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Optimization of refueling processes in metal-hydride based hydrogen storage systems

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We developed models based on experimental data to enable the development of a new H2 storage system

Sandia and GM partnered to develop enabling technology for automotive H2 storage systems based on solid sorbents:

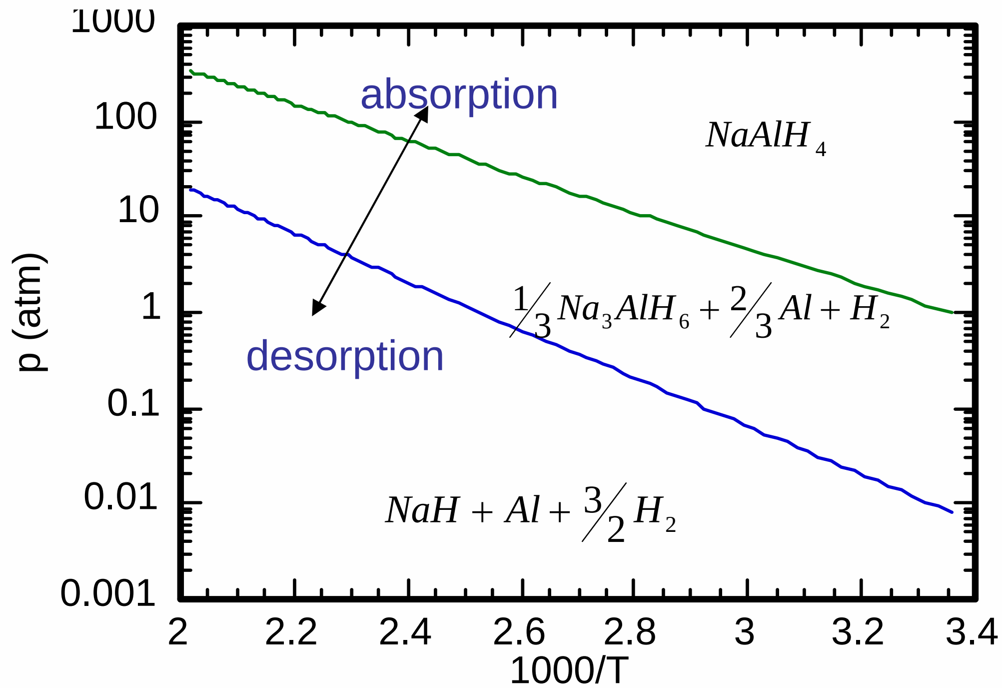
- **System drive-cycle simulation**
- **Structural design**
- **Heat and mass transfer design**
- **Prototype demonstration**

Goal of this presentation is two-fold:

- Describe the model development process for coupled heat transfer, mass transfer, and chemical kinetics
- Demonstrate the use of these models for optimization of transportation systems.

Catalyzed sodium alanates are prototypical reversible complex hydride materials

Van ‘t Hoff diagram (equilibrium P vs. T)

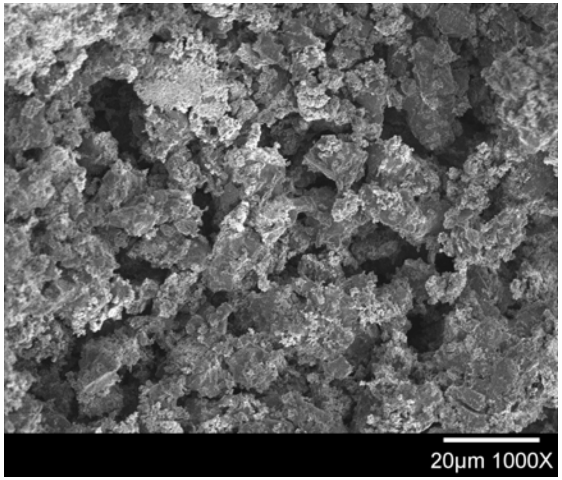


Significant changes occur:

-Physical properties (ρ , k_{th}, etc)

-Morphology, porosity

-Reactivity

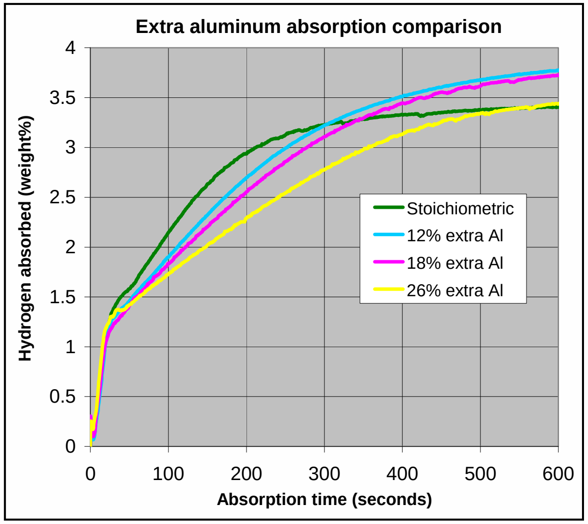


- Hydrogen uptake is exothermic (-40 kJ/mol-H2)
- Hydrogen release is equally (opposite) endothermic
- Characteristics are similar for other H2 storage materials

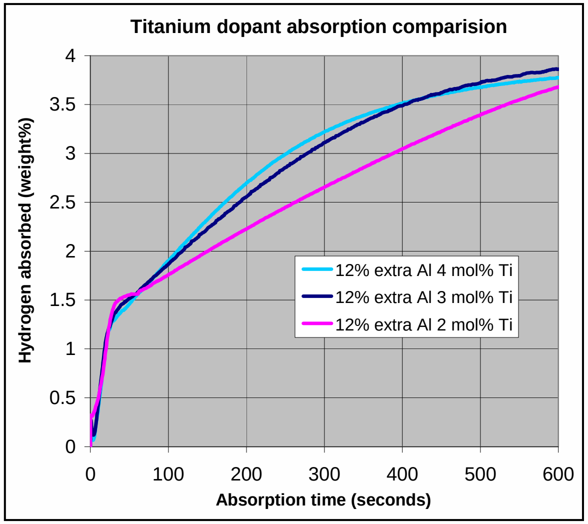
Material properties are modified to optimize the 5 and 10 min hydrogen refill

- *Stoichimetric sodium alanates have **poor kinetics** and **thermal conducvity***
- *However, optimization is possible*

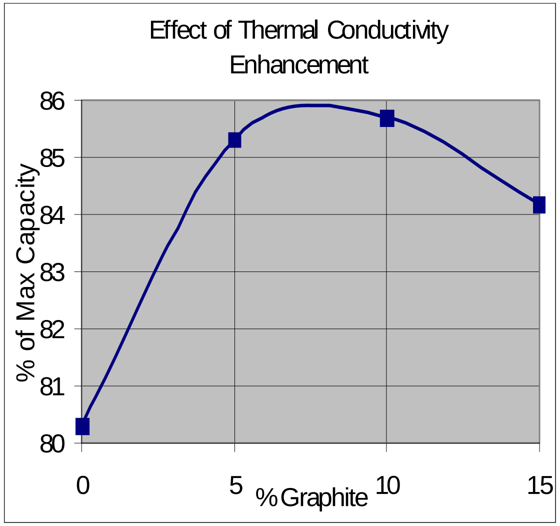
Excess Aluminum



Catalyst loading



Graphite flake



US Patent Pending 20070178042,
'Sodium Alanate Hydrogen Storage Material'

Optimized sodium alanate formulation:
- 10 wt% ENG flake
- 18 wt% excess aluminum

The models include momentum, species, and energy transport with chemical reactions

Momentum transport (Brinkman-Forchheimer equation): Darcy term Forchheimer term

$$\frac{\rho \partial \mathbf{v}}{\phi \partial t} + \frac{\rho}{\phi} \mathbf{v} \cdot \nabla \boldsymbol{u} = -\nabla p + \nabla \cdot \left[\frac{\mu}{\phi} \left(\nabla \mathbf{v} + \nabla \mathbf{v}^T \right) \right] - \frac{\mu}{K} \mathbf{v} - \frac{\rho F}{\sqrt{K}} |v| \mathbf{v}$$

Superficial velocity (Darcy velocity): $\boldsymbol{v} = \phi \boldsymbol{u}$

$\boldsymbol{u}$ is the seepage velocity (intrinsic velocity)

K is the permeability

ϕ is porosity

Energy transport:

$$(\rho c_p)_m \frac{\partial T}{\partial t} + (\rho c_p)_g \mathbf{v} \cdot \nabla T = k_m \nabla^2 T + R \Delta H$$

Species transport:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (v_i c_i) = R_i$$

Closure is accomplished empirically

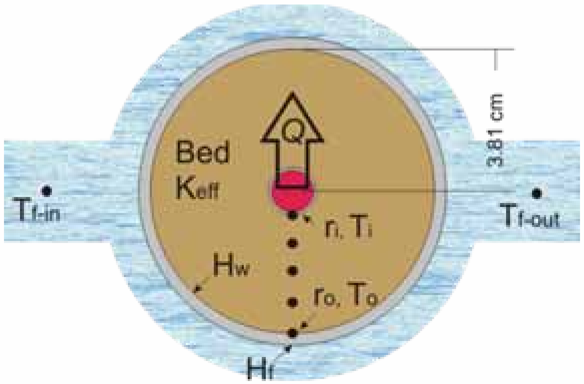
Mass continuity:

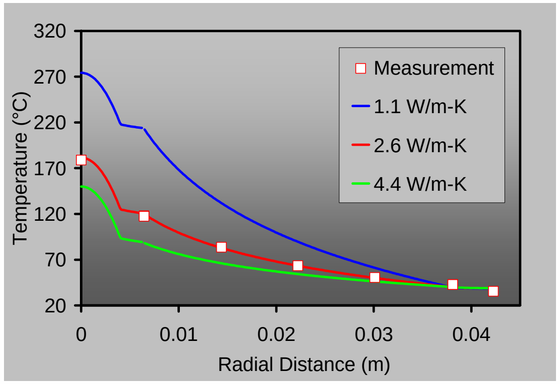
$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho v) = MR$$

Exchange of mass between gas and solid phases

Heat Transfer properties were experimentally optimized and quantified

Experimental apparatus:



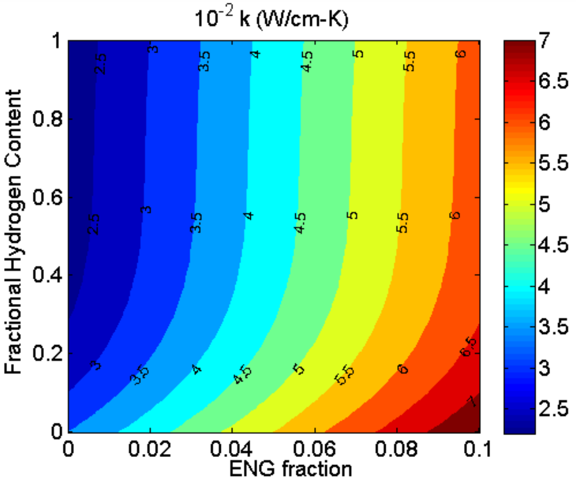


FE model parameter fit for Kth and wall resistance

Thermal conductivity measured as a function of

- **H_2 pressure**
- **ENG content**
- **H_2 content**

Empirical formula for K_{th}:



$$k(\psi, E) = 11.7\psi^4 - 32.5\psi^3 + 33.2\psi^2 - 14.8\psi + 40E + 3.4$$

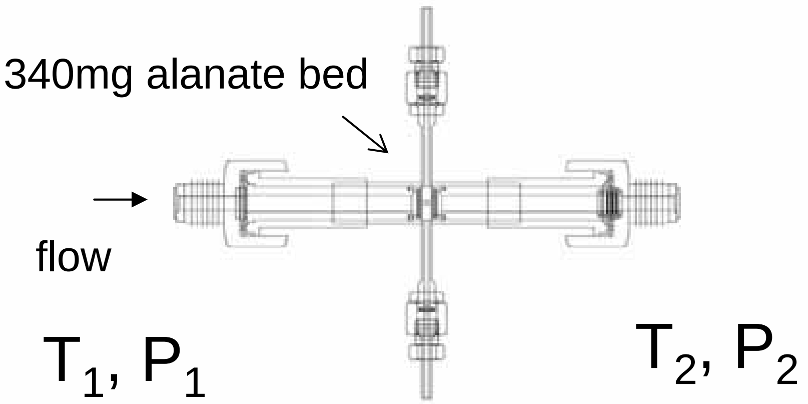
Mass Transfer permeability (K) model chosen based on flow regimes found in a typical metal hydride bed

Permeability model

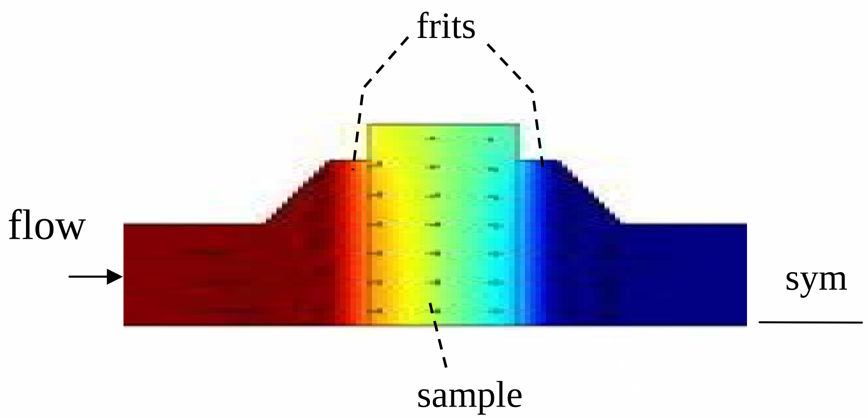
We use a model by Young & Todd that includes Knudsen number effects due to the small particle and pore sizes that characterize some materials:

$$K = \frac{\phi}{\tau^2} d_p^2 \left[\frac{1}{32} + \frac{5}{12} Kn \right]$$

Experimental measurement



FEM model parameter fit



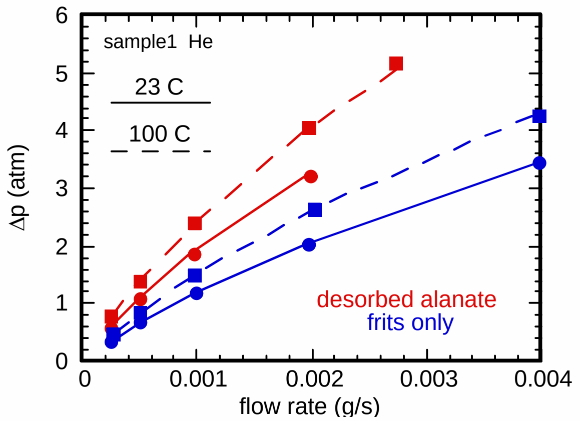
Results

Permeability model parameters:

$\phi = 0.806$

$d_p = 3\ \mu m$

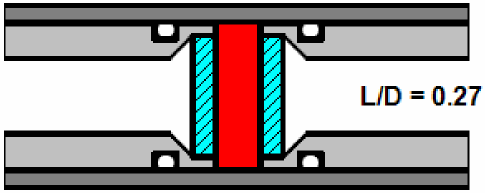
$\tau = 2$



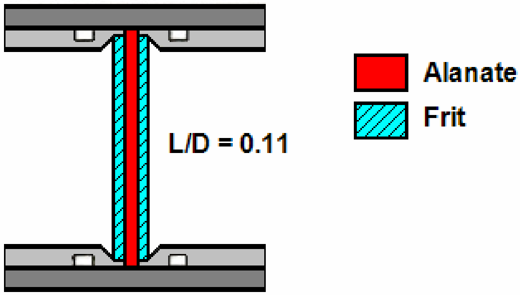
A channeling model was developed by considering additional experimental geometries

Three aspect ratios targeted to elucidate channeling:

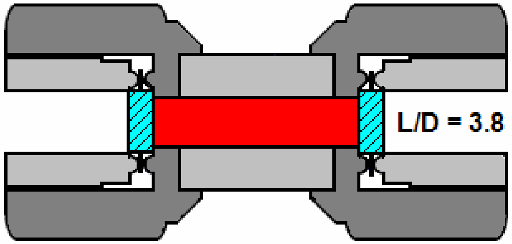
"Standard" aspect ratio



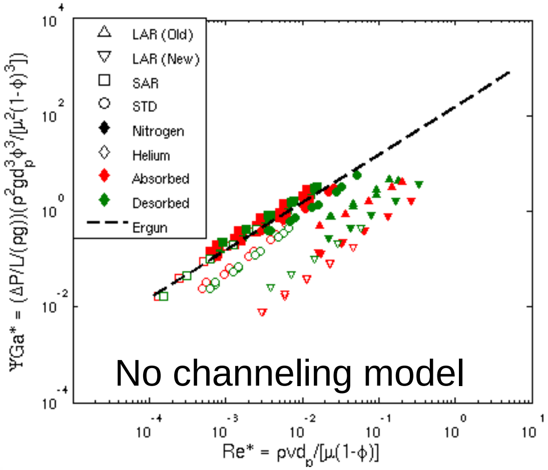
"Short" aspect ratio

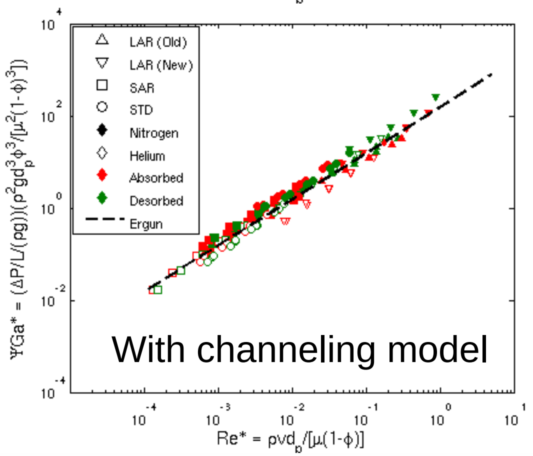


"Long" aspect ratio



Non-dimensional pressure vs flow:

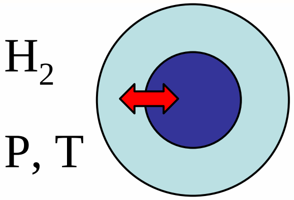


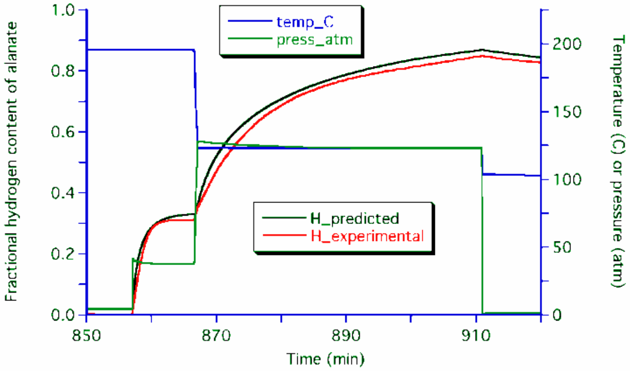


Wall channeling model of 2.08% of total cross-sectional area found to be appropriate

Chemical kinetics model parameters determined using experimental measurement

- Modeled as a shrinking core with the reaction occurring at the moving interface
- Model parameters are empirically derived on small samples to exclude transport limitations
- The experimental data is fit with Arrhenius expressions
- Model parameters verified to have general applicability over entire range of operating conditions





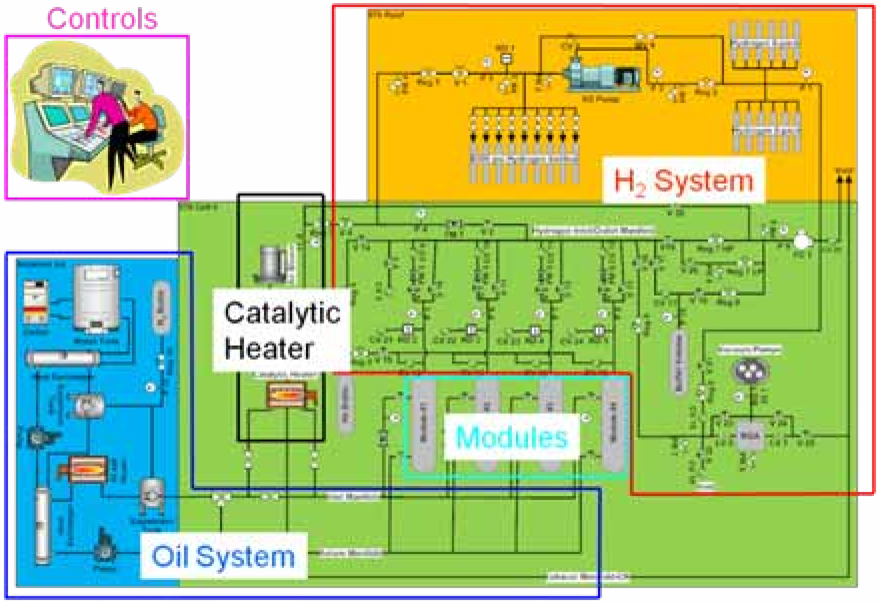
$$R_i = f_i\left(p_{eq-i} - p_{H_2}\right)A_i e^{\frac{-E_i}{RT}}$$

$$\frac{\partial [H_2]}{\partial t} = \sum R_i$$

$$q = -\sum Q_i R_i$$

process	reaction, i	f_i	$p_{eq\text{-}i}(T)$
desorption	1	$[NaAlH_4]$	tetrahydride
desorption	2	$[Na_3AlH_6]$	hexahydride
absorption	3	$[NaH]$	hexahydride
absorption	4	$[Na_3AlH_6]^2$	tetrahydride

Validation at the automotive scale

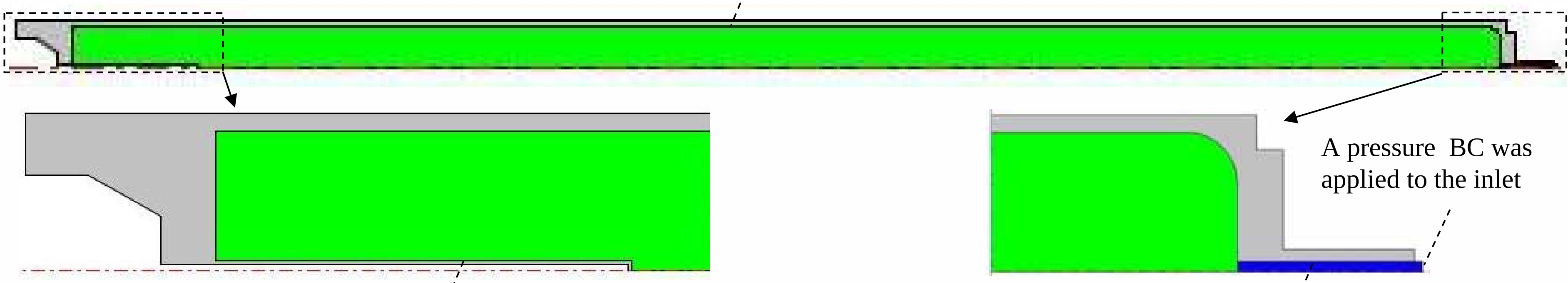


Extensive data collection:

- Pressure, mass flow
- 18 total external shell thermocouples
- 48 thermocouples installed into end caps
- 26 RTDs on tube surfaces

A FE model of a module tube was constructed

A convection bc was applied to the outer tube surface: $q = h(T_{oil} - T)$; $h = 0.065$w/cmK, $T_{oil}(t,z)$

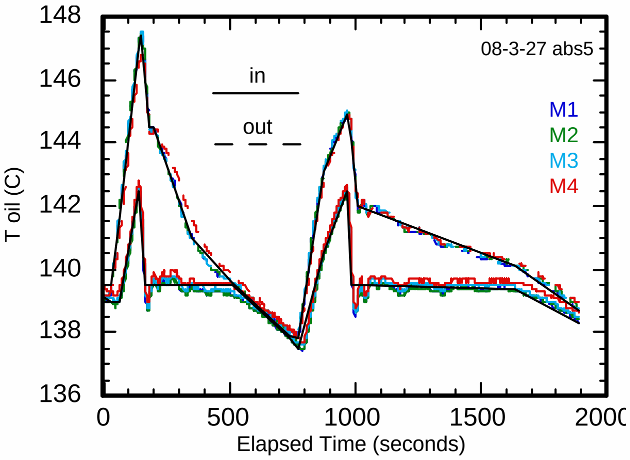


A pressure BC was applied to the inlet

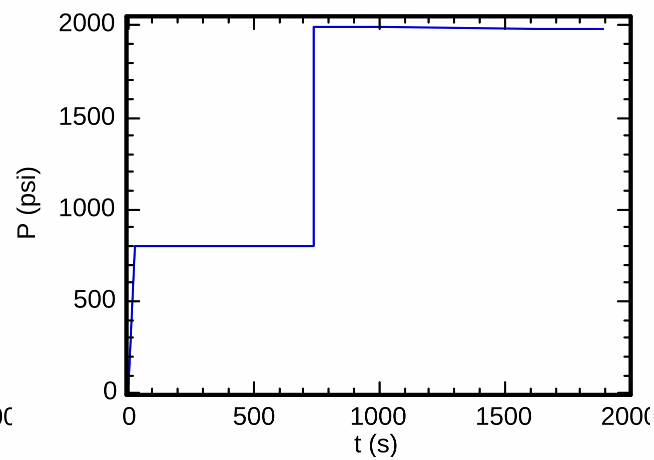
Thermocouple well

Hydrogen inlet tube is filled with sodium alanate

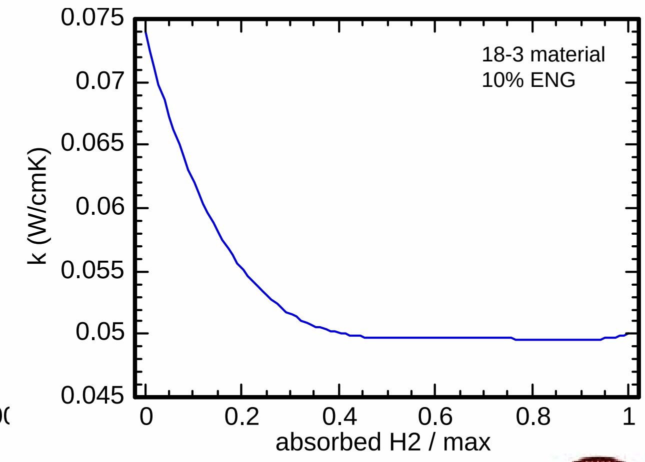
T_{oil} based on measurement



Pressure boundary condition based on measurement

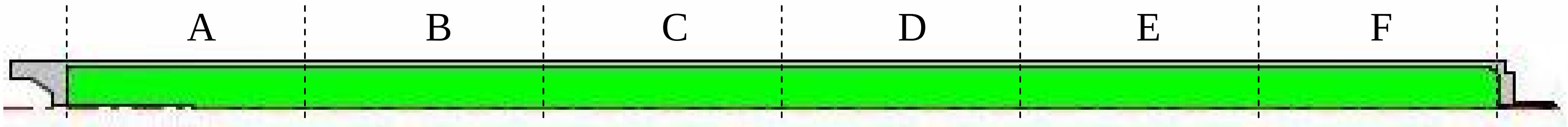


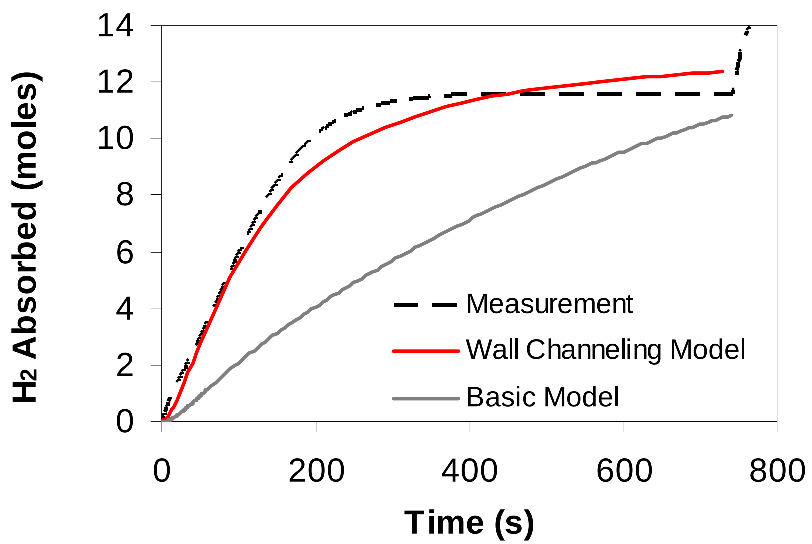
Empirical alanate conductivity model



Permeability model with channeling applied to full scale measurement

Tube baffle sections





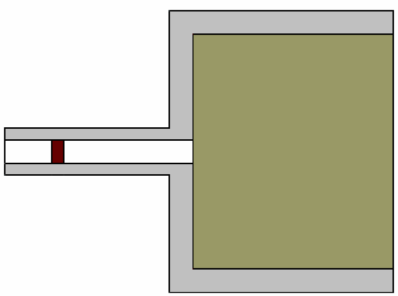
Some evidence of wall channel observed

Wall channeling model accounts for apparent high permeability in full scale system

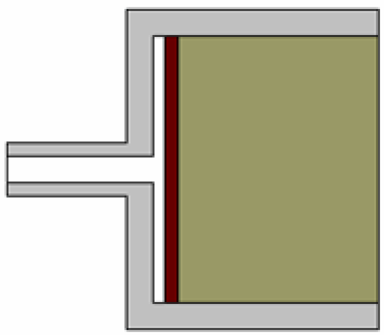
Validated transport model enables optimization

Example of three design cases considered:

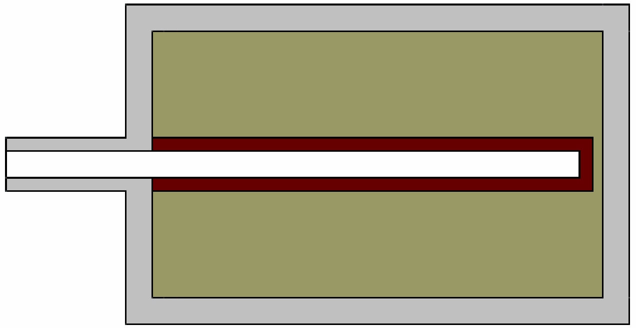
Baseline



Entry plenum



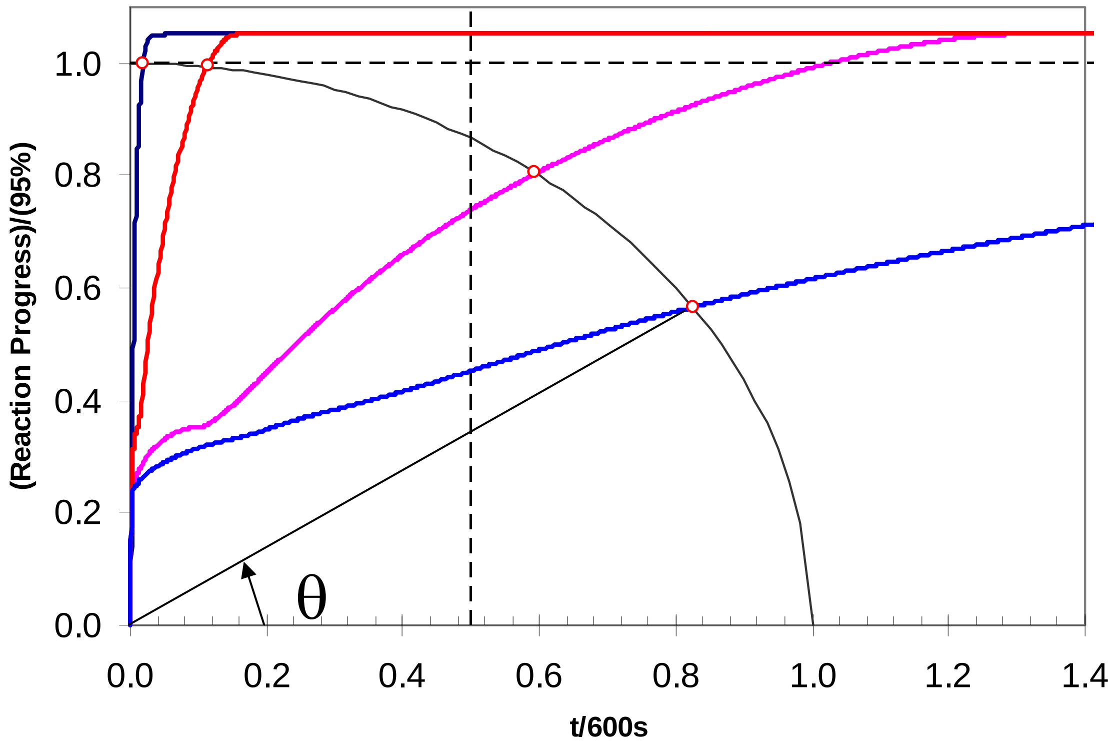
Axial Frit



A reaction progress evaluation metric is useful to evaluate design options

Angular position leaving normalized unit circle

Consider the 2 step sodium alanate absorption process:

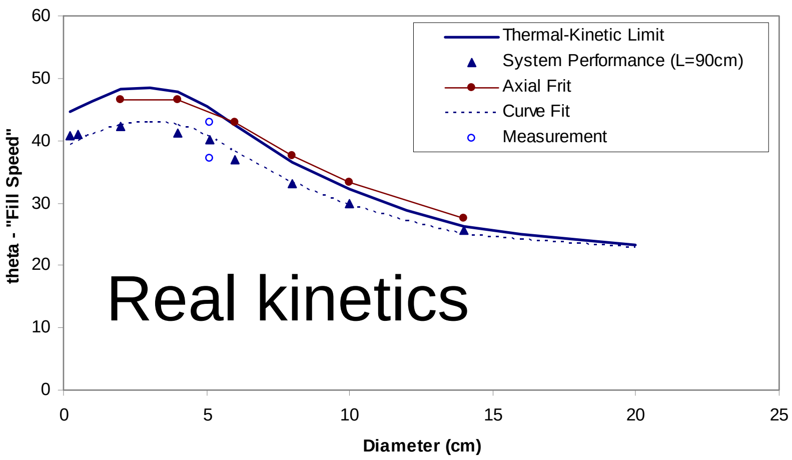


The theoretical performance of the axial frit design approaches the thermal kinetic limit

The thermal/kinetic limit (TKL) represents the maximum fill speed possible

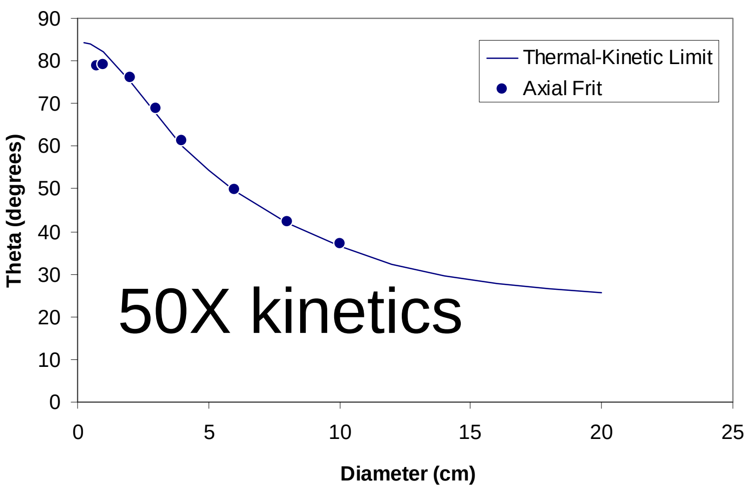
Case 1 - Real sodium alanate kinetics:

- The axial frit design enables a 10% improvement in fill speed
- At larger diameters, the axial frit design exceeds TKL due to added cooling



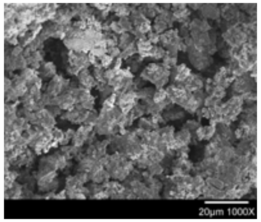
Case 2 - Theoretical kinetics (50X):

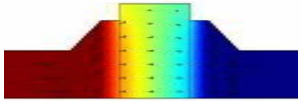
- Sodium alanates with enhanced kinetics (50X) and existing thermal properties
- The use of the axial frit allows performance to reach the TKL

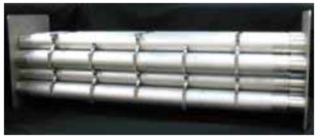


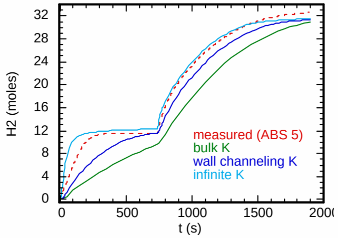
Conclusions

- Robust model of transport in an enhanced sodium alanate system has been developed
- We have resolved the individual transport mechanisms and their impact on the rate of hydrogen uptake
- Channeling along the wall of the vessel appears to be a dominant hydrogen gas transport mechanism
- The model can be used to optimize transport and can lead to near ideal hydrogen absorption and delivery rates in scaled-up systems
- The application of these transport models is generally applicable to a variety of condensed-phase hydrogen sorption materials









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