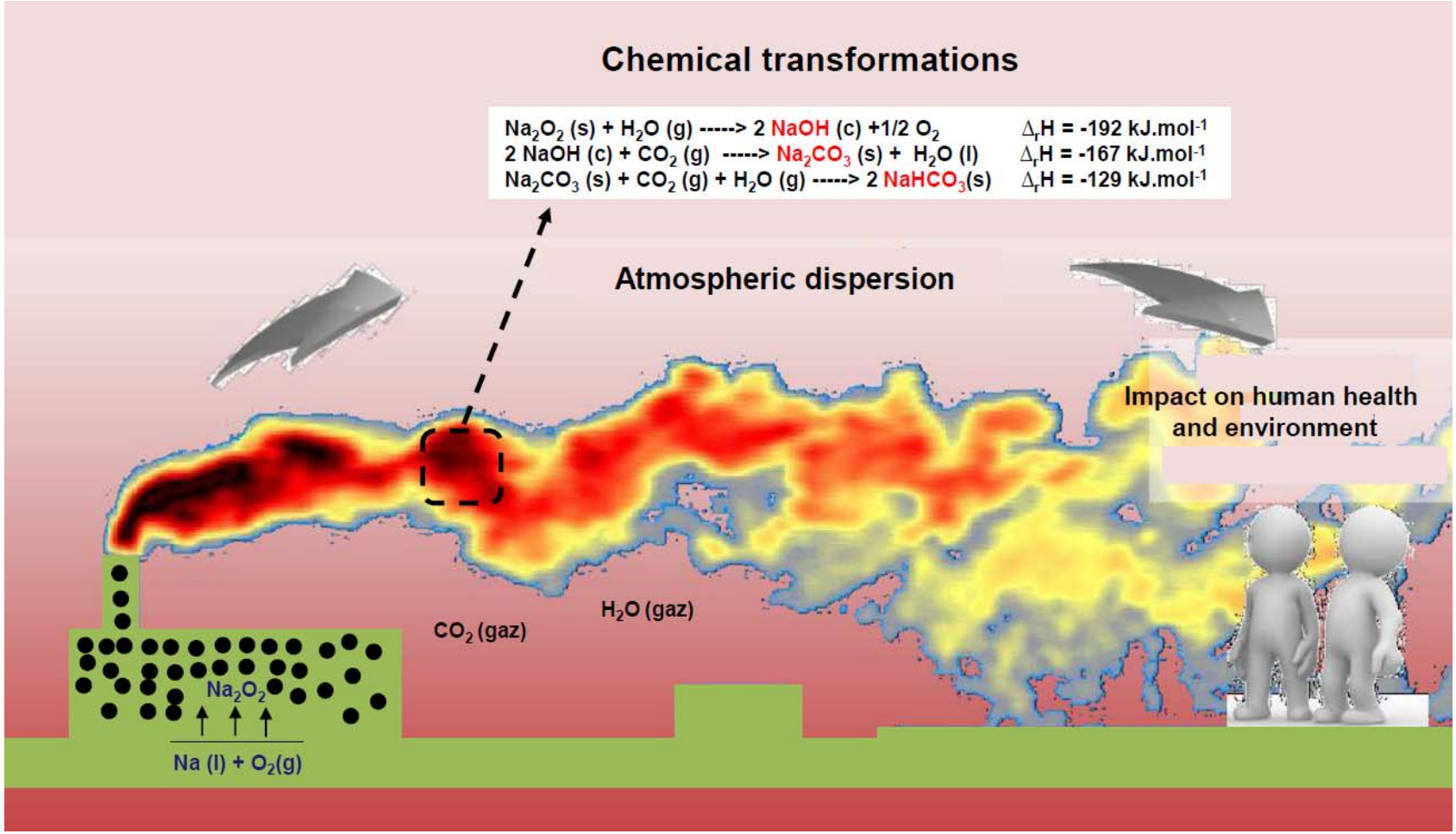
Modeling of the chemical behavior of sodium aerosols during atmospheric dispersion

Rémy Nsir, Karine Sartelet, Raphael Bresson, Luc Musson-Genon, Lynda Porcheron

Outline

1. **Context and Objectives**
2. **Chemical transformation of Na aerosol in the atmosphere**
3. **Development of a kinetic model**
   - Shrinking core model (Mathé, 2012)
   - Reactive adsorption model (Plantamp, 2016)
4. **Introduction of the developed model in the atmospheric dispersion simulator (Code_Saturne)**
5. **Preliminary validation of the global model**
   - Comparison to existent models (0D simulations)
   - Comparison to experimental data from literature (0D simulations)
   - Sensibility study (3D Simulations)
6. **Conclusions and perspectives**

Context : Toxicological impact of sodium fire aerosols



Description of the aerosol formation in a sodium fire

Combustion

==> sodium oxides Na_2O and Na_2O_2

$$Na(l \text{ or } g),\ O_2\ (g) \Longrightarrow Na_2O\ (s),\ Na_2O_2\ (s)$$

Hydration

Soda

ΔH=-192 kJ.mol-1

$$Na_2O_2\ (s) + H_2O\ (g) \Longrightarrow 2\ NaOH\ (s \text{ or } l) + \frac{1}{2}\ O_2$$

Sodium peroxyde

humidity

Sodium Hydroxide

Carbonation

$$2\ NaOH\ (s \text{ or } l) + CO_2\ (g) \Longrightarrow Na_2CO_3\ (s) + H_2O\ (l)$$

Sodium hydroxide

Carbon dioxide atmosphere

Sodium carbonate

ΔH=-167 kJ.mol-1

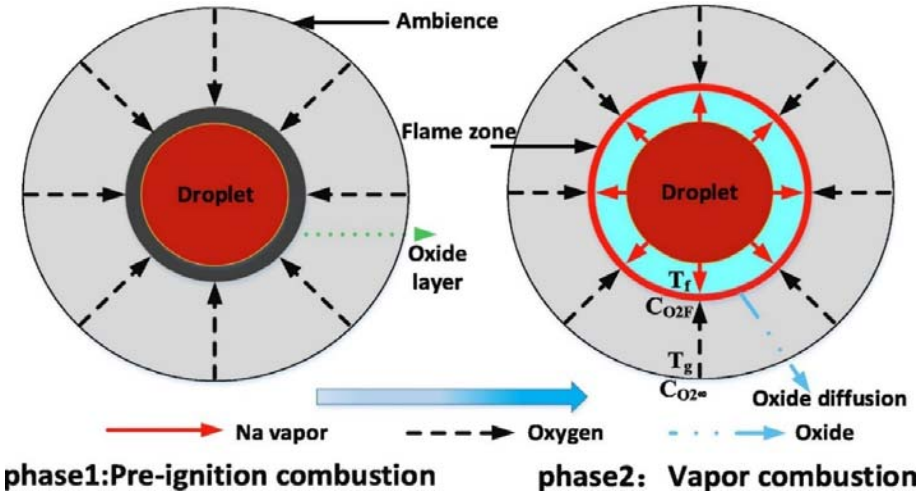
Bi-Carbonation

$$Na_2CO_3\ (s) + CO_2\ (g) + H_2O\ (g) \Longrightarrow 2NaHCO_3\ (s)$$

ΔH=-129kJ.mol-1

Sodium carbonate

Sodium bicarbonate



Process of Na liquid droplet combustion,
H. Sun et al./Annals of Nuclear Energy 147 (2020) 107674

Objectives and scientific approach

Objectives

- Development of a kinetic model
  - Aerosol reaction with H_2O
  - Aerosol reaction with CO_2

Na_2O_2 (s) + H_2O (g) -----> 2 NaOH (c) + ½ O_2 $\Delta_r H$ = -192 kJ.mol-1

2 NaOH (c) + CO_2 (g) -----> Na_2CO_3 (s) + H2O (l) $\Delta_r H$ = -167 kJ.mol-1

Na_2CO_3 (s) + CO_2 (g) + H_2O (g) -----> 2 $NaHCO_3$ (s) $\Delta_r H$ = -129 kJ.mol-1

- Introduction of the kinetic modeling in an atmospheric dispersion simulator
- Consideration of aerosol interaction with the surrounding air (sedimentation,deposition)

Methodology

- Review analysis of existing models and collection of experimental data
- Elaboration of a development strategy (conceptual model, hypothesis, numerical scheme,…)
- Evaluation of the developed model

Chemical transformations of sodium aerosols : review

❑ Aerodynamic diameter of primary sodium aerosol (before transformation)

- AMMD ≈ 0.9 µm (Cherdronet al., 1985)
- AMMD ≈ 1 µm (Jordan et al., 1988)
- AMMD ≈ 1.2 µm (Subramanianet Baskaran, 2007)

❑ Reaction with H_2O : Hydration

- Very fast reaction (transfer time **tr<1 s**)
  - tr≈ 2.10^{-4}-1s , RH ≈ 40-70% (Hofmann et al. 1979)
  - tr≈ 6.10^{-6}-3.10^{-2} s , dp≈ 0,1-10 µm (Cooper, 1980)
- NaOH aerosol is very harmful
- Formation of liquid droplet for **RH>35%**

❑ Reaction with CO_2 : Carbonation & Bicarbonation

- Slow reaction (transfer time **tr≈ few minutes**)
  - tr≈ 260 s , RH=20% (Cherdronet al., 1985)
  - tr≈ 500 s , RH=50-65% (Subramanian et al., 2009)
  - tr≈ 1300 s , RH=80% (Misraet al., 2012)
- Na_2CO_3 is only irritant
- Lack of studies on bicarbonation reaction
- NaHCO3 is inert

- Carbonation seems to be the limiting process of the aerosol chemical transformation
- Modeling hydration reaction by assuming liquid-vapour equilibrium on the aerosol surface (Cooper, 1981)

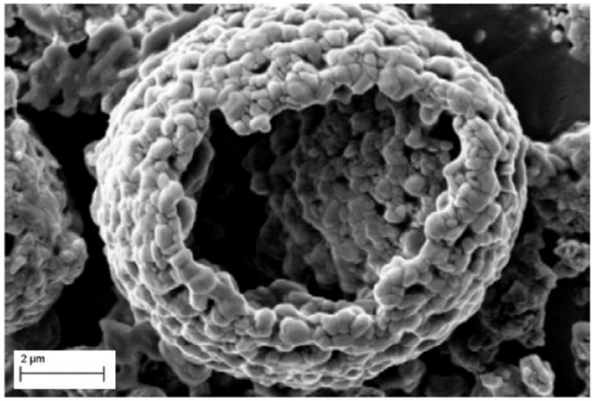
$$R_0 = R_p \frac{0.87}{(1-RH)^{1/3}}$$

RH : Relative humidity – R0 : Initial Radius of the hydrated aerosol - Rp Aerosol Particle radius

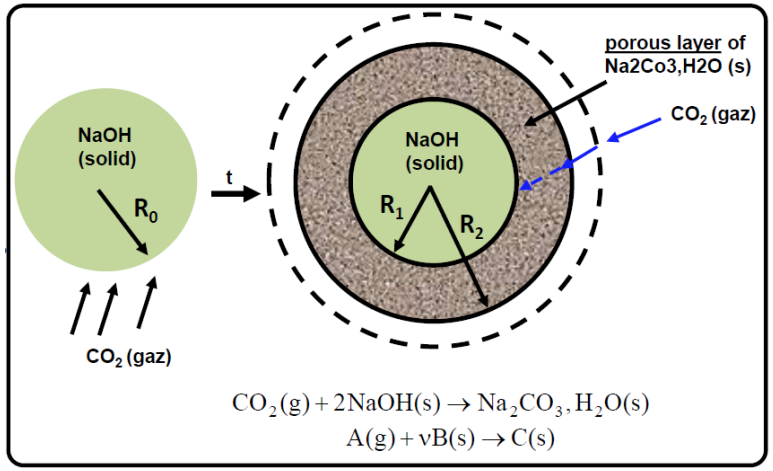
Development of a kinetic model

Shrinking core model (Mathé, 2012)
Reactive adsorption model (Plantamp, 2016)

❑ Conceptual model for carbonation reaction



Carbonate aerosol image (Plantamp, 2016)



❑ Hypothesis

- Heterogeneous reaction (gas/solid)
- Transfer limitation by internal diffusion
- Instantaneous surface reaction (1st order)

❑ Transfer flow rate (mole/s)

$$J_{CO_2} = 4\pi DeC_{CO_2} \frac{R_1 R_2}{R_2 - R_1}$$

Physical evolution of the aerosol

Initial radius

$$R_0 = R_s \frac{0.87}{(1-RH)^{1/3}}$$

Internal radius

$$R_1 = \left(\frac{3(m_{NaOH})}{4\pi\rho_{aerosol}}\right)^{1/3}$$

External radius

$$R_2 = \left(R_1^3 + \frac{3m_{Na_2CO_3,H_2O})}{4\pi\rho_{Na_2CO_3(1-\varepsilon)}}\right)^{1/3}$$

Development of a kinetic model

Shrinking core model (Mathé, 2012)
Reactive adsorption model (Plantamp, 2016)

❑ Application for all reactions (hydration, carbonation, bicarbonation)

- $Na_2O_2(s) + H_2O\ (g) \text{ -----> } 2\ NaOH(c) + ½\ O_2(g)$ (hydration)

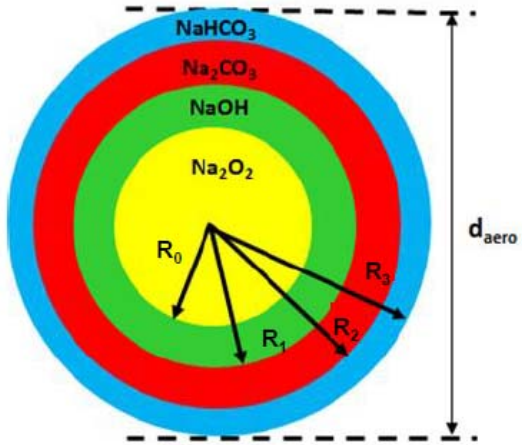
$$J_{H_2O} = \frac{4\pi C_{H_2O} D_e R_3 R_0}{R_3 - R_0}$$

- $2\ NaOH(c) + CO_2(g) \text{ -----> } Na_2CO_3\ (c) + H_2O\ (l)$ (carbonation)

$$J_{CO_2} = \frac{4\pi C_{CO_2} D_e R_3 R_1}{R_3 - R_1}$$

- $Na_2CO_3(c) + CO_2(g) + H_2O\ (g) \text{ -----> } 2\ NaHCO_3(c)$ (bicarbonation)

$$J_{H_2O,CO_2} = \frac{4\pi \min(C_{H_2O}, C_{CO_2}) D_e R_3 R_2}{R_3 - R_2}$$



Configuration of a aerosol sodium

❑ Aerosol size evolution

$$R_0 = \left(\frac{3(m_{Na_2O_2})}{4\pi\rho_{aerosol}}\right)^{1/3} \qquad R_1 = \left(\frac{3m_{NaOH}}{4\pi\rho_{aero}} + R_0^3\right)^{1/3}$$

$$R_2 = \left(\frac{3m_{Na_2CO_3}}{4\pi\rho_{aero}} + R_1^3\right)^{1/3} \qquad R_3 = \left(\frac{3m_{NaCHO_3}}{4\pi\rho_{aero}} + R_2^3\right)^{1/3}$$

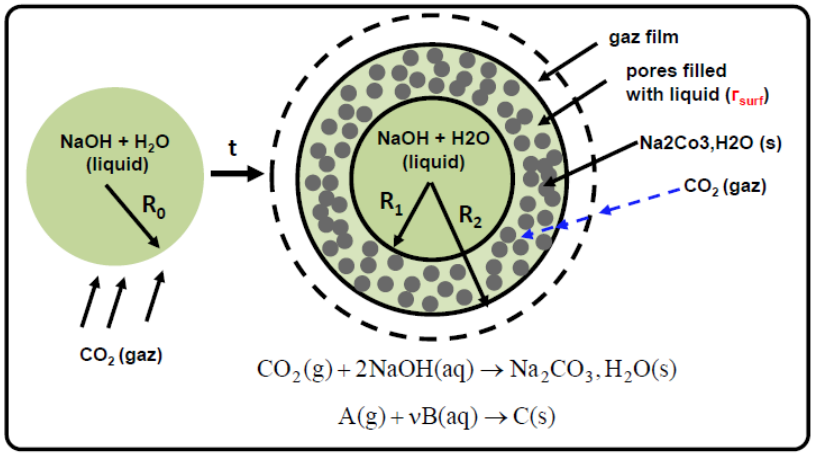
Incremental-Iterative schemas with fixed step time

ρ_{aero}: aerosol density (cst) ; mk: chemical compound mass

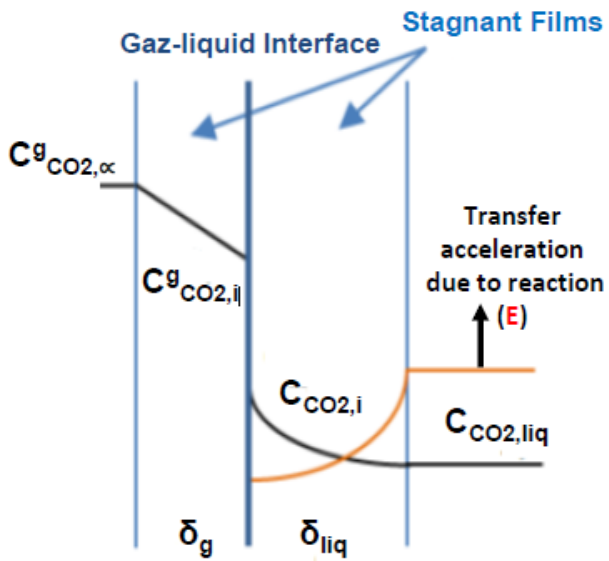
Development of a kinetic model

Shrinking core model (Mathé, 2012)
Reactive adsorption model (Plantamp, 2016)

❑ Conceptual model



Two-film theory



❑ Equation of the transfer flow rate (mole/s)

✓ **Gas film** $J_{CO_2} = 4\pi R^2 k_g (C^g_{CO_2,\infty} - C^g_{CO_2,i})$

✓ **Liquid film** $J_{CO_2} = 4\pi R^2 k_{liq} \tau_{surf} E (C_{CO_2,i} - C_{CO_2,liq})$

Since $C_{CO_2,i} = H C^g_{CO_2,i} R_{gaz} T$ **Henry law**

$$J_{CO_2} = 4\pi R_2^2 C^g_{CO_2,\infty} \times \left(\frac{1}{k_g} + \frac{1}{k_{liq} E \tau_{surf} R_{gaz} T}\right)$$

E: enhancement factor of reaction; Tsurf : ratio of accessible surface

Physical evolution of aerosol

Internal radius $R_1 = \left(\frac{3(m_{H_2O} + m_{NaOH})}{4\rho_{solt}}\right)^{1/3}$

External radius $R_2 = \left(R_0^3 + \frac{3m_{Na_2CO_3,crist}}{4\pi\rho_{Na_2CO_3(1-\varepsilon)}}\right)^{1/3}$

Development of a kinetic model

Shrinking core model (Mathé, 2012)
Reactive adsorption model (Plantamp, 2016)

Calculation of model parameters

- Enhancement factor H

$$Ha = \frac{\sqrt{C_{OH^-,L}\, k_{OH^-}\, D_{CO_2,L}}}{k_L}$$

$$E_{inst} = 1 + \frac{1}{2}\frac{D_{OH^-,L}\, C_{OH^-,L}}{D_{CO_2,L}\, C_{CO_2,i}}$$

$$Ha^2 = \frac{Kinetic\ rate\ of\ reaction\ in\ a\ liquid\ film}{Transfer\ flow\ rate\ by\ diffusion\ through\ film}$$

If E_{inst}>>Ha ⇒ $E = \frac{Ha}{tang(Ha)}$

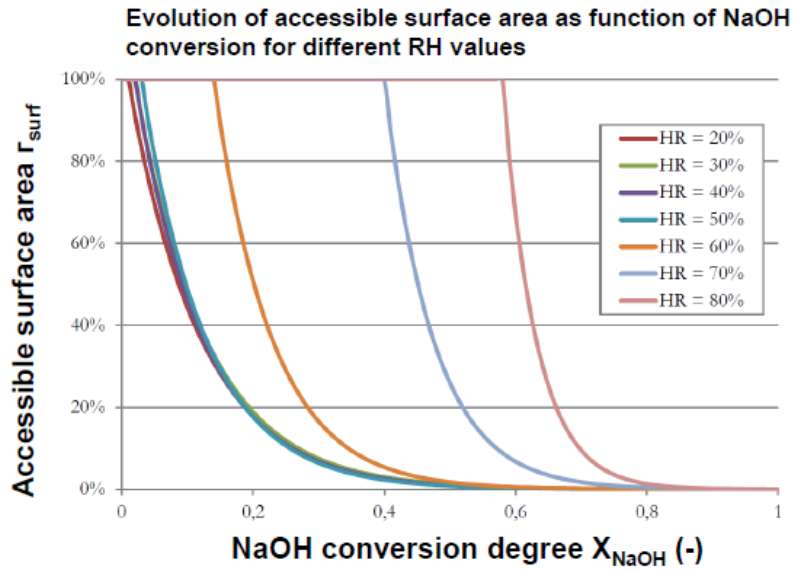
k_{OH^-}: reaction rate constant (m_3,mol_{-1}.s_{-1})
$D_{CO2,L}$: diffusion coefficient of CO2 in the liquid (m_2.s_{-1})
$D_{OH^-,L}$: diffusion coefficient of OH in the liquid (m_2.s_{-1})
$C_{OH^-,L}$: OH concentration in the liquid (mol.m_{-3})

- Accessible surface area τ_{surf}

$$\tau_{surf} = \beta \exp(pX_{NaOH})$$

$$p = \frac{-0.5289}{(1-RH)^2} - 8.626$$

$$X_{NaOH} = \frac{n^0_{NaOH} - n_{NaOH}}{n^0_{NaOH}}$$



Coupling with atmospheric dispersion calculation

CFD-based simulation : Eulerian Approach

- Eulerian approach is preferable because sodium aerosol inertia is negligible
- Aerosol concentration is considered as a scalar transported in the flow field
- Chemical transformation of aerosol is introduced as a source term in the transport equation

Transport equation

$$\frac{\partial(\rho X_k)}{\partial t} + \mathrm{div}((\rho \underline{u}) \cdot X_k) = \mathrm{div}(K_e \, \mathrm{grad}(X_k)) + TS_{X_k}$$

$$TS_{X_k} = \nu J_{gaz} \frac{M_k}{M_{gaz}}$$

X_k: mass fraction (kg_k/kg_{airl})
M_k: molar mass (mol/kg)
k : Chemical species (NaOH, Na_2CO_3, CO_2,…)

- Modeling of aerosol sedimentation

$$\rho \underline{u} = \rho \underline{u} + \rho \underline{v_{sed}}$$

drift-flux model

Integration of the gravitational settling effect of aerosols into the convection term

$$v_{sed} = \frac{\rho_p d_{aero}^2}{18 \mu_{air}} |g = \tau_{aero} g$$

τ_{aero}: relaxation time

Coupling with atmospheric dispersion calculation

❑ CFD-based simulation : Eulerian Approach

- **Modeling of aerosol release**

$$\frac{\partial \rho}{\partial t} + \mathrm{div}(\rho \underline{u}) = \Gamma$$

$$\frac{\partial(\rho X_k)}{\partial t} + \mathrm{div}((\rho \underline{u}) \cdot X_k) = \mathrm{div}(K_e \, \mathrm{grad}(X_k)) + TS_{X_k} + (X_{k,inj} - X_k)\Gamma$$

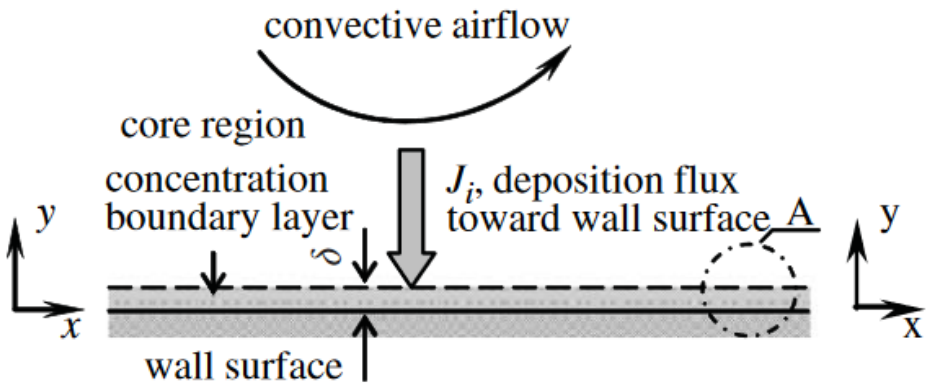
Γ: release rate(kg_{air}/s)
$X_{k,inj}$: mass fraction in the release rate

- **Modeling of aerosol deposition**

$$J = v_{dep} C_{aero}^{wall}$$

$$v_{dep} = v_{sed} + \underbrace{\frac{1}{R_a + R_b + R_a R_b v_{sed}}}_{= cst}$$

Integration of aerosols deposition as a wall flux into the boundary condition



Methodology modeling of aerosol deposition,
F. Chen et al. / Atmospheric Environment 40 (2006) 357–367

Coupling with atmospheric dispersion calculation

❑ Modeling of reaction heat

- Heat balance

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p \underline{u}.\mathrm{grad}(T) = \mathrm{div}(\lambda_e \mathrm{grad} T) + TS_T + v_r(-\Delta_r H)$$

$\Delta_r H$: heat of the reaction, J.mol-1
V_r : rate of the chemical reaction, mol.s-1

- Atmospheric application : potential temperature

$$\theta = T\left(\frac{P_{ref}}{P}\right)^{R_{gaz}/C_p}$$

P_{ref}: standard reference pressure
R_g: gazconstant

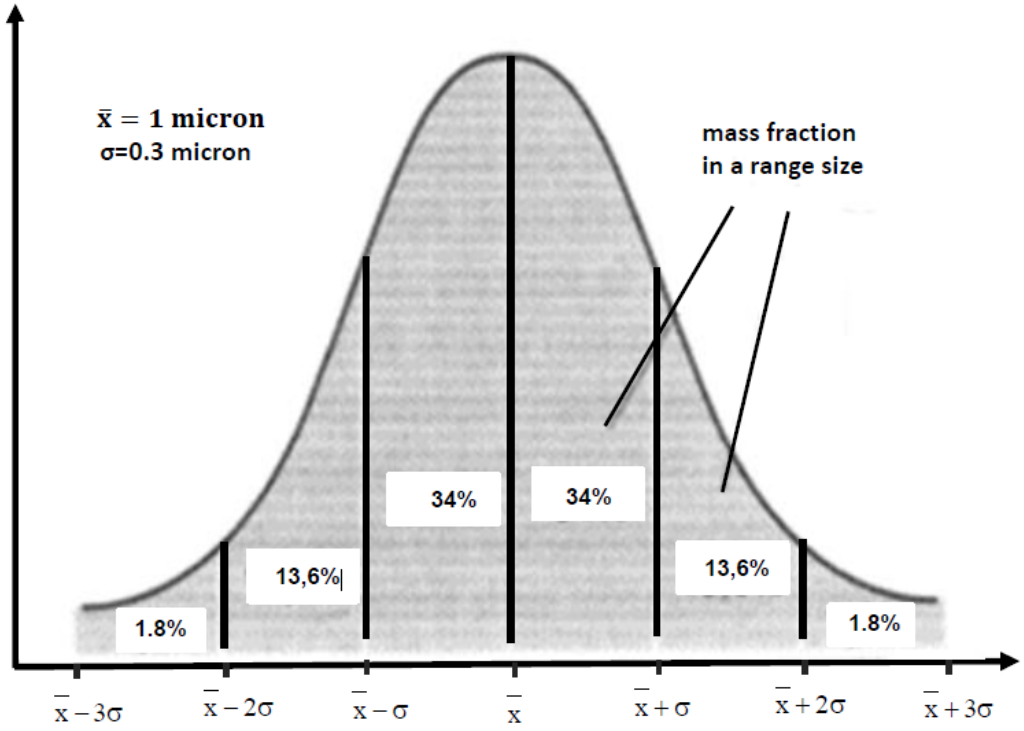
$$\rho C_p \frac{\partial \theta}{\partial t} + \rho C_p \underline{u}.\mathrm{grad}(\theta) = \mathrm{div}(\lambda_e \mathrm{grad}\theta) + TS_T + \frac{\theta}{T}\frac{dC_{H2O}}{dt}\left(\frac{\Delta_r H_{hydration}}{Mm_{H2O}}\right) + \frac{\theta}{T}\frac{dC_{CO2}}{dt}\left(\frac{\Delta_r H_{carbonation} + \Delta_r H_{bicarbonation}}{Mm_{CO2}}\right)$$

Cp: specific heat of the gas, J.Kg-1.mol-1
λe : effective thermal conductivity, W.m-1.K-1

Coupling with atmospheric dispersion calculation

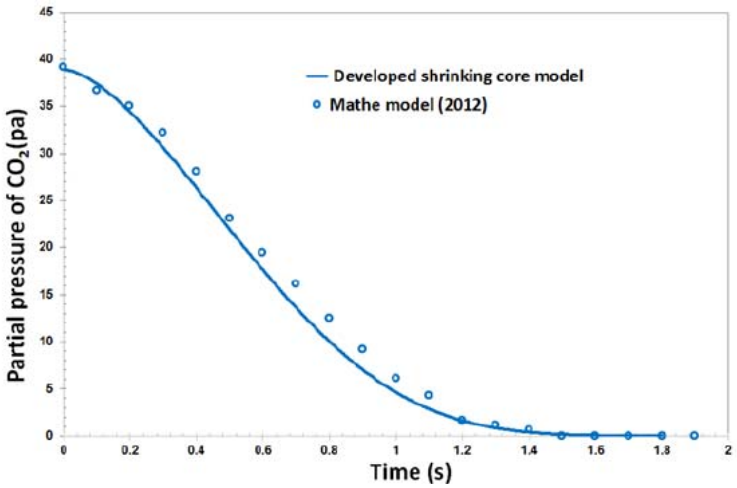
Discretization of the aerosol granulometry

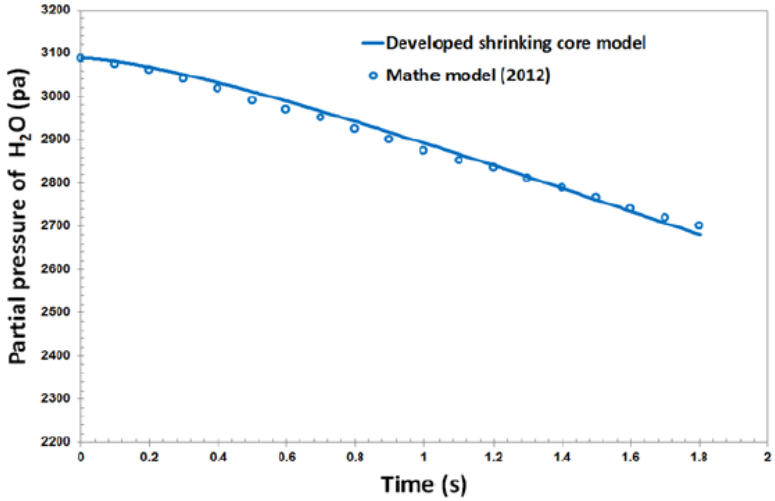
- Application of a normal distribution
- Choice of a 6 range sizes
- Possibility to integrate more realistic spectral distribution

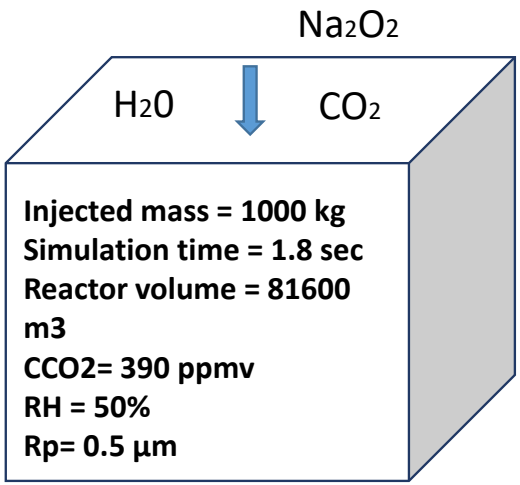


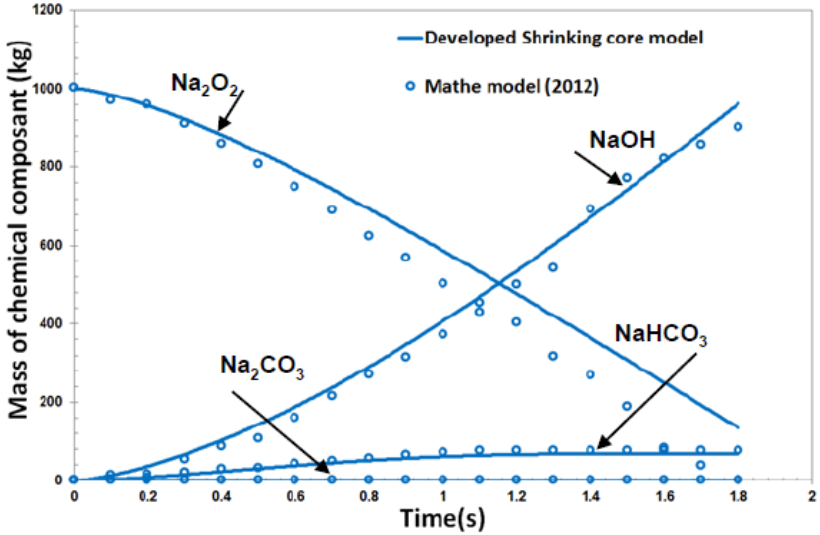
Evaluation of the kinetic model

Model vs. Stark simulation (Mathé, 2012)



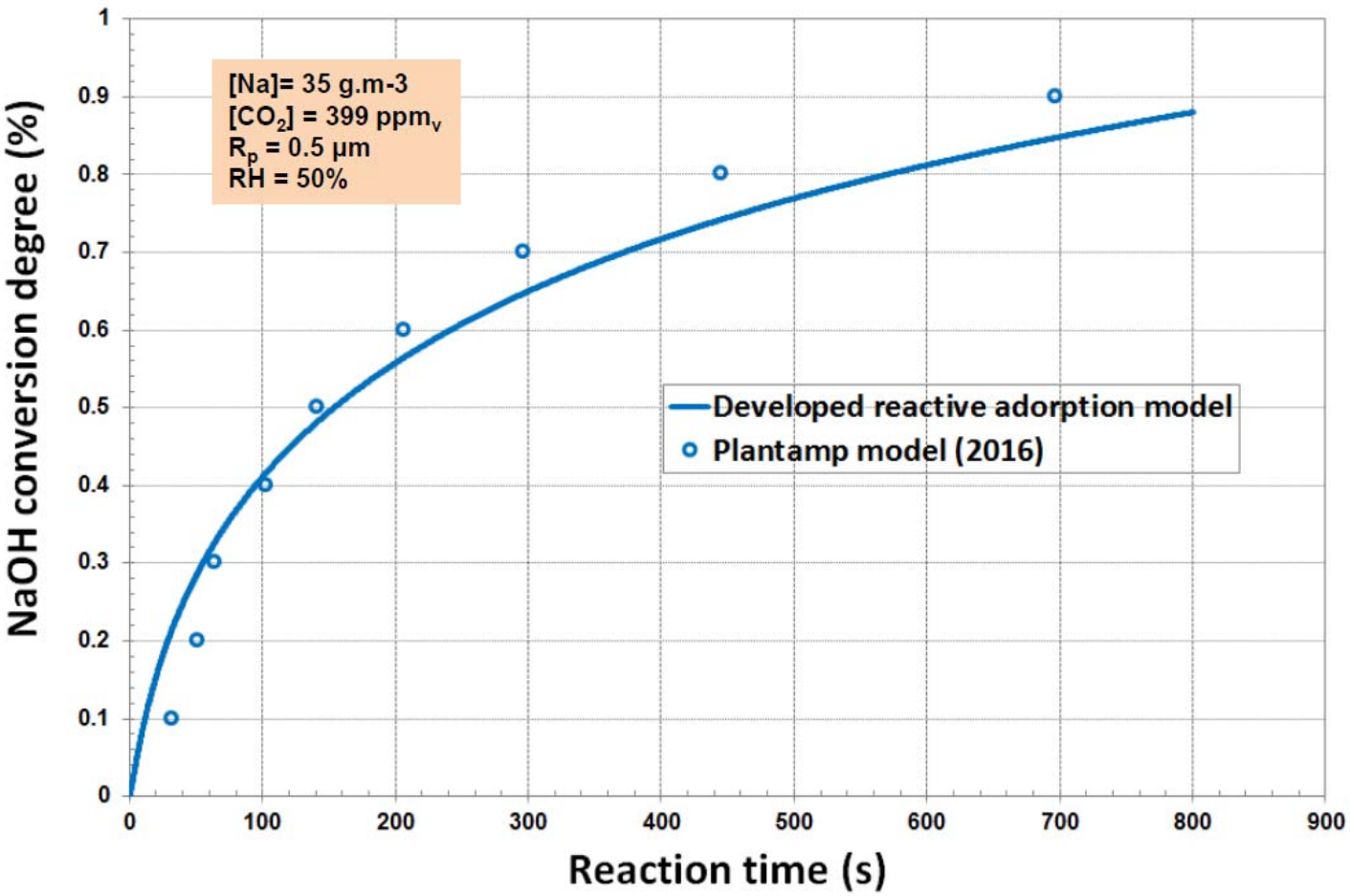






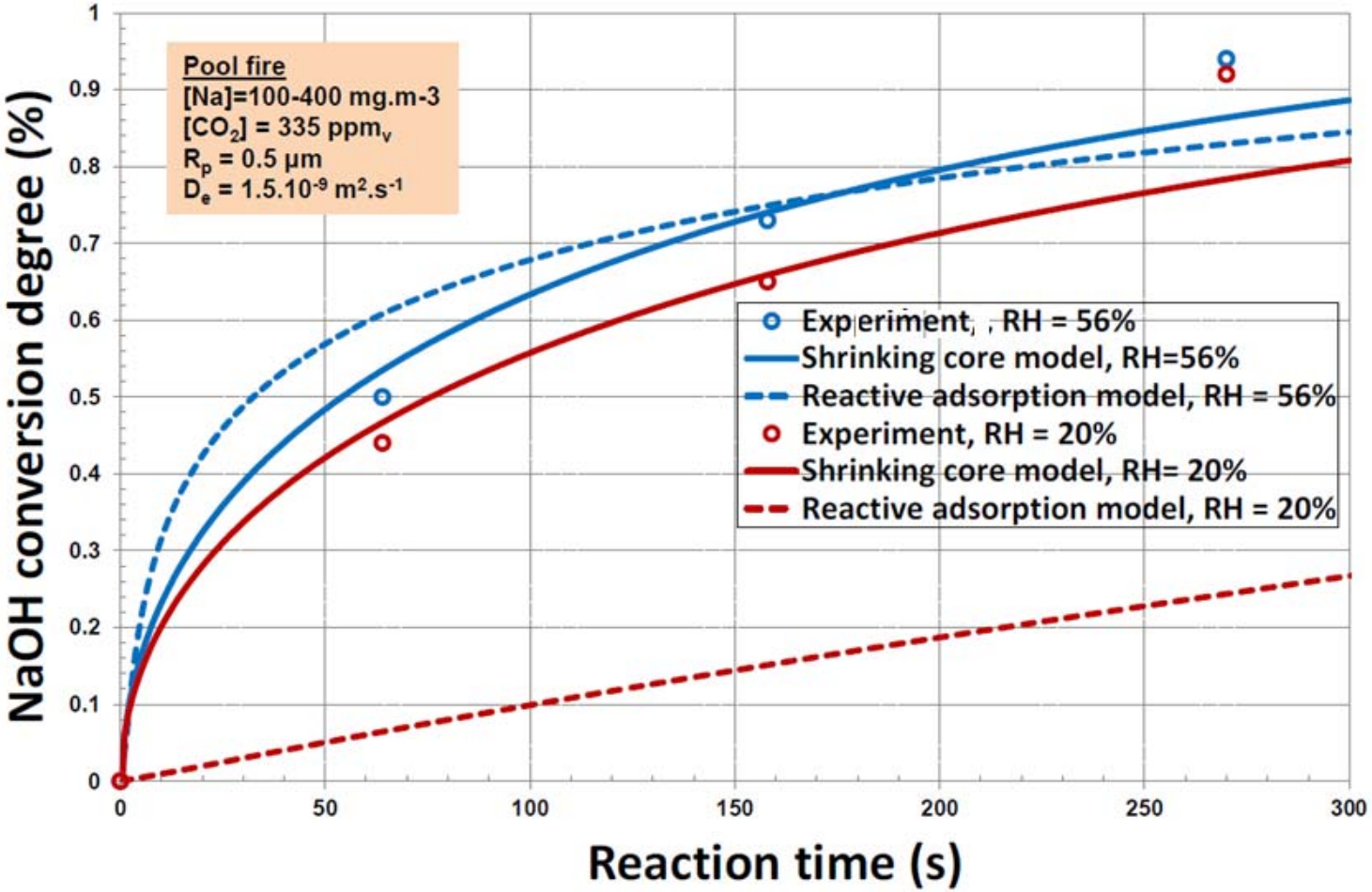
Evaluation of the kinetic model

Model vs. Simulation Plantamp(Plantamp, 2016)



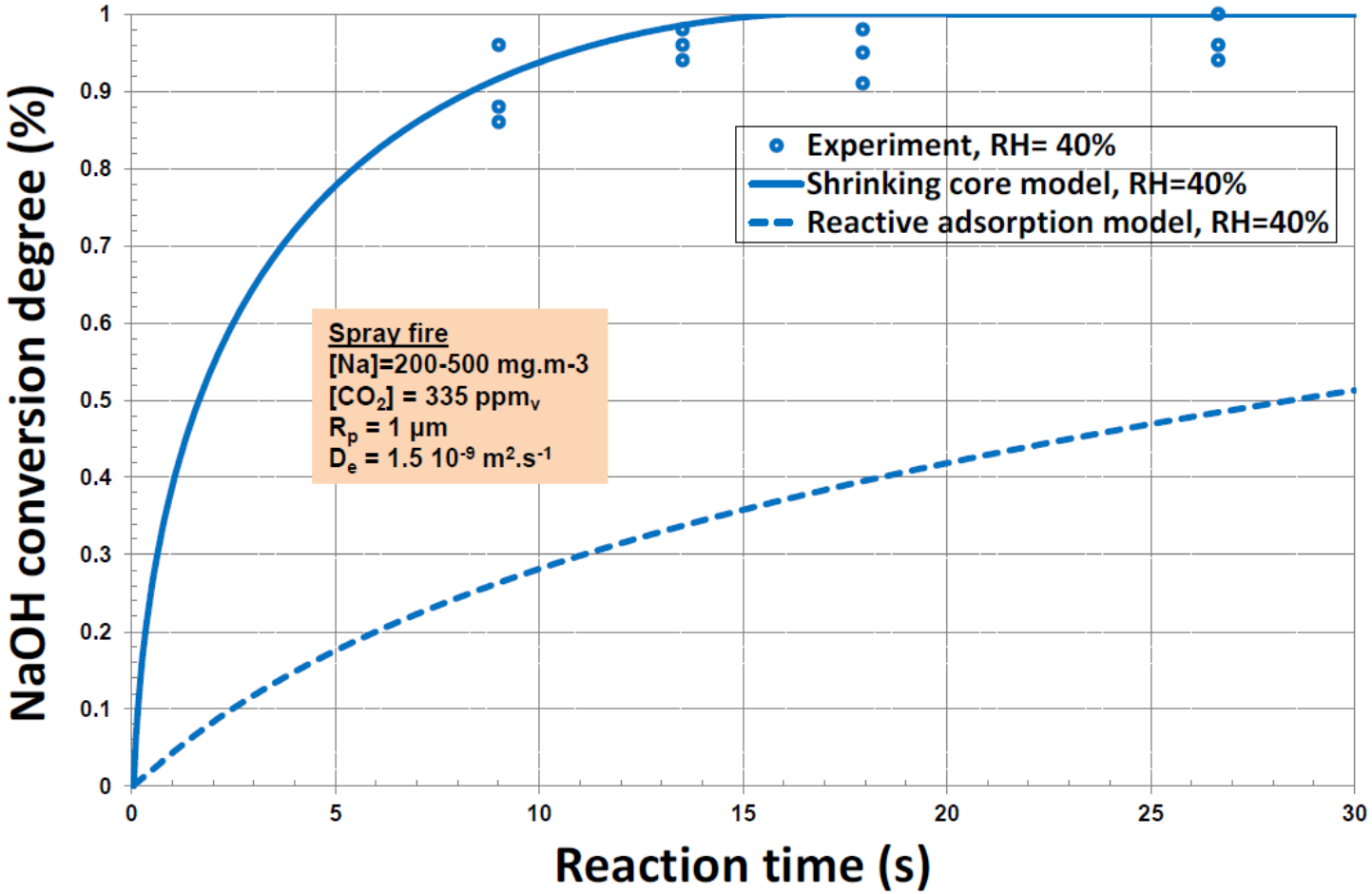
Evaluation of the kinetic model

❑ Model vs. experiments of Cheldron et al., 1984



Evaluation of the kinetic model

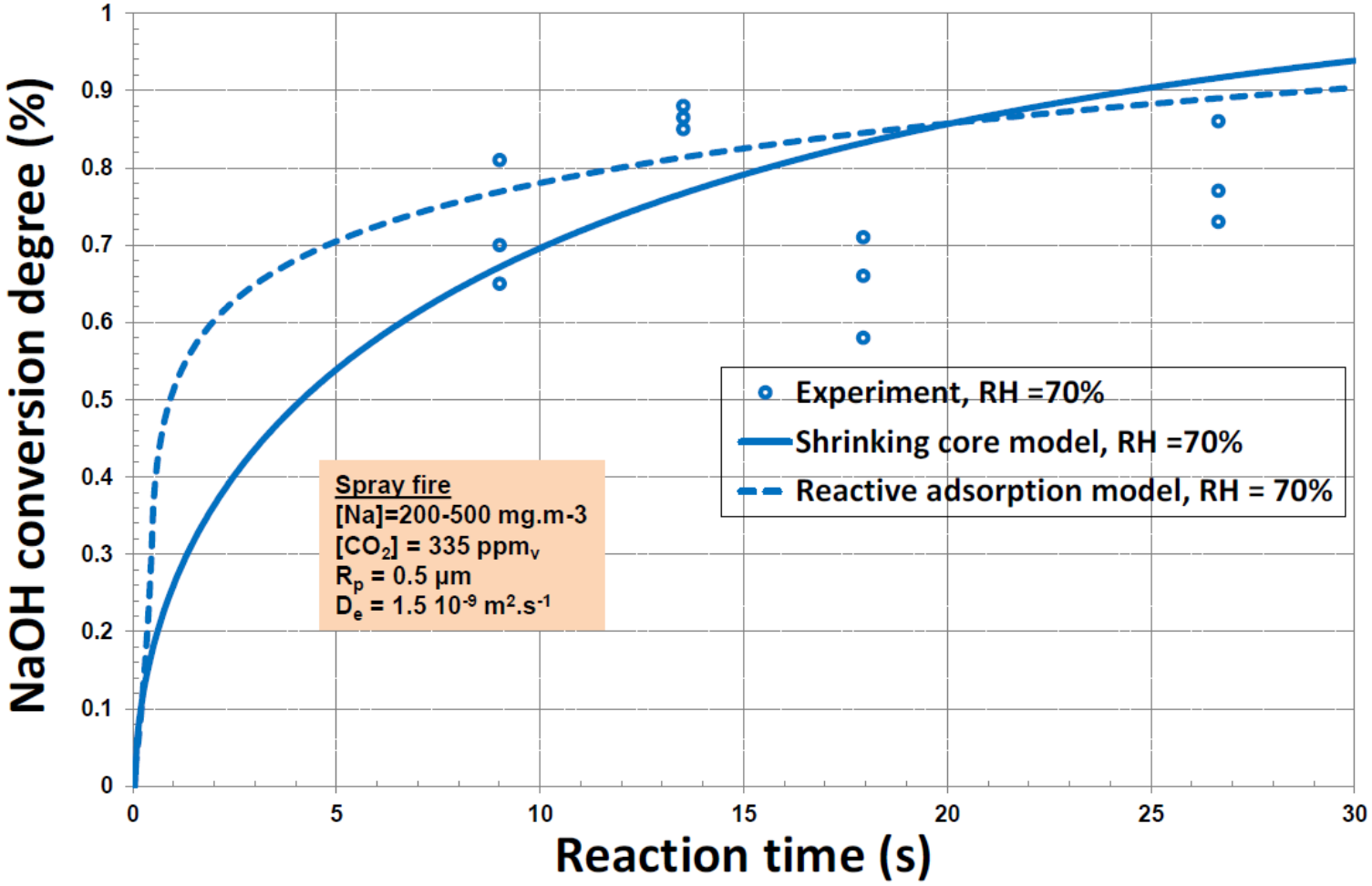
Model vs. experiments of Hofmann et al., 1979 (RH = 40%)



Evaluation of the kinetic model

Comparison to existent model
Comparison to experimental data from literature
Sensibility study – 3D simulations

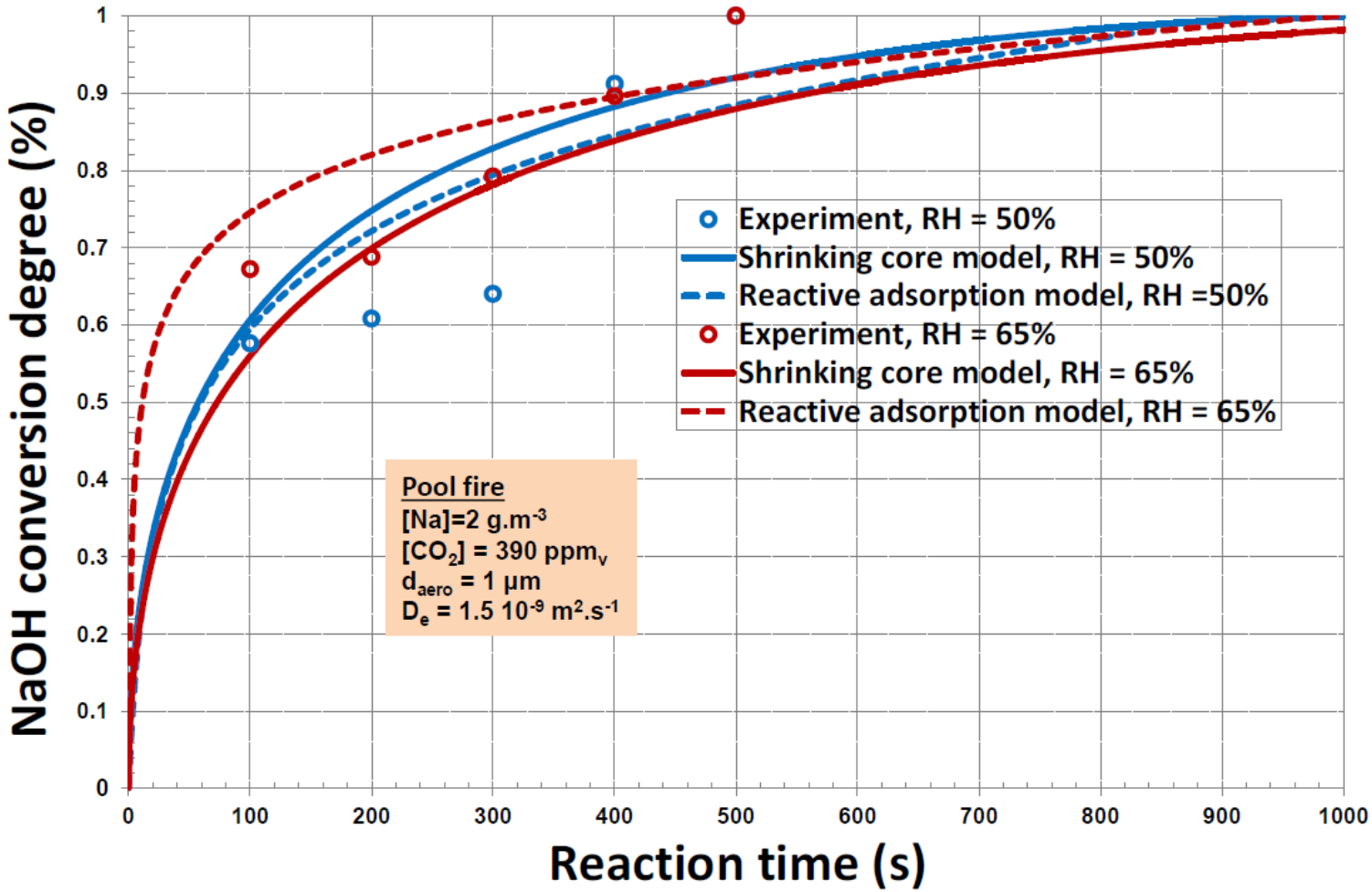
Model vs. experiments of Hofmann et al., 1979 (RH = 70%)



Evaluation of the kinetic model

Comparison to existent model
Comparison to experimental data from literature
Sensibility study – 3D simulations

Model vs. experiments of Subramanian et al., 2009

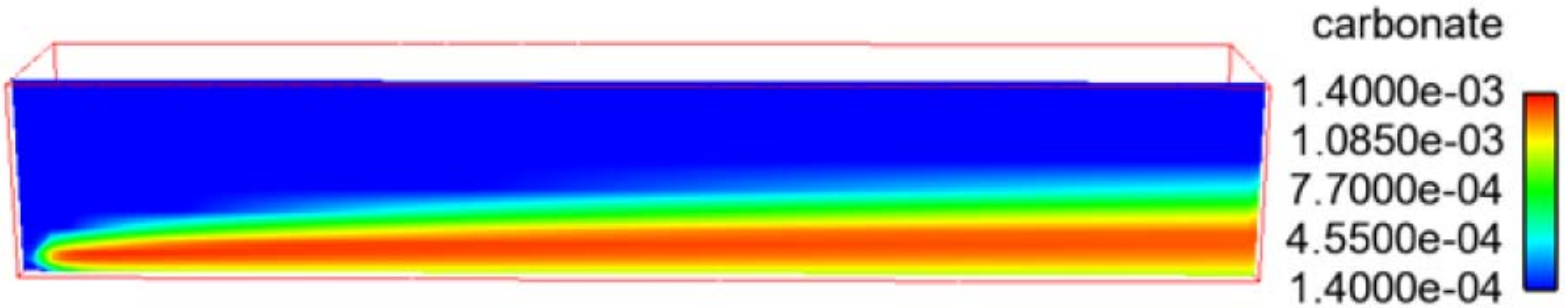


Evaluation of the kinetic model

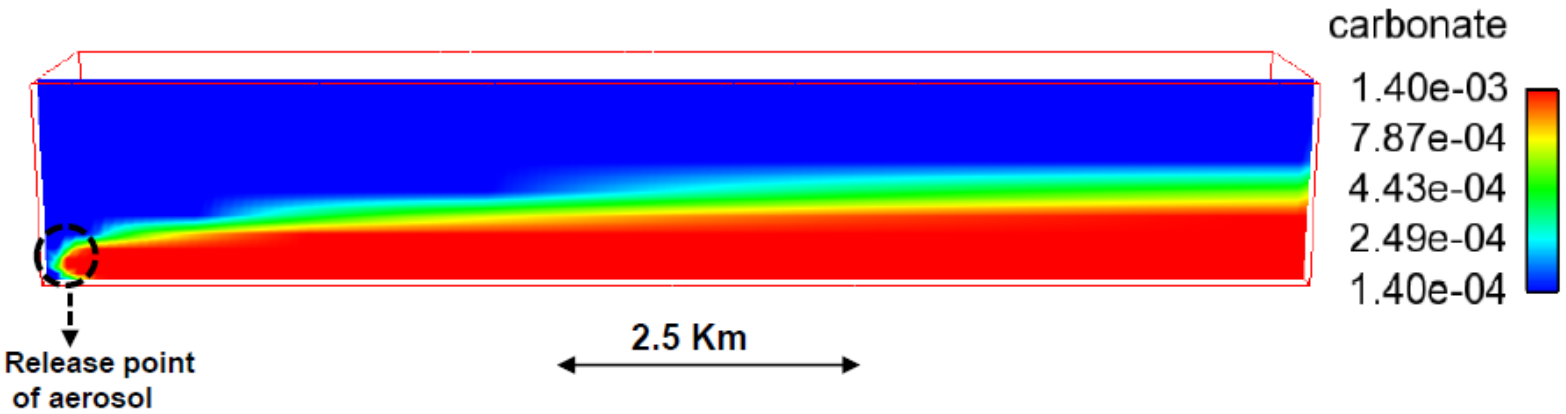
Comparison to existent model
Comparison to experimental data from literature
Sensibility study – 3D simulations

❑ Modelling of aerosol deposition process: shrinking core model

Deposition process: considered monodisperse size distribution case



Deposition process: not considered monodisperse size distribution case

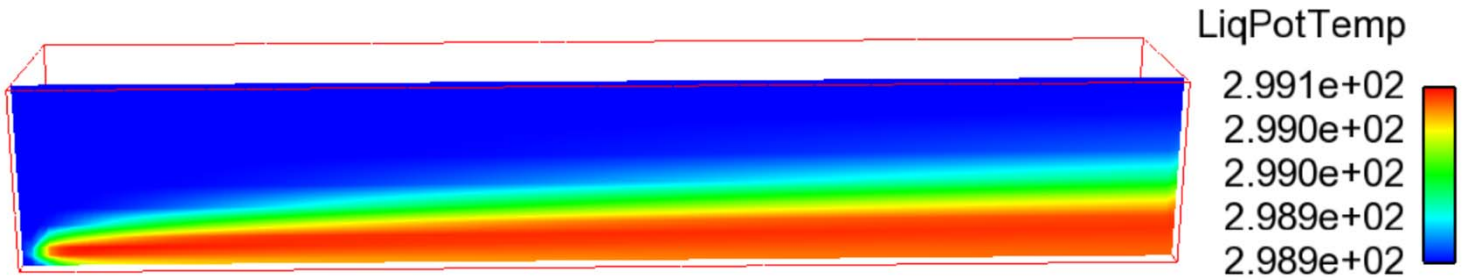


- ✓ Homogenous domain
- ✓ Domain size: 1000x400x400
- ✓ Source release : 30 m up soil
- ✓ RH = 50%
- ✓ Neutral atmosphere
- ✓ Release rate : 100 Kg/s
- ✓ Simulation time : 1000 s

Evaluation of the kinetic model

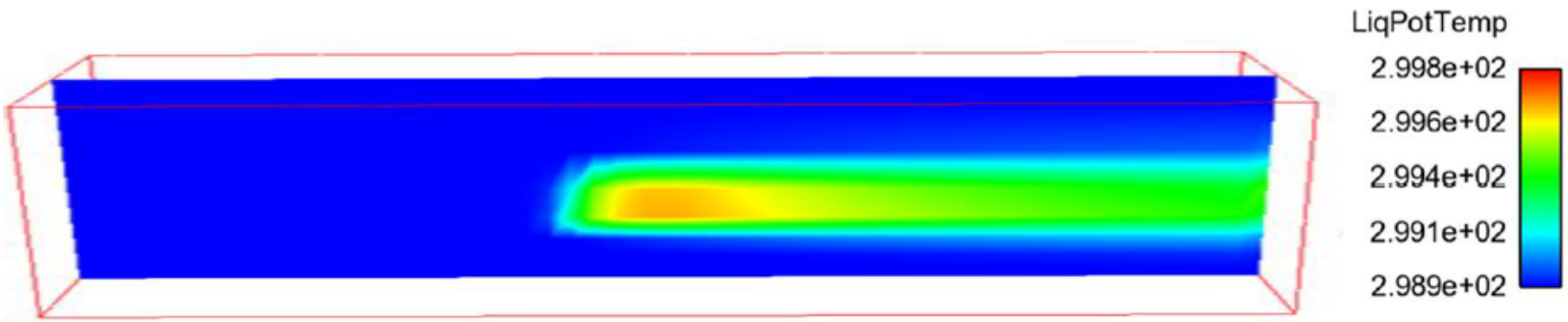
❑ Modelling of the aerosol deposition process : shrinking core model

Only carbonation reaction is considered



- ✓ Homogenous domain
- ✓ Domain size: 1000x400x400
- ✓ Source release : 30 m up soil
- ✓ RH = 50%
- ✓ Neutral atmosphere
- ✓ Release rate : 100 Kg/s
- ✓ Simulation time : 1000 s

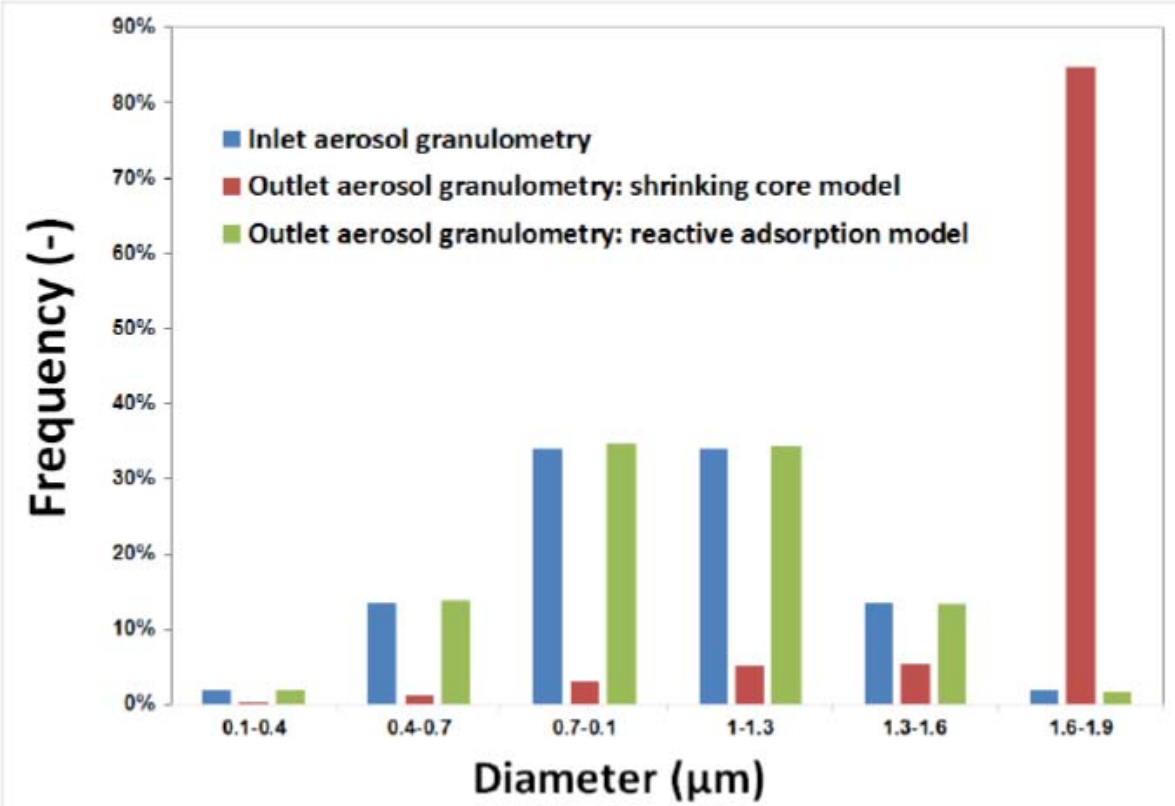
All reaction are considered (<u>hydration</u>, <u>carbonation</u>, <u>bicarbonation</u>)

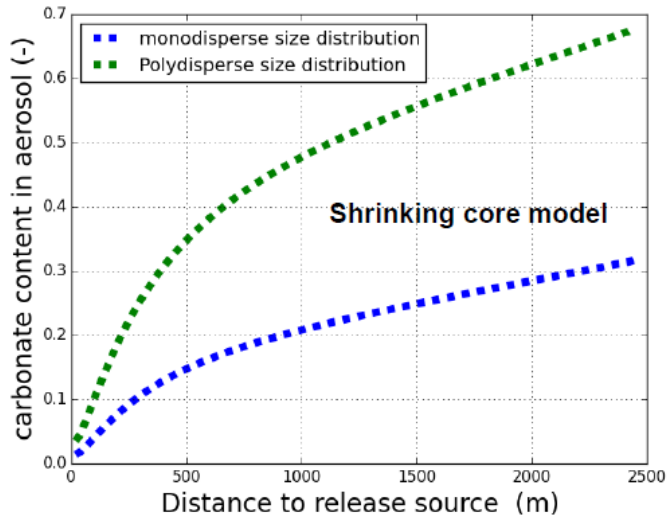


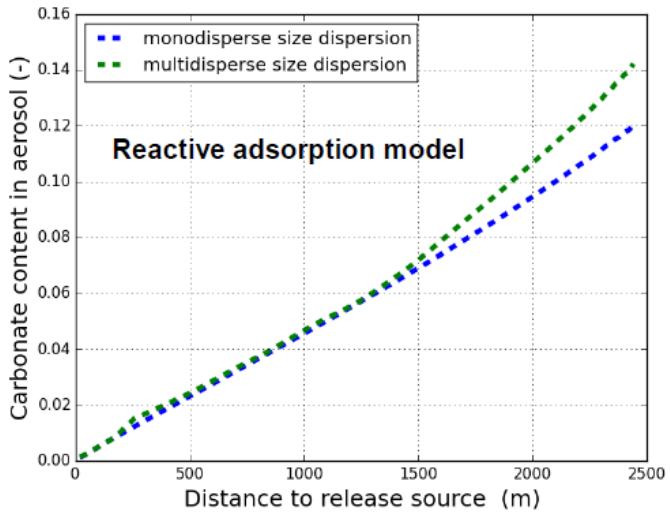
Evaluation of the kinetic model

Comparison to existent model
Comparison to experimental data from literature
Sensibility study – 3D simulations

❑ Effect of the aerosol size discretization

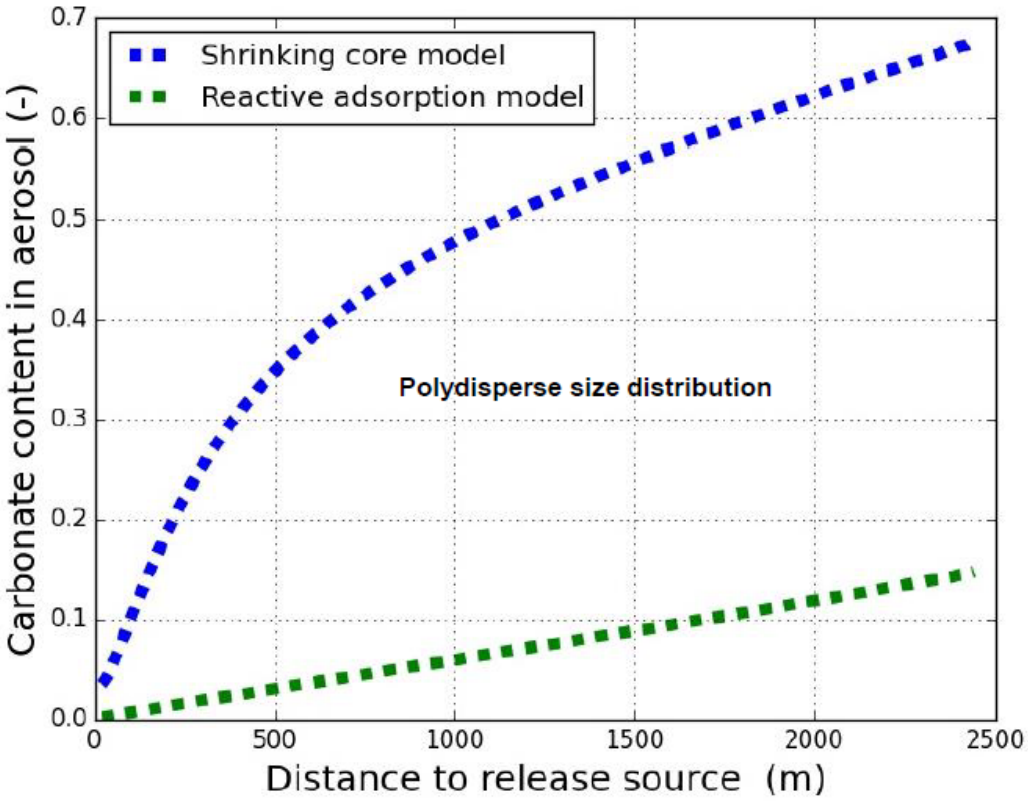


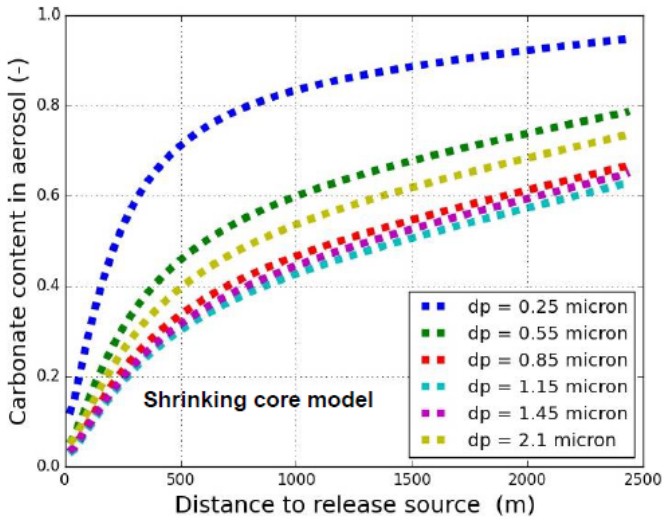


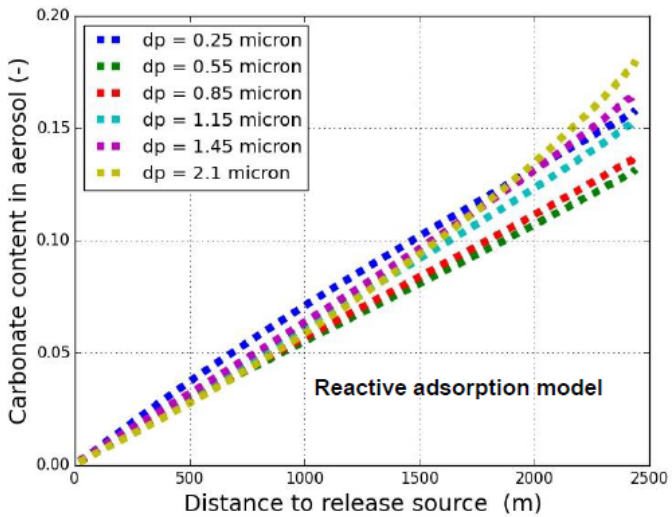


Evaluation of the kinetic model

❑ Effect of the aerosol size : shrinking core model



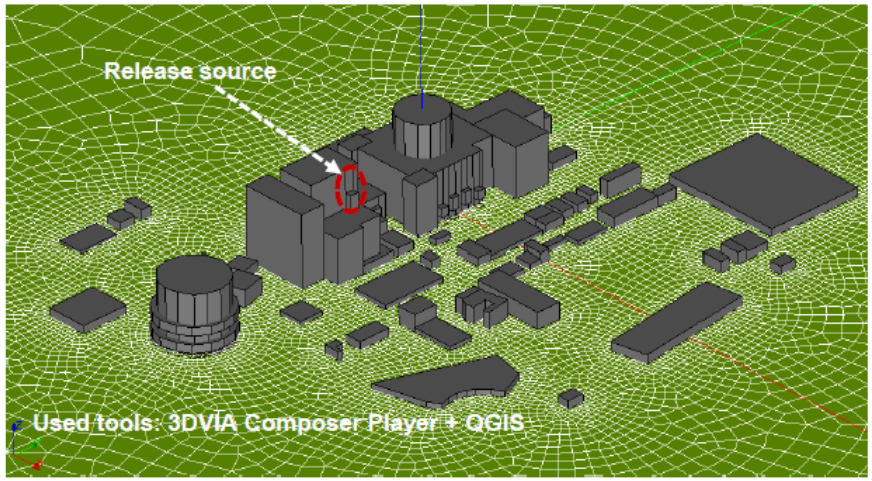


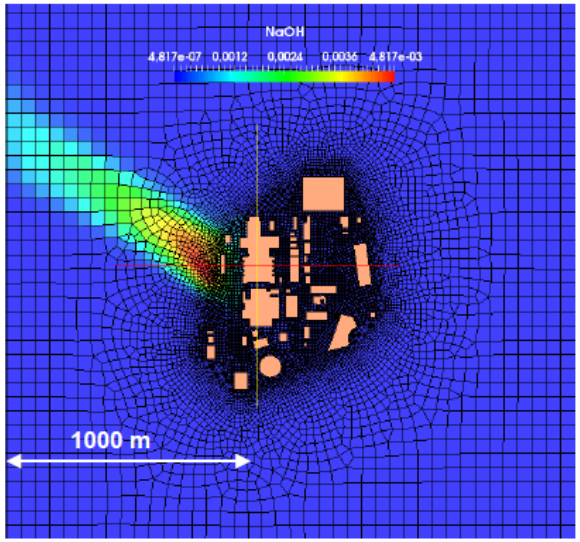


Evaluation of the kinetic model

Comparison to existent model
Comparison to experimental data from literature
Sensibility study – 3D simulations

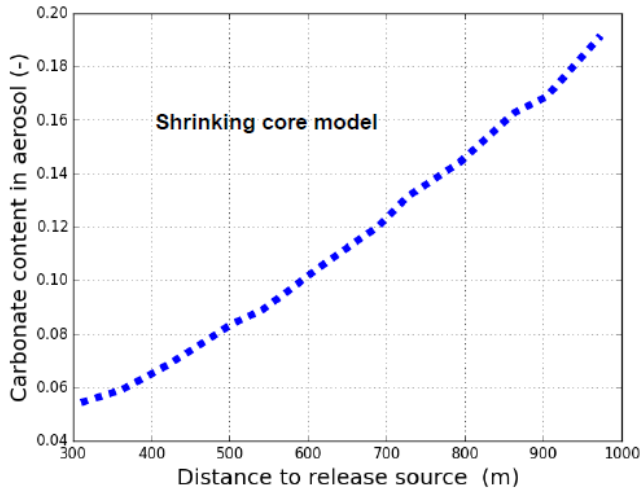
❑ Modeling the conditions of a release scenario





Domain with building

- ✓ Domain size : 2000x2000x1000
- ✓ source release : 70 m up soil
- ✓ RH = 50%
- ✓ Rp= 0,5 µm
- ✓ Neutral atmosphere
- ✓ Release rate :100 Kg/s
- ✓ Simulation time : 1000 s
- ✓ Monodisperse size distribution



Conclusions and Perspectives

Conclusions

- Quantitative kinetic model but 0D validation is not sufficient
- High sensitivity of the carbonation process to the aerosol granulometry and to RH
- Shrinking core model more adapted to low RH whereas reactive adsorption model gives better satisfaction at high RH
- Easy incorporation in atmospheric dispersion simulator
- K. Nsir, et al. *Journal of Aerosol Science 137 (2019) 105433*

Perspectives

- Further experimental validations under different atmosphere conditions
- Consideration of more realistic meteorological conditions in dispersion simulation
- More precisions about the bicarbonation chemical kinetic is needed
- Evaluation of sodium aerosol toxicological impact at a larger scale

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