TFM simulations of membrane-assisted fluidized bed reactors for H_2 production

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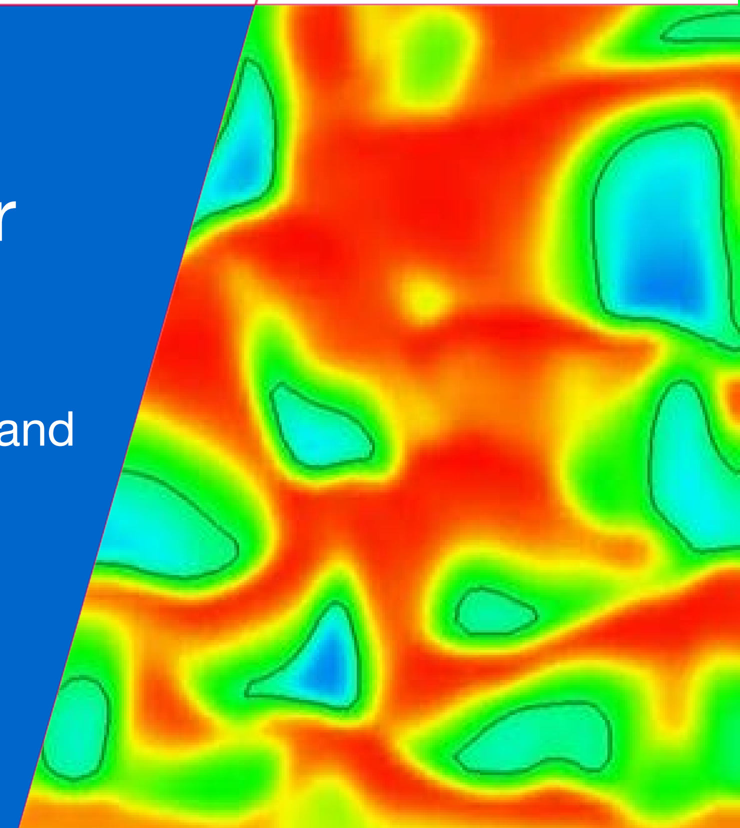
Chemical process intensification – Multiphase reactors group



Process Intensification Network (PIN) Meeting,

21 June 2017, Newcastle University.

Multiphase Reactors Group
Department of Chemical Engineering & Chemistry

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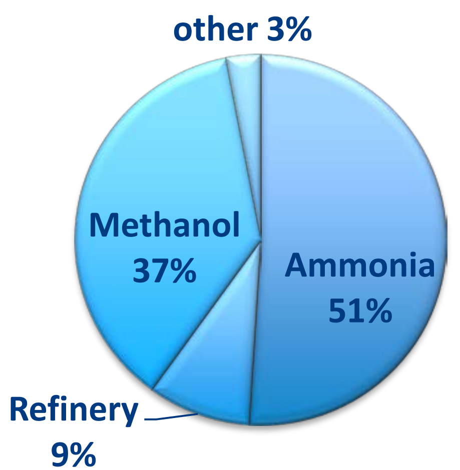
Where innovation starts

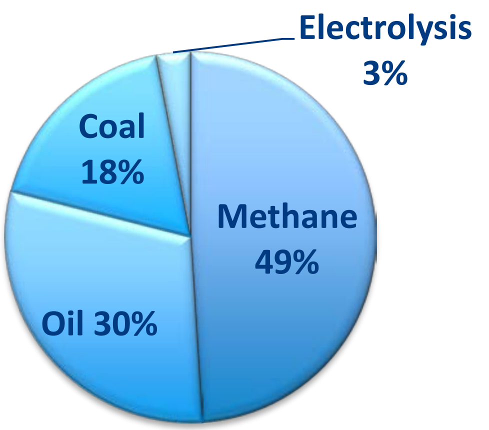
Fluidized bed membrane reactors for H_2

- **Motivation**
  - What are the advantages & challenges of FBMRs
- **CFD: Two-Fluid modelling**
  - How to model hydrodynamics, extraction and reaction?
- **Vertically inserted membranes**
  - Can we quantify the effect of concentration polarization?
- **Horizontally inserted membranes**
  - What are the hydrodynamic effects of horizontal membranes?
- **Reactive systems**
  - Can we intensify reactions by using membranes?
- **Conclusions**

Motivation

Motivation





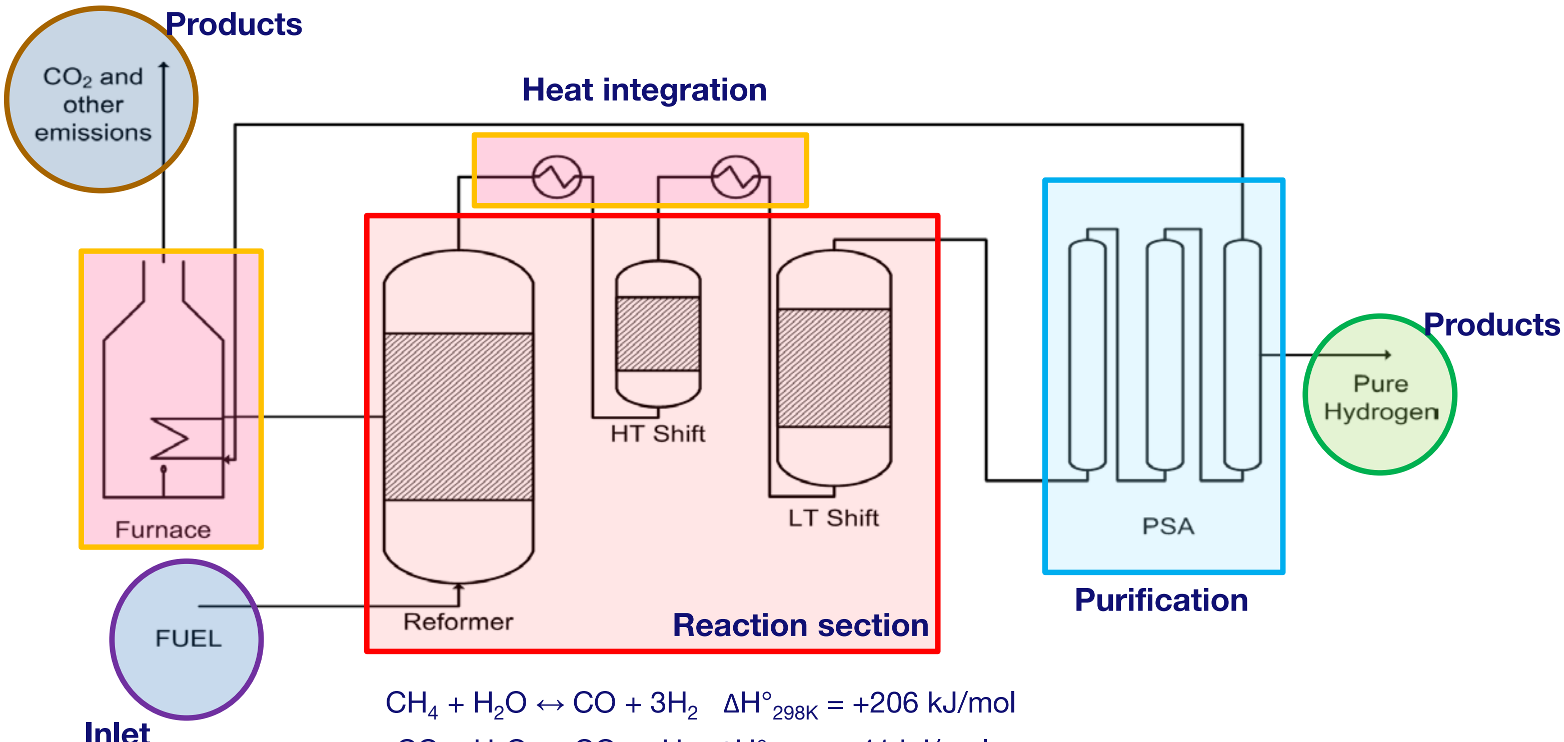
Global CO_2 emissions:
Coal (power) 59%
NG (power) 12%
Refineries 7%

- H_2 production contributes to about 2% of the global CO_2 emissions ☺, **BUT….**
- For H_2-to-power and H_2-to-transport: integrated CO_2 capture in H_2 plant required!
- H_2 production based on conventional steam methane reforming with CO_2 capture results in large energy penalty ☹

⇒ *Ambition: make H_2 production more **environmental friendly** & **less costly** via Process Intensification*

Conventional H_2 production

Steam methane reforming



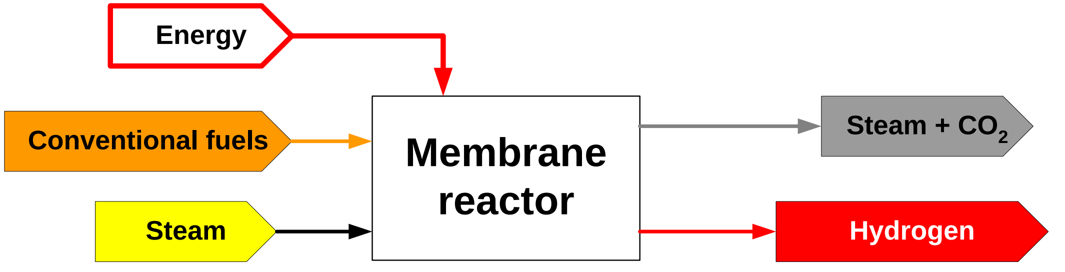
$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H^\circ_{298K} = +206 \text{ kJ/mol}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^\circ_{298K} = -41 \text{ kJ/mol}$$

- Many process units
- Complicated heat integration
- Low carbon efficiency & CO_2 capture not integrated

Membrane reactors for H_2 production

Membrane reactor concept:

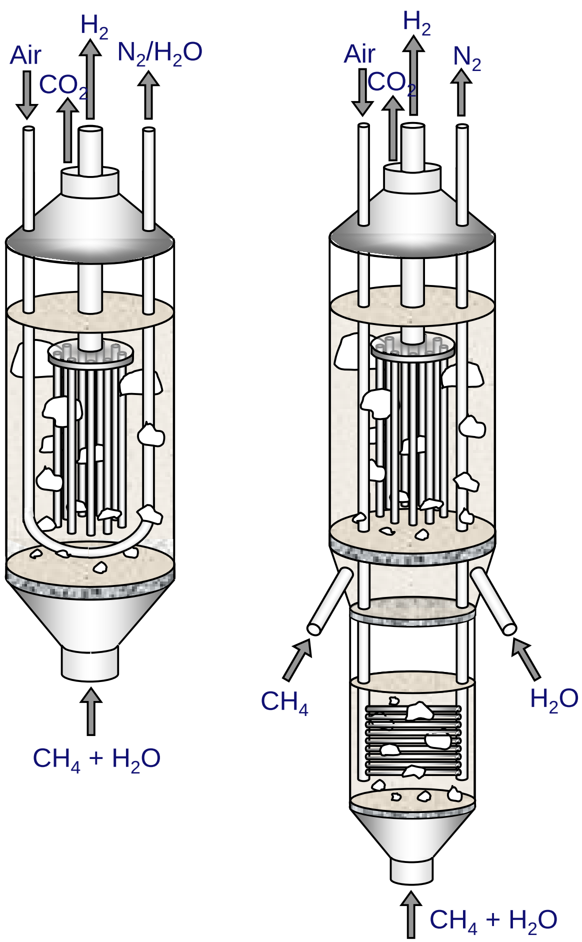


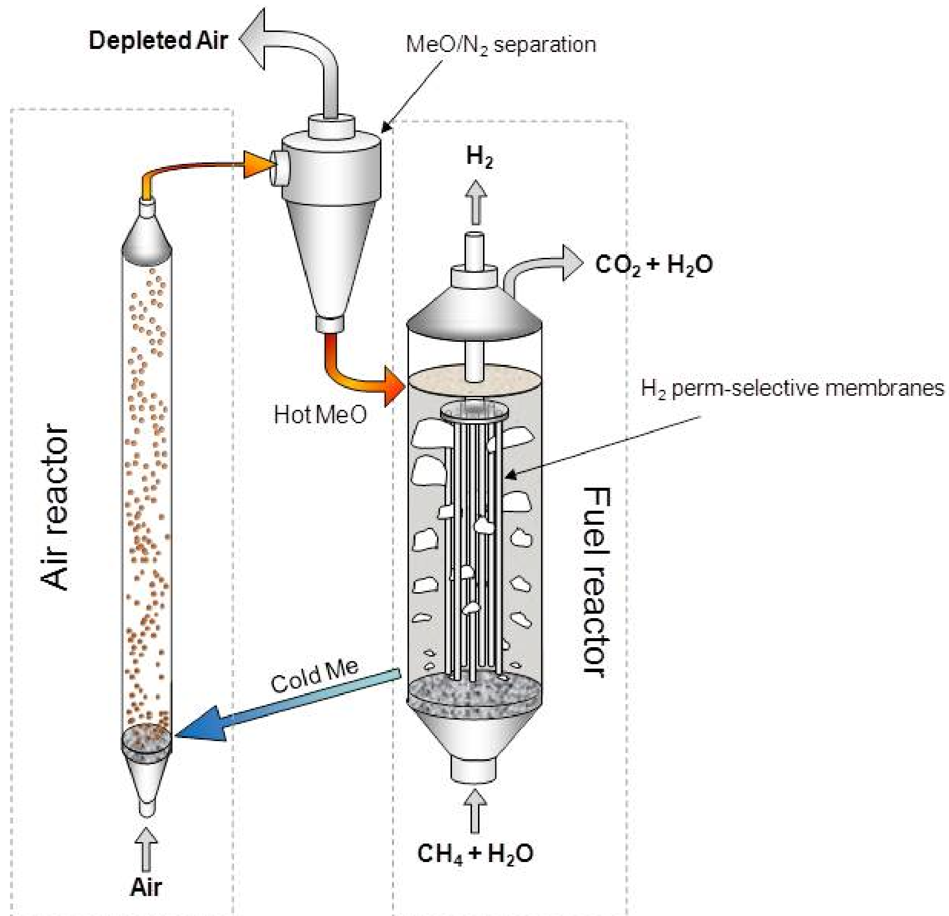
Intensification by integration into a single apparatus:

- Use perm-selective membranes to extract H_2 product
  (obtain directly ultra-pure H_2 & shift equilibrium for complete CH_4 conversion)
- Auto thermal operation via integration with CH_4 or H_2 combustion
- Intrinsic CO_2 capture

Multiple concepts

The oxygen can be supplied via a membrane…





…or via a circulating metal oxygen carrier (eg. Ni-NiO)

Why use fluidized bed membrane reactors?

- ✓ Great mixing, no temperature profiles
- ✓ Reduced pressure drops
- ✓ No internal mass transfer limitations
- ✓ Decreased concentration polarization
- ✓ Synergy between membranes and FBR

- X **Better sealing solutions**
- X **Durability of membranes**
- X **Membranes need better resistance against impurities**
- X **Largely unknown interaction between membranes and FBR**

Two-Fluid Modelling

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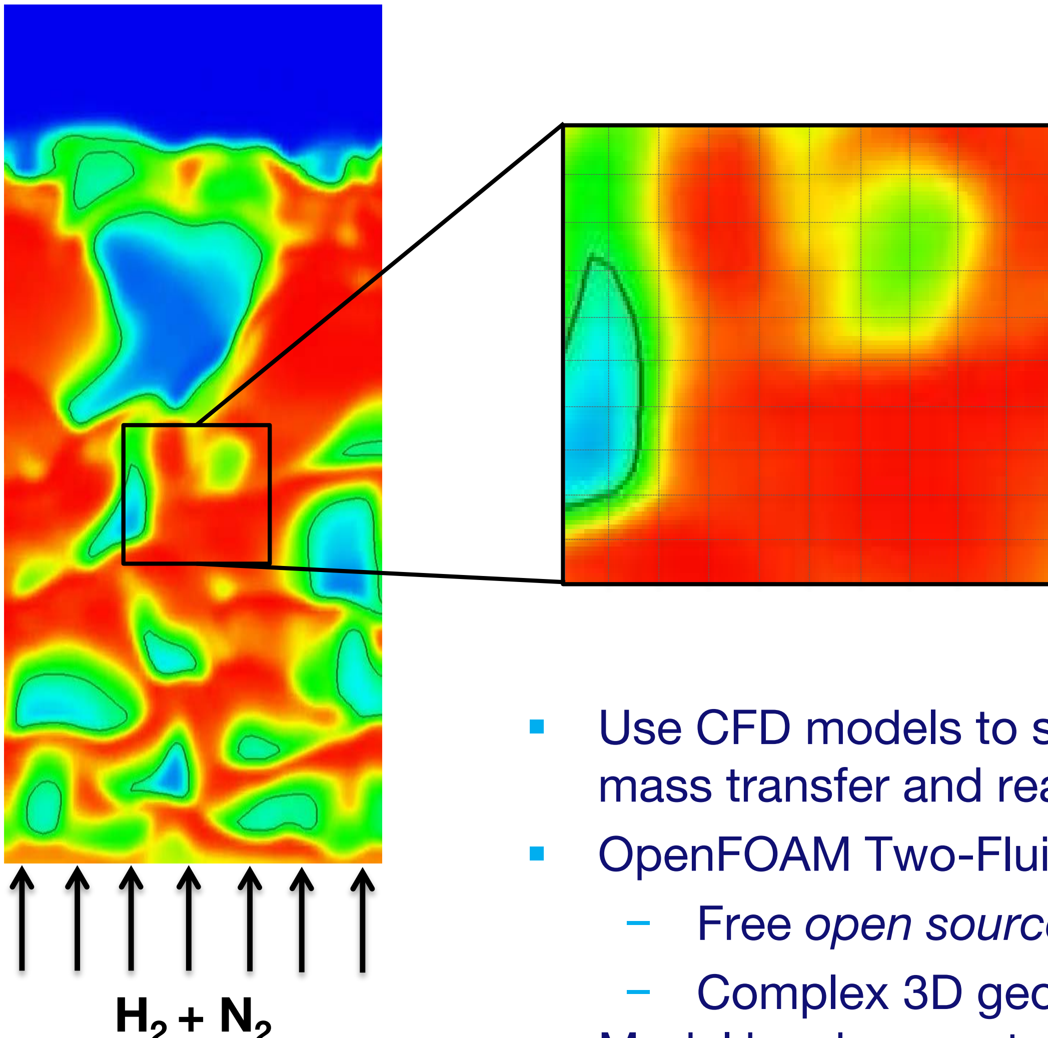
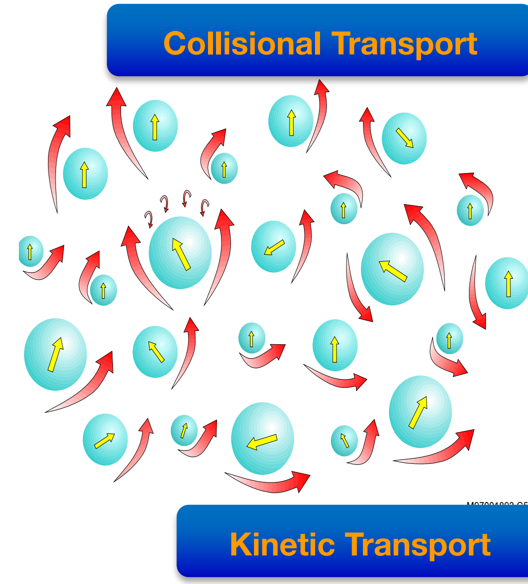
Two-Fluid Model

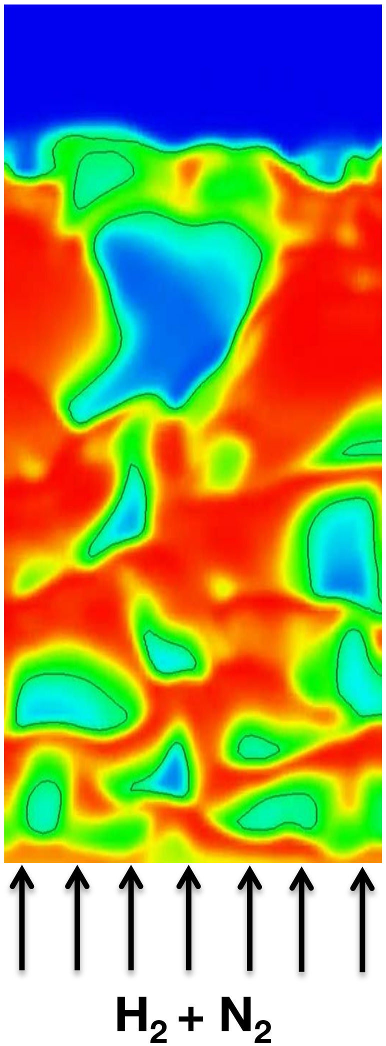


KTGF ≈



- Use CFD models to simulate detailed hydrodynamics, mass transfer and reactions in FBMRs
- OpenFOAM Two-Fluid Model:
  - Free *open source* CFD code
  - Complex 3D geometries (membranes)
- Model has been extended, validated and verified

Two-Fluid Model



Continuity equations:

$$\frac{\partial \alpha_g \rho_g}{\partial t} + \nabla \cdot (\alpha_g \rho_g \mathbf{u}_g) = S_m \qquad \frac{\partial \alpha_s \rho_s}{\partial t} + \nabla \cdot (\alpha_s \rho_s \mathbf{u}_s) = 0$$

Momentum conservation gas:

$$\frac{\partial \alpha_g \rho_g \mathbf{u}_g}{\partial t} + \nabla \cdot (\alpha_g \rho_g \mathbf{u}_g \mathbf{u}_g) = -\left(\nabla \cdot \alpha_g \boldsymbol{\tau}_g\right) - \alpha_g \nabla p - \beta \cdot (\mathbf{u}_g - \mathbf{u}_s) + \alpha_g \rho_g \boldsymbol{g}$$

Momentum exchange

Momentum conservation solids:

$$\frac{\partial \alpha_s \rho_s \mathbf{u}_s}{\partial t} + \nabla \cdot (\alpha_s \rho_s \mathbf{u}_s \mathbf{u}_s) = -\left(\nabla \cdot \alpha_s \boldsymbol{\tau}_s\right) - \alpha_s \nabla p - \nabla p_s + \beta \cdot (\mathbf{u}_g - \mathbf{u}_s) + \alpha_s \rho_s \boldsymbol{g}$$

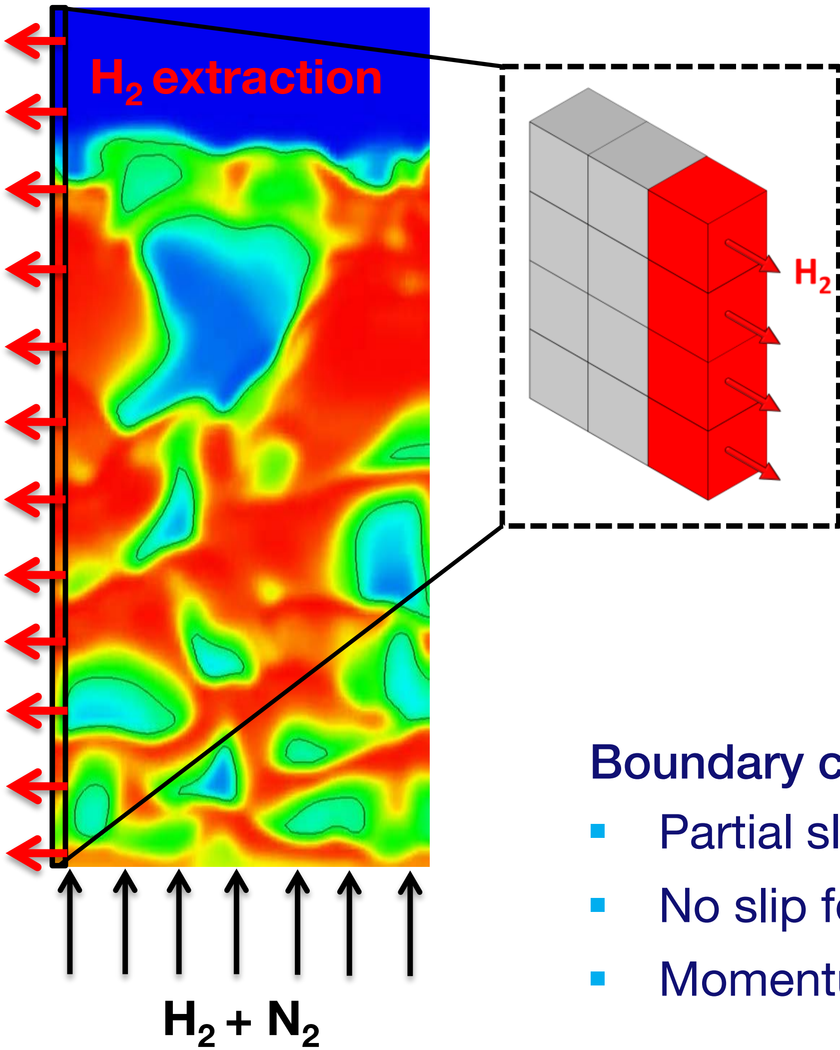
Solids rheology

Granular temperature equations:

$$\frac{3}{2}\left(\frac{\partial(\alpha_s \rho_s \theta)}{\partial t} + \nabla \cdot (\alpha_s \rho_s \mathbf{u}_s \theta)\right) = \left(-p_s \overline{\overline{I}} + \alpha_s \boldsymbol{\tau}_s\right) : \nabla \mathbf{u}_s + \nabla \cdot \left(\kappa_s \nabla \theta\right) - \gamma_s - J_s$$

Random fluctuating velocity of particles → Collisional, kinetic and frictional

Two-Fluid Model



Species balance:

$$\frac{\partial \alpha_g \rho_g Y_{H_2}}{\partial t} + \nabla\cdot\left(\alpha_g \rho_g \mathbf{u}_g Y_{H_2}\right) = \nabla\cdot\left(\alpha_g \rho_g D_{H_2} \nabla Y_{H_2}\right) + \frac{A_c}{V_c} S + R$$

Sieverts' law (applied on red cells):

$$S = Q_{Pd}\cdot\left[\left(X_{H_2}^{ret} p_{tot}\right)^n - \left(X_{H_2}^{perm} p_{tot}\right)^n\right]$$

Boundary conditions:

- Partial slip for particles
- No slip for gas phase on walls
- Momentum extraction of gas via membrane $u_m = \frac{SRT}{pM}$

Kinetics

Kinetics

- Numaguchi & Kikuchi (1988)

SMR: $CH_4 + H_2O \rightleftharpoons CO + 3\,H_2$

$$R_{SMR} = k_{SMR} \frac{P_{CH_4} P_{H_2O} - \dfrac{P_{CO} P_{H_2}{}^3}{K_{eq,SMR}}}{P_{H_2O}{}^{1.596}}$$

WGS: $CO + H_2O \rightleftharpoons CO_2 + H_2$

$$R_{WGS} = k_{WGS} \frac{P_{CO} P_{H_2O} - \dfrac{P_{CO_2} P_{H_2}}{K_{eq,WGS}}}{P_{H_2O}}$$

Reaction rate constant & equilibrium constant

$$k_i = A_i \exp\left(-\frac{E_{act}}{RT}\right)$$

$$K_{eq,i} = B_i \exp\left(\frac{-\Delta G_i}{RT}\right)$$

$$i = SMR,\ WGS$$

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Summary: modelling of membrane FB reactors

Fluidized bed membrane reactors have significant advantages for hydrogen production over conventional technologies

A Two-Fluid Model was developed to perform detailed hydrodynamics and mass transfer studies

Vertically inserted membranes

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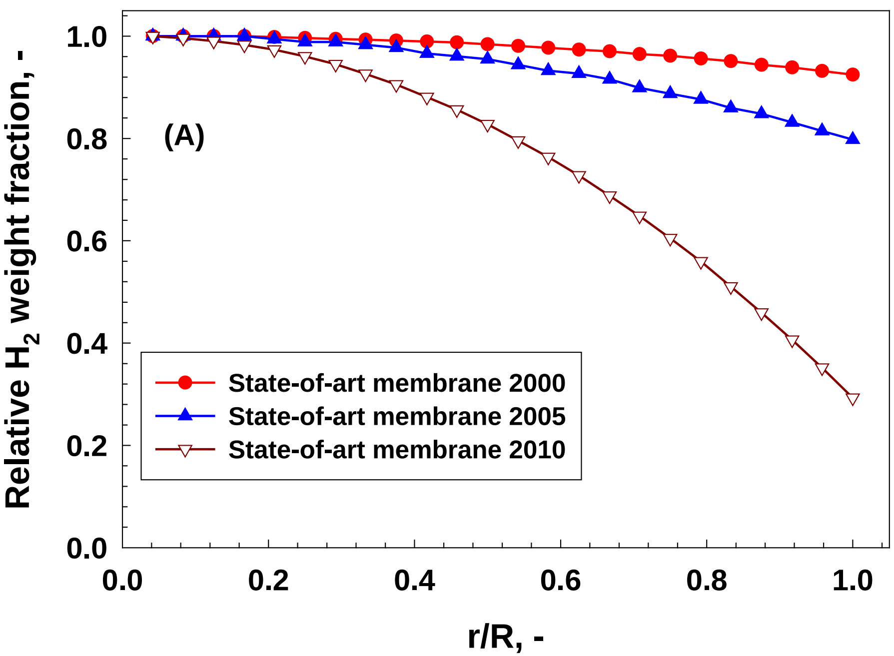
Concentration polarization

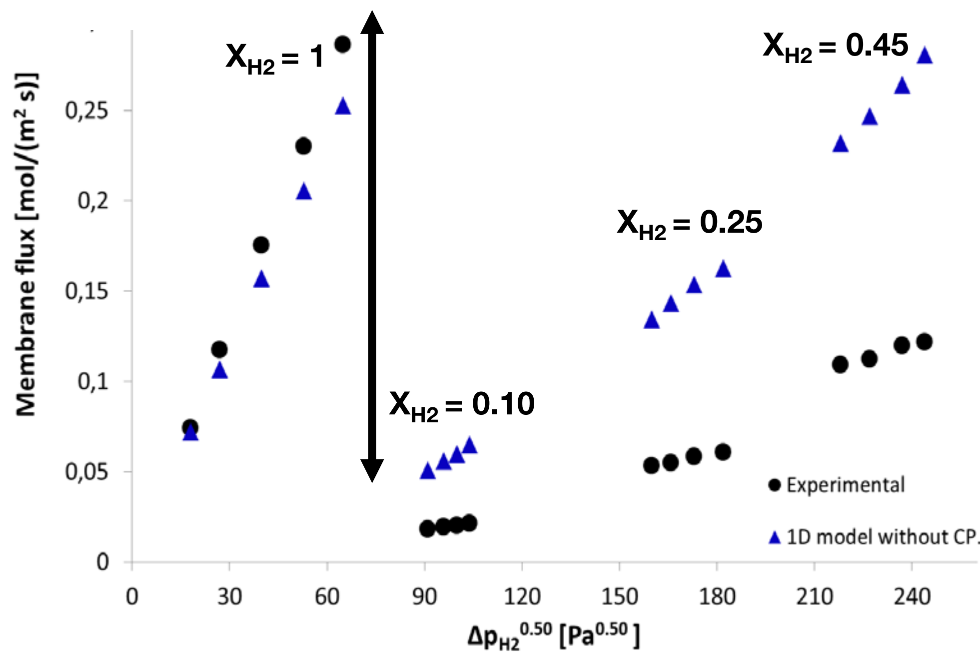
What is <u>concentration polarization</u> (and why do we care)?

"Bed-to-membrane mass transfer limitations"

Effect of improving membranes



Pure H_2 vs. binary N_2/H_2 mixtures



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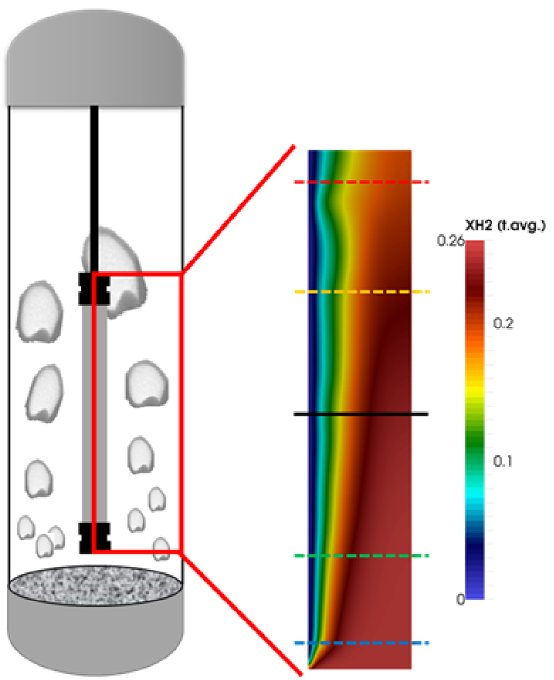
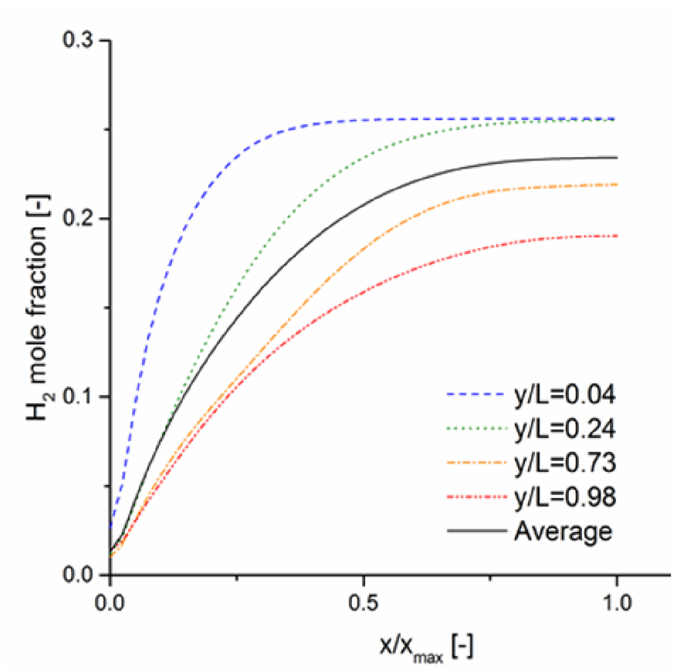
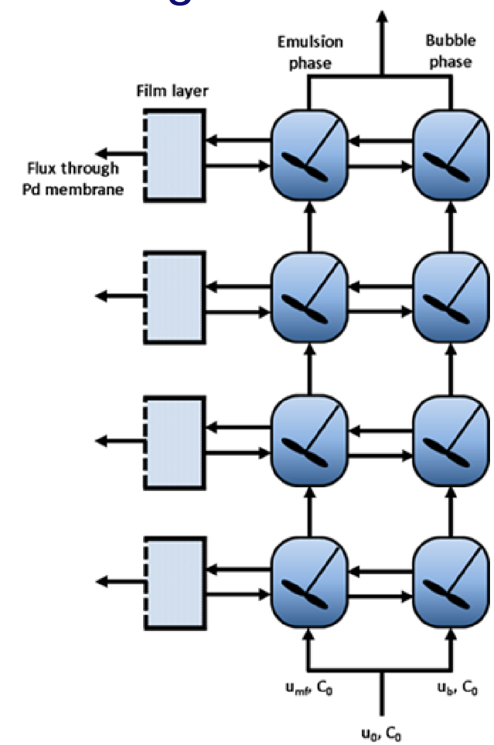
Quantification of concentration polarization

- Experiments in FBMR with 1 membrane
- Concentration profiles obtained from 2D TFM simulations to estimate thickness of mass transfer boundary layer
- Include boundary layer resistance to 1D phenomenological model

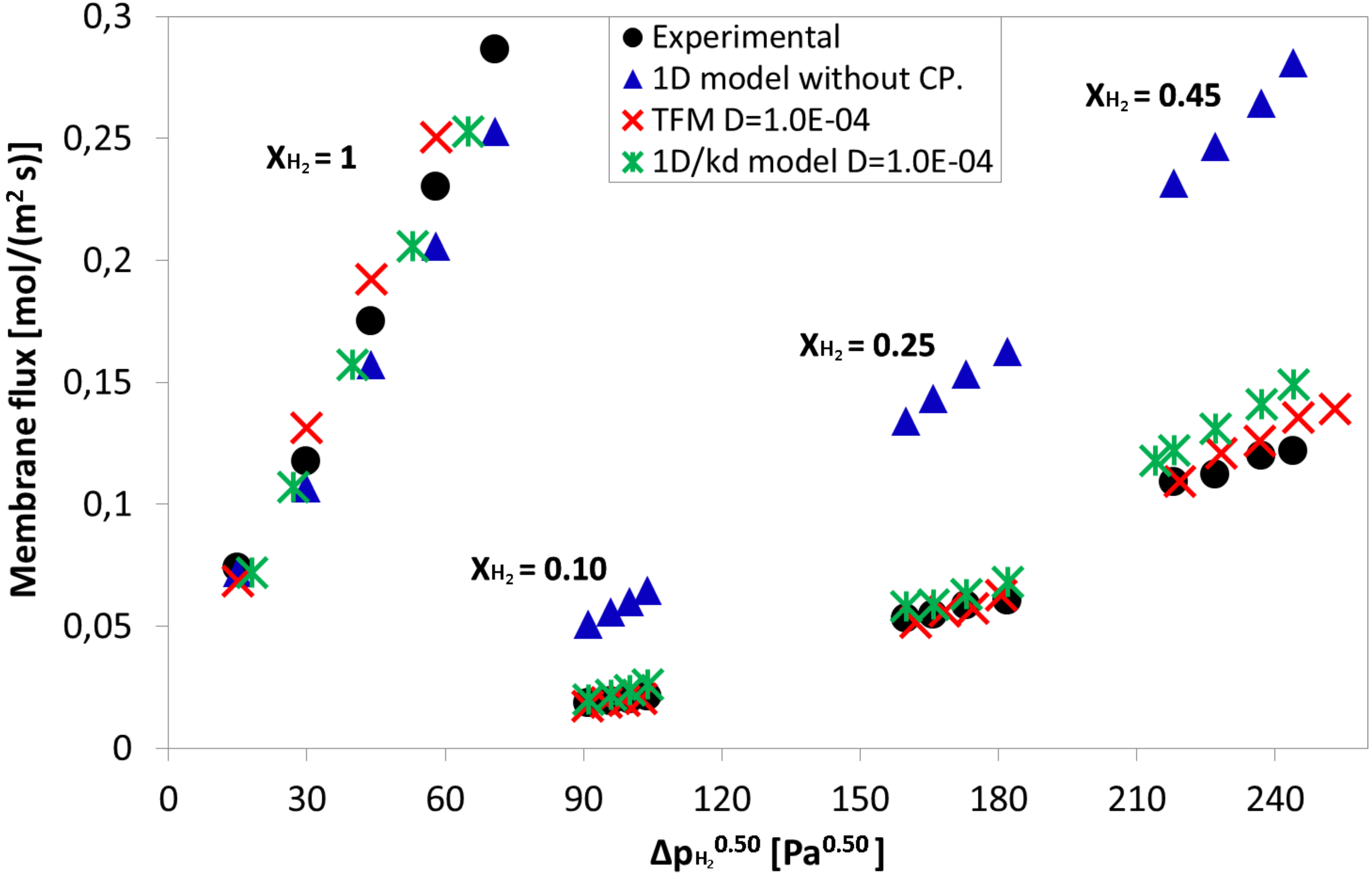






Two Fluid Model → **Concentration profiles** → **1-dimensional model**

Using TFM results to improve 1D model



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Vertically inserted membranes

TFM simulations 3D

- Clear build up of a mass transfer boundary
- Some fluctuations induced by bubbles passing by
- Average thickness of the mass transfer boundary for the considered case estimated at 1 cm

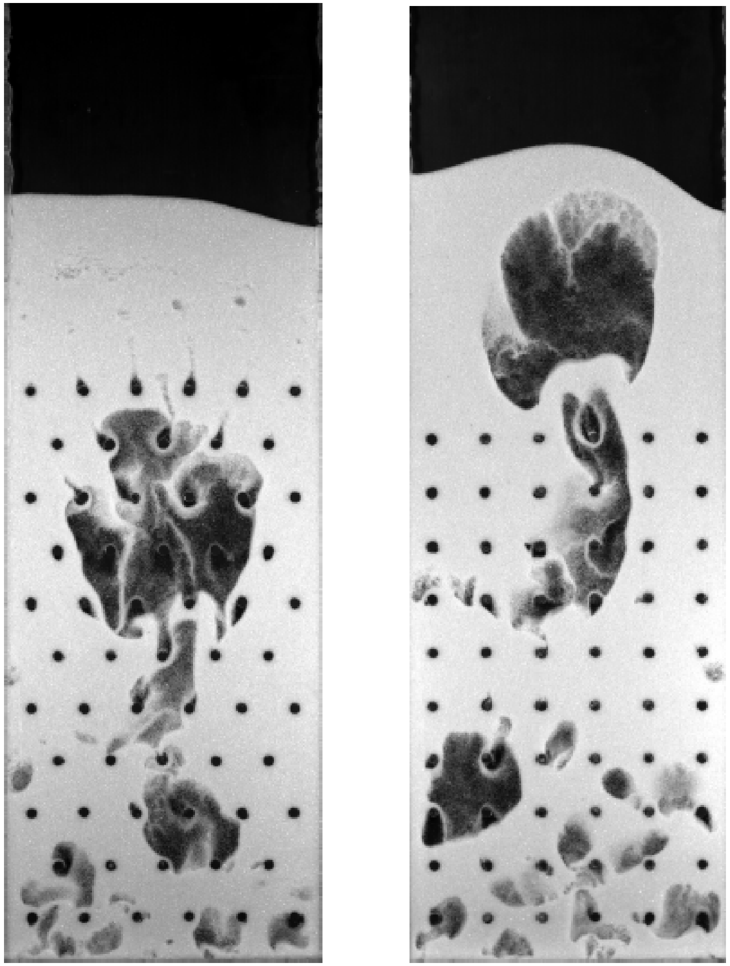
Summary: vertical membranes

Concentration polarization emerges due to very high-flux membranes!

We can quantify the concentration boundary layer thickness with TFM in order to improve phenomenological models

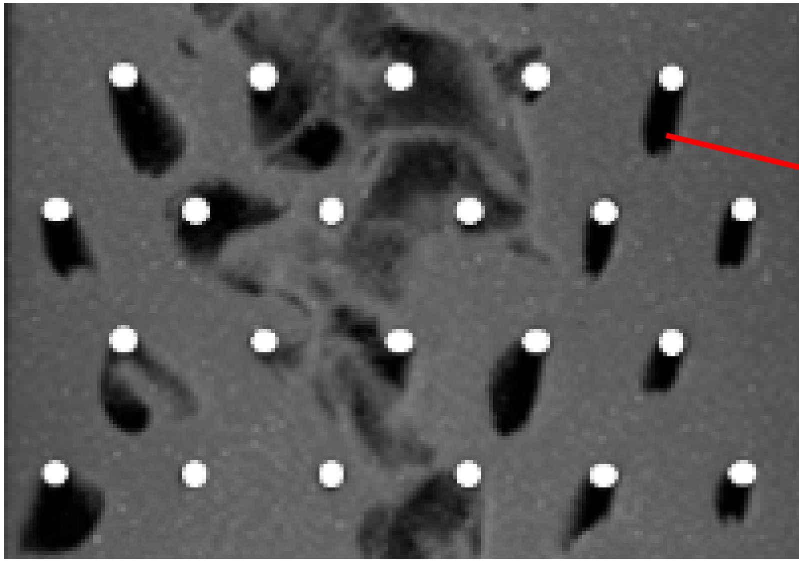
Horizontally inserted membranes

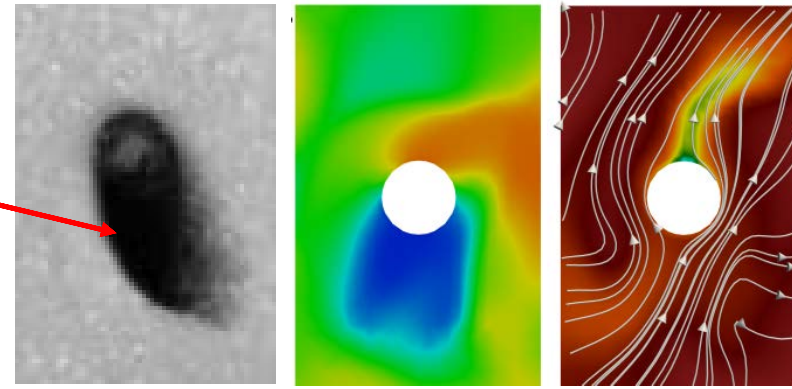
Horizontally inserted membranes

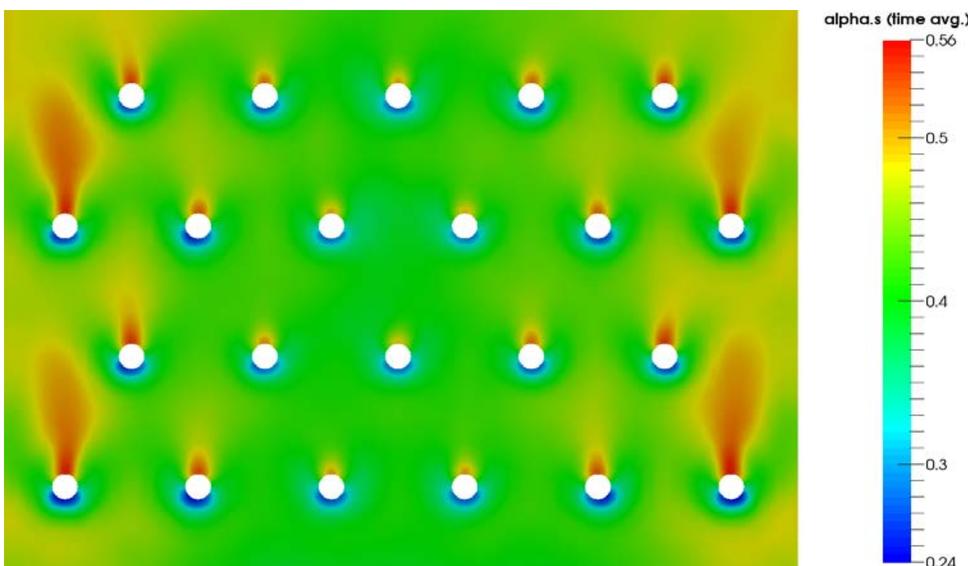


(bed width: 30 cm)

Gas pockets: zoomed in

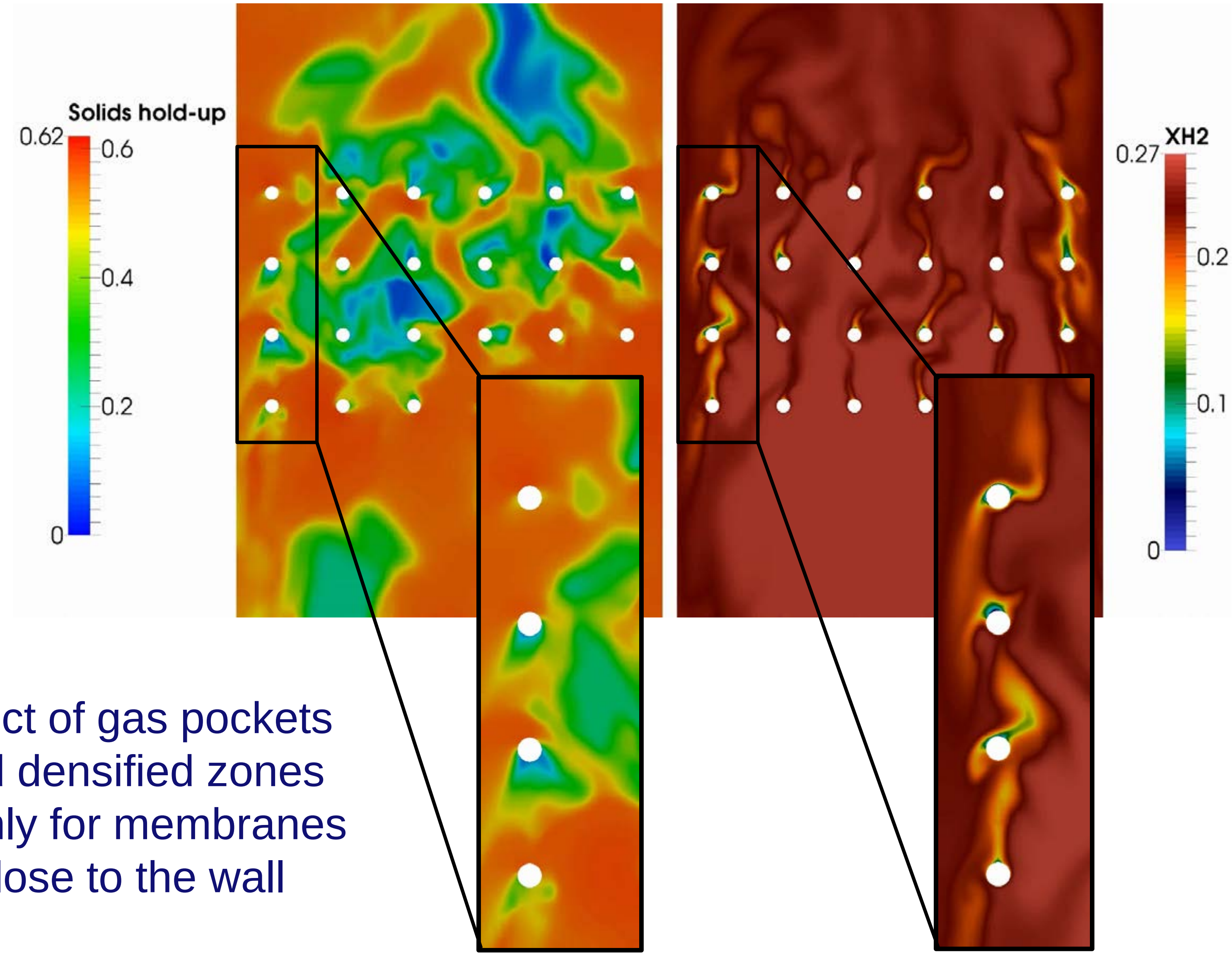






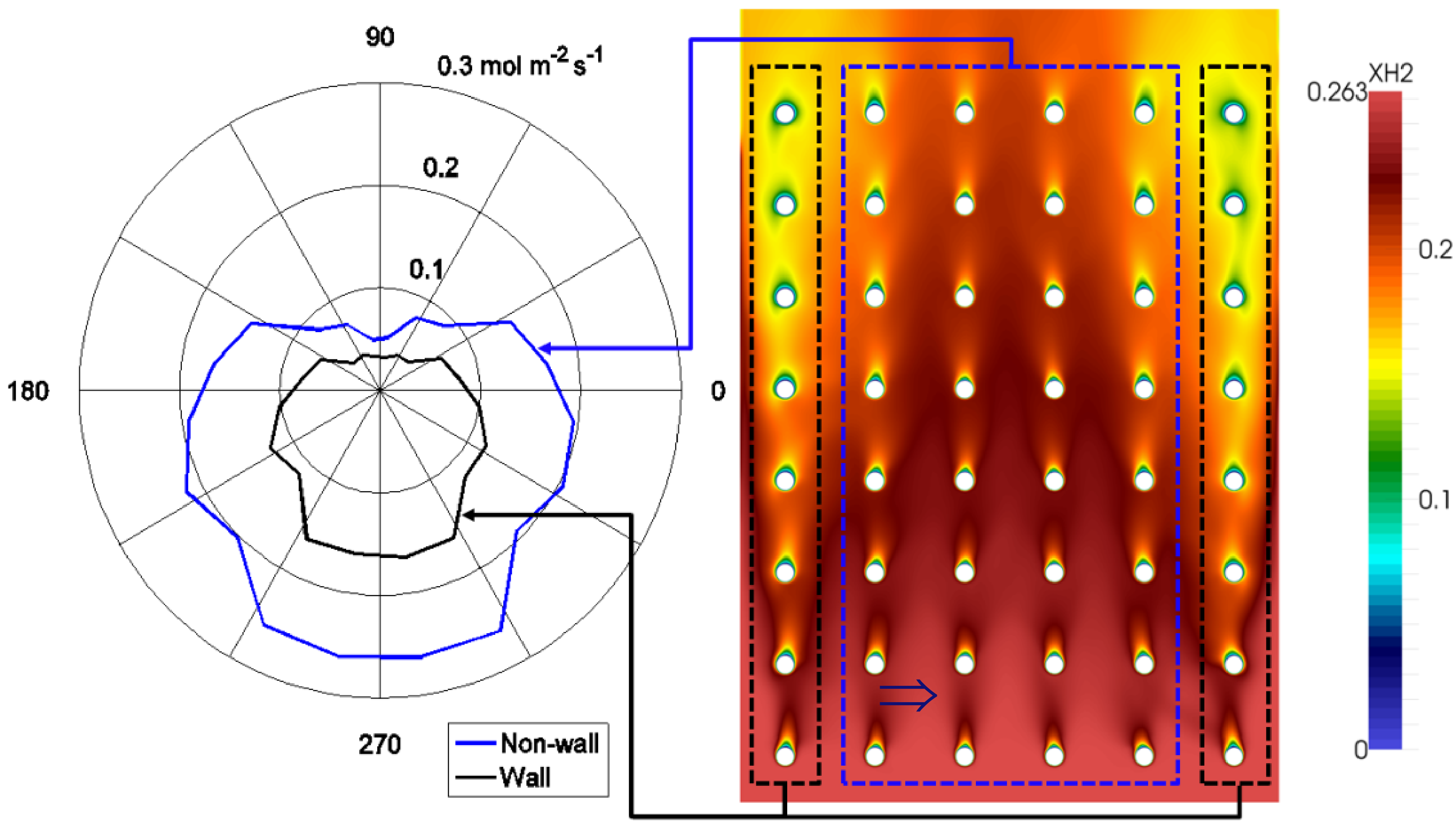
- Gas pockets
  - ‘Attached’ to membrane
  - Contain very little amount of solids
  - May cause mass transfer limitations
- Main mass transfer limitations are on top of the membranes case by densified (defluidized) zones
- Gas pockets and densified zones mostly at membranes near walls

Gas pockets: overview

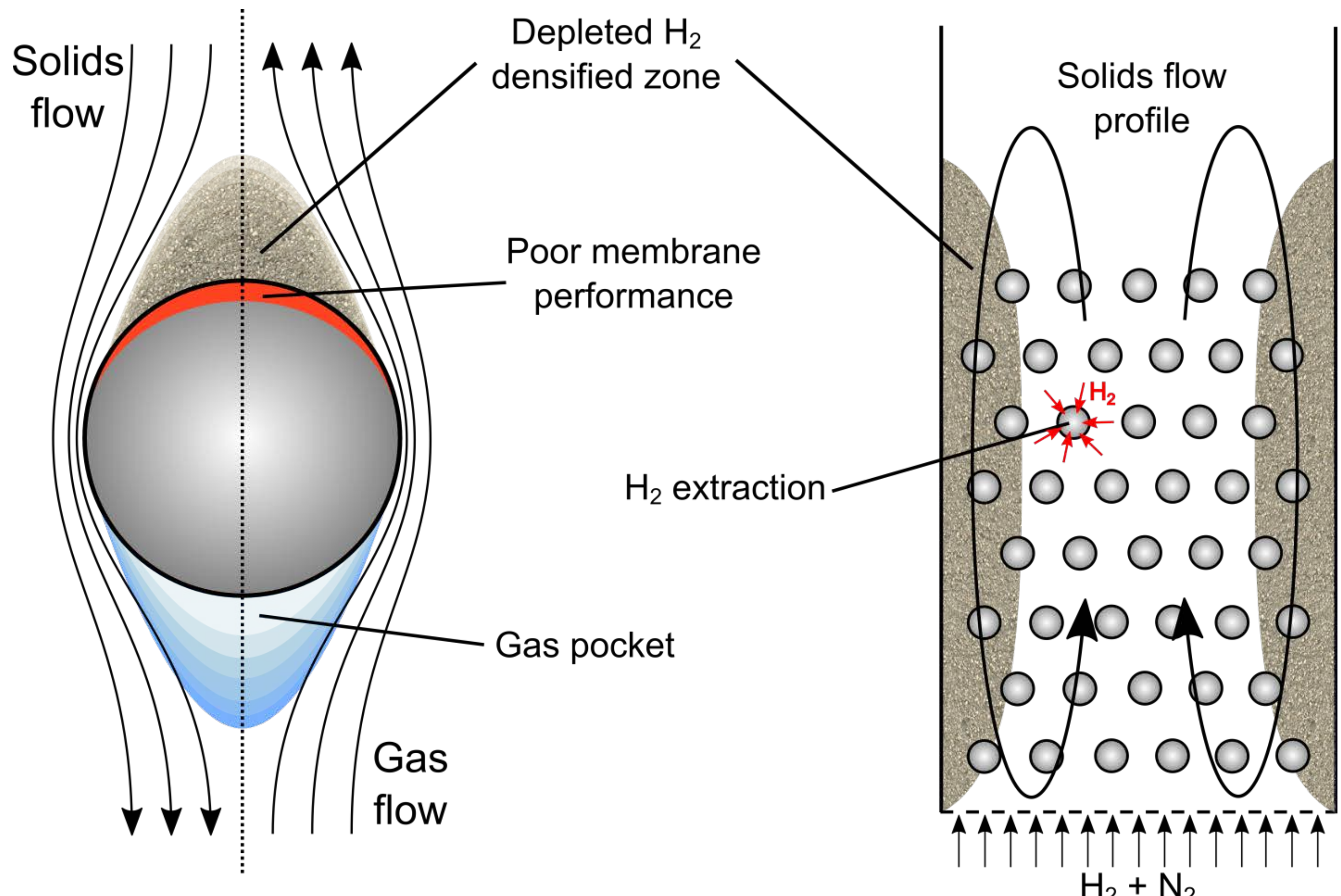


Effect of gas pockets and densified zones mainly for membranes close to the wall

Wall vs. centre membranes: radial flux profile



Putting it all together

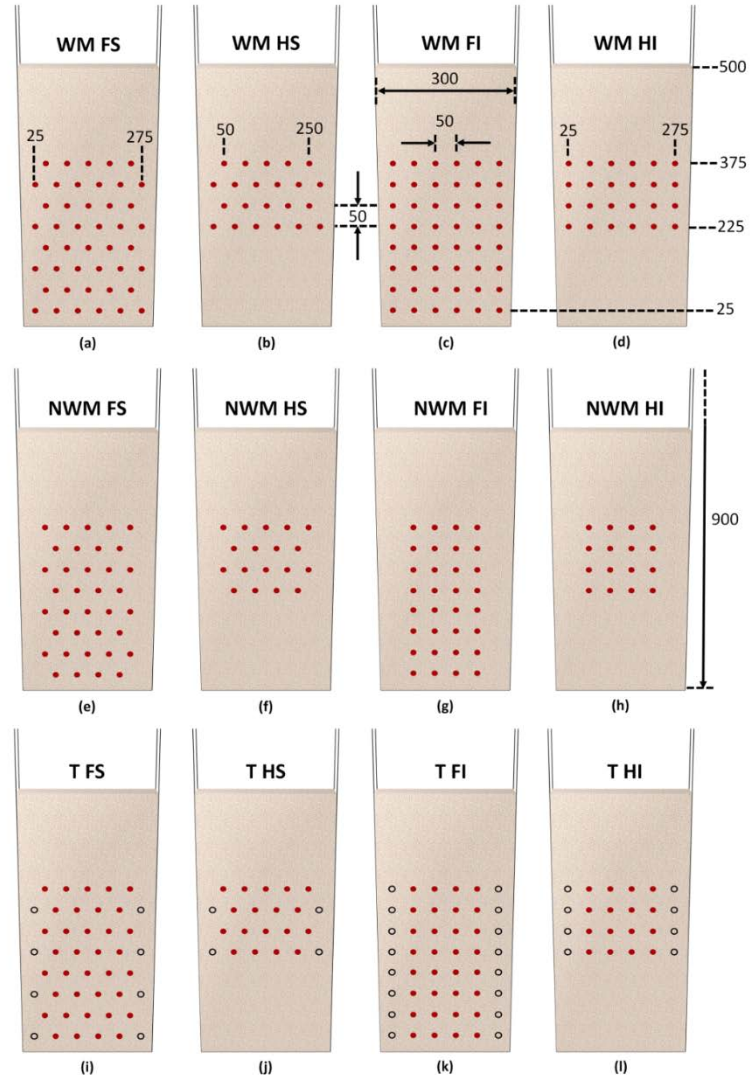


Membrane configurations

Wall membranes present

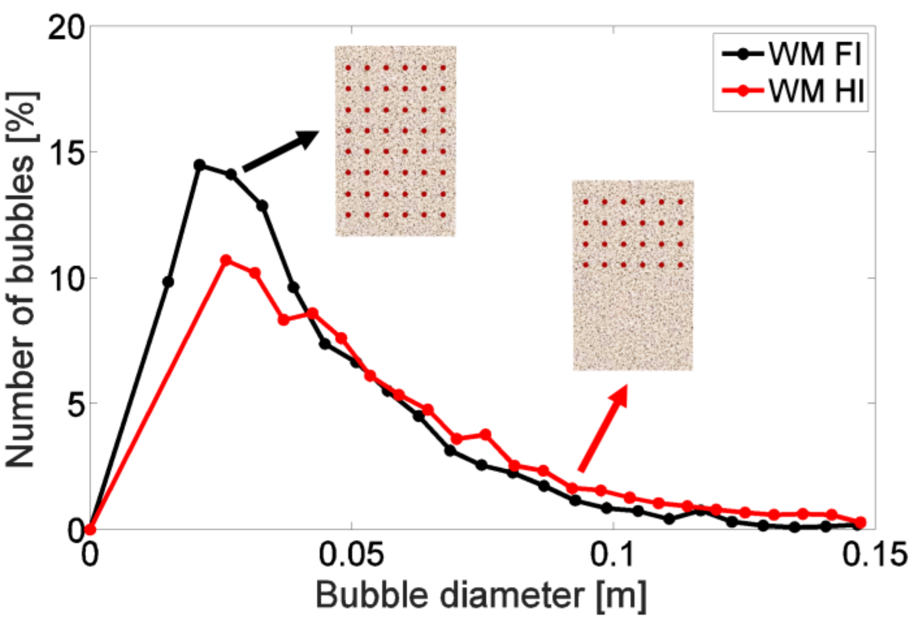
Wall membranes removed

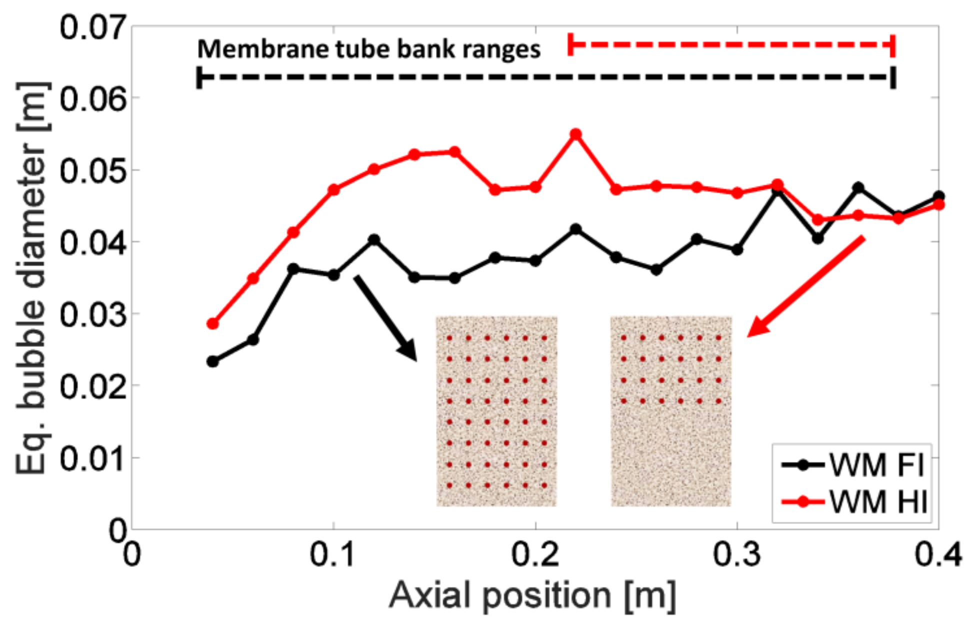
Inactive tubes near walls



Bubble cutting by membrane tube banks

- No hydrodynamic effect from removal of membranes near walls or addition of inactive wall tubes
- More membranes in tube bank = more small bubbles
- Slower increase in bubble diameter with more membranes





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Summary: horizontal membranes

When placing membranes horizontally in the fluidized bed, gas pockets and densified zones occur around them

Horizontal membranes placed near the reactor walls perform worse due to densified zones and gas back-mixing

Membrane tube banks in fluidized beds significantly cut gas bubbles

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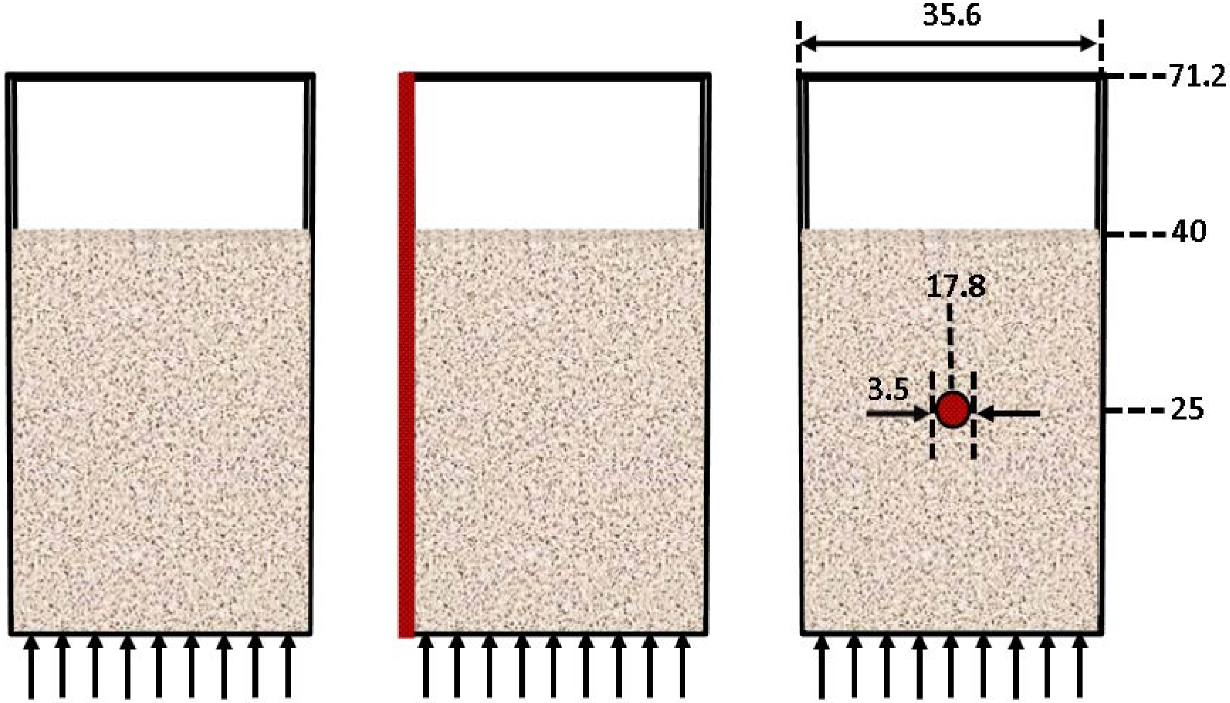
Reactive systems

Simulation settings

- Compare system without membranes and with vertical and horizontally immersed membranes
- Bubbling fluidization regime
- Simulations were performed at laboratory pressures

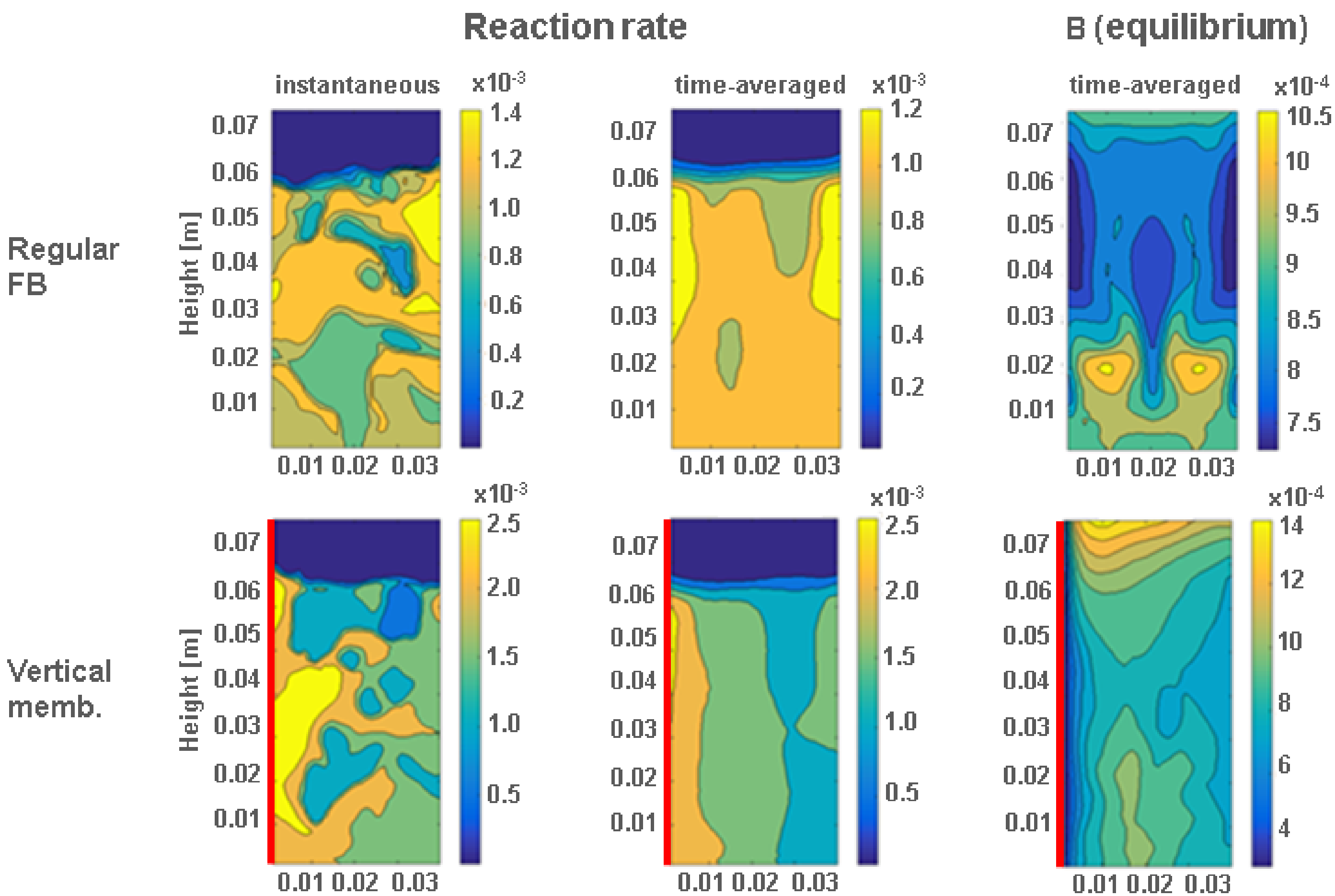


Quantity	Value	Unit
d_p	250	μm
ρ_p	1700	kg/m^3
e_{pp}, e_{pw}	0.97	-
u/u_{mf}	3	-
D	$1.0 \cdot 10^{-4}$	m^2/s
Q_{pd}	$4.3 \cdot 10^{-3}$	$mol/(m^2 s Pa^n)$
n	0.50	-
T	678	K
X_{H2}	0.1	-
X_{CH4}	0.1	-
X_{H2O}	0.35	-
X_{CO}	0.35	-
X_{CO2}	0.1	-
ω_{cat}	0.10	-
p_{outlet}	3	bar
p_{perm}	$0.01 \cdot 10^5$	Pa
t_{sim}	10	s
Δt	$5 \cdot 10^{-6}$	s

H_2 production and extraction

- Increased reaction rates near membranes
- Reaction shifts further away from equilibrium

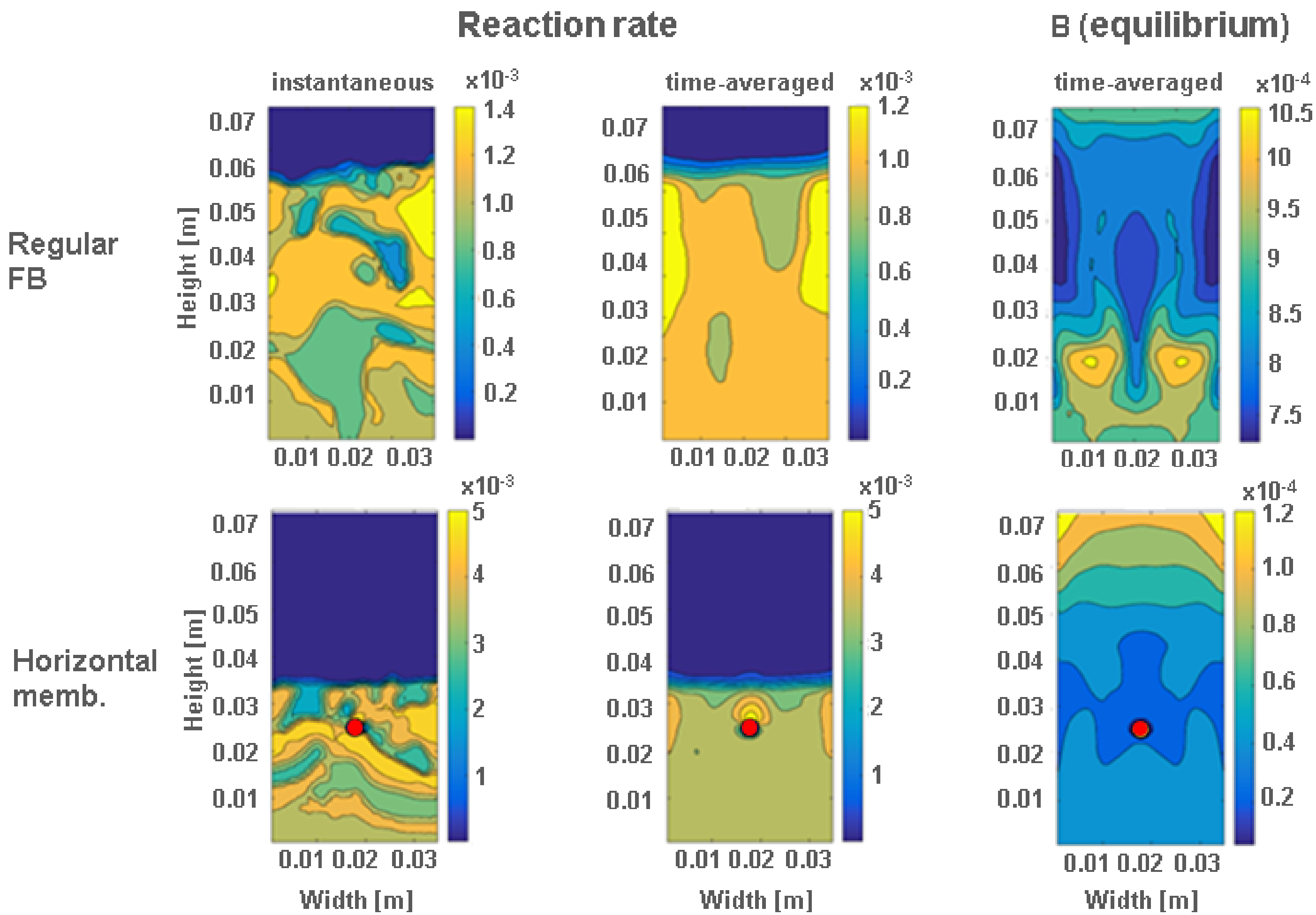
$$B = \frac{\frac{[CO_2][H_2]}{[CO][H_2O]}}{K_{eq}}$$



H_2 production and extraction

- Densified zones and gas pockets around membrane
- Significant effect on reaction rate

$$B = \frac{\frac{[CO_2][H_2]}{[CO][H_2O]}}{K_{eq}}$$



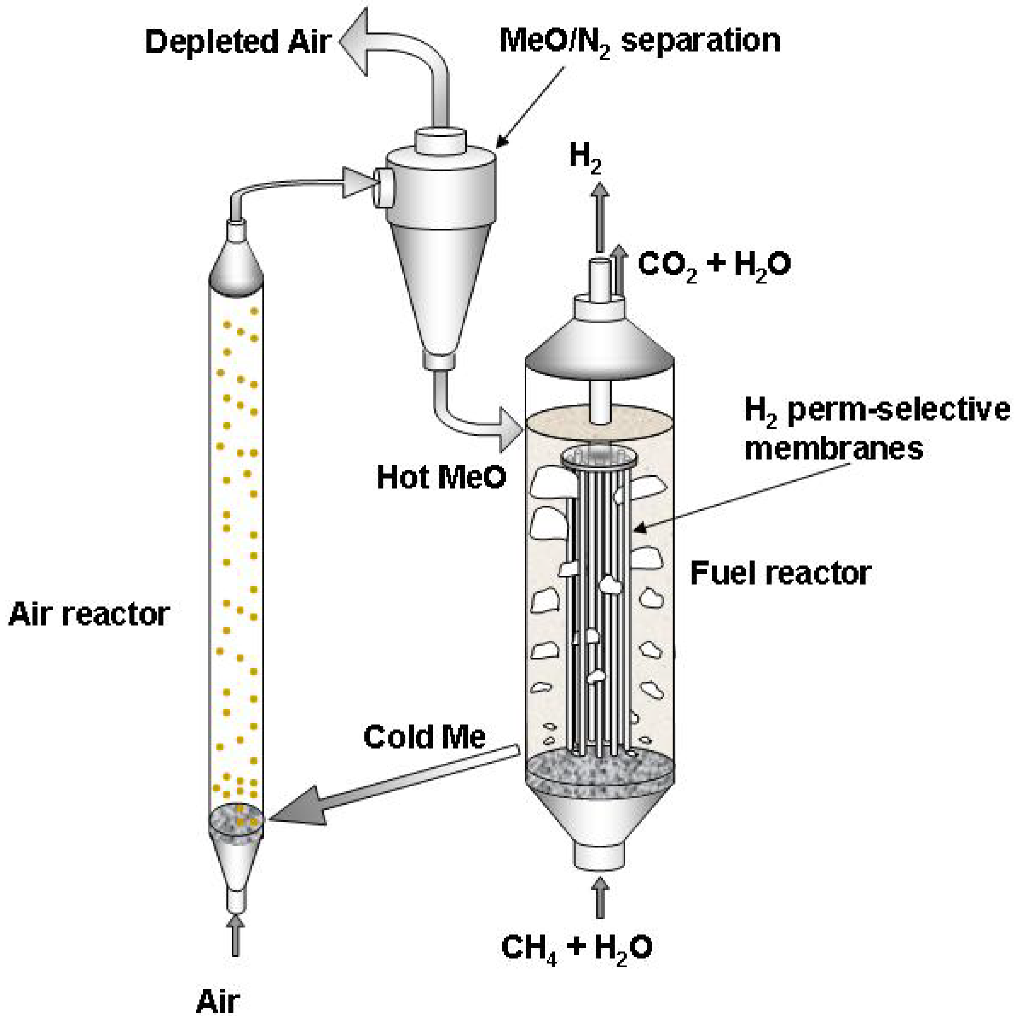
Summary: reactive systems

Extraction of hydrogen via membranes shifts the equilibrium towards the product size and increases the reaction rates

Densified zones and gas pockets around horizontally immersed membranes affect the local reaction rates

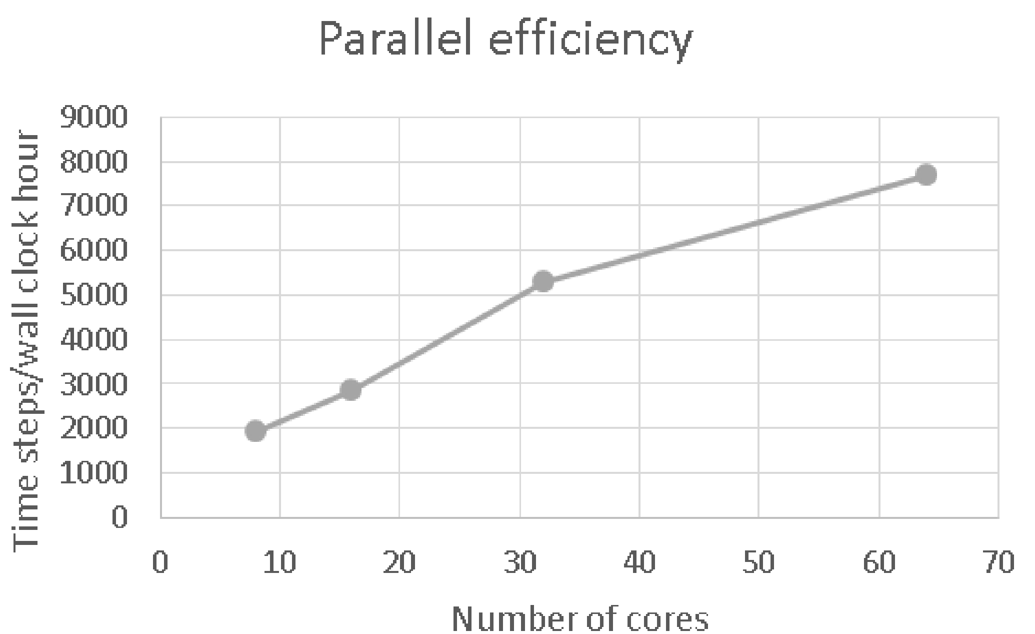
Outlook and conclusions

MA-CLR concept: solids conversion

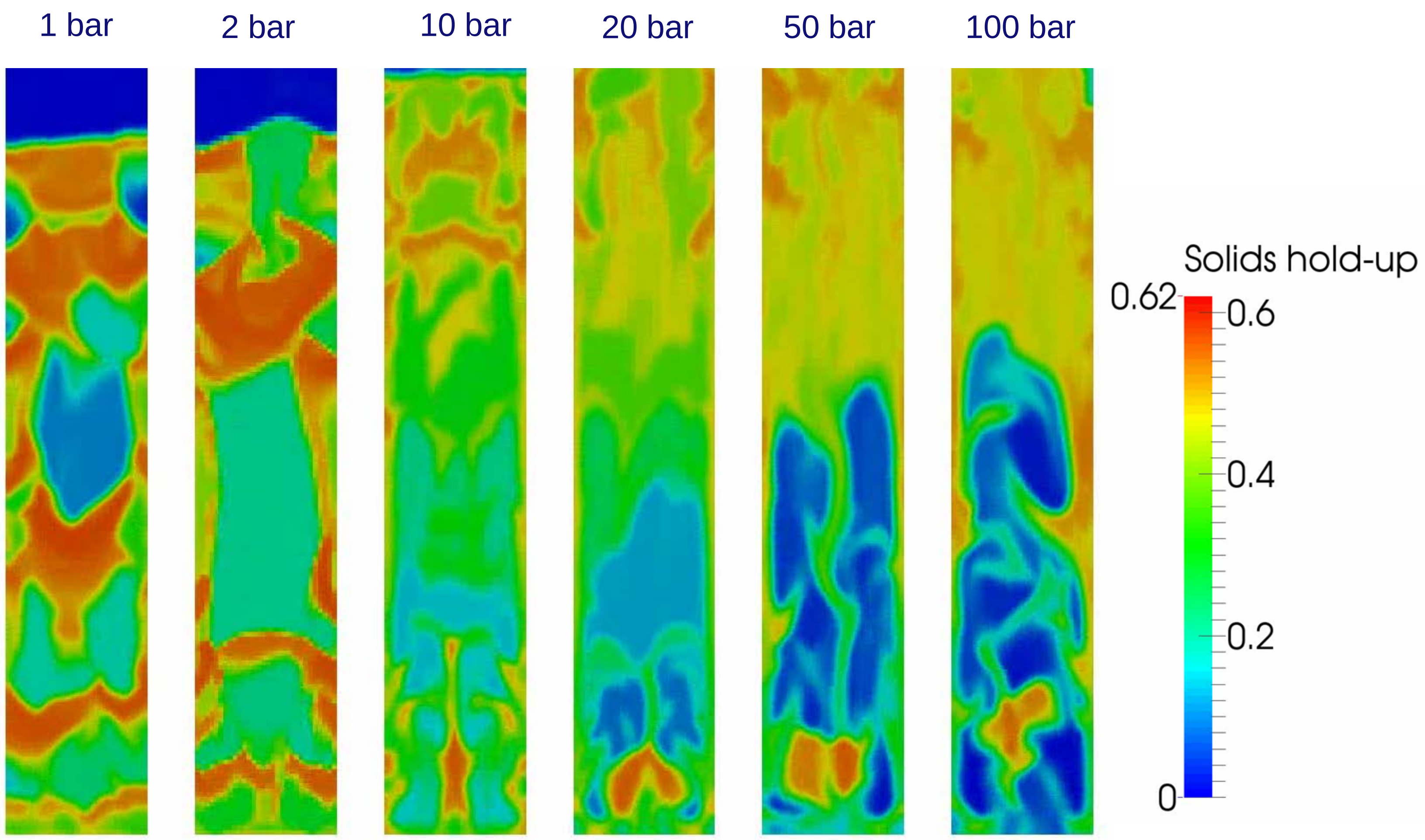


Parallel simulations with OpenFOAM

- Most simulations were run with 6 cores
- Scotch algorithm minimization of communication between processors
- Simulations performed on HPC and workstation computers
- Parallel efficiency (~350k cells) measured on SurfSara cluster, Amsterdam
- Infiniband

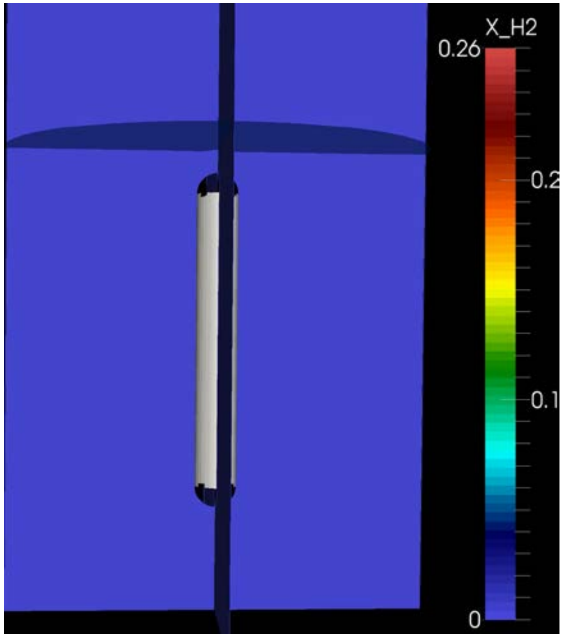


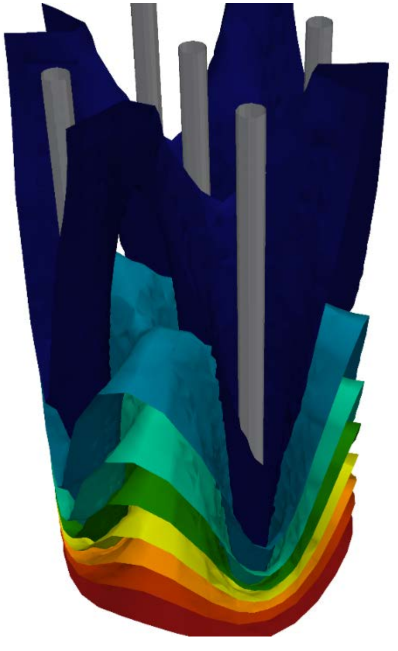
High-pressure fluidization

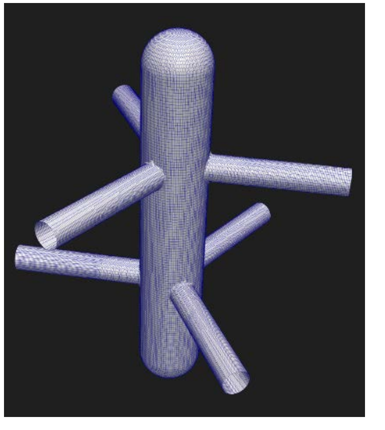


Complex geometries and full 3D simulations

- 3D cylindrical lab-scale FBMRS
- Single membrane, multiple membranes
- Quantify boundary layer
- Add horizontal tubes, change inlet flow conditions







Take home messages

Fluidized bed membrane reactors have significant advantages for hydrogen production over conventional technologies

From CFD to phenomenological; the TFM can greatly improve a 1D model by accounting for concentration polarization

Horizontal membranes at the walls are a waste; in the center they have higher fluxes and help cutting the bubbles!

Membranes help to speed-up equilibrium reactions

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