Modelling and simulation of simultaneous **intrinsic kinetics**, **hydrogen transport** and **heat transfer** in complex hydride hydrogen storage systems

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Outline

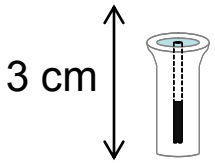
- Motivation
- Modelling of H_2 sorption in COMSOL
- Intrinsic kinetics approach
- Simulation results
- Summary and Conclusions

Motivation

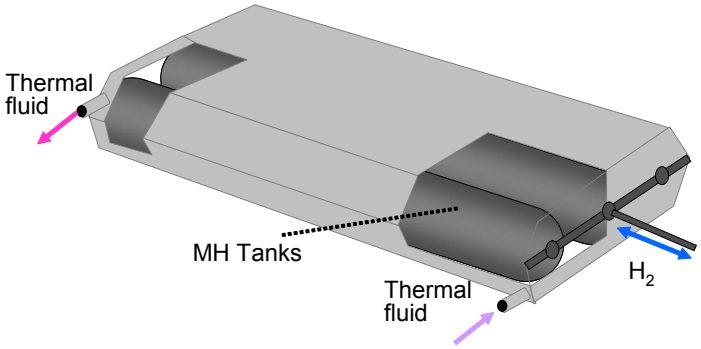
Scale-up of solid-state hydrogen storage in metal hydrides

- Metal hydrides: Highest hydrogen volumetric density

Basic research



(Lab cell, mass ≈ mg)



Scaled-up systems **(mass > kg)**

Intrinsic kinetics

Heat transfer

Hydrogen flow

- Simulation used for design and the evaluation of performance of the storage systems: dynamics, capacities, temperature levels.
- Final goal: Hydrogen storage systems with low volume and weight

Model Material: Sodium Alanate ($NaAlH_4$)

First step: $$NaH + \frac{1}{3}Al + \frac{1}{2}H_2 \xleftrightarrow{cat.} \frac{1}{3}Na_3AlH_6$$

Second step: $$\frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al + H_2 \xleftrightarrow{cat.} NaAlH_4$$

- Compromise between relatively high capacity (5 wt%) and moderate operation temperatures (125 °C – 160 °C)

Model configuration: tubular reactor

Modelling of H_2 Sorption in COMSOL

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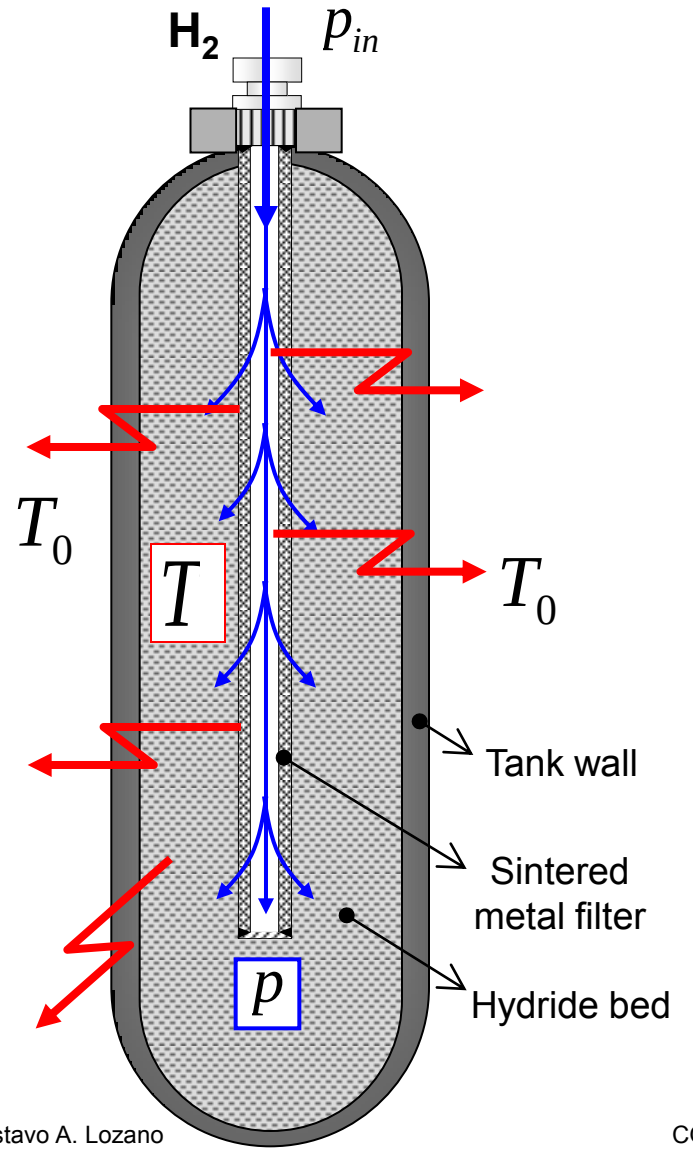

3 sequential subprocesses with different driving forces (d.f.):

1. **Hydrogen flow**
2. **Intrinsic kinetics**
3. **Heat Transfer**

Implementation in COMSOL 4.2

Hydrogen flow

$$\underbrace{\frac{\partial(\rho_g \varepsilon)}{\partial t}}_{\text{Accumulation}} + \underbrace{\vec{\nabla}\cdot(\rho_g \vec{u}_g)}_{\text{Flow}} = \underbrace{-r'_{abs}}_{\text{Source Term}}$$

Darcy's law: $\vec{u}_g = -\frac{\kappa}{\mu}\vec{\nabla}p$

Dependent variable: Pressure p

(COMSOL 4.2: Fluid Flow ⇒ Porous Media and Subsurface Flow ⇒ Darcy's Law)

Heat transfer

$$\underbrace{\left[\varepsilon(c_p\rho)_g + (1-\varepsilon)(c_p\rho)_s\right]\frac{\partial T}{\partial t}}_{\text{Accumulation}} + \underbrace{\left(-\lambda_{eff}\nabla^2 T\right)}_{\text{Fourier's law}} + \underbrace{(c_p\rho)_g(\vec{u}_g\cdot\vec{\nabla}T)}_{\text{Convection}} = \underbrace{r'_{abs}\left(\frac{-\Delta H_R}{MW_{H_2}}\right)}_{\text{Source Term}}$$

Dependent variable: Temperature T

(COMSOL 4.2: Heat Transfer ⇒ Heat Transfer in Porous Media)

Intrinsic kinetics approach

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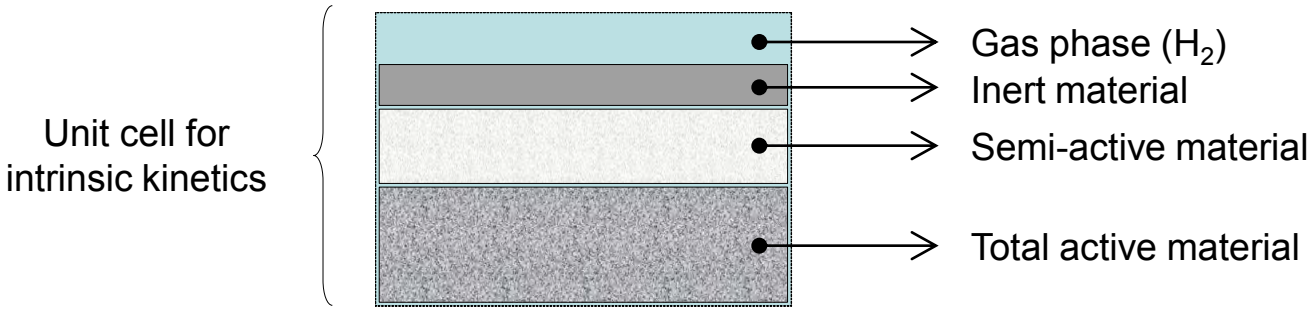
Following the kinetics of a solid-gas reaction: metal hydrides sorption

- Deviations between theoretical and experimental obtained capacities
- Classical approach:

  use of “artificial terms” in the kinetics equations related to the experimental capacities

- New approach:

  Hydride (solid reactant) considered as a mixture of different types of reacting materials



Intrinsic kinetics

- Simplified reaction system description

Total active material

$$S_I \xrightarrow{r'_{a1S}} S_{II} \xrightarrow{r'_{a2S}} S_{III}$$

$\frac{d\gamma_{S_I}}{dt} = -r'_{a1S}$	$\frac{d\gamma_{S_{II}}}{dt} = r'_{a1S} - r'_{a2S}$	$\frac{d\gamma_{S_{III}}}{dt} = r'_{a2S}$

Semi-active material

$$Z_I \xrightarrow{r'_{a1Z}} Z_{II}$$

$\frac{d\gamma_{Z_I}}{dt} = -r'_{a1Z}$	$\frac{d\gamma_{Z_I}}{dt} = r'_{a1Z}$

Dependent variable: Mass concentrations

(COMSOL 4.2: Chemical species transport ⇒ Transport of diluted species)

- Kinetic model developed and validated by experimental results

Lozano G.A., et al. Empirical kinetic model of sodium alanate reacting system (I). Hydrogen absorption. Int. J. Hydrogen Energy 2010;35:6763-6772.
Lozano G.A., et al. Empirical kinetic model of sodium alanate reacting system (II). Hydrogen desorption. Int. J. Hydrogen Energy 2010;35:7539-7546.
Lozano G.A., et al. Optimization of hydrogen storage tubular tanks based on light weight hydrides. Int. J. Hydrogen Energy 2011;
doi: 10.1016/j.ijhydene.2011.03.043..

Simulation results

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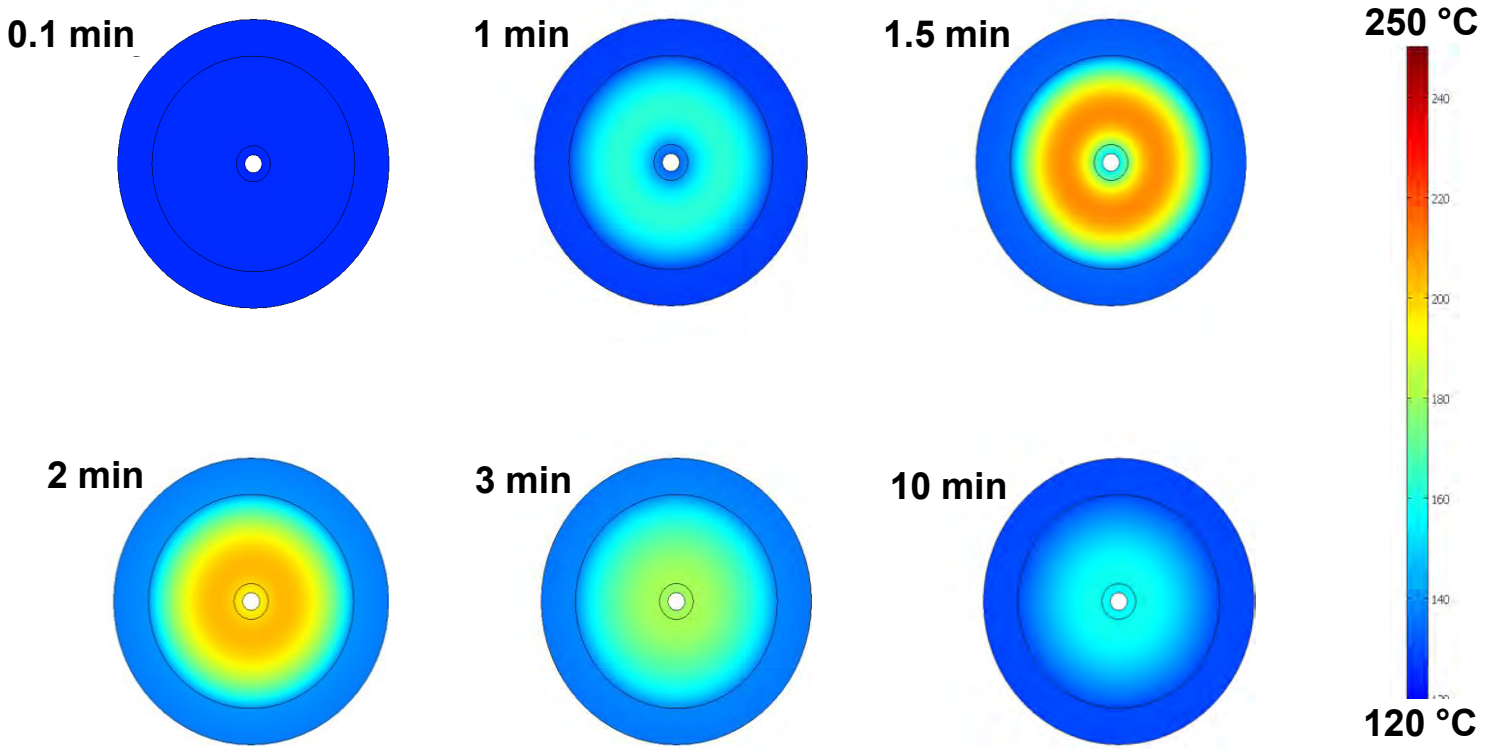
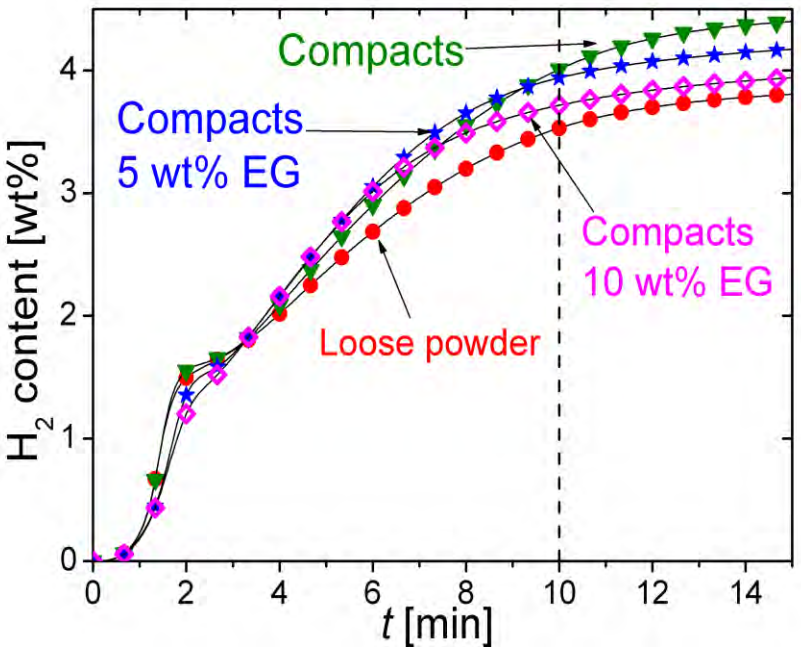
Example: Temperature profile



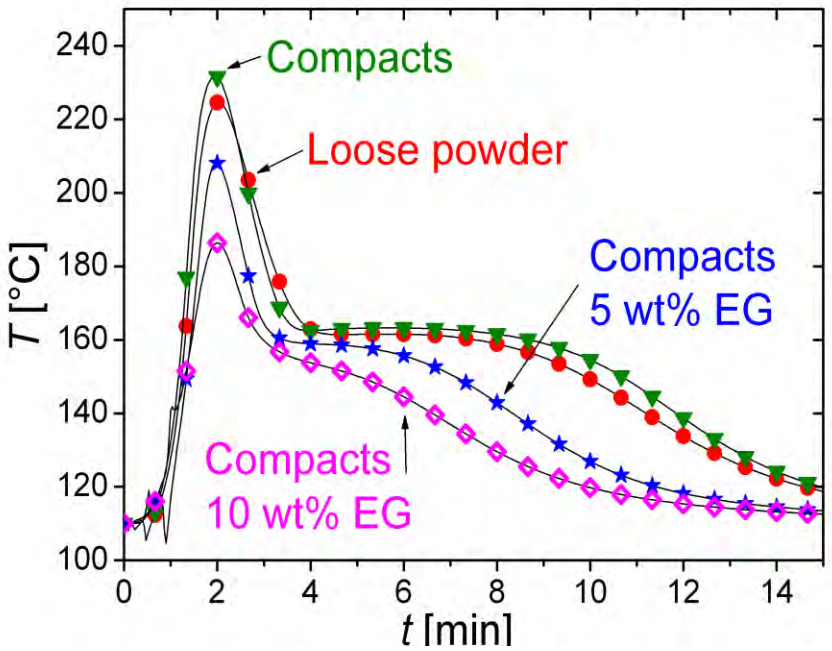
- Main result of the simulation: the prediction of the total mass of hydrogen stored in the system as a function of time.

Example: 35 mm internal diameter

Hydrogen content



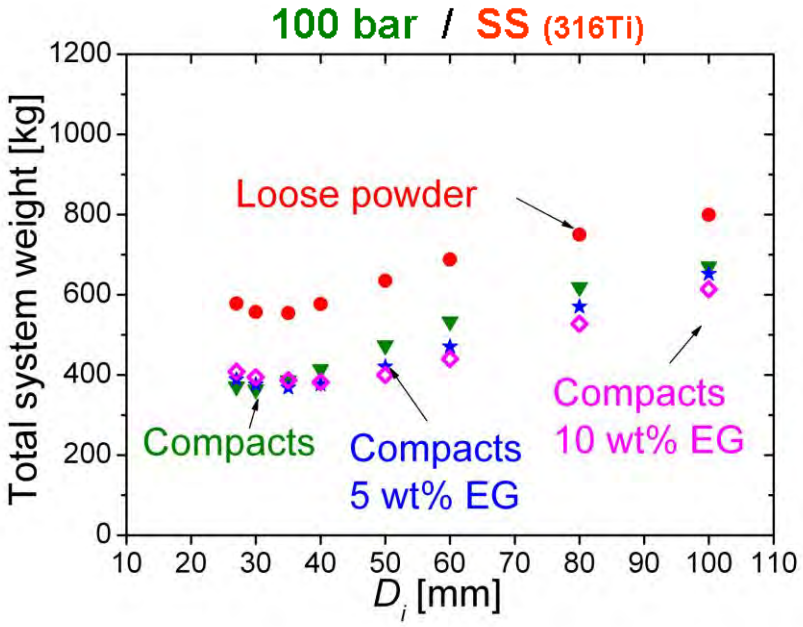
Temperature (bed centre)

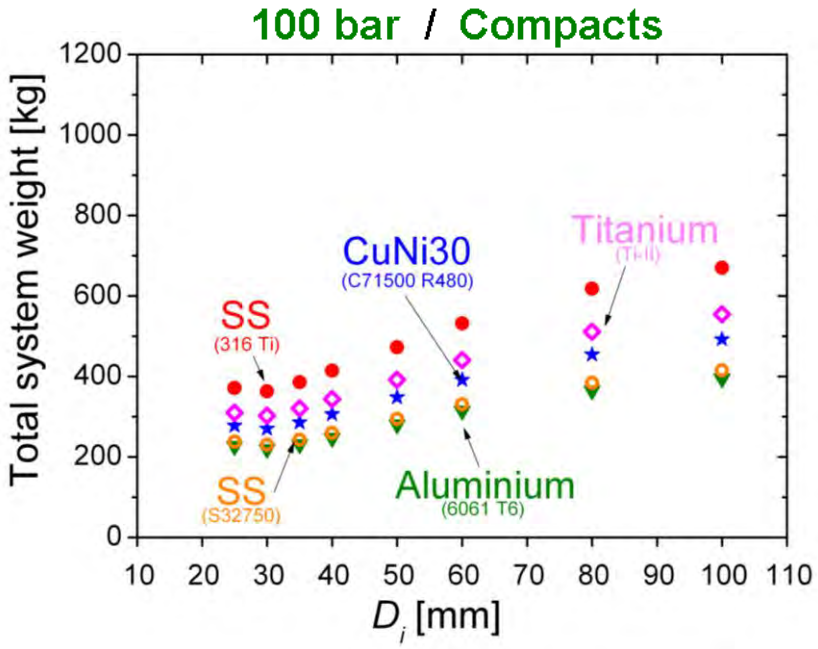


Case studie: Optimisation definition of sodium alanate tanks

Issue	Definition
Conditions and constraints	1. Basic configuration: tubular reactor 2. Time to charge 4.5 kg H_2: 10 min 3. Total hydrogen capacity $\geq$ 5 kg H_2 4. Tank wall calculated possible max T_{eq}
Function to be minimised	Weight (Volume) of the hydrogen storage system
Variables	1. Internal diameter of the tubular tank 2. Compaction level 3. Addition of expanded graphite (EG) 4. Hydrogen pressure 5. Tank wall material

Optimization results





- Compacted material shows the lowest required system weight compared to loose powder.
- System weight: reduction potential for Aluminium (6061 T6) and Super Duplex Steel (SS S32750). .

Summary and Conclusions

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- Succesfully developed simulation including 3 sub-processes: intrinsic kinetics, heat transfer and hydrogen transport

- New approach for intrinsic kinetics through definition of different active materials.

- Great potential of weight reduction in hydrogen storage systems based on metal hydrides by compaction and by stronger and/or lighter tank wall materials