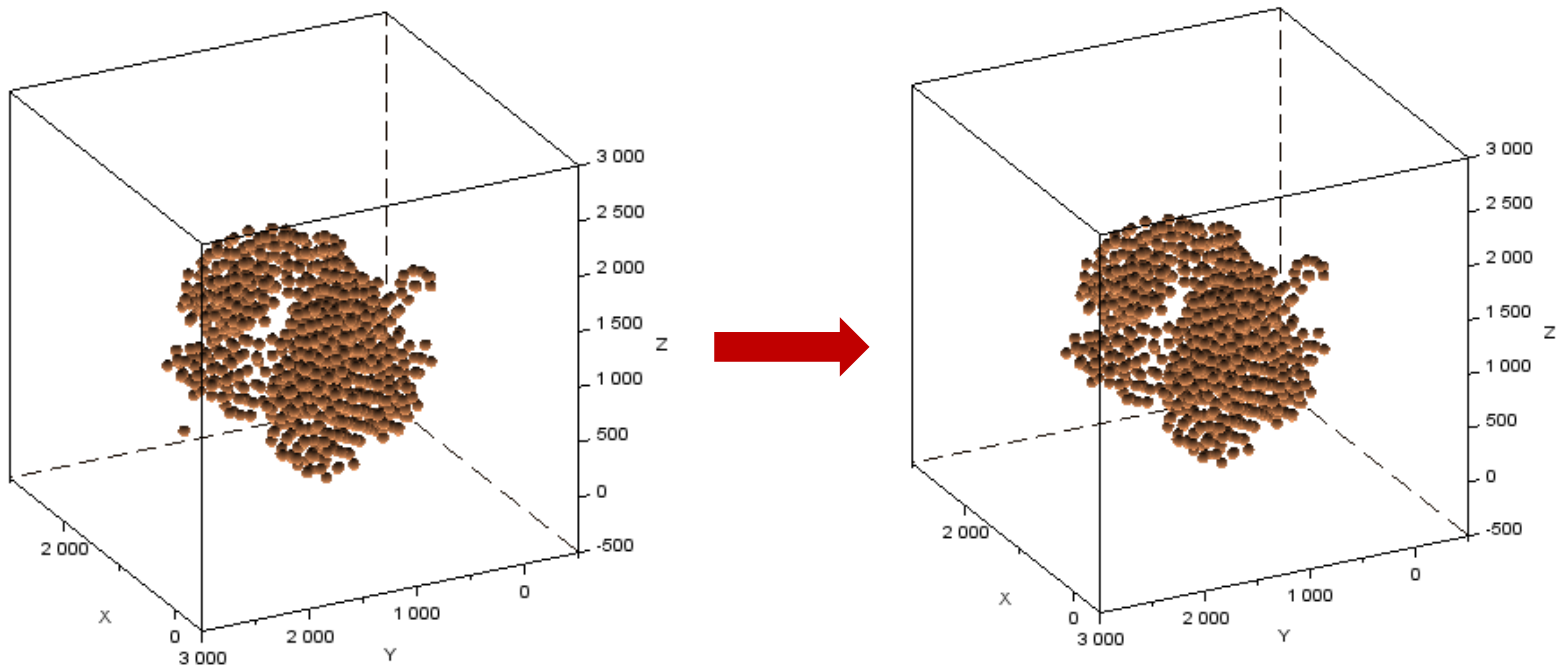
Cluster4

AGGREGATION AND GELATION MODELING

- Fractal dimension: Ionic strength = 0.003 mol/l
  - Calculation on the basis of 3D DLVO aggregation modeling

$$d_f = \frac{ln\left(\frac{n_i}{k_f}\right)}{ln\left(\frac{R_{g,i}}{R_p}\right)}$$

cluster number	R_gyr cluster (nm)	Rp (nm)	np_cluster	dim fractal
1	806.34	50	988	2.48



Cluster 1

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AGGREGATION AND GELATION MODELING

- Aggregation kernel
  - 2 terms for this kernel
    - Brownian agglomeration characterized by:
      - Fuchs stability ratio **W**
    - Shear induced agglomeration characterized by:
      - Collision efficiency **a**
      - Shear rate $\dot{\gamma}$

$$K_{ij} = \min \begin{cases} \dfrac{2kT}{3\eta W}\left(i^{\frac{1}{d_f}} + j^{\frac{1}{d_f}}\right)\left(i^{-\frac{1}{d_f}} + j^{-\frac{1}{d_f}}\right) \\ \dfrac{4}{a\frac{3}{3}}\dot{\gamma} R_p{}^3 \left(i^{\frac{1}{d_f}} + j^{\frac{1}{d_f}}\right)^3 \end{cases}$$

Lattuada, Marco; Zaccone, Alessio; Wu, Hua; Morbidelli, Massimo (2016) Population-balance description of shear induced clustering, gelation and suspension viscosity in sheared DLVO colloids. In : Soft Matter, vol. 12, 2016, p. 5313–5324.

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AGGREGATION AND GELATION MODELING

HYDROCARBURES RESPONSABLES

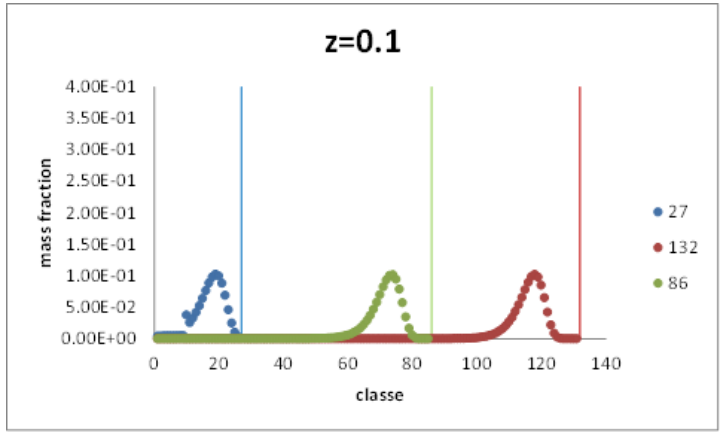
- Breakage kernel
  - Power-law model proposed by Harshe et al.

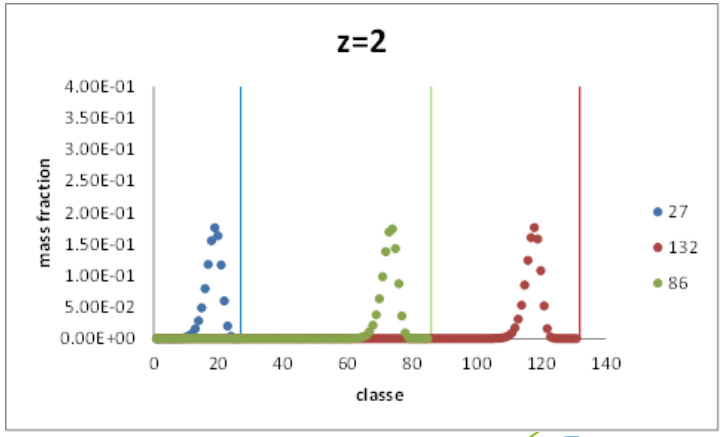
$$K_i^{\mathrm{B}} = c_1(\eta\dot{\gamma})^n \, R_{g,i}^m.$$

  - According to the population balance equation we need to define the distribution G_{im} of the clusters issued from the breakage of a given aggregate

$$\frac{\mathrm{d}N_m}{\mathrm{d}t} = \frac{1}{2}\sum_{i,j=1}^{i+j=m} K_{ij}^{\mathrm{A}} N_i N_j - N_m \sum_{i=1}^{\infty} K_{im}^{\mathrm{A}} N_i - K_m^{\mathrm{B}} N_m + \sum_{i=m+1}^{\infty} K_i^{\mathrm{B}} G_{im} N_i$$

aggregation — breakage





  - The broken aggregates are given by a Schultz-Zimm distribution
    - z is a parameter determining the width
    - This formalism ensure that only smaller clusters are formed

$$f_{m,k} = (a)^{z+1}(N_{\mathrm{fr}}^{\mathrm{s}})^z \exp[-(a \cdot N_{\mathrm{fr}}^{\mathrm{s}})]\frac{1}{\Gamma(z+1)}$$

Harshe, Y. M.; Lattuada, M. (2012) Breakage Rate of Colloidal Aggregates in Shear Flow through Stokesian Dynamics. In : Langmuir, vol. 28, 2012, p. 283–292.

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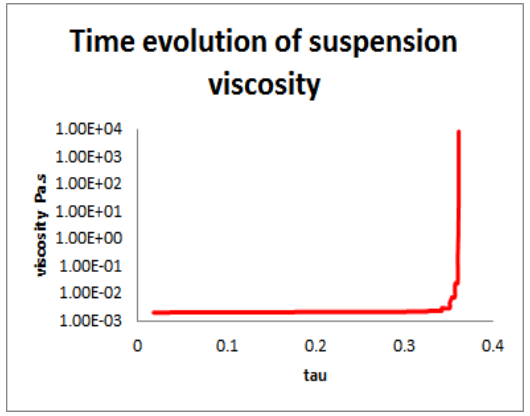
AGGREGATION AND GELATION MODELING

HYDROCARBURES RESPONSABLES

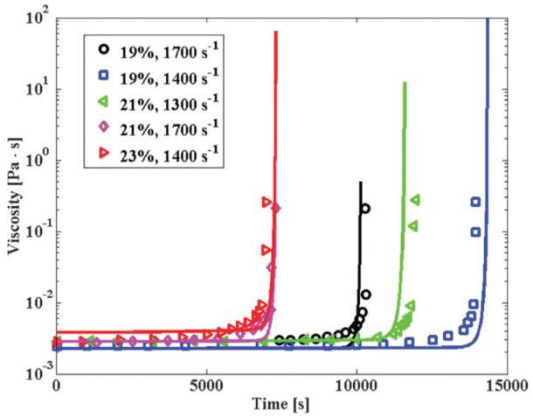
- Solid holdup
  - $\varepsilon_s = \sum_i N_i \cdot \frac{4}{3} \cdot \pi \cdot R_{g,i}^3$
- Viscosity: $\varepsilon_s \equiv \emptyset$
  - Equation proposed by van de Ven and Takamura

$$\eta_s = \eta \left(\frac{1 - \frac{\phi}{\phi_c}}{\left(1 - (k_0\phi_c - 1)\frac{\phi}{\phi_c}\right)} \right)^{-\frac{5\phi_c}{2(2-k_0\phi_c)}}$$

Our simulation

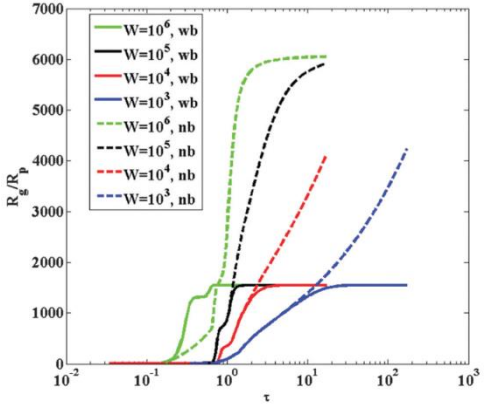


Lattuada et al. (2016)

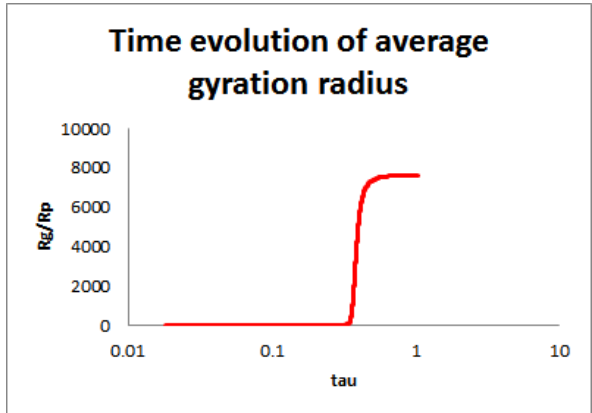


- Average gyration radius
  - $R_g = \frac{1}{N_o} \cdot \sum_i N_i \cdot n_i \cdot R_{g,i}$

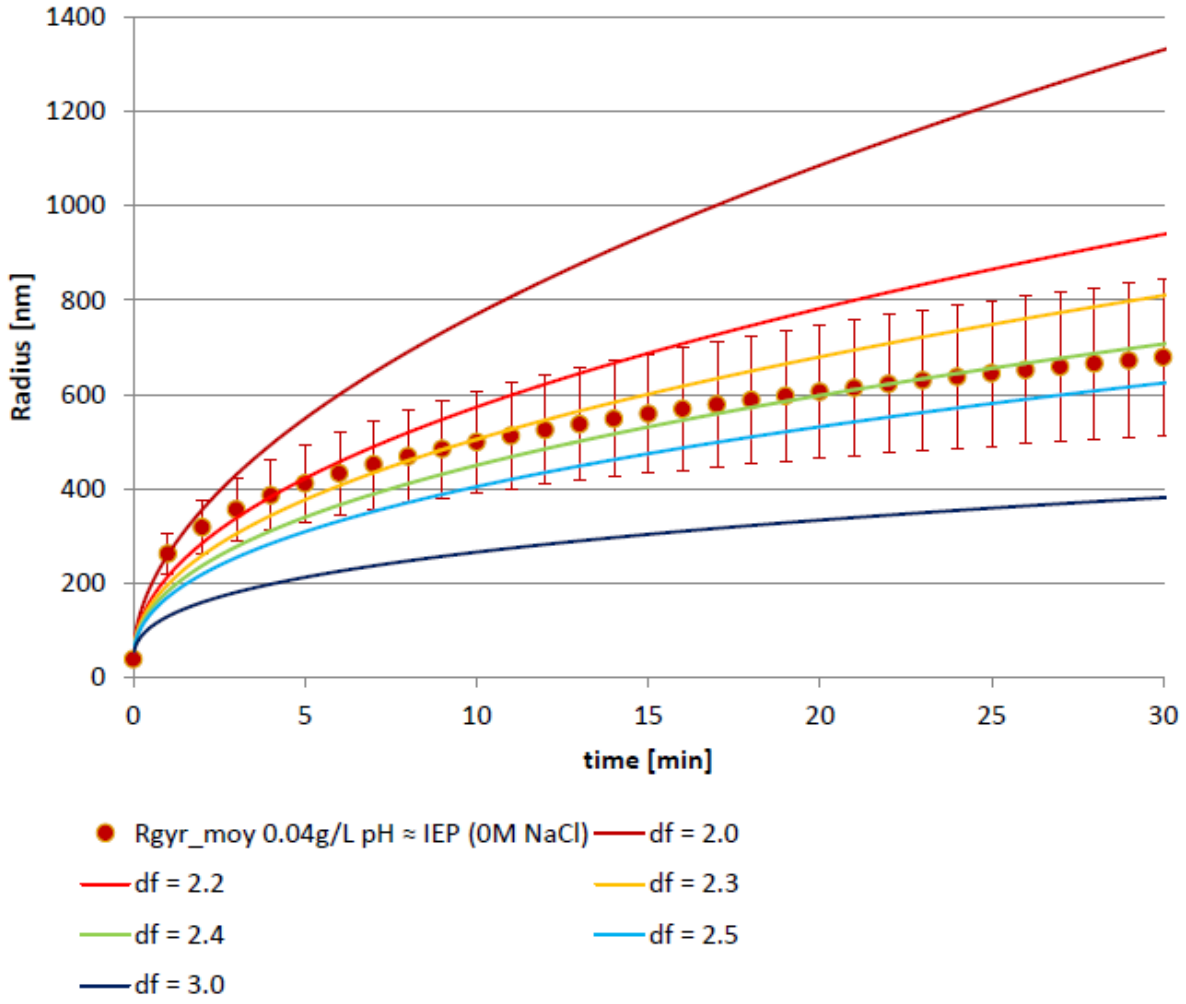
Lattuada et al. (2016)



Our simulation



FIRST COMPARISON BETWEEN EXPERIMENTAL RESULTS AND PHYSICAL MODELS



Colloidal aggregation in Brownian conditions → inspected with Dynamic Light Scattering (DLS)

No shear → $\dot{\gamma} = 0$

Only aggregation kernel *

→ $\beta_{ij}^{A} = \frac{2k_BT}{3\eta W}\left(i^{\frac{1}{df}} + j^{\frac{1}{df}}\right)\left(i^{-\frac{1}{df}} + j^{-\frac{1}{df}}\right)$

Near to IEP → the aggregation process is faster

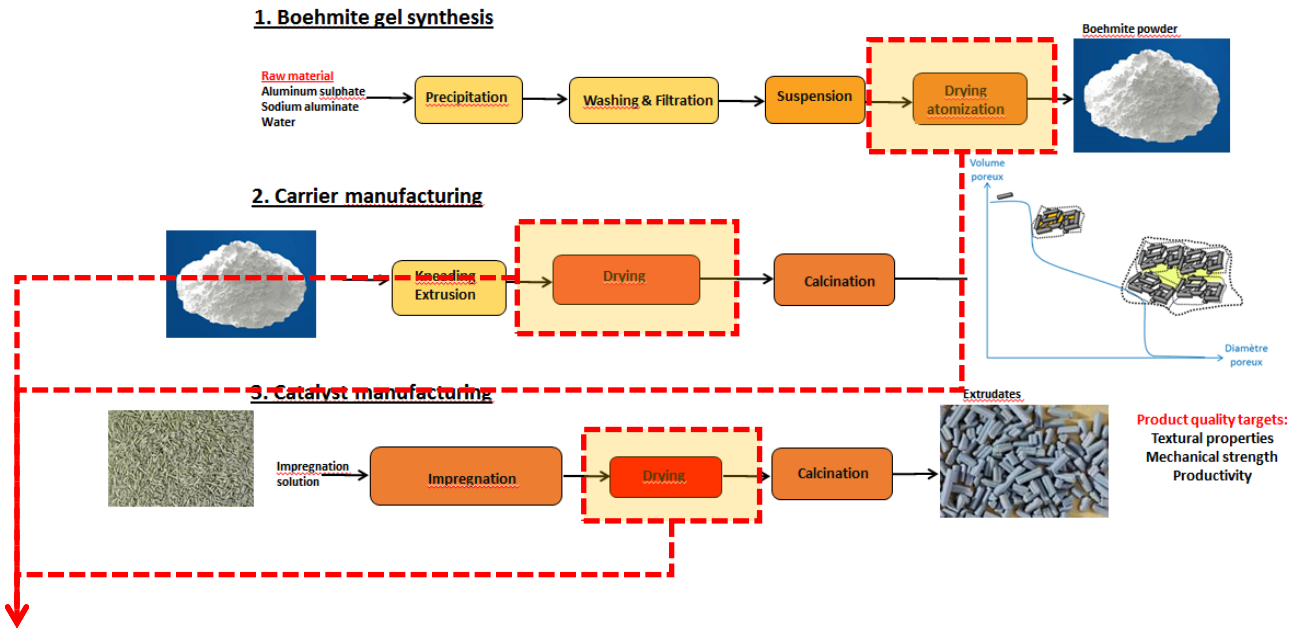
W = 1 → *df* free parameter

Far IEP → the aggregation process is slower

W > 1 → W and *df* free parameters

IN SUMMARY

- DLVO modeling leads to an estimate of the aggregate fractal dimension
- Population balance modeling with aggregation and breakage kernels proposed by Lattuada et al. (2016) leads to the prediction of the cluster size distribution and the time evolution of suspension viscosity
- Good trends are obtained for viscosity and average gyration radius
- Population balance model is tested on an IFPEN experimental case
- This model is a tool to drive the unit operations by adapting the hydrodynamic constraints and the chemical formulation of the suspension



GEL DRYING

CONSTRUCTION OF THE BUILDING BLOCK

Alumina gel drying

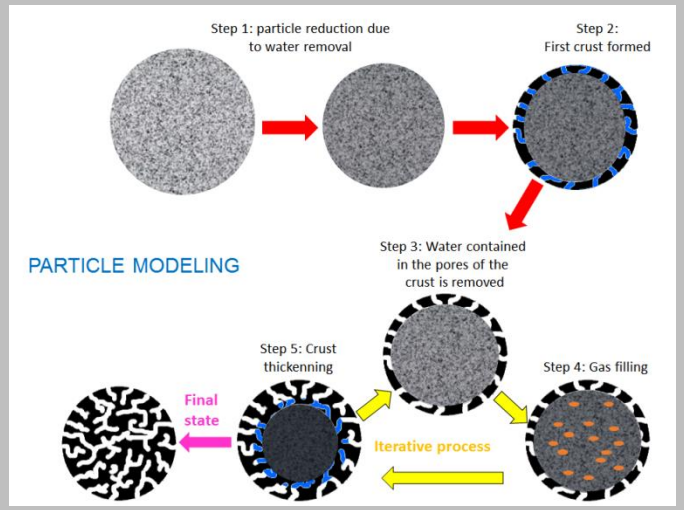
Objectives

Construction of a drying building block (particle drying model)

1- allow to evaluate the effects of operating conditions

2- allow to evaluate the mechanical resistance of the dry particle

3- useful to scale-up industrial dryers (belt dryer, atomizer)



Lab tool

Particle model

Different steps during drying

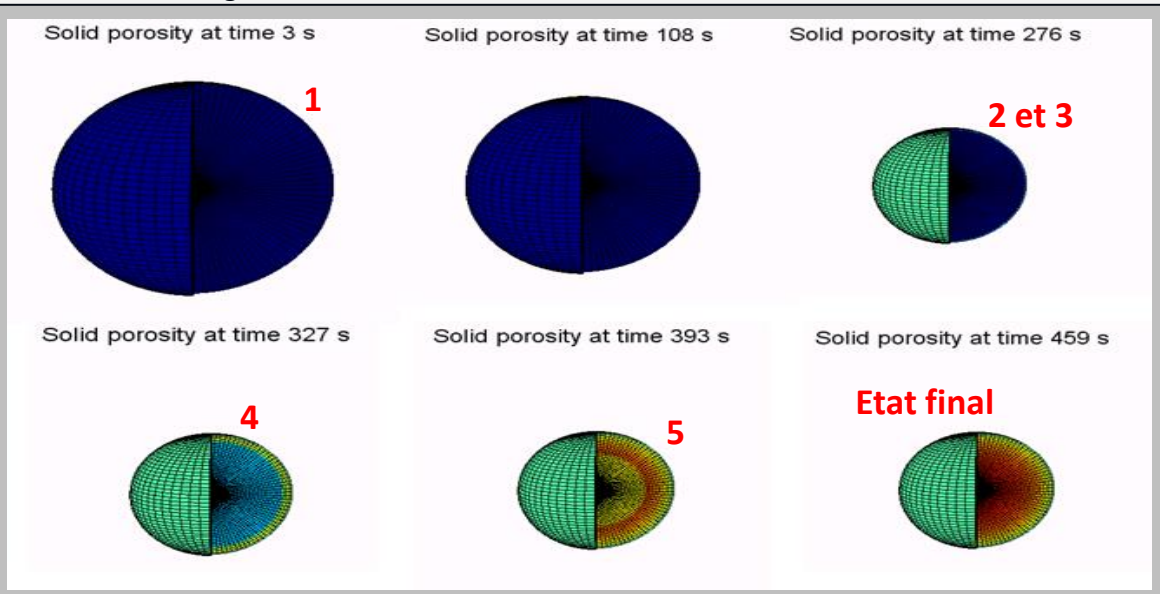
1- Particle reduction due to water evaporation

2- Crust formation

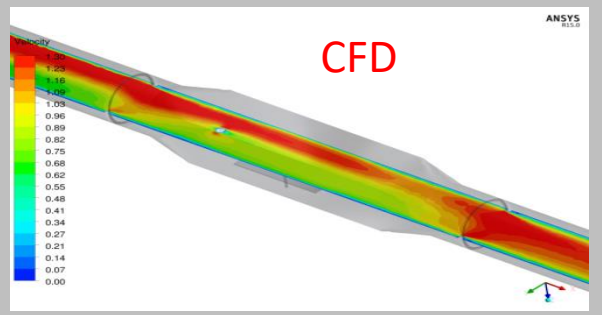
3- Elimination of water contained in the crust

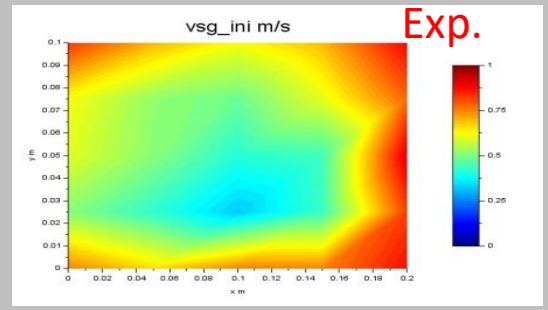
4- Gas feeding

5- Crust thickening

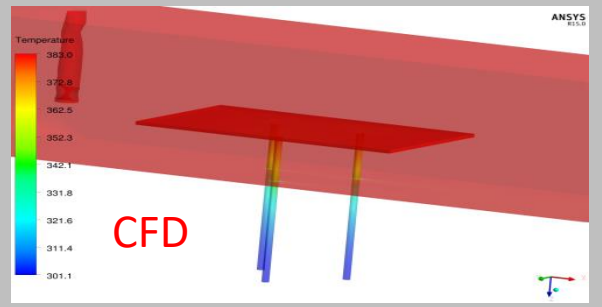


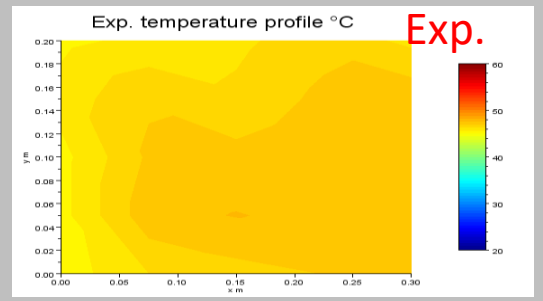
Heterogeneity of gas velocity field





Isothermal conditions





Alumina gel drying

Plate model

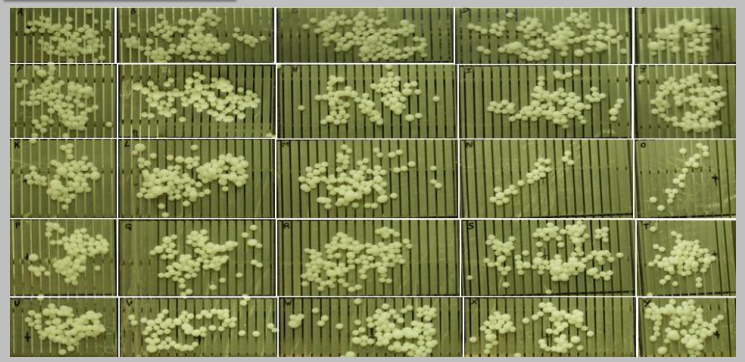
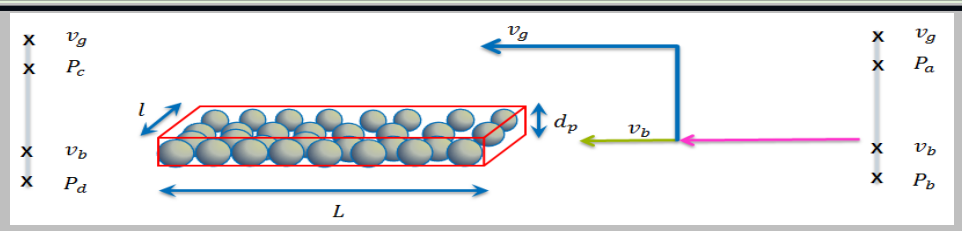
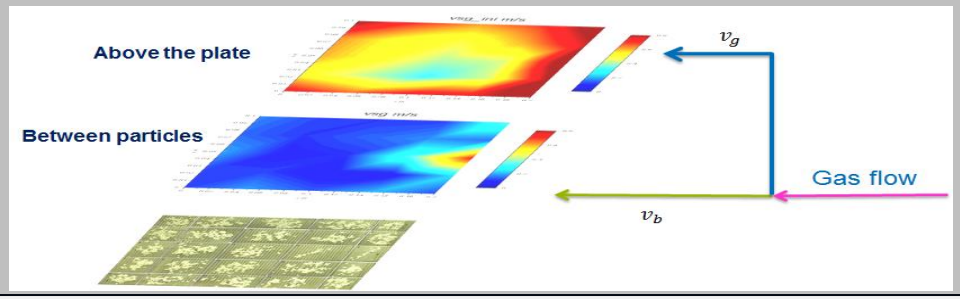


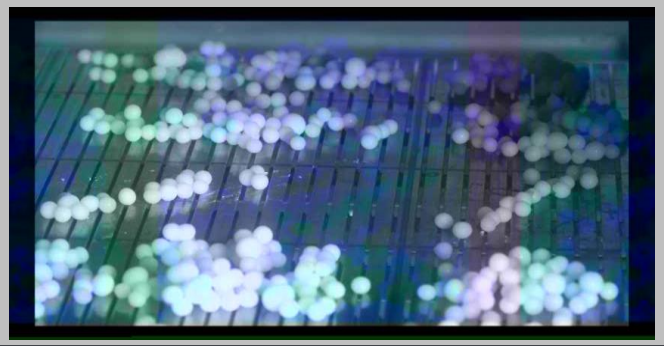
Plate divided into 25 cells



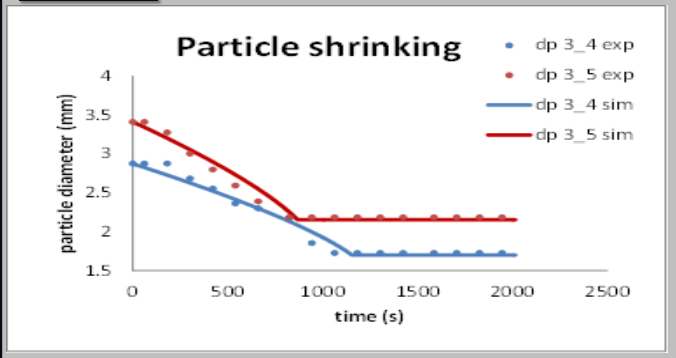


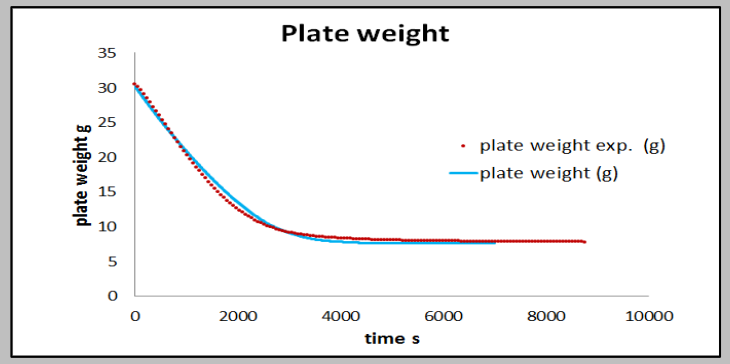
Gas velocity between particles ≠ Gas velocity above the plate

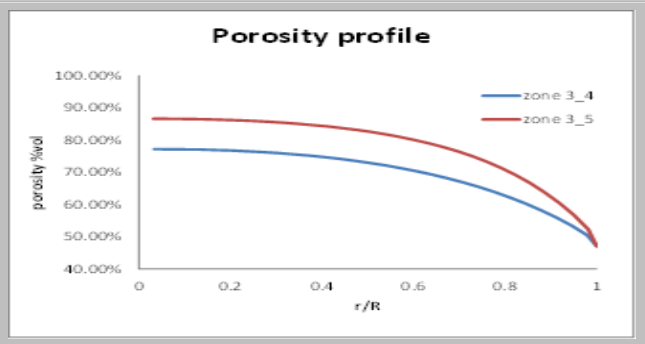
Drying evolution

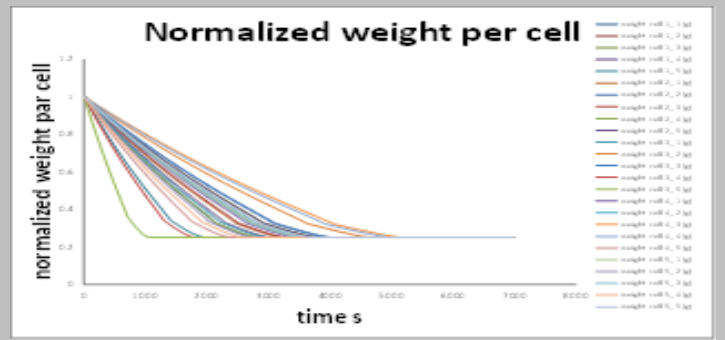


Results









Perspectives

Particle model (Building block) used for

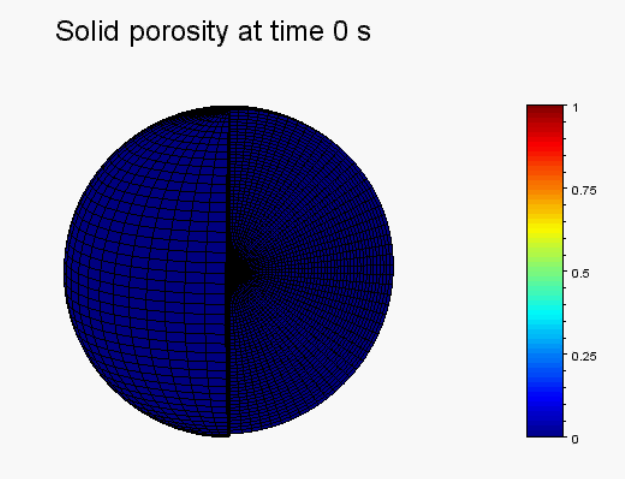
1- prediction of the dry particle mechanical resistance (coupled with a mechanical model)

2- Industrial belt dryer modeling

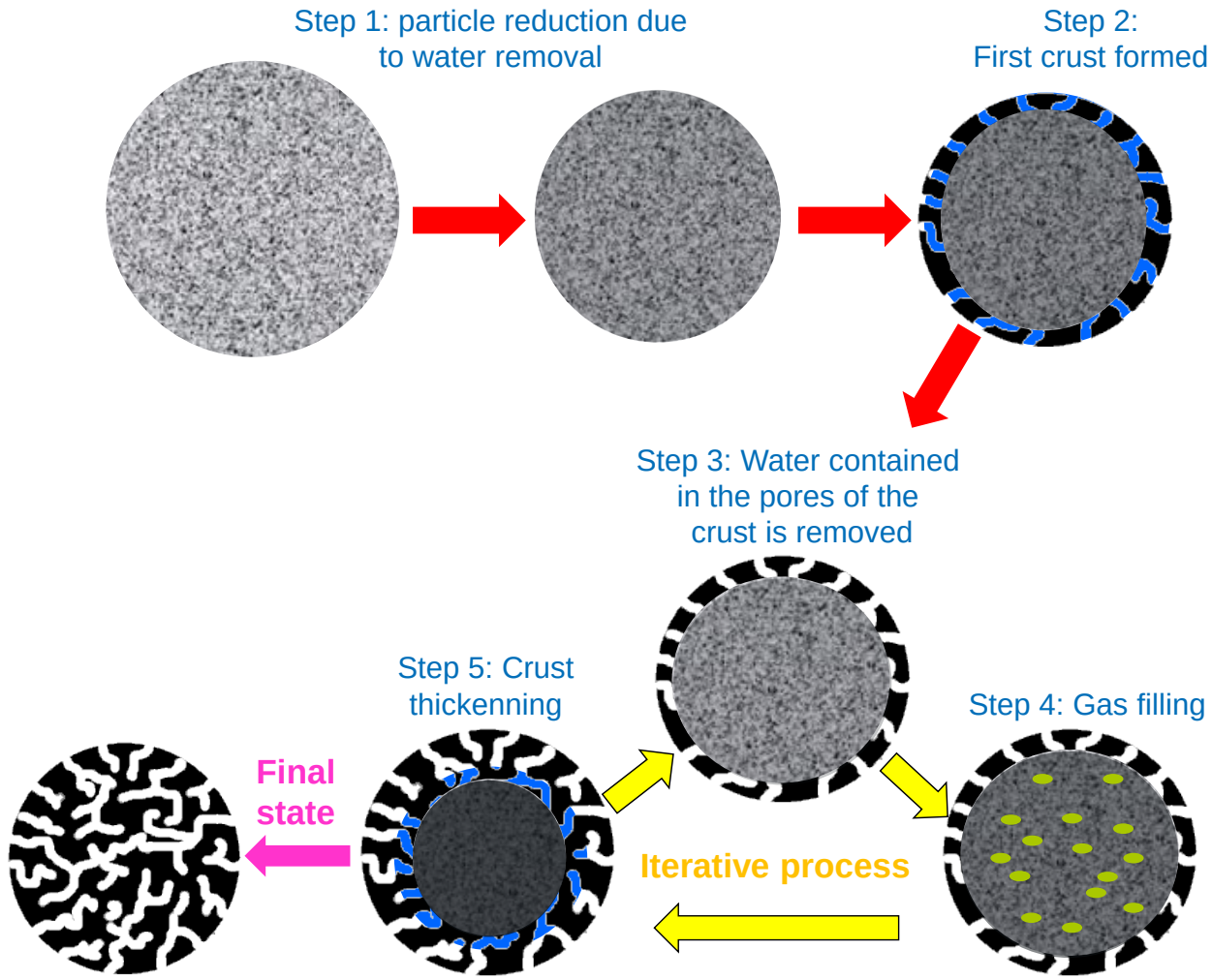
3- Atomizer modeling

BUILDING BLOCK: PARTICLE MODEL

Particle model for drying



Drying with v_{gas} = 1 m/s



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BELT DRYER

RESPONSIBLE
OIL AND GAS

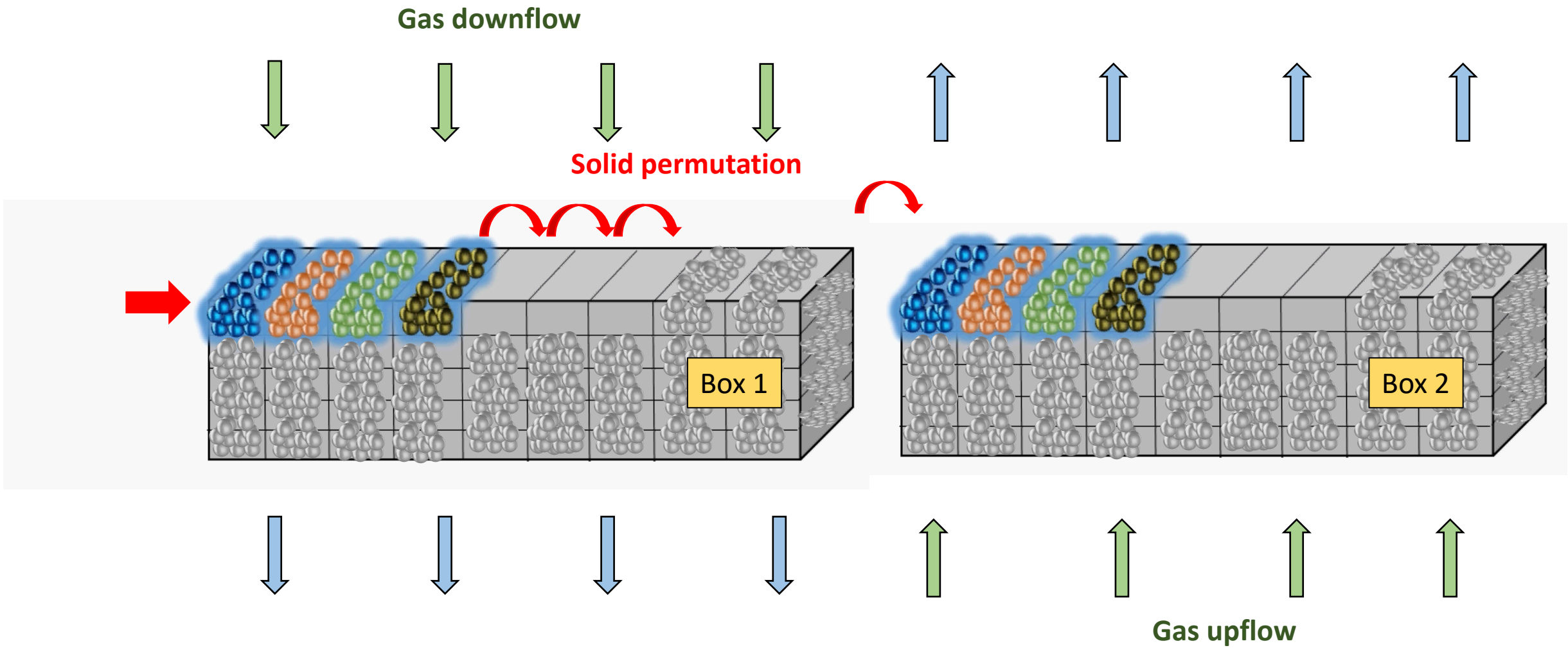
Inlet

Outlet

THE COMPLETE BOX

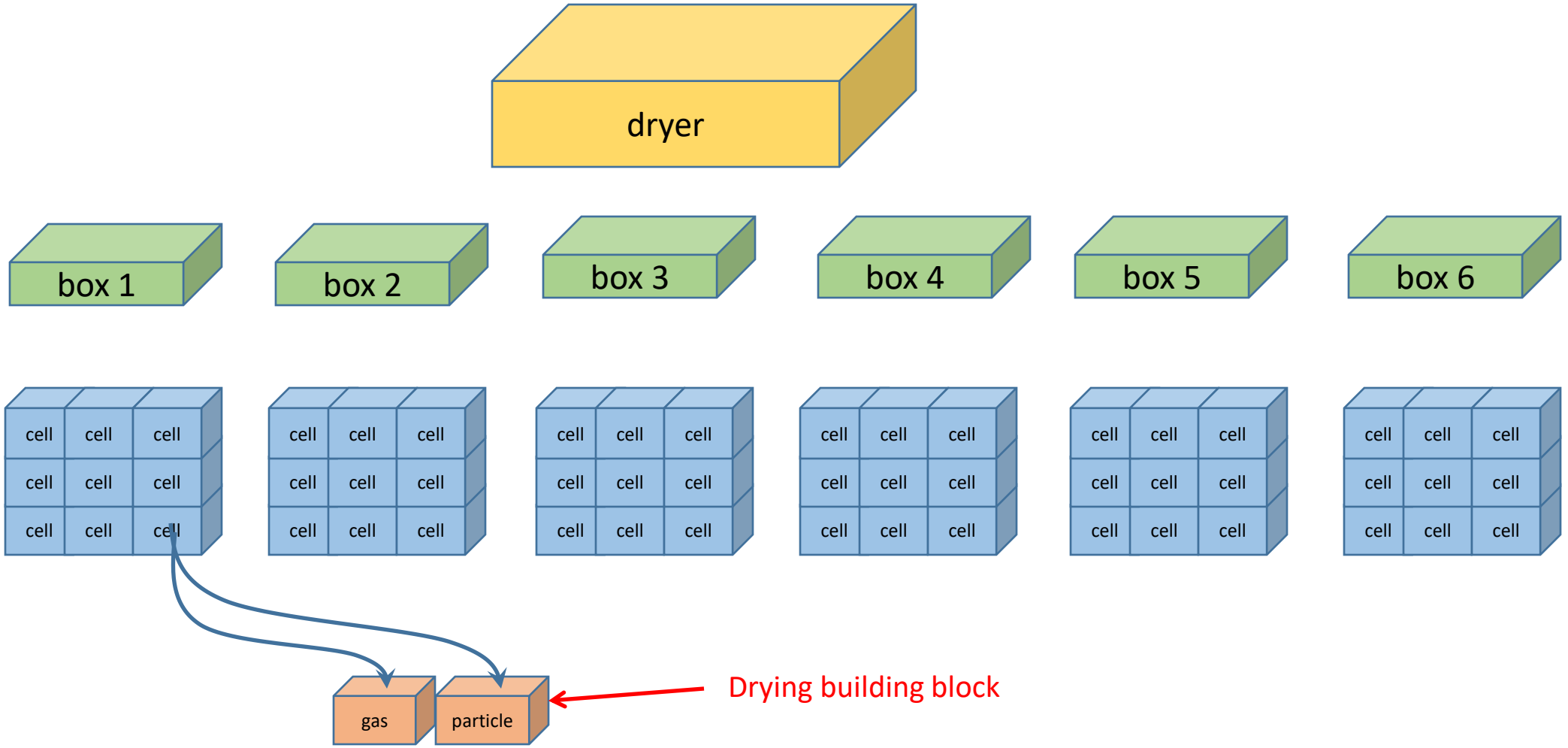
Solid: Lagrangian description
Gas: Eulerian description

RESPONSIBLE OIL AND GAS



OBJECTS DEFINITION

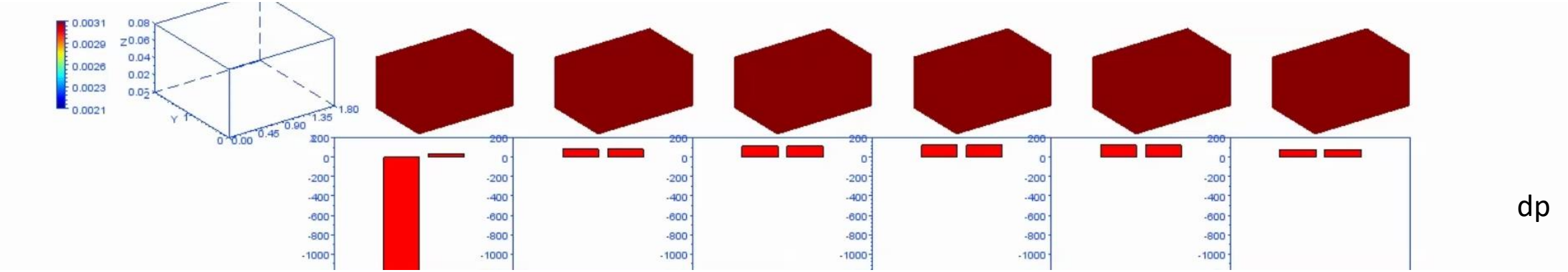
RESPONSIBLE
OIL AND GAS



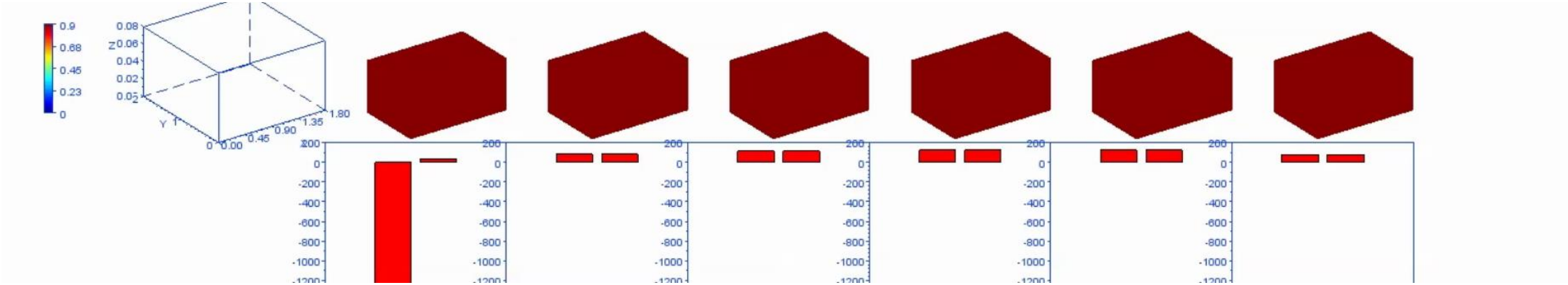
- d_p
- % vol. water

SIMULATION

RESPONSIBLE
OIL AND GAS



dp



% vol water

ATOMIZER MODELING

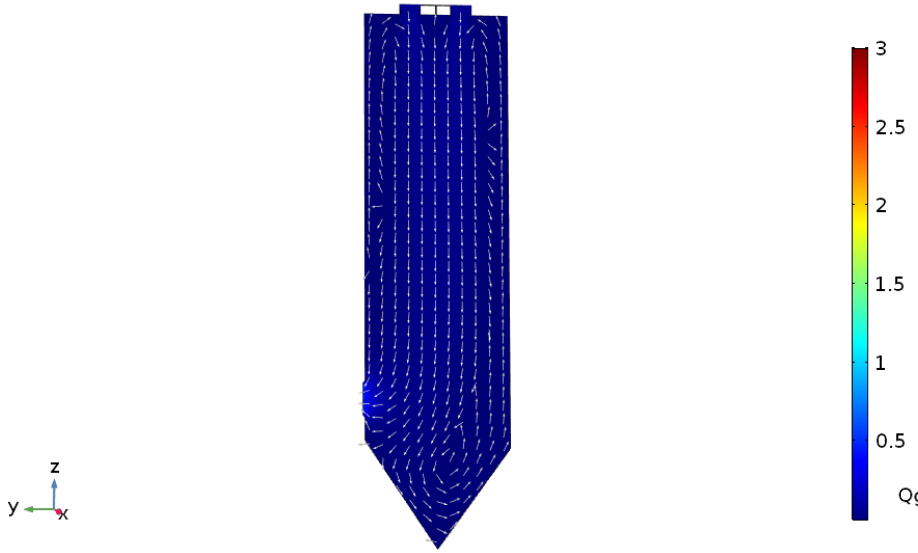
RESPONSIBLE
OIL AND GAS

- Development of an atomizer model which includes
  - The gel drying particle model developed and validated at lab scale
  - A stochastic gel droplet ejection model taking into account
    - Droplet size distribution
    - Ejection angles
    - Ejection velocity
  - A momentum balance for each particle taking into account friction forces and gravity
  - A elastic collision model between dried particles and the wall
  - Particle-Particle collisions will be neglected (coalescence phenomenon is not preponderant in a spray)
  - The gas velocity field in an atomizer (calculated from 3D Comsol simulations)
- This model is developed for a lab scale atomizer (Buchi)
- This model isvalidated with experiments carried out on this atomizer
- This model provides
  - A statistical evaluation of the atomizer performances
  - An 3D animation of the particle trajectories

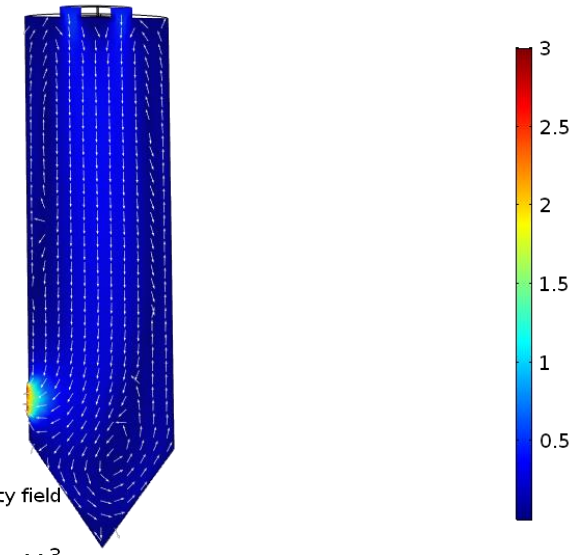
GAS VELOCITY FIELD

- 3D simulations with gas only using Comsol: Velocity fields for 2, 10 and 30 m3/h

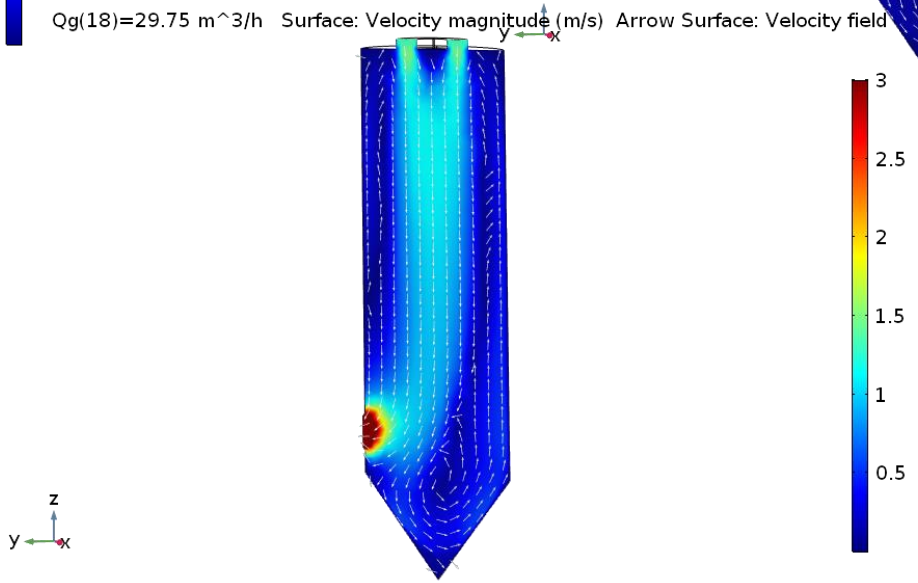
Qg(2)=2 m^3/h Surface: Velocity magnitude (m/s) Arrow Surface: Velocity field



Qg(6)=10 m^3/h Surface: Velocity magnitude (m/s) Arrow Surface: Velocity field



Qg(18)=29.75 m^3/h Surface: Velocity magnitude (m/s) Arrow Surface: Velocity field



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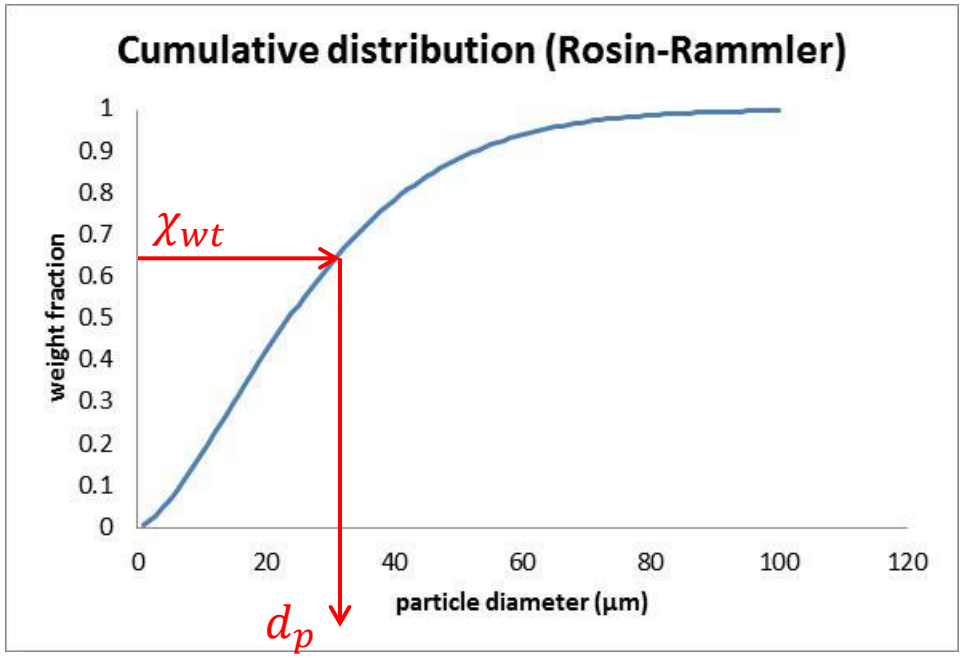
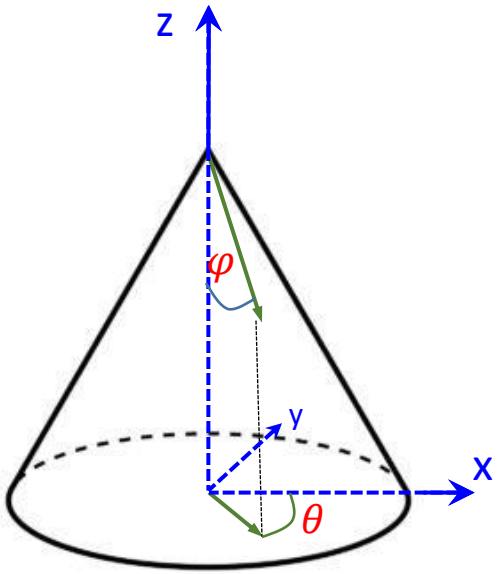
STOCHASTIC PROCEDURE

- For a given particle
  - Generate a random number χ_{wt} (between 0 and 1) for the particle size



Ejection cone



  - Generate a random number χ_θ (between 0 and 1) for initial θ angle $\quad \theta = \chi_\theta \cdot 2\pi$
  - Generate a random number χ_φ (between 0 and 1) for initial φ angle $\quad \varphi = \chi_\varphi \cdot Atan(R/H)$
  - Initial ejection velocity is set at 10 m/s
  - Start the simulation

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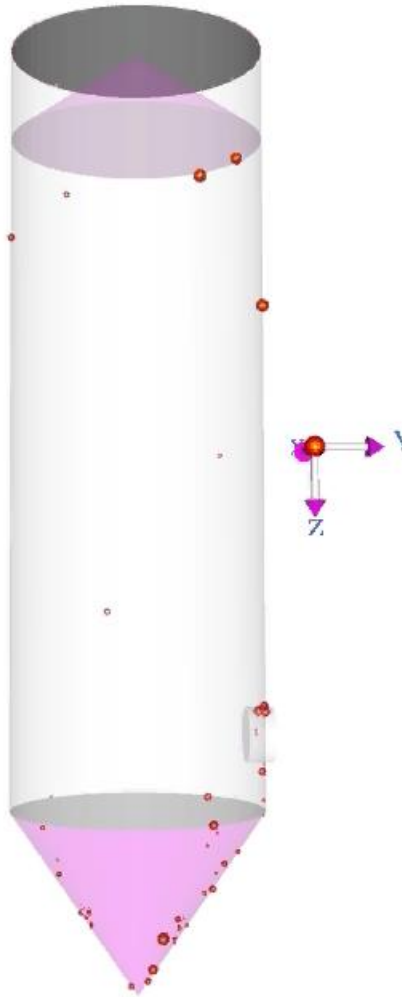
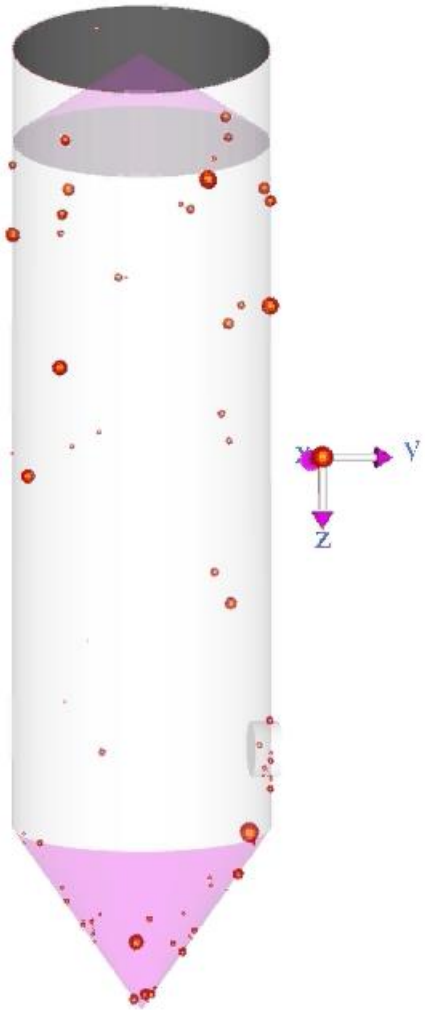
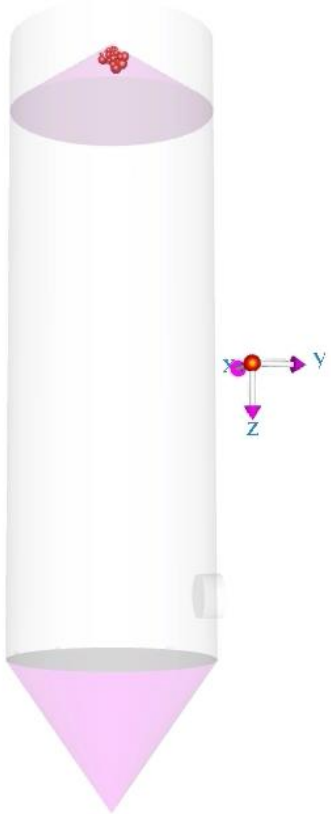
EFFECT OF GAS FLOWRATE



30 µ



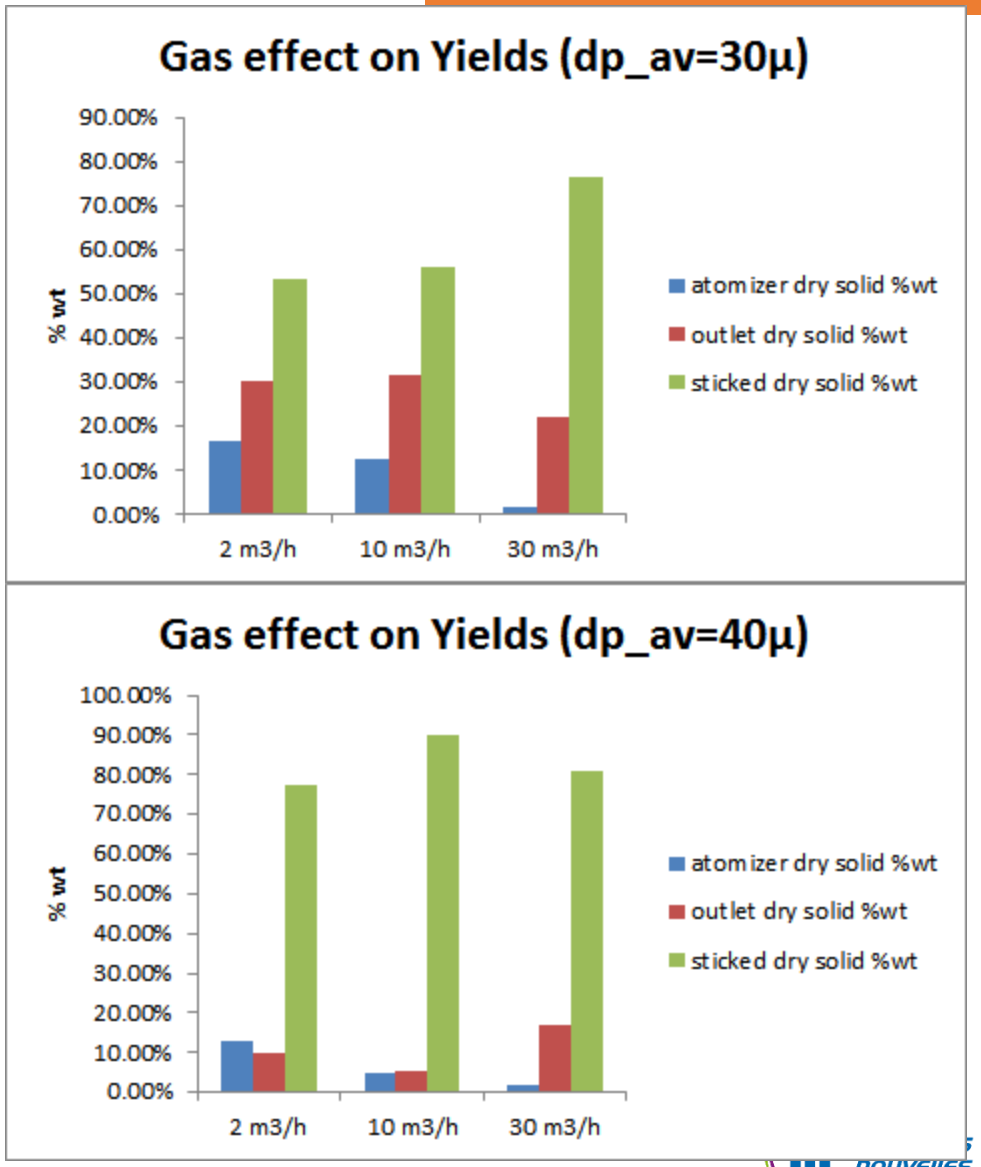
30 m3/h



40 µ

On Yields
ejection

time/100 → 0.1 s



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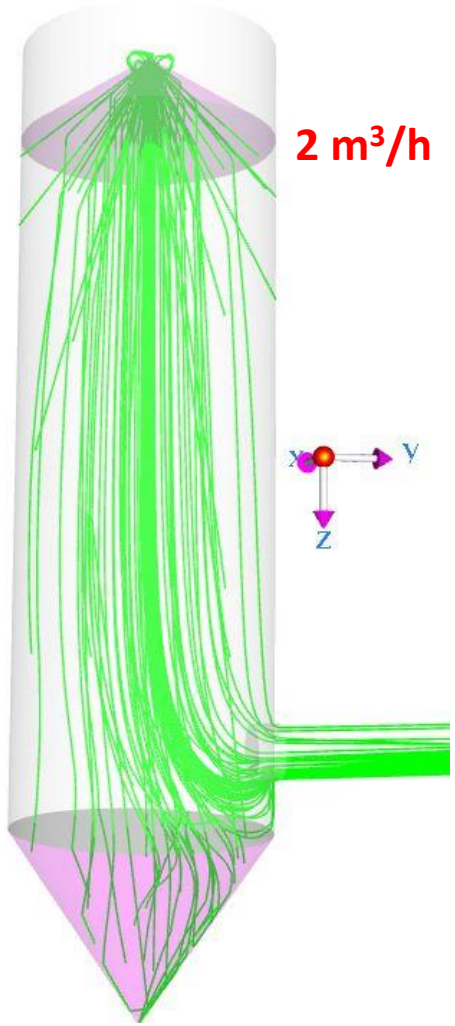
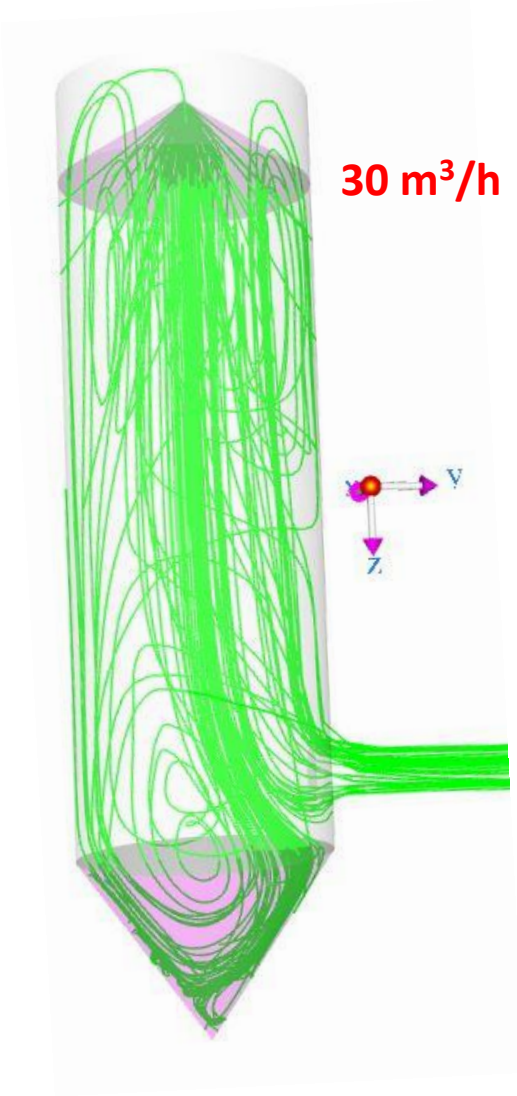
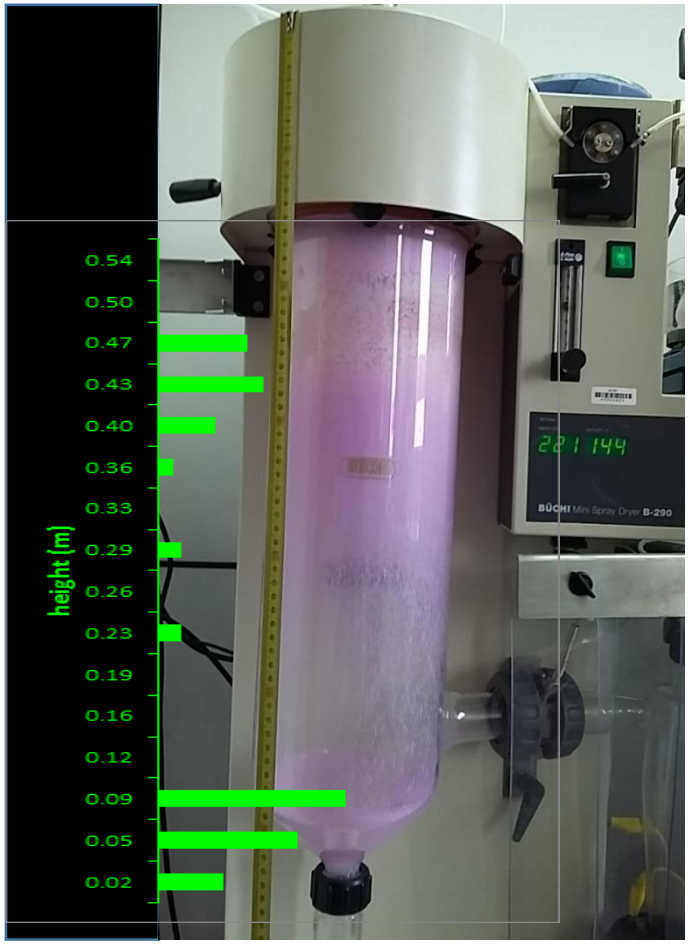
STATIC TRAJECTORIES FOR 40 µ

RESPONSIBLE
OIL AND GAS

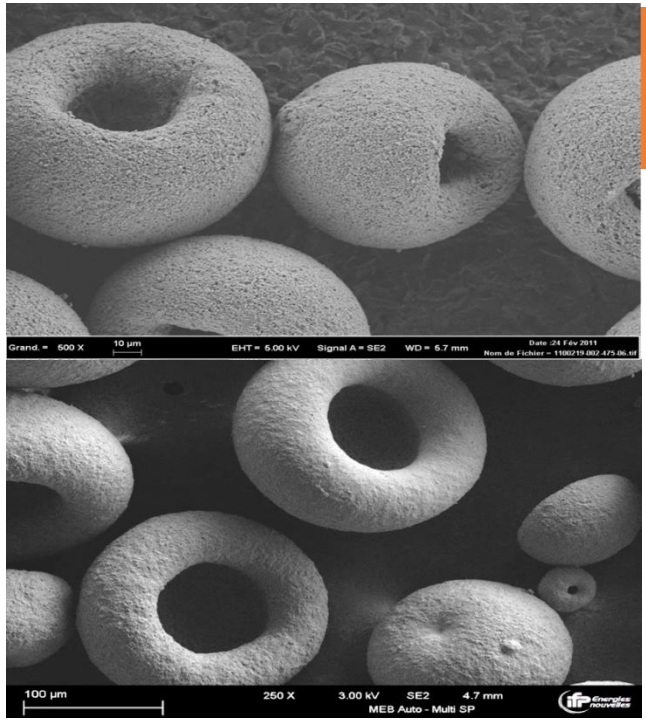




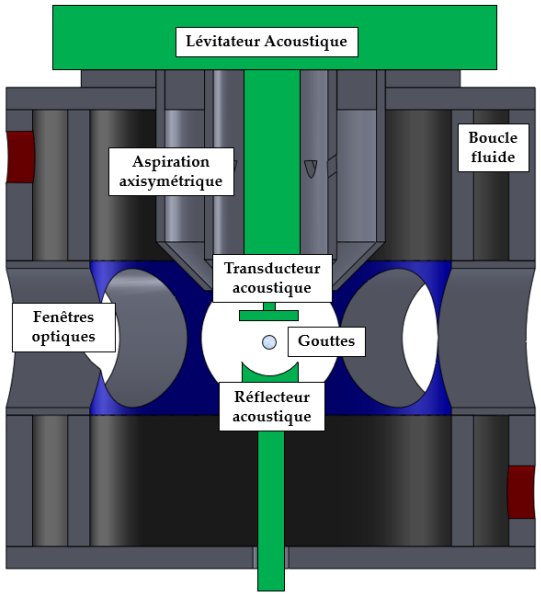


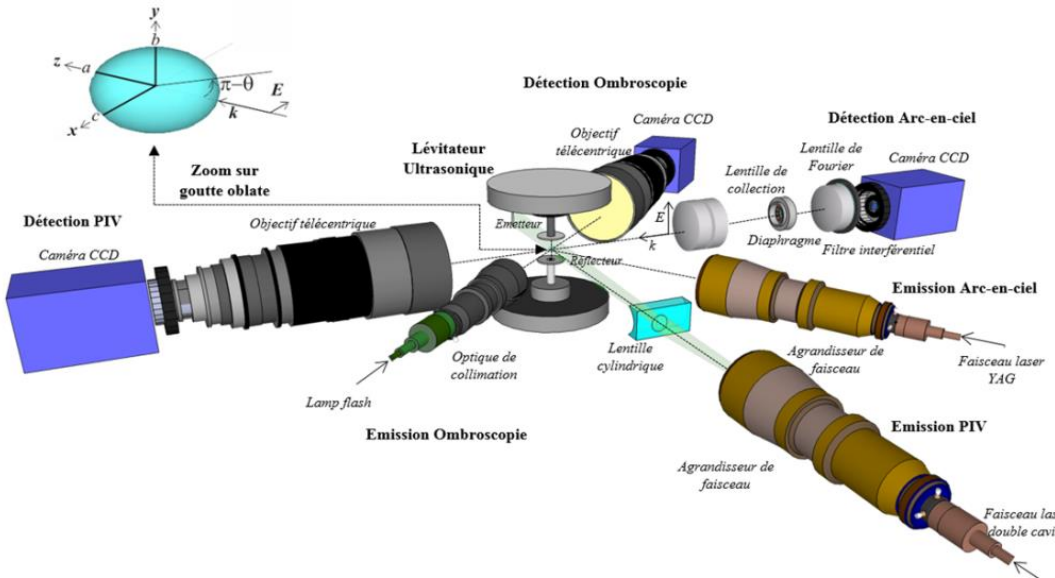
Evolution of the drying building block

- In some cases the particle shape is changing during drying
- Experimentally observed in a isotropic drying device (PhD Quentin Gaubert IFPEN/IUSTI)



- Single droplet levitation under drying conditions
  - Droplet levitation system using an acoustic wave
  - Optimization of the gas velocity field in order to reach isotropic conditions





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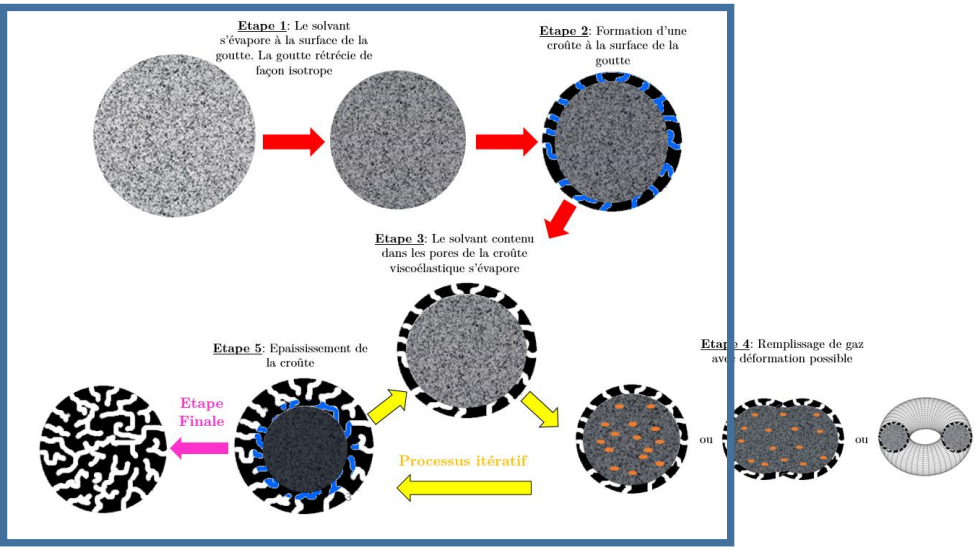
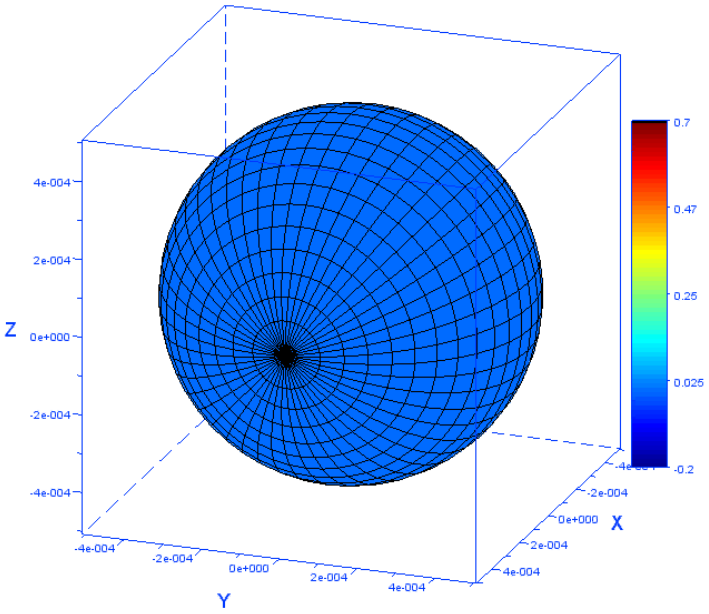
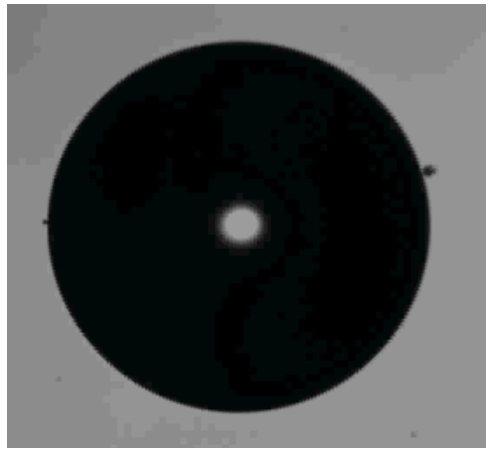
Deformation model: validation

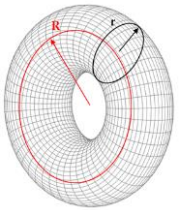
Particle model V1.0



Transient evolution of radius and porosity



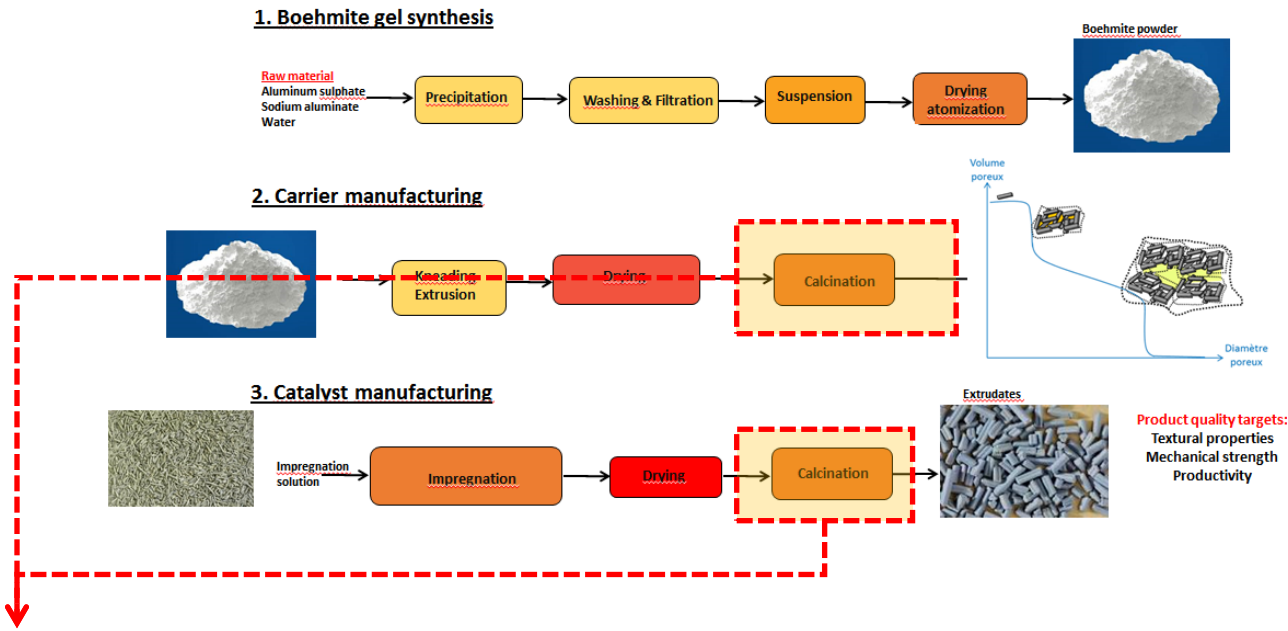




$$\begin{cases} x = (R + r\cos(v))\cos(u) \\ y = (R + r\cos(v))\sin(u) \\ z = r\sin(v) \end{cases}$$

$$\begin{cases} \dfrac{dV_{gaz}}{dt} = (1-\alpha)Q_{vap} \\ R + r = R_{cr} \\ \dfrac{dV_{tore}}{dt} = -\alpha Q_{vap} \\ V_{tore} = 2\pi\left(Rr^2\left(\theta_1 - \dfrac{\sin(2\theta_1)}{2}\right) + \dfrac{2}{3}r^3\sin^3(\theta_1)\right) \quad \text{si } R \le r \\ V_{tore} = 2\pi^2 r^2 R \quad \text{si } R > r \end{cases}$$

In progress: deformation=f(operating conditions)



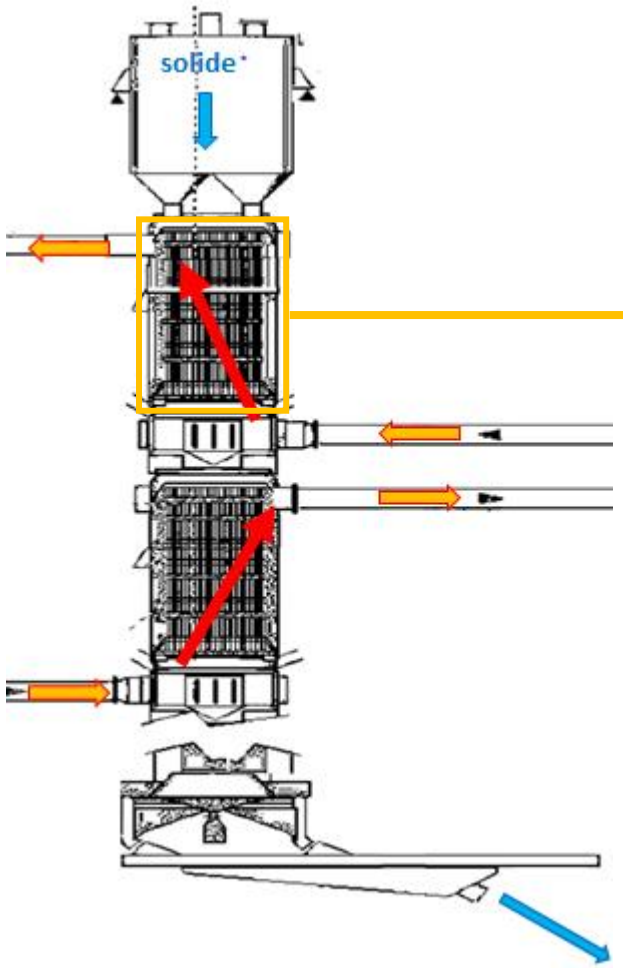
CALCINATION

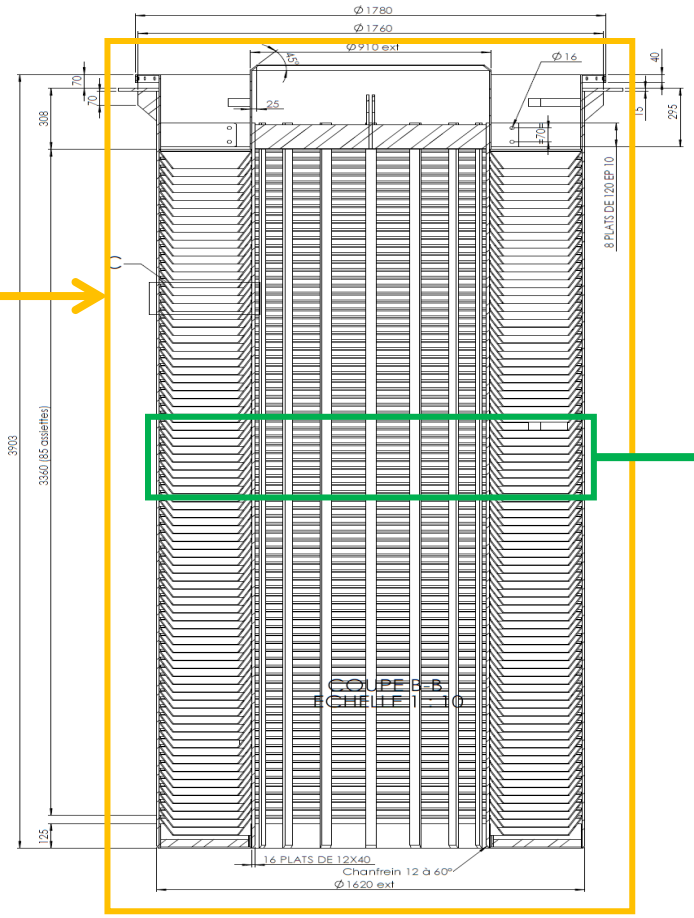
MOVING BED MODELING

REACTOR SCHEME

RESPONSIBLE
OIL AND GAS

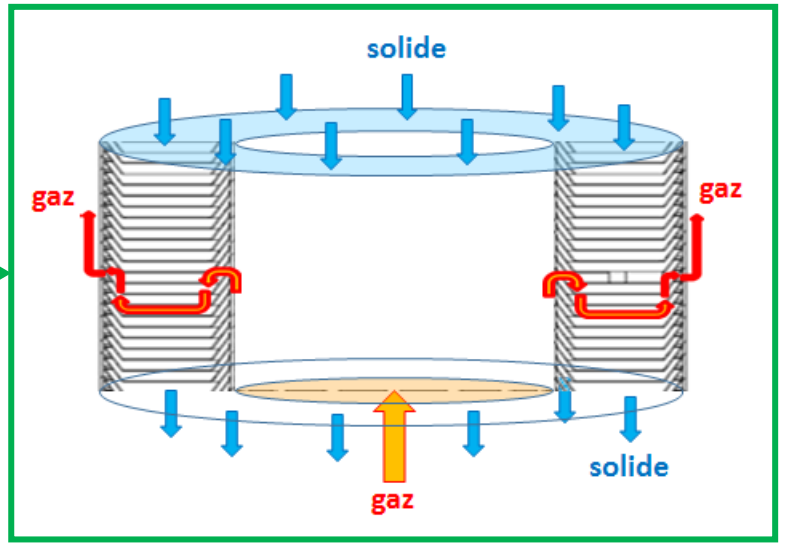
Multi-zone calcinator





Catalyst : downflow circulation in a ring

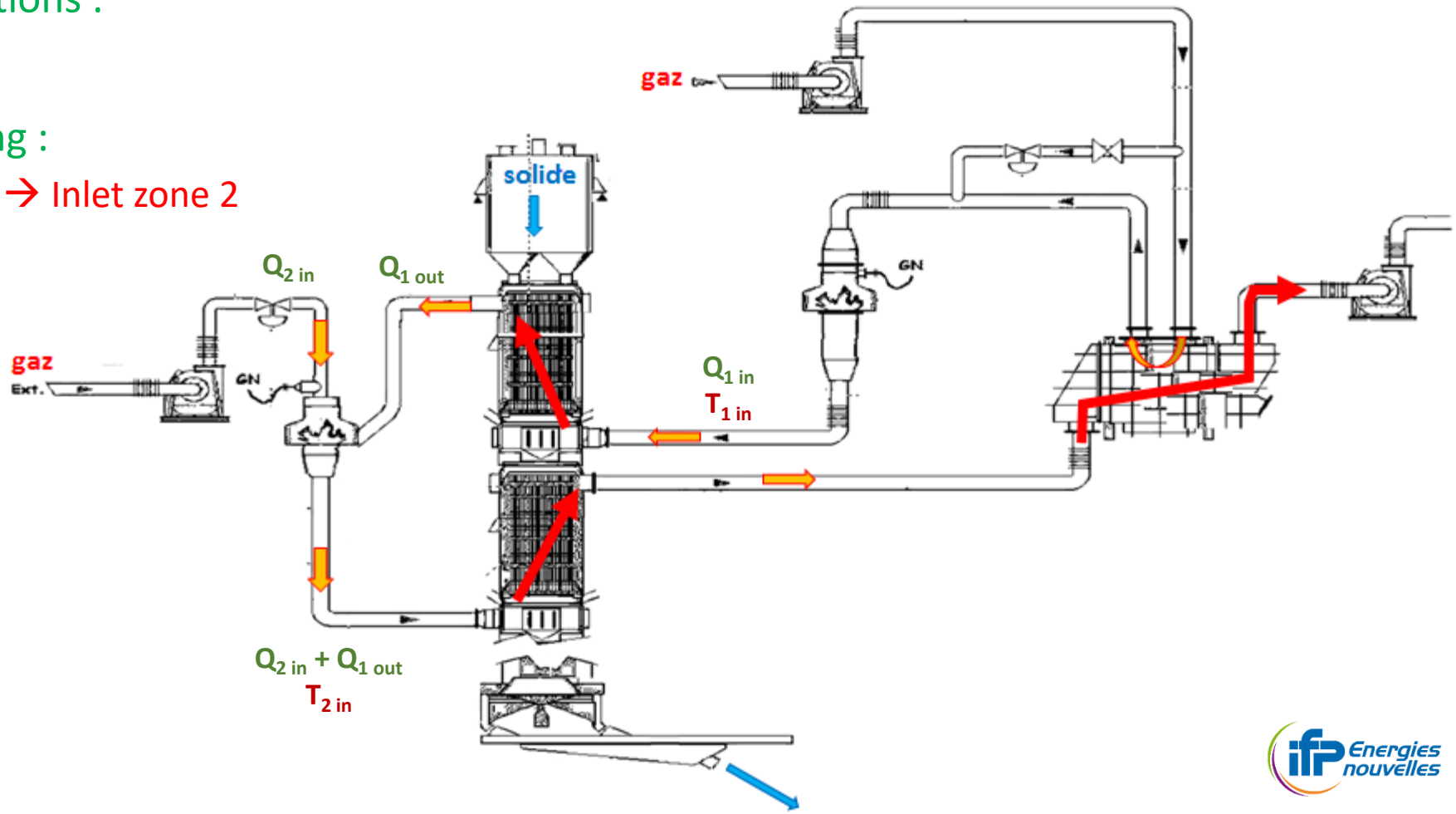
Gas : radial circulation inside the ring



REACTOR SCHEME

RESPONSIBLE
OIL AND GAS

- **On each calcination zone :**
  - Gas operating conditions :
    - T_g, Q_g, moisture
  - Optional gas recycling :
    - Outlet gas zone 1 → Inlet zone 2



REACTION SCHEME AND RATES

RESPONSIBLE
OIL AND GAS

- Desorption of physisorbed and chemisorbed water

$$H_2O_{(s)} \xrightarrow[k_1]{} H_2O_{(g)}$$

- Conversion of boehmite to alumina through a reaction intermediate

$$AlOOH \xrightarrow[k_2]{} \frac{1}{2}\underbrace{Al_2O_{3-x/2}(OH)_x}_{Al_{int}{}^*} + \frac{2-x}{4}H_2O_{(g)}$$

$$Al_2O_{3-x/2}(OH)_x \xrightarrow[k_3]{} Al_2O_3 + \frac{x}{2}H_2O_{(g)}$$

Hypothesis :
First order kinetics

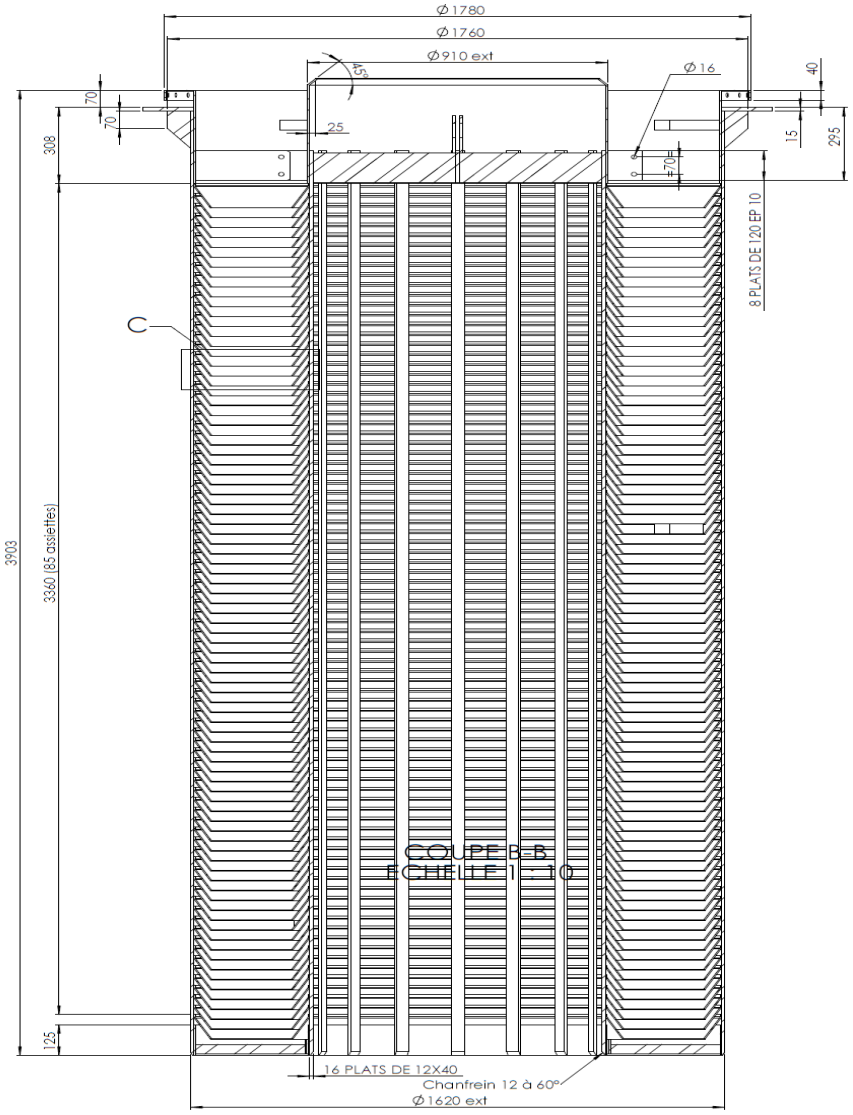
$$r_1 = k_1[H_2O_{(s)}]$$

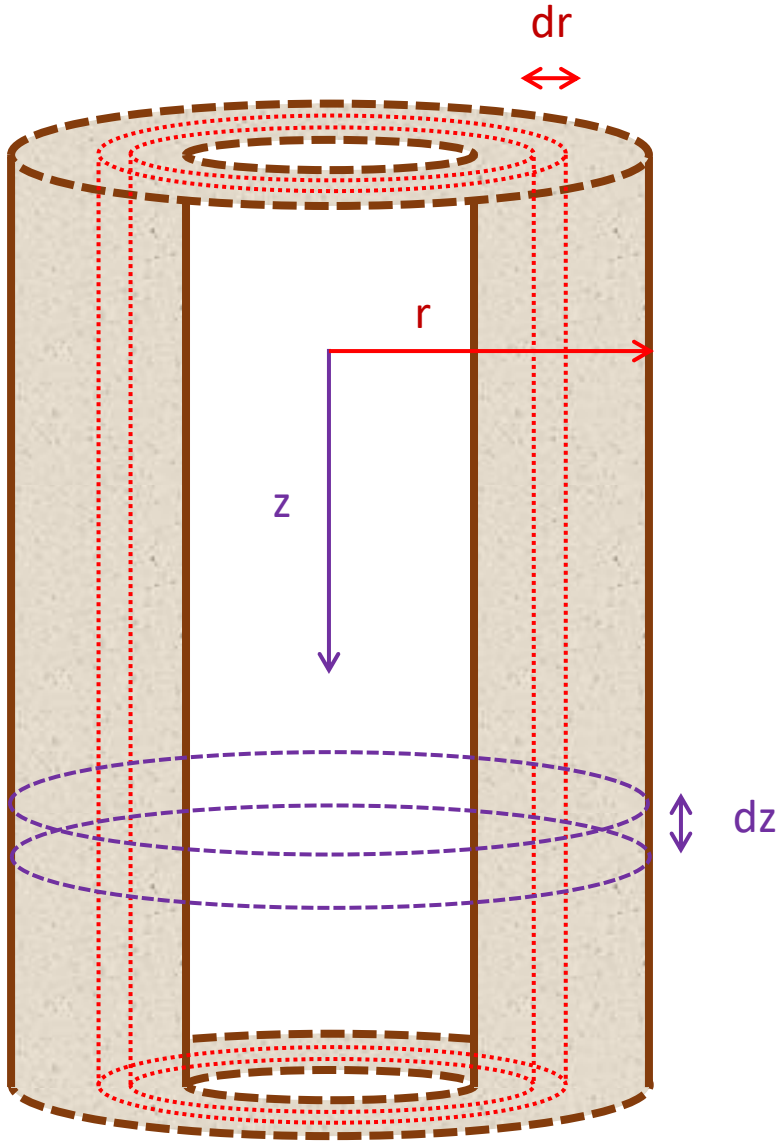
$$r_2 = k_2[AlOOH]$$

$$r_3 = k_3[Al_{int}]$$

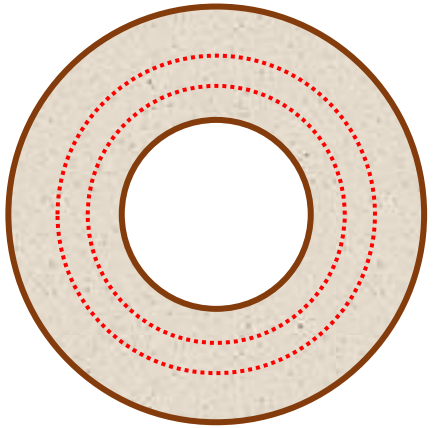
* *Thèse F Karouia (2014)*

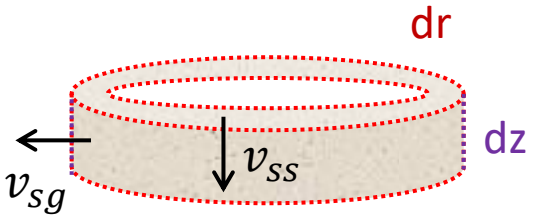
REACTOR DISCRETIZATION





2D model (r,z)





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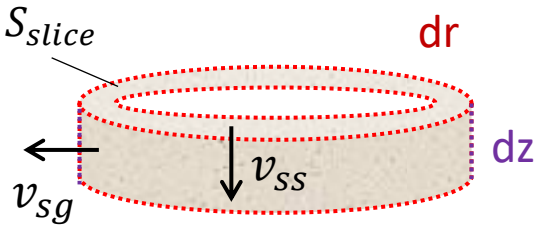
MASS BALANCES



- **Solid molar balances :**

$$C_i{}^s \leftrightarrow \left[mol_s \cdot m^{-3}{}_{particle}\right]$$

$$\varepsilon_s \cdot \frac{\partial C_i{}^s}{\partial t} = -\frac{\partial (v_{ss} \cdot C_i{}^s)}{\partial z} + \sum_j \mu_{ij} \cdot r_j \cdot \varepsilon_s$$

- **Gas molar balances :**

$$(\varepsilon_g + \varepsilon_p \varepsilon_s) \cdot \frac{\partial C_i{}^g}{\partial t} = -\frac{1}{r} \cdot \frac{\partial (r \cdot v_{sg} \cdot C_i{}^g)}{\partial r} + \sum_j \mu_{ij} \cdot r_j \cdot \varepsilon_s$$

- **Equation of state:**

$$\frac{\partial}{\partial r}\left(\frac{r \cdot v_{sg}}{T_g}\right) = -(\varepsilon_g + \varepsilon_p \varepsilon_s) \cdot \frac{r}{T_g{}^2} \cdot \frac{\partial T_g}{\partial t} + r \cdot \frac{R}{P_{tot}} \cdot \sum_i \sum_j \mu_{ij} \cdot r_j \cdot \varepsilon_s$$

THERMAL BALANCES

Solid thermal balance :

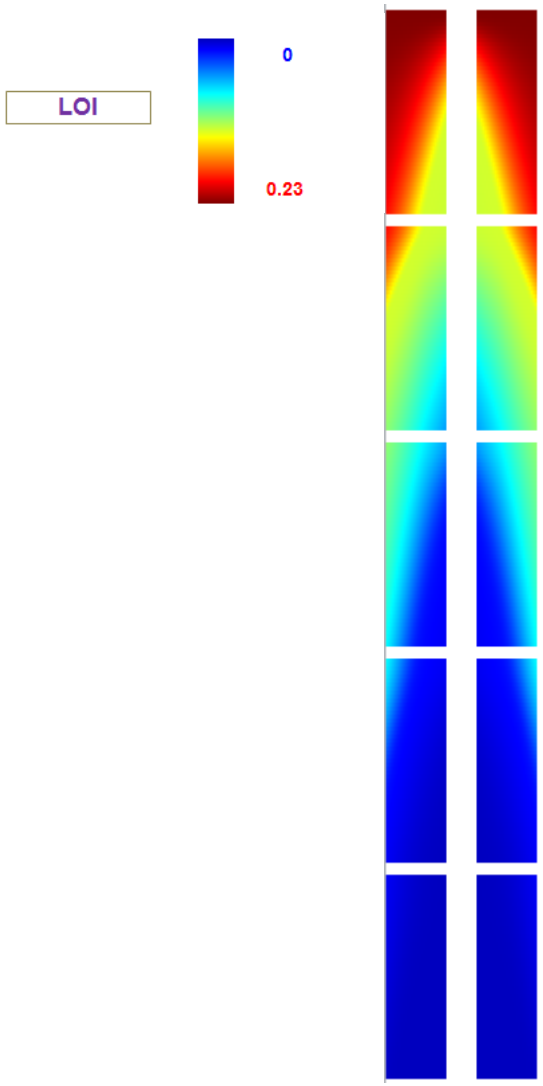
$$\rho_s \cdot C_{ps} \cdot \varepsilon_s \cdot \frac{\partial T_s}{\partial t} = -v_{ss} \cdot \rho_s \cdot C_{ps} \cdot \frac{\partial T_s}{\partial z} + \sum_j r_j \cdot \left(-\Delta H r_j\right) \cdot \varepsilon_s + h_{gs} \frac{A_p}{V_p} \cdot \varepsilon_s \cdot \left(T_g - T_s\right)$$

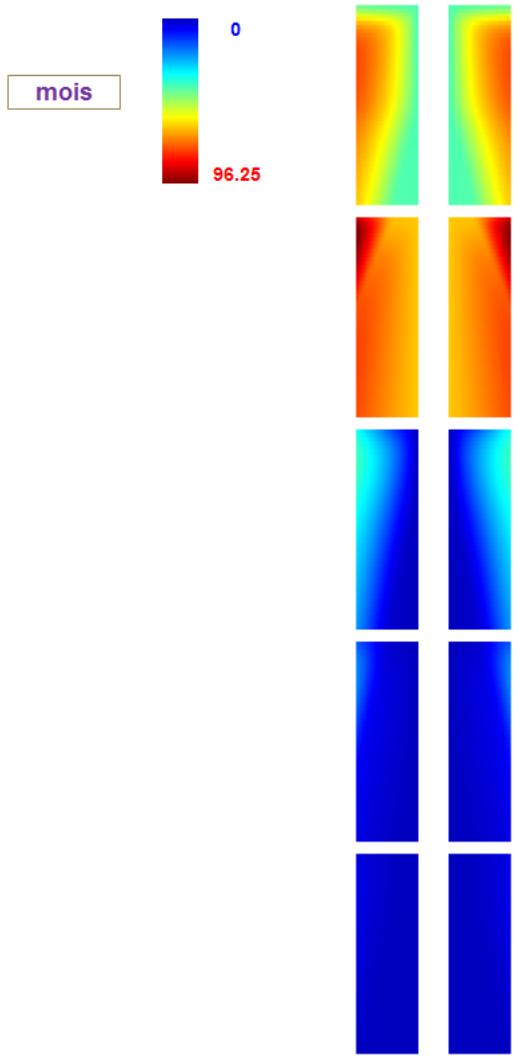
Gas thermal balance :

$$\rho_g \cdot C_{pg} \cdot \varepsilon_g \cdot \frac{\partial T_g}{\partial t} = -v_{sg} \cdot \rho_g \cdot C_{pg} \cdot \frac{\partial T_g}{\partial r} - h_{gs} \frac{A_p}{V_p} \cdot \varepsilon_g \cdot \left(T_g - T_s\right)$$

MODEL RESULTS

- **Sheet “color_map” :**





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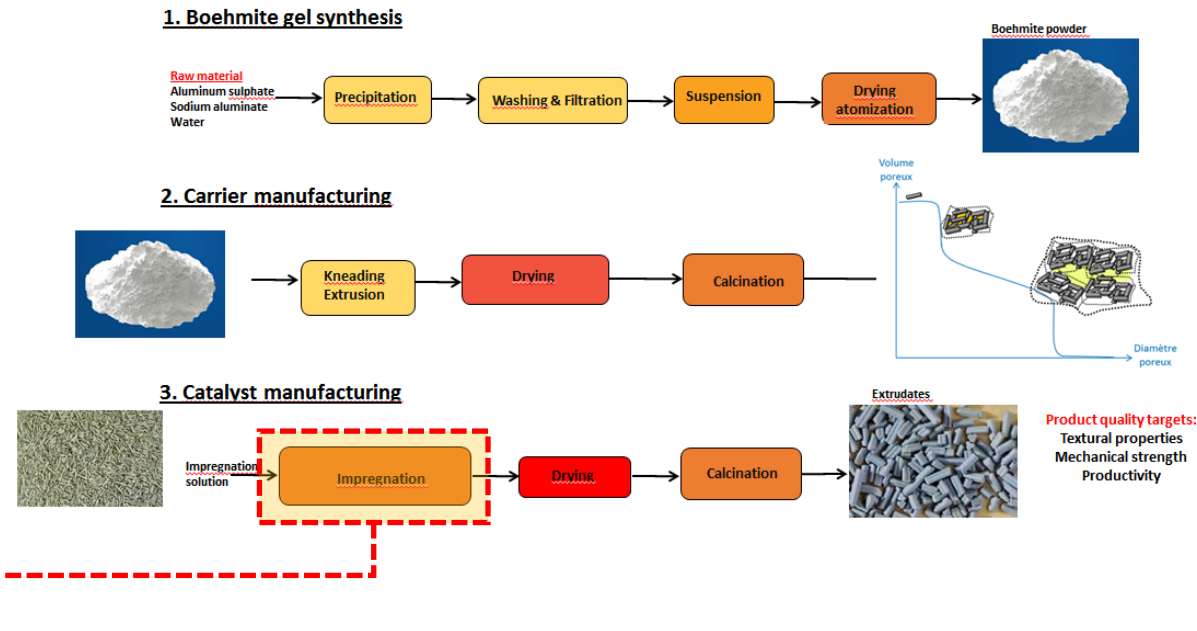


IMPREGNATION

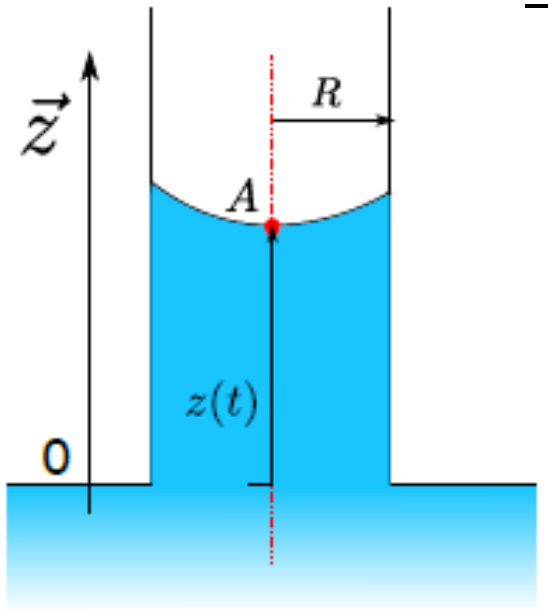
IMPREGNATION MODELING

OBJECTIVES

- Development of particle model for impregnation
  - Dry impregnation
  - Wet impregnation
- Comparison with experimental work based on MRI measurements
- Optimization of the impregnation step in the catalyst manfucturing procedure

 |

CAPILLARY SUCTION MODELING



$$\frac{d(m.\vec{v})}{dt} = \vec{F}_{capillary} + \vec{F}_{friction}$$

$$F_{capillary} = \Delta P_{Laplace} \cdot S$$

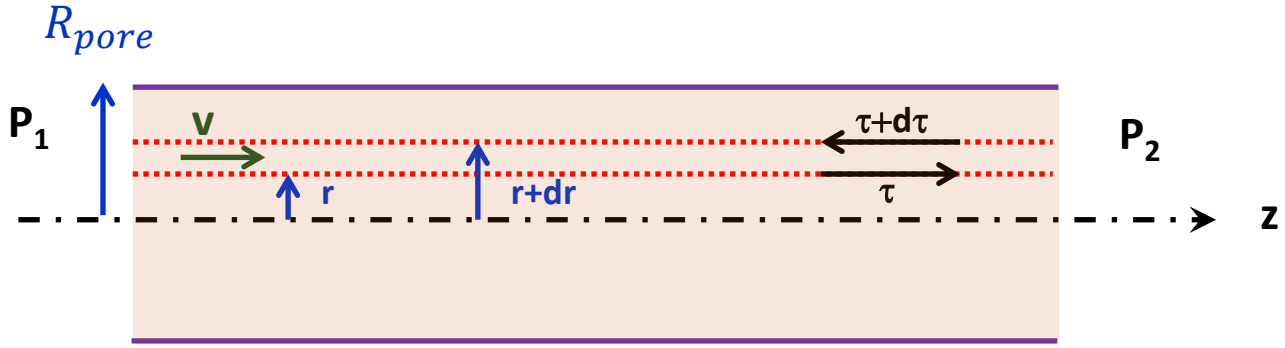
$$\Delta P_{Laplace} = \frac{2 \cdot \gamma \cdot cos\theta}{R_{pore}}$$

$$S = \pi \cdot R_{pore}^2$$

$$F_{capillary} = 2 \cdot \pi \cdot R_{pore} \cdot \gamma \cdot cos\theta$$

 |

CAPILLARY SUCTION MODELING



$$(P_1 - P_2) \cdot 2 \cdot \pi \cdot r \cdot dr + 2 \cdot \pi \cdot r \cdot z \cdot \tau - 2 \cdot \pi \cdot (r + dr) \cdot z \cdot (\tau + d\tau) = 0$$

$$d(r \cdot \tau) = \frac{\Delta P_{friction} \cdot r \cdot dr}{2 \cdot z}$$

$$\tau = -\mu \cdot \frac{dv}{dr}$$

$$\int_r^{wall} dv = \int_r^{R_{pore}} -\frac{\Delta P_{friction} \cdot r \cdot dr}{2 \cdot \mu \cdot z}$$

$$v(r) = \frac{\Delta P_{friction}}{4 \cdot \mu \cdot z} \cdot \left(R_{pore}^2 - r^2\right)$$

$$\bar{v} = \frac{\Delta P_{friction} \cdot R_{pore}^2}{8 \cdot \mu \cdot z}$$

$$F_{friction} = \Delta P_{friction} \cdot S$$

$$F_{friction} = 8 \cdot \pi \cdot \mu \cdot z . \bar{v}$$

CONVECTION-DIFFUSION-ADSORPTION MODELING

- For a cylindrical particle

  - Compounds in pores during capillary suction

Washburn model

$$\varepsilon_p \cdot \frac{\partial C_i^p}{\partial t} = \frac{D_{eff}}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \frac{\partial C_i^p}{\partial r}\right) + \frac{\varepsilon_p}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \bar{v} \cdot C_i^p\right) + \sum_j \mu_{ij} \cdot r_{kin} \cdot \rho_s$$

Volumetric flowrate conservation

$$\frac{\partial}{\partial r}(r \cdot \bar{v}) = 0$$

  - Compounds in pores when the particle is completly wetted

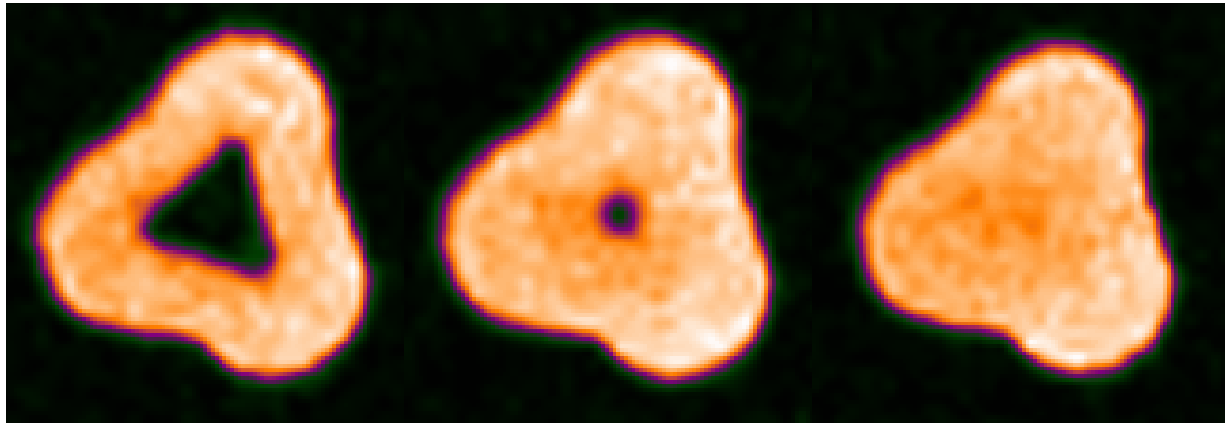
$$\varepsilon_p \cdot \frac{\partial C_i^p}{\partial t} = \frac{D_{eff}}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \frac{\partial C_i^p}{\partial r}\right) + \sum_j \mu_{ij} \cdot r_{kin} \cdot \rho_s$$

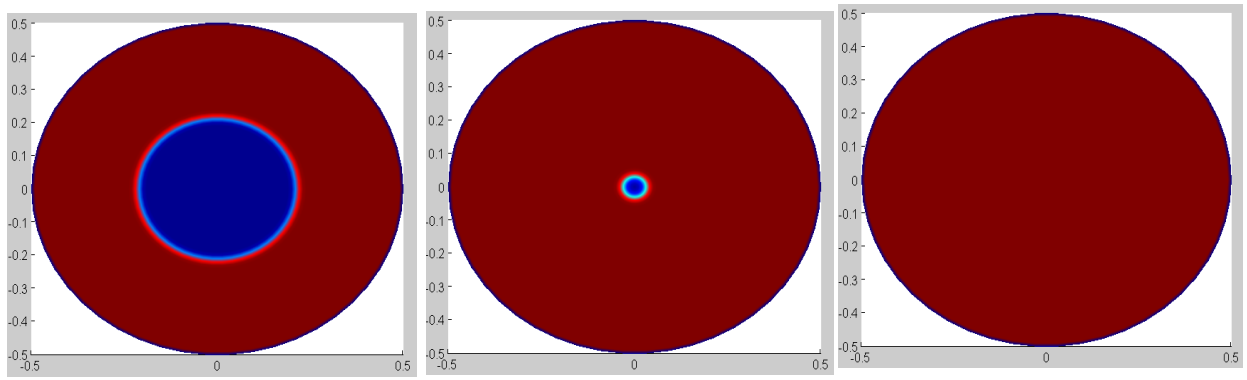
  - Compounds on the solid surface

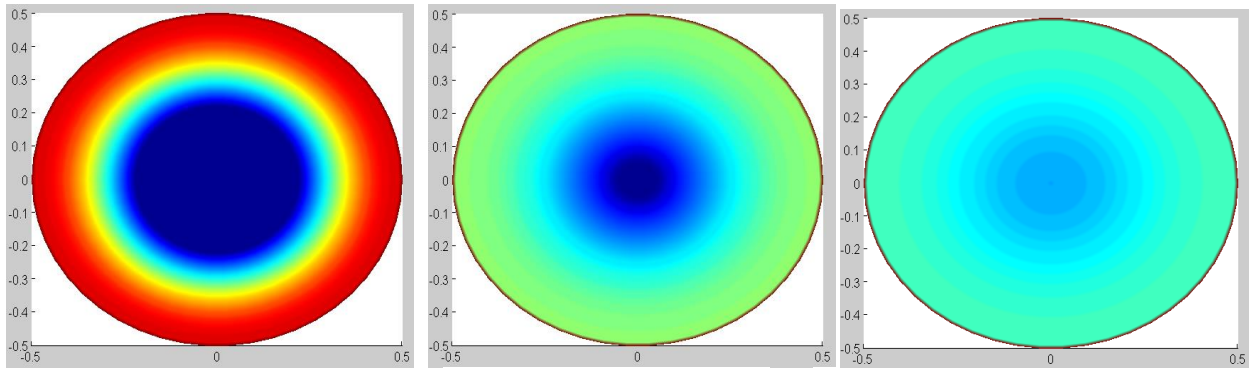
$$\frac{\partial C_i^*}{\partial t} = \frac{D_s}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \frac{\partial C_i^*}{\partial r}\right) + \sum_j \mu_{ij} \cdot r_{kin}$$

MODEL VALIDATION: DRY IMPREGNATION

5 min 22 min 31 min







3 min 20 min 29 min

Case of 0,2M [Ni^{2+}]

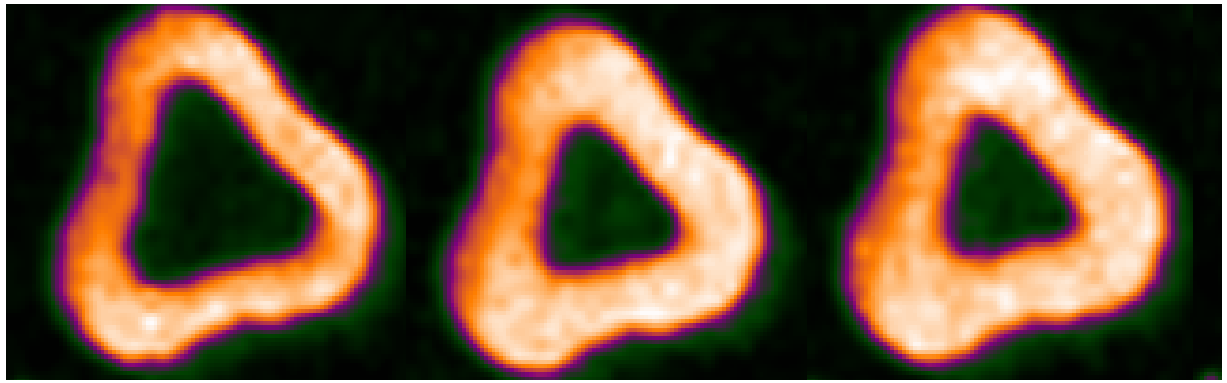
Adsorbed Nickel

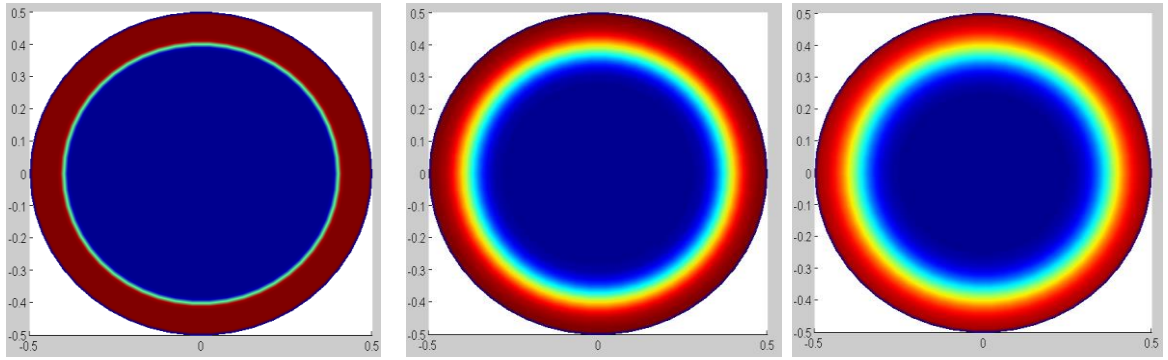
Nickel in pores

MODEL VALIDATION: WET IMPREGNATION

HYDROCARBURES RESPONSABLES

5 min 22 min 31 min





Case of 0,2M [Ni^{2+}]

Adsorbed Nickel

Nickel in pores

3 min 20 min 29 min

Thesis starting in 2018

Giullia Ferri

IDENTIFICATION AND STUDY OF RELEVANT SOLID DESCRIPTORS DURING BOEHMITE SYNTHESIS

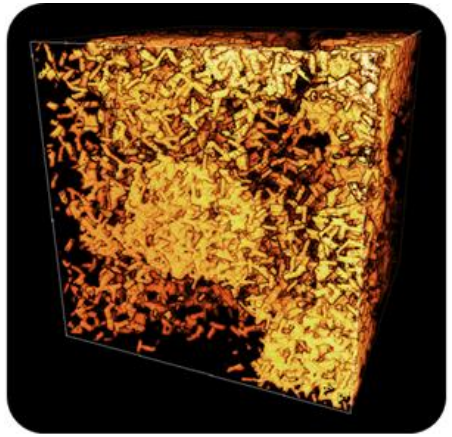
OBJECTIVES

- Construction of an unique solid structure model where the empirical parameters are adjusted for each unit operation step
- Variations of these parameters through the different steps should:
  - allow to evaluate their sensitivities
  - allow to evaluate their impact on the final textural properties
- The final objective is to estimate the values of those parameters for different unit operation in order to reach a given set of textural properties.

STRATEGY

RESPONSIBLE
OIL AND GAS

- **1. Improvement of the solid construction model (dry and wet media)**
  - Solid structural model: Stochastic assembly of elementary particles. The stochastic methodology is based on specific distribution functions such as:
    - Fractal dimension
    - Agglomerates size
    - Aggregates size
    - Preferential sticking faces of the elementary particles
    - …
  - Distribution functions
    - Continuous or discretes
    - Different types (log-normal, gaussian,…)
    - Characterized by a limited number of parameters (mean, standard deviation,…)
  - Calculation of the global properties of the reconstructed solid
    - Size pore distribution
    - Porous volume
    - SBET
    - Crystal size distribution
    - …



Morphological Modeling and Transport Properties of mesoporous alumina

Haisheng Wang

Thèse Haisheng Wang (Mines de Paris / IFPEN 2016)

2 scales model

Model parameters

Elementary particle size

Size of aggregates

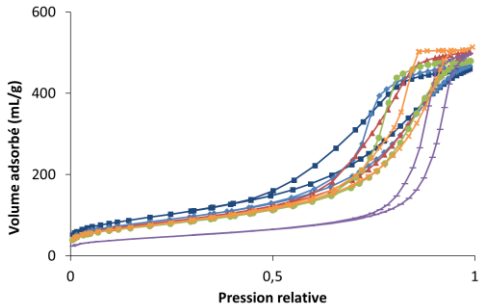
Number of elementary particles in aggregates

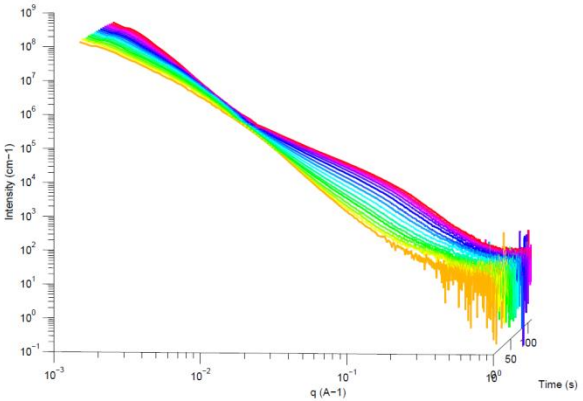
…

Validation on SBET, Vp, TEM images, Nitrogen desorption, …

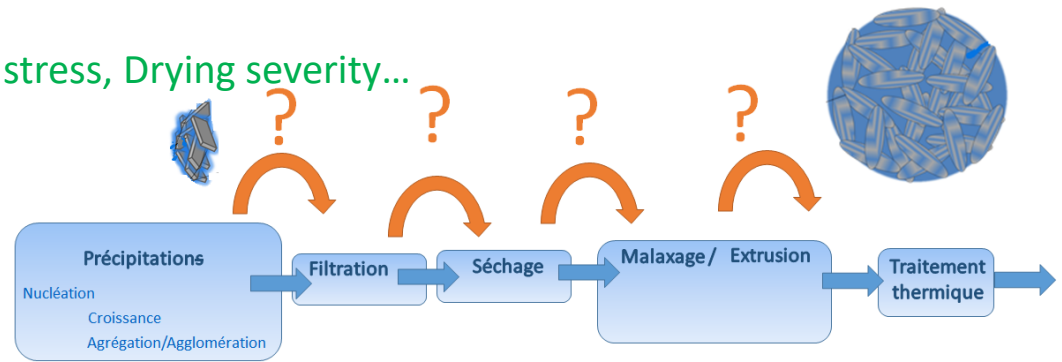
STRATEGY

- **2. Solid analytical characterization at each step**
  - What are the analytical techniques available?
    - SAXS
    - Mercury porosity
    - MEB
    - …
  - Reliability in wet conditions
  - Development or modification of specific analytical methods in order to define new descriptors
  - Are all these methods enough to sensitize the global set of textural properties?





- **3. Optimization of distribution function parameters in order to reproduce the analytical results obtained at each steps.**
  - Follow their evolution after each steps
  - Sensitivity analysis to identify which steps are critical for the final textural properties
- **4. Modeling of the distribution parameters based on physical-chemical descriptors (interaction with the DLVO model)**
  - pH, zeta potential, Re, shear stress, Drying severity…



Thesis starting in 2019

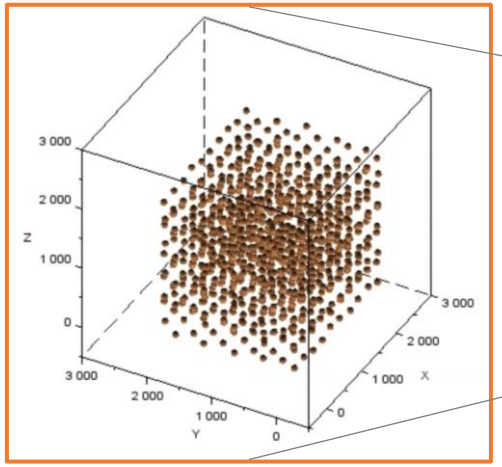
Iana Sudreau

EXPERIMENTAL STUDY AND MODELLING OF A COLLOIDAL GEL RHEOLOGY UNDER PHYSICO-CHEMICAL AND HYDRODYNAMIC CONSTRAINTS

STRATEGY - GLOBAL

structuration and breakage modeling of colloids aggregates

scale : nm
observation : colloidal structure

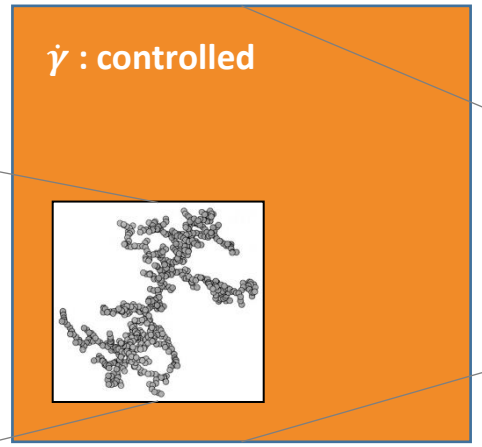


pH, C_s, r_c, ζ

S : D_f

Population balance modeling of gelation process

scale : rheometer
observation : $\mu(t)$

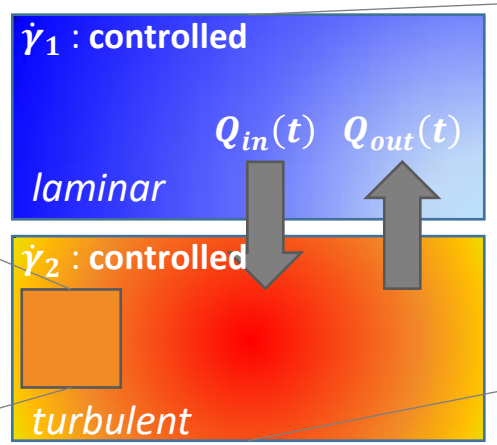


D_f, $\dot{\gamma}(t)$

S : $|\mu(t)|_{\dot{\gamma}=cte}$

compartmental model coupled with population balance

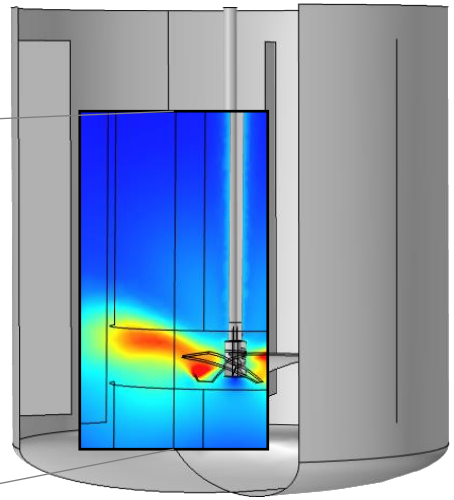
macroscopic scale,
observation $\mu(t)$, $\dot{\gamma}(t)$



S : $|\mu(t)|_{\dot{\gamma}=cte}$, $\dot{\gamma}(x, y, z)$

S : $\mu(t, \dot{\gamma})$

From lab to ind. scale

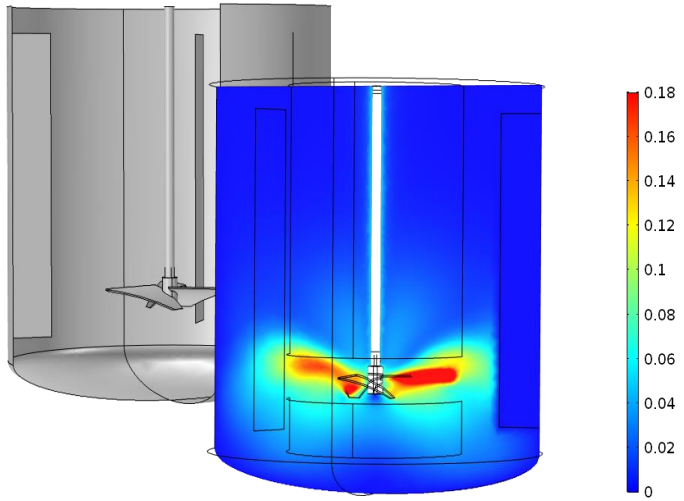


complementary phD proposal (2020)

- *CFD development with complex fluid*
- *population balance implementation*
- *CFD + fluid model validation*

C_s : salt concentration, r_c : colloid radius, ζ : zeta potential, D_f : fractal dimension, μ : viscosity, $\dot{\gamma}$: shear rate

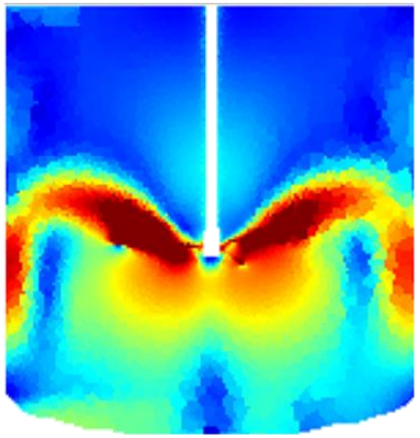
STRATEGY – COMPARTMENTAL MODELING



velocity field from CFD simulation – [m.s^{-1}]

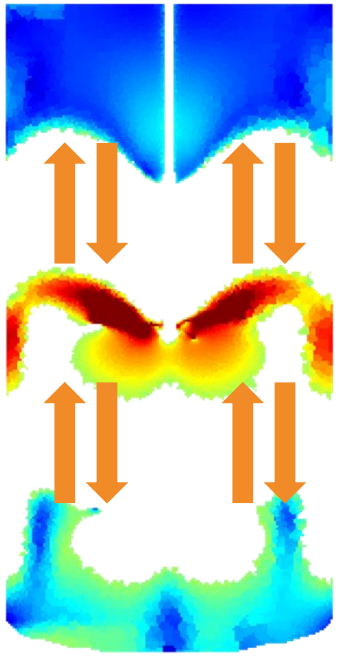
- shear rate field obtained from CFD simulation (COMSOL / FLUENT)
- shear rate data transposed to a structured grid (FORTRAN code)
- compartmentalization according to the shear rate field
- calculation of mean entrance and outlet compartmental flow rate
- population balance modeling inside each compartment

structured mesh



shear rate compartmentalization

determination of mean entrance and outlet compartment flow rate



population balance modelling run inside each compartment

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