OPTIMAL PARTICLE PARAMETERS FOR CLC AND CLR PROCESSES

PREDICTIONS BY INTRA-PARTICLE TRANSPORT MODELS AND EXPERIMENTAL VALIDATION

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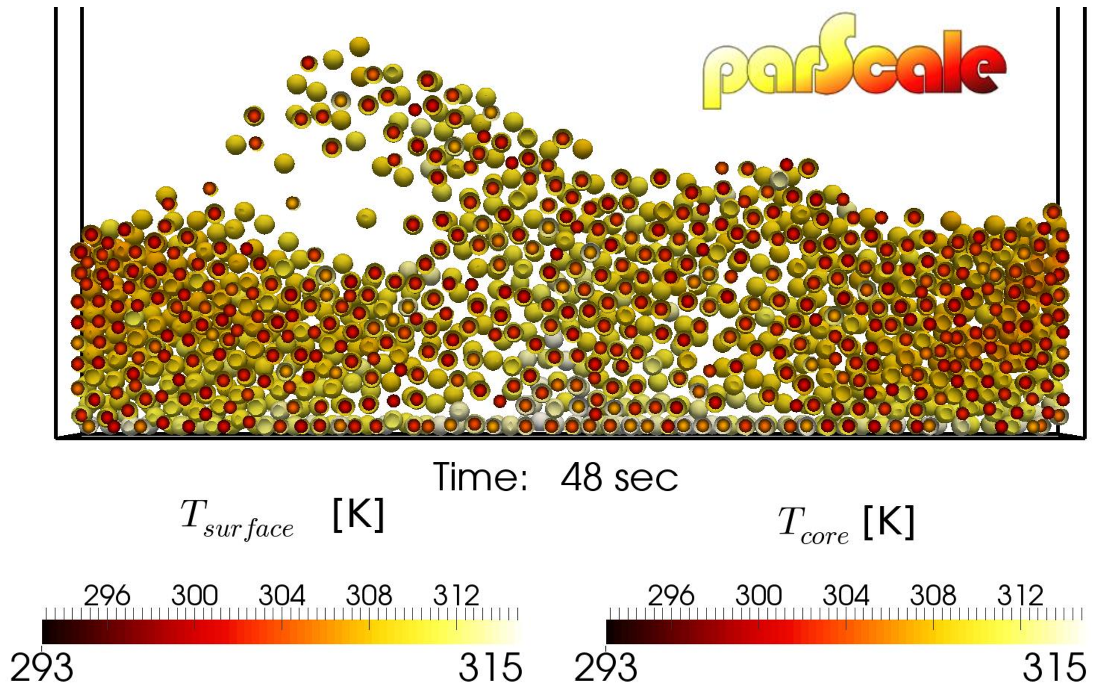


Institute for Process and Particle Engineering 2015

Motivation

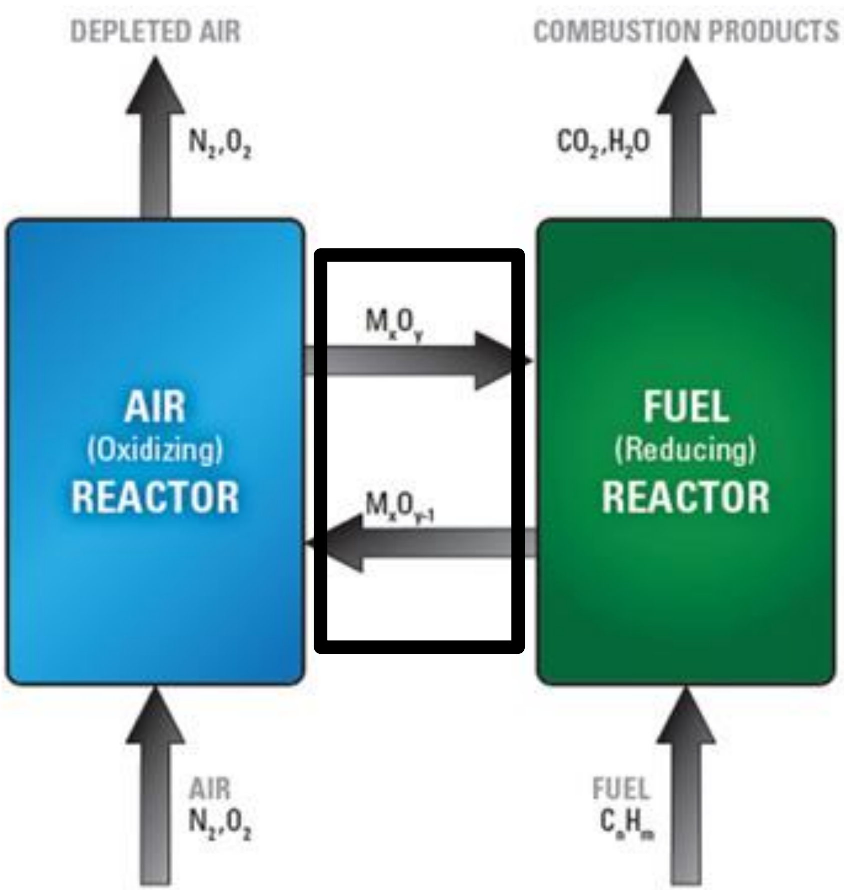


Figure 1: Schematic CLC process

Particle Parameter Set

- Composition
- Porosity
- Pore size
- Particle size
- ...

↓

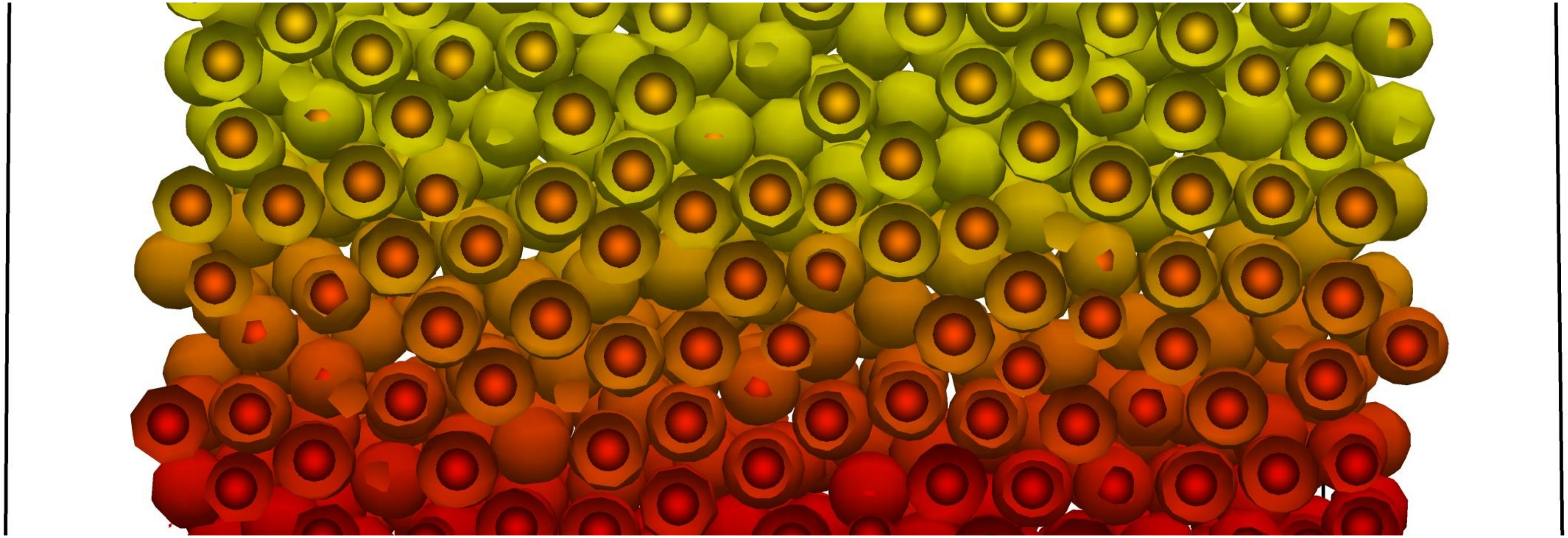
Rate limiting steps

↓

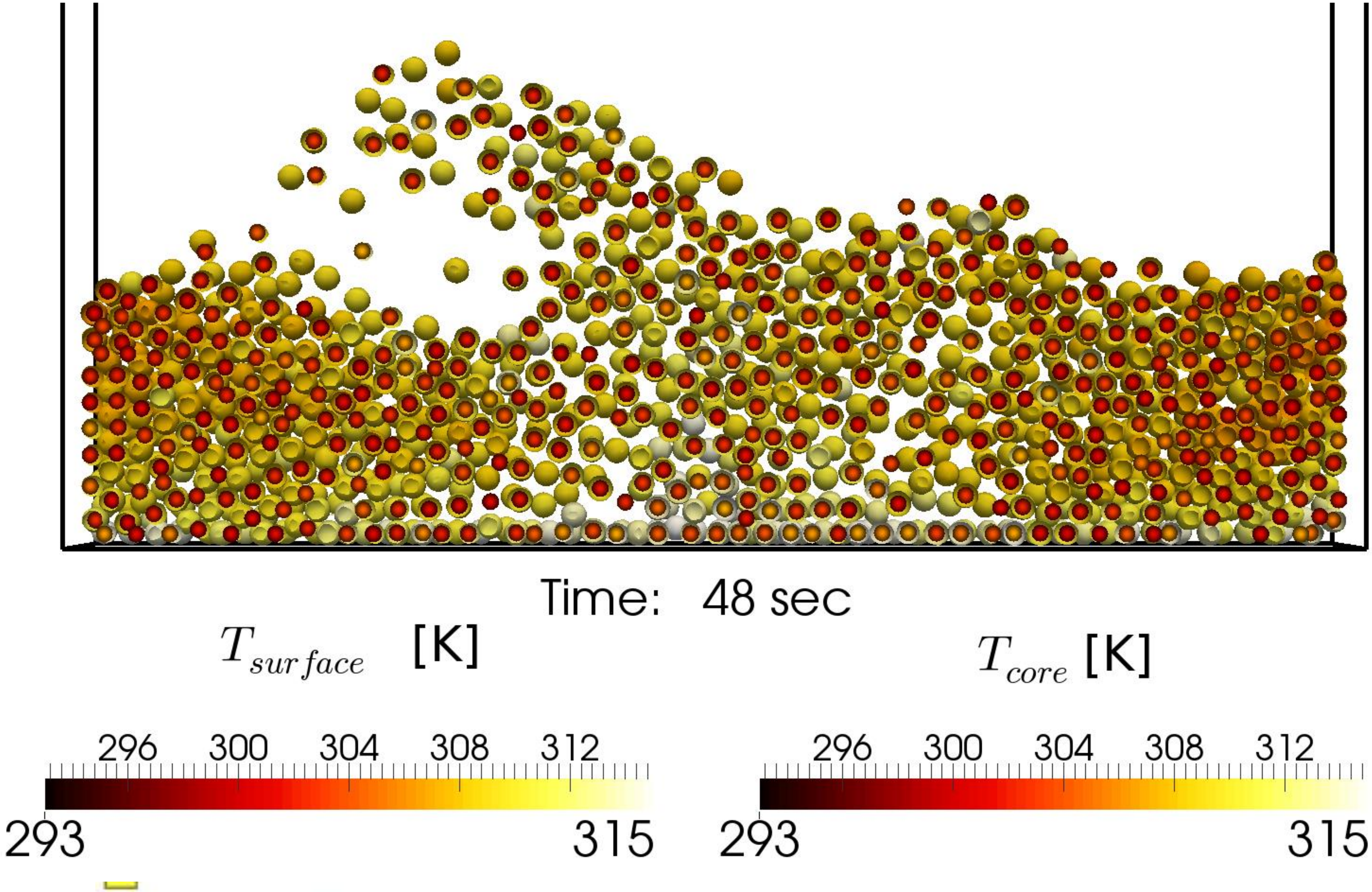
Optimization study

(Most) Economic Process

Motivation



Motivation


Time: 48 sec
$T_{surface}$ [K]
T_{core} [K]
296 300 304 308 312
293
315
296 300 304 308 312
293
315

Governing equations

Chem. reaction source term

$$s_i = \nu_i \, k \, c_s^m \, c_i^n$$

Dimensionless transport eqn. gaseous species

$$\partial_{t^*}\left(\varepsilon \, c_i^*\right) = \frac{1}{\xi^2}\partial_\xi\left(\xi^2 \, \partial_\xi c_i^*\right) + \nu_i^* \Phi^2 c_i^{*n}$$

Dimensionless transport eqn. solid species

$$\partial_{t^*}\left(c_s^*\right) = \nu_s^* \Phi^2 c_i^{*n} \frac{c_{i,0}}{c_{s,0}} \frac{|\nu_s|}{|\nu_i|}$$

Thiele modulus

$$\Phi^2 = \frac{d_p^2 \, |\nu_i| \, k \, c_s^m \, c_{i,0}^{n_i - 1}}{4 D_{eff}}$$

Reference Thiele modulus

$$\Phi_{ref}^2 = d_p^2 \, |\nu_i| \, k_{\max} \, / \left(4 \, D_{eff,support}\right)$$

Numerical model for optimal parameters for first order reaction

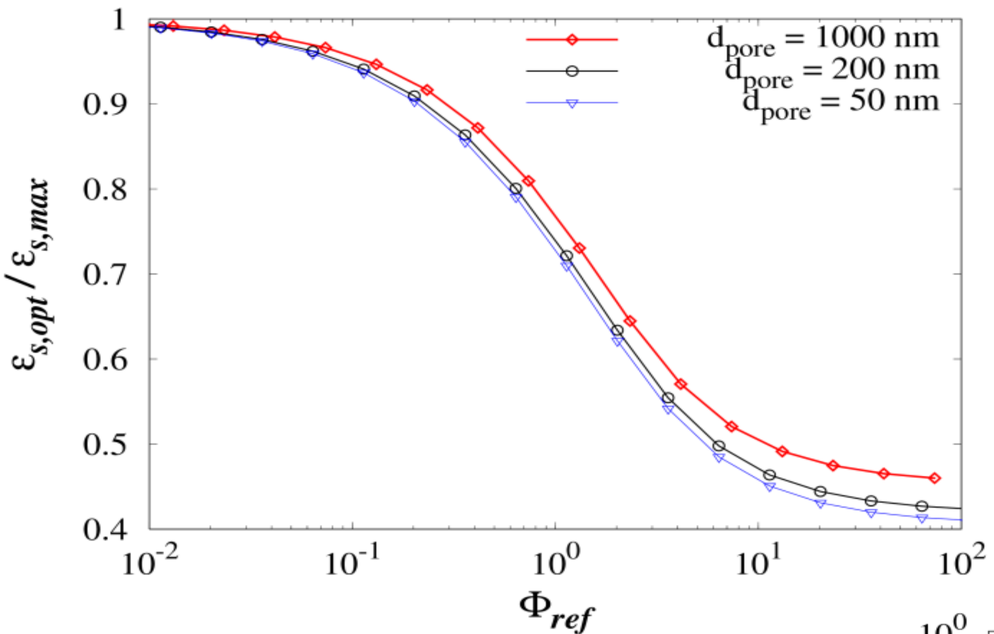
- Single reaction model
  - 0th order w.r.t solid, **1st order w.r.t gas**
  - No grain effect

- Optimization by
  - Maximze k_s (surface-area specific reaction rate)
  - Maximize c_i (gas concentration)
  - Minimize grain diameter
  - ***Maximize (ε η), with η = f(Bi,Thiele)***

Parameter	Value	Parameter	Value
ε	0.5	ν	-4
τ	1.5	T	1089 [K]
d_p	100 [µm]	p	1 [bar]
d_{pore}	20 ... 1000 [nm]	Sh	2
θ	0.5	*gas prop.*	CH_4 in N_2

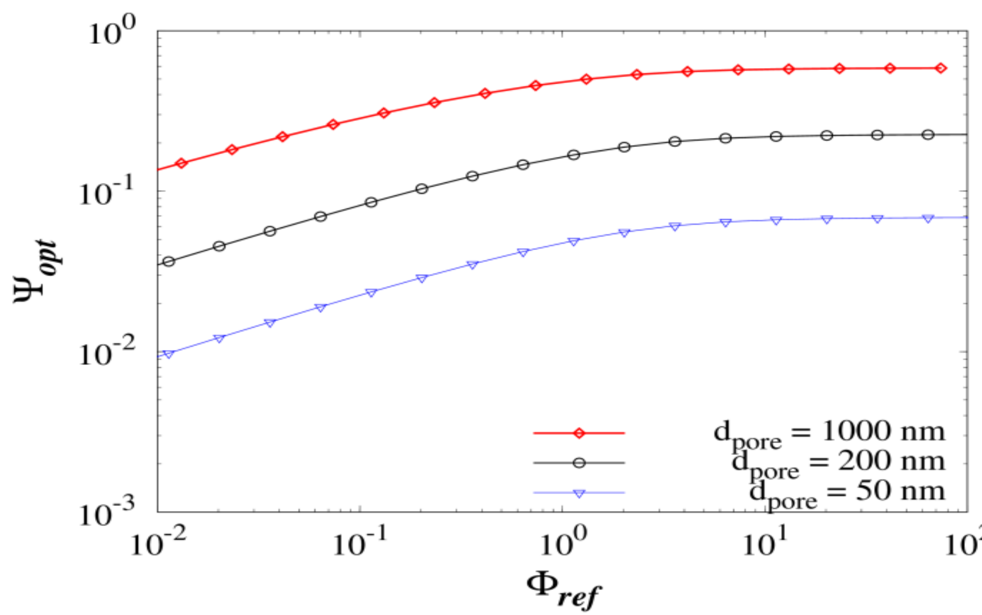
Table 1. Base case parameters used for optimization.

Simulations and Results



- Slow reacting systems
  - optimal solid loading close to maximum solid loading
- Fast reacting systems
  - optimal solid loading 40 to 50 % of maximum solid loading
- Minor effect of pore size

- Knudsen diffusion increases for smaller pore size
- Should always be considered ($\psi_{opt} << 1$)



Simulations and Results

Numerical model for optimal metal oxide loading for the reduction of hematite

R. 1 $$4CH_4 + 27Fe_2O_3 \rightarrow 18Fe_3O_4 + 2CO_2 + 2CO + 3H_2O + 5H_2$$

R. 2 $$3CH_4 + 8Fe_3O_4 \rightarrow 24FeO + 2CO_2 + CO + 3H_2O + 3H_2$$

Conversion Rate $$\partial_t X_i = w_i \, X_\infty \, y_{CH_4}^{n_i} \, k_i \exp\left[-E_{A,i} / T\right]$$

Molar Reaction Rate $$s_{Fe_2O_3,i} = \partial_t X_i \frac{(1-\varepsilon)\,\rho_{Fe_2O_3}}{MW_{Fe_2O_3}}$$

Parameter	Value	Parameter	Value
ε	0.5	y_{CH4}	0.2
τ	1.5	T	1089 [K]
d_p	1 [mm]	p	1 [bar]
(R.1) t_{react}	60 [s]	Bi	∞
s_{Fe2O3}	0.11 [kmol/m³/s]	R_{R1}	$4 \cdot 10^{-3}$ [kmol/m³/s]

Table 2. Case parameters for reduction of hematite

Simulations and Results

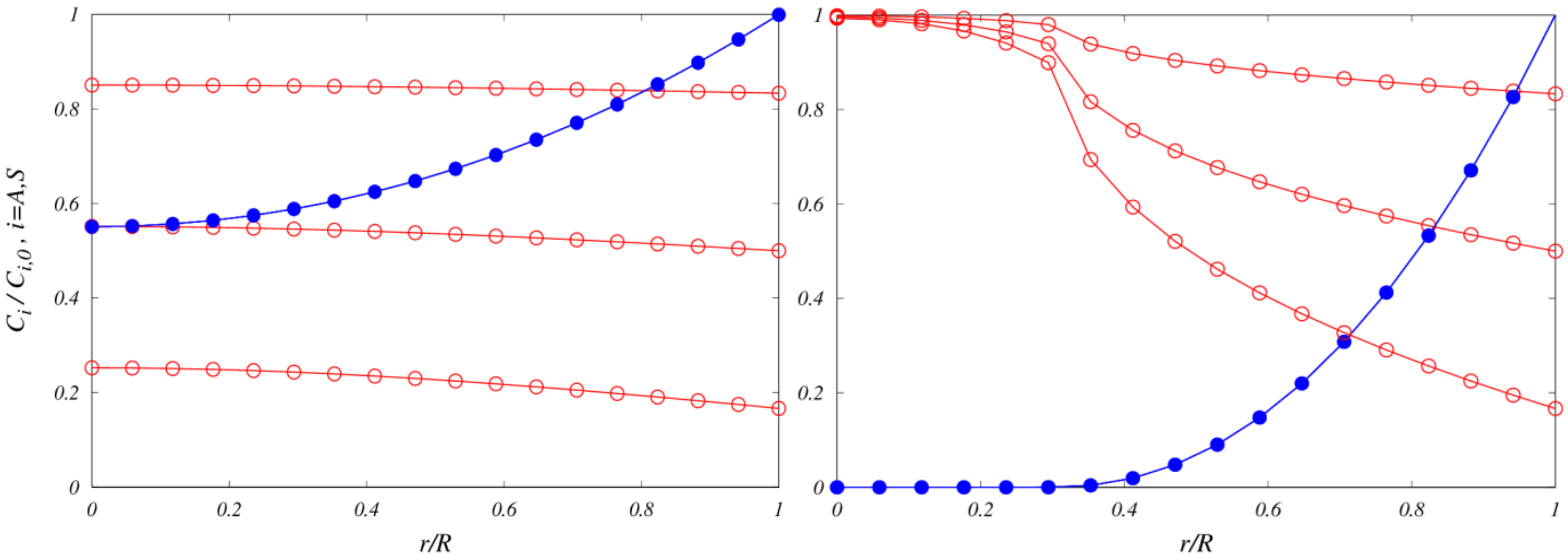


Figure 4. Normalized concentration profiles of gas (blue dots) and Fe_2O_3 (red circles, t = 10, 30, 50 [s] from top to bottom; Left: $\varepsilon_s / \varepsilon_{s,max}$ = 0.9, Φ = 1.70; Right: $\varepsilon_s / \varepsilon_{s,max}$ = 0.96, Φ = 3.39.

- Sharp hematite concentration front at r/R = 0.3 (right panel)
  - due to relatively high Thiele modulus → diffusion limitation
- Sharp front vanish for smaller Thiele modulus, uniform concentration profiles
- Significant gradient in gas concentration
  - due to insensitivity of reaction rate on methane concentration (small n)

Simulations and Results

Optimal solids loading

$$c_{s,t_{res}} = c_{s,0} X_s(t_{res}) \quad \text{with} \quad c_{s,0} = \varepsilon_s \rho_s / MW_s \qquad (t_{res} = 100\ s)$$

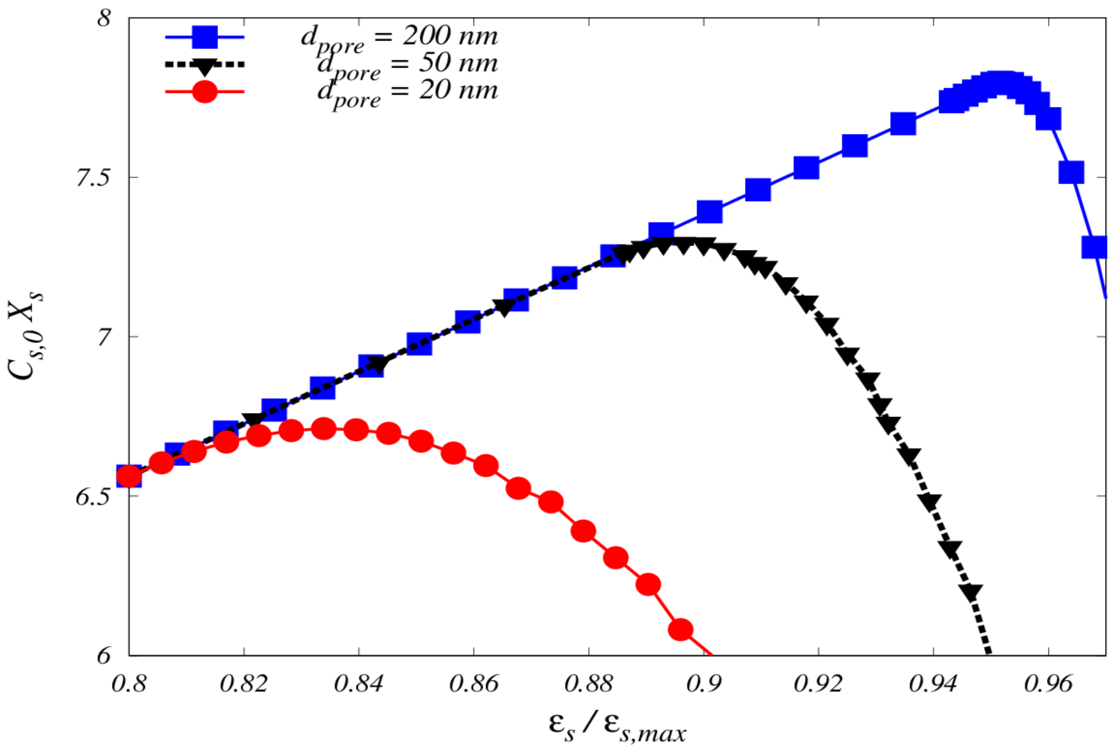


Figure 5. Normalized metal consumption as a function of the relative metal loading and pore size of the support

- Optimal solids loading close to maximum solid loading
- No influence for ≤ 80 %
- Depending on pore size
  - ≈ 84 % for 20 nm
  - ≈ 90 % for 50 nm
  - ≈ 95 % for 200 nm

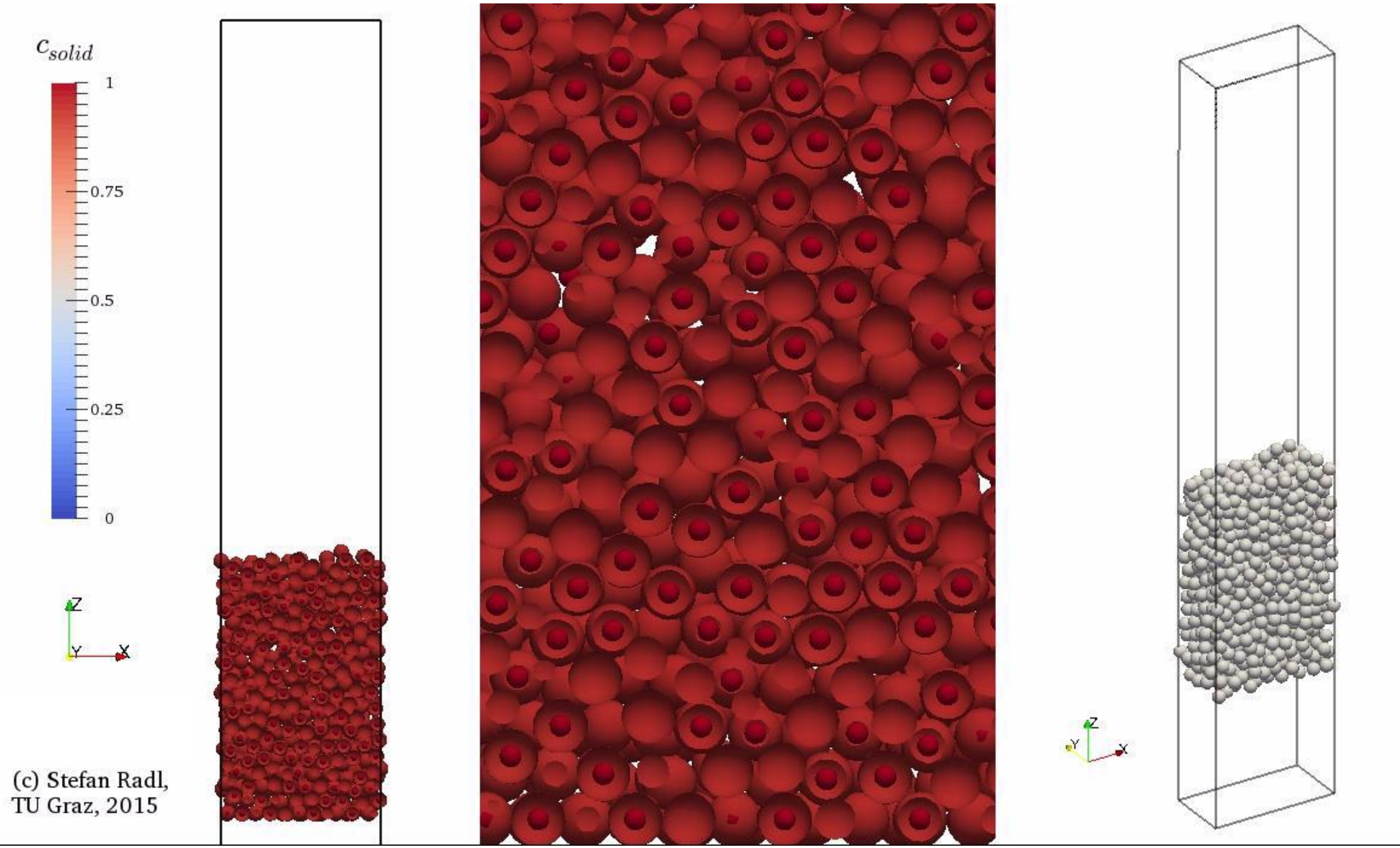
Conclusion

- Model for reacting-diffusion problems in porous particles
- Included in *ParScale*, published under LGPL
- Linkable to any open-source and commercial particle-based flow solver
  - *LIGGGHTS, CFDEMcoupling*

- Active solid optimal loading close to porosity of support
  - 85% - 95% depending on pore size

- If solid is highly active (i.e., high Thiele Modulus)
  - 45% of pore volume should be filled

Outlook



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Thank you!

Acknowledgement and Disclaimer

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http://www.sintef.no/projectweb/nanosim/