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Predictions of solid-state hydrogen storage system contamination processes

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DOE Hydrogen Program

International Partnership for the Hydrogen Economy

HYDROGEN IMPLEMENTING AGREEMENT

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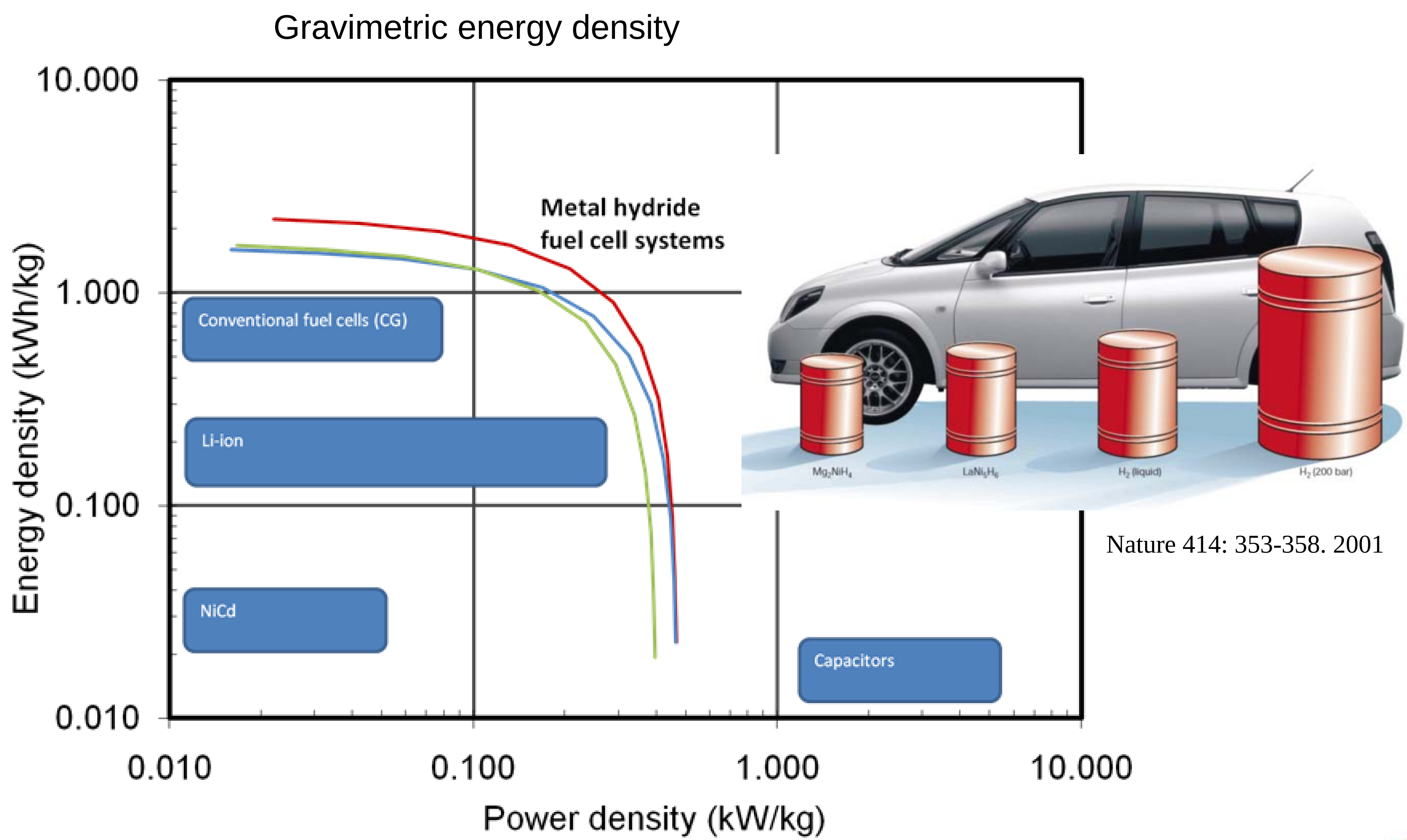
Metal hydride systems enable a large amount of energy storage per unit mass – easily exceeding Li-ion batteries



Nature 414: 353-358. 2001

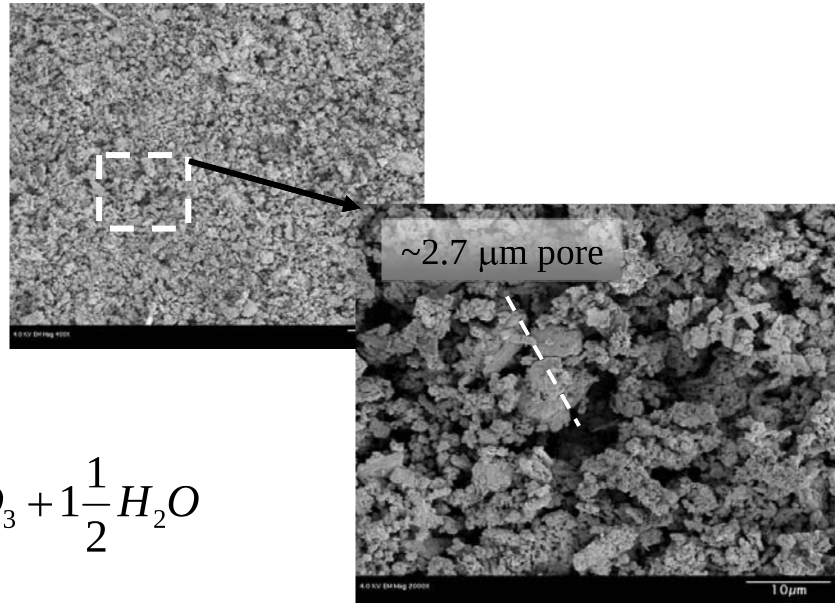
Hydrogen storage materials are reactive

- Solid hydrogen sorbents (metal hydrides and complexes) are being developed for automotive applications

$$M + \frac{x}{2} H_2 \leftrightarrow MH_x + HEAT$$

- There are a variety of materials being considered
  - Interstitial hydrides, Laves phase, etc (AB , AB_2 , AB_5 , A_2B)
  - Complexes (alanates, borohydrides, amides, etc)

- Generally, the materials are highly reactive
  - Pyrophoric
  - Water reactive
  - High surface area



$$1\frac{1}{2} O_2 + AlH_3 \rightarrow \frac{1}{2} Al_2O_3 + 1\frac{1}{2} H_2O$$

Overall Objective

Understand and predict chemical and physical hazards associated with metal hydride system accident scenarios

Impact:

- Enable the design, handling and operation of effective hydrogen storage systems.
- Design hazard mitigation strategies to enable consumer technology deployment
- *Provide a technical basis for eventual Codes and Standards development*

Accident scenarios focus on most credible events as identified by hazards analysis

Breach in plumbing/tank

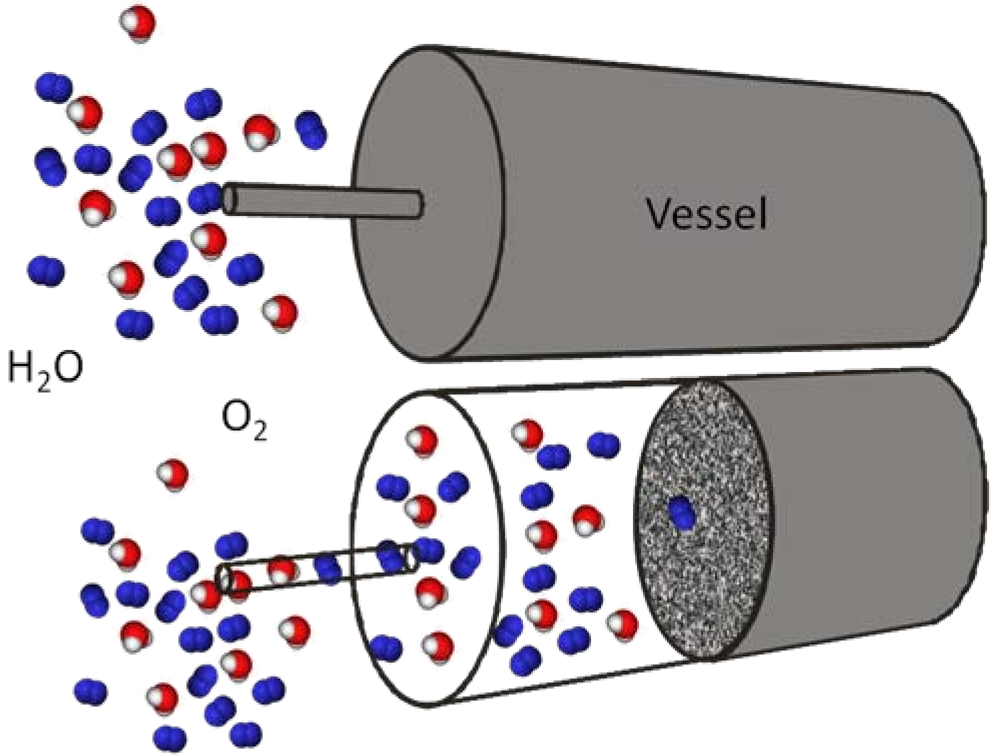
1. Overpressure venting
2. Back diffusion of air
3. Exothermic reaction within bed

Contaminated refueling stream

1. Hydrogen depleted material at temperature
2. Entrance of contamination with refueling gas
3. Exothermic reaction within bed

Possible outcomes:

1. Thermal run-away/fire
2. Formation of hazardous products
3. Loss of containment



Example:
Alane, α-AlH_3

How do we confidently predict outcomes of these accident scenarios to evaluate and mitigate risk?

A robust model includes momentum, species, and energy transport with chemical reactions

Momentum transport (Brinkman-Forchheimer equation):

Darcy term

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

Forchheimer term

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

u is the seepage velocity (intrinsic velocity)

K is the permeability

ϕ is porosity

Energy transport:

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

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

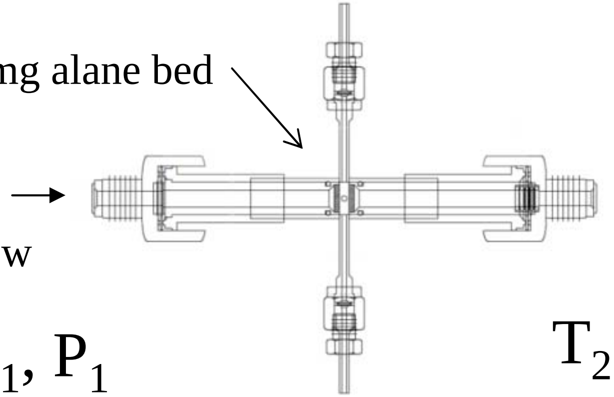
Permeability (K) model chosen based on flow regimes found in a typical metal hydride bed

Permeability model

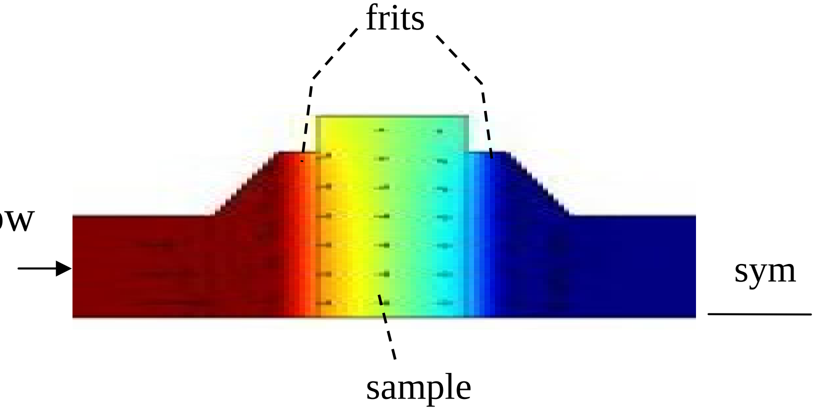
We use a model by Young & Todd that includes Knudsen number effects due to the small particle and pore sizes that characterize some materials:

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

Experimental measurement



FEM parameter determination



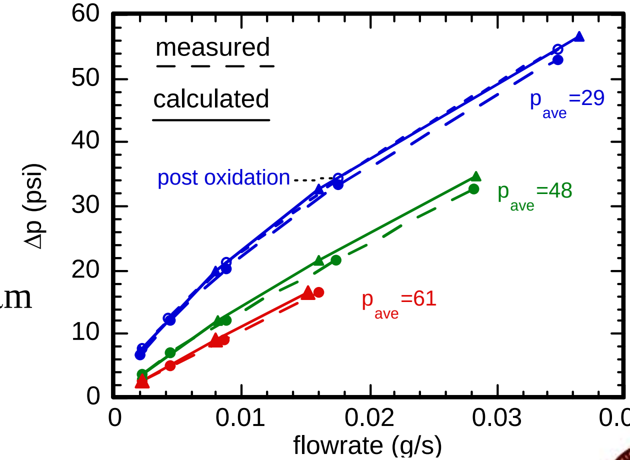
Results (AlH_3)

Permeability model parameters:

ϕ= 0 .68-0.81

d_p = 1.6 – 3 μm

τ = 2



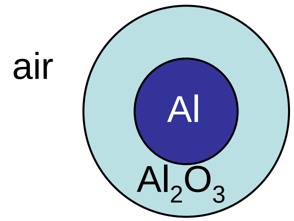
Alane oxidation *chemical kinetics* and *thermal conductivity* models

Chemical kinetics model

Shrinking core mechanism in a packed bed of spheres:

O_2 dissociates and dissolves at outer surface:

$O_2 \Leftrightarrow 2\ O(s)$



Dissolved oxygen diffuses through oxide layer and aluminum is oxidized at inner surface:

$$Al + \frac{3}{2} O(s) \rightarrow \frac{1}{2} Al_2O_3$$

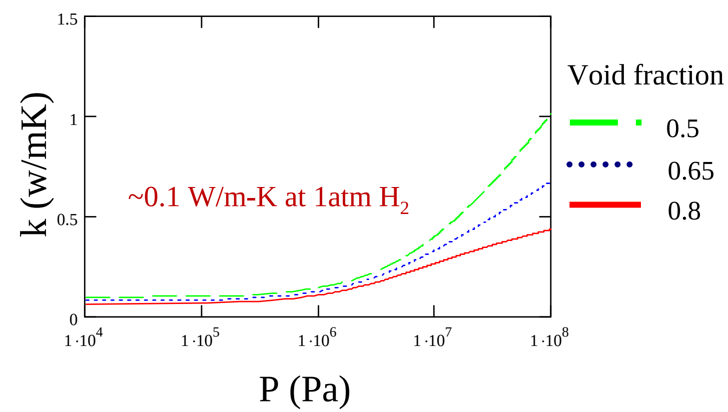
The **bulk** reaction rate takes the form for a thin oxide layer

$$R = -k p_{O_2}^{1/2} Al_0 \left[1 - \beta \left(1 - \frac{Al}{Al_0} \right) \right]$$

Thermal Conductivity

Thermal conductivity is a function of:

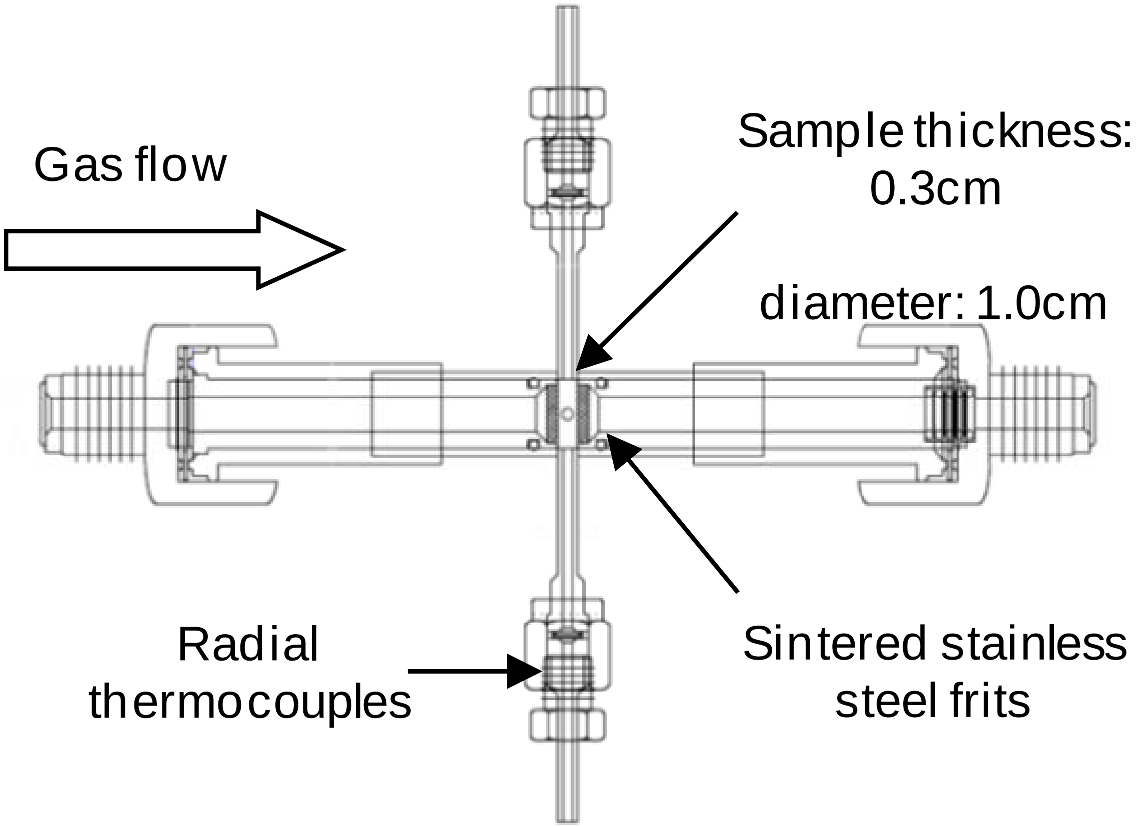
- hydrogen pressure
- thermal conductivity of the particle
- porosity
- particle diameter
- quality of thermal contact



* Rodriguez-Sanchez et al. International Journal of Hydrogen Energy 28 (2003) 515 – 527

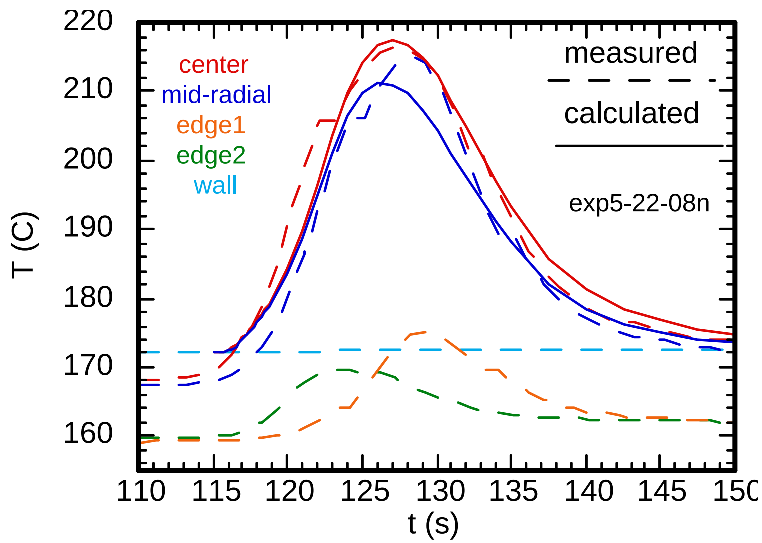
Models coupled and validated through experiments

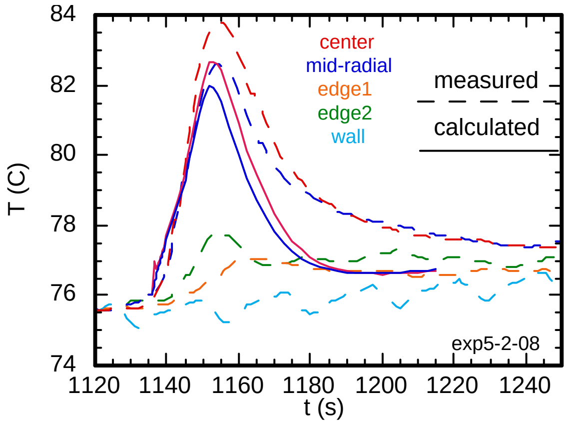
Oxidation flow-through reactor:



A robust set of chemical kinetics parameters determined experimentally

Exotherms resulting from exposure of 100mg beds to dry air



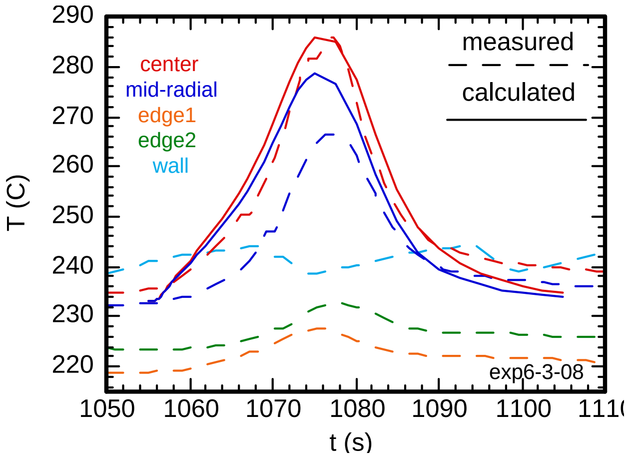


kinetics model:

$$\frac{d[Al]}{dt} = -\frac{6(1-\phi)\sqrt{Kp}k_0 e^{-Q/RT}}{D}\left[1-\frac{2+\alpha D k_1 e^{Q1/RT}}{6}\left(1-\frac{[Al]}{[Al]_0}\right)\right]$$

Parameters: $\sqrt{K}k_0 = 6.854e-12,\quad k_1 = 1200000,\quad Q = 1.73e11,$

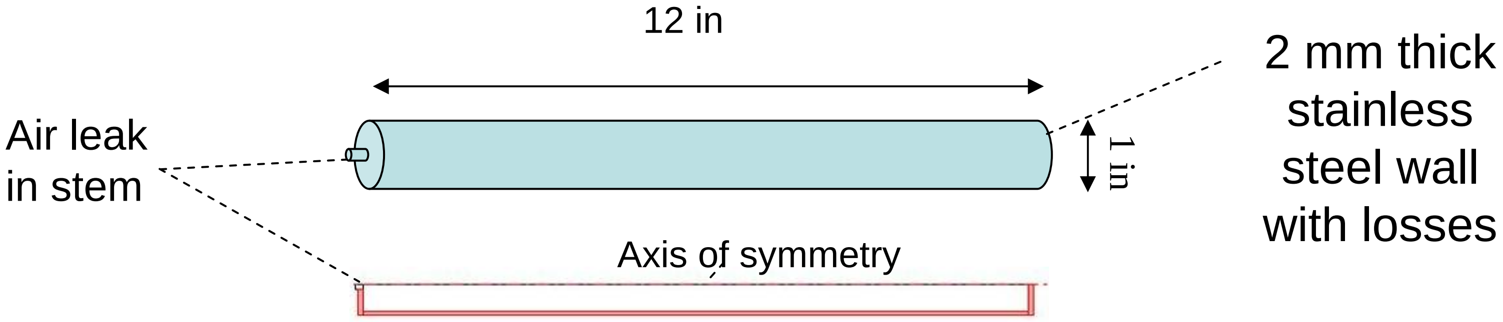
$Q1 = 1.66e11,\quad \alpha = 1,\quad D = 150nm,\quad R = 8.315e7$



We are now confident in the usefulness of our model to predict accident scenarios

Scaled-up system simulations utilized to predict processes during alane breach-in-tank scenario

A dead-end cylindrical vessel with a inlet/outlet stem filled with alane



Breach in tank (worst case):

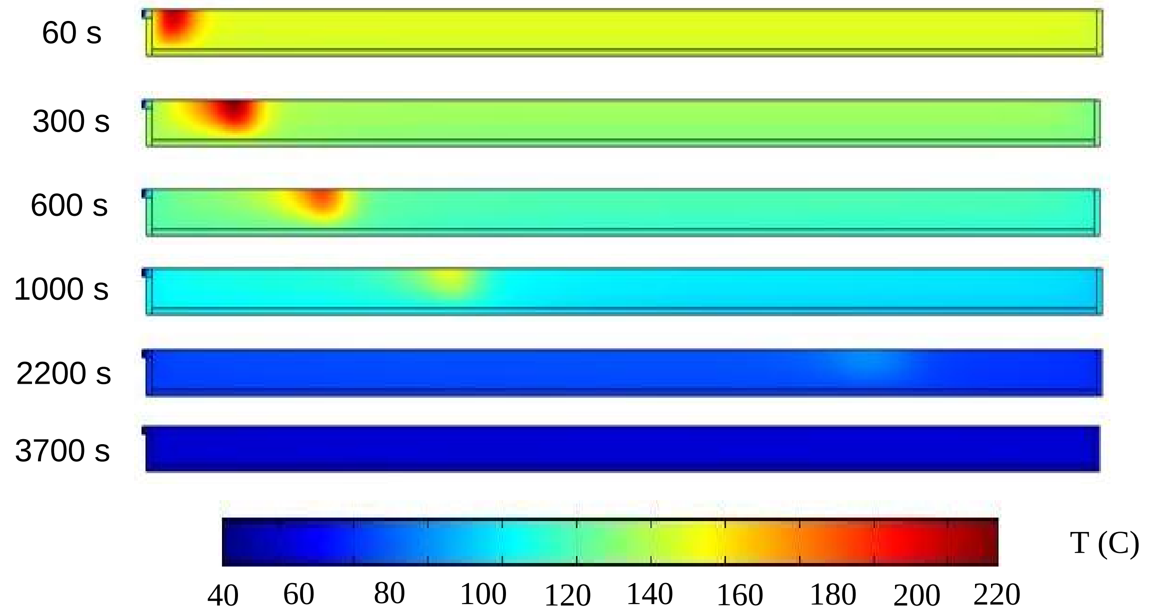
- Empty bed – no H_2 evolution
- Bed at 150 °C and ΔP = 0
- Air leak at stem
- Diffusion/advection of air into bed
- Heat loss to the environment

Prediction of scaled up contamination event indicate a propagating reaction front

Simulation results:

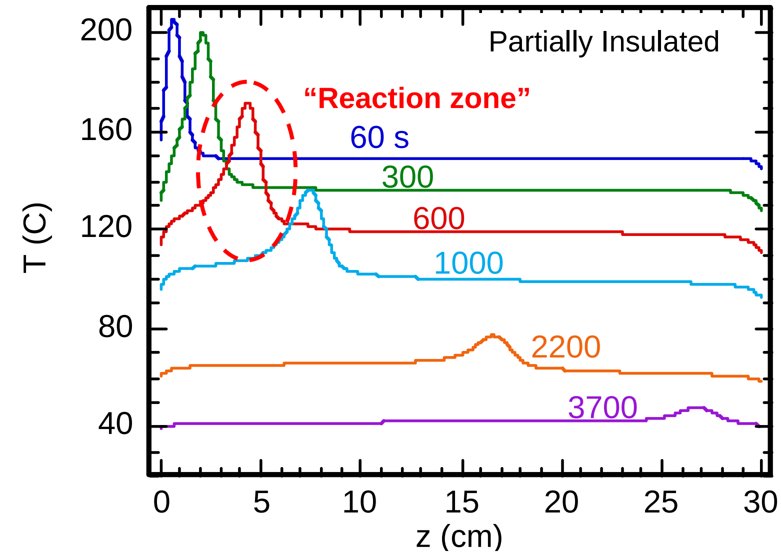
A reaction front propagates for over 1 hour, while the bed cools by natural convection (5.5 W/m^2-K)

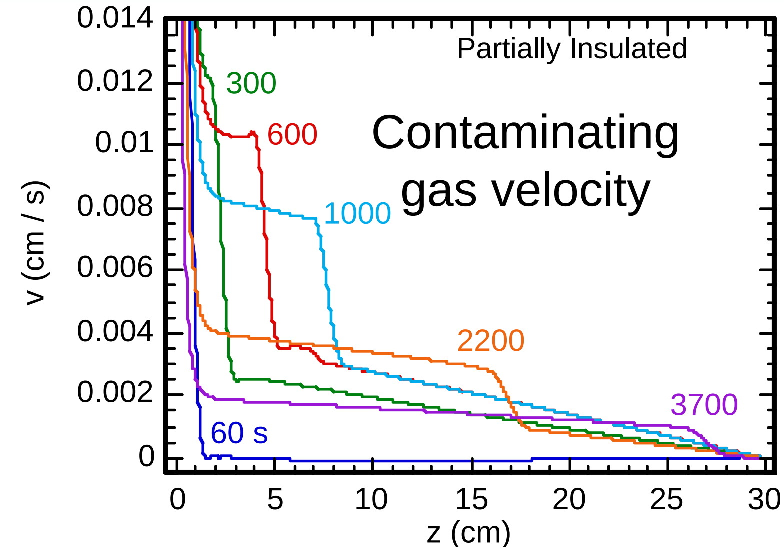
Time-lapse of reaction front propagation:

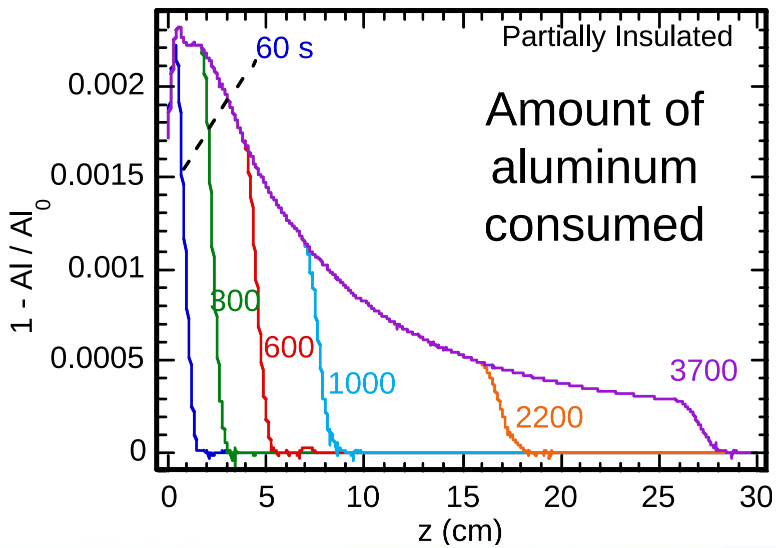


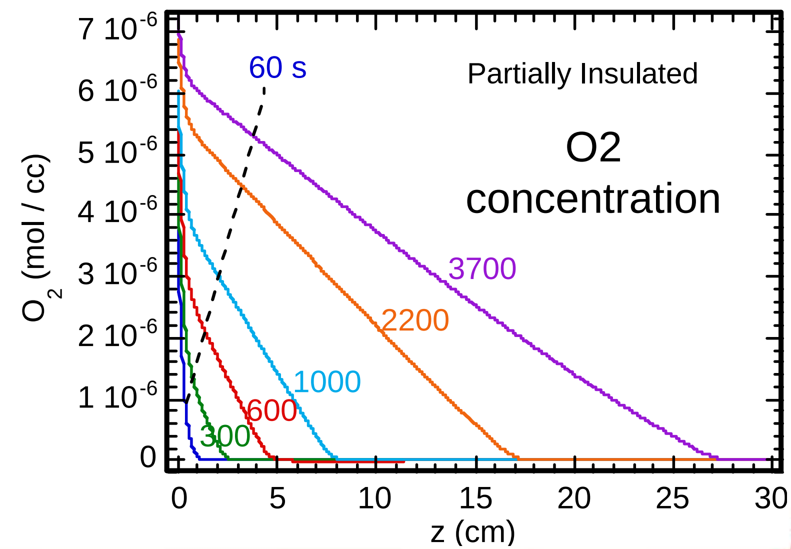
Alane, α-AlH_3

Simulation results indicate self-quenching due to limited oxygen diffusion









We can now predict scenarios with different initial and boundary conditions to help understand risk

Insulating the system:

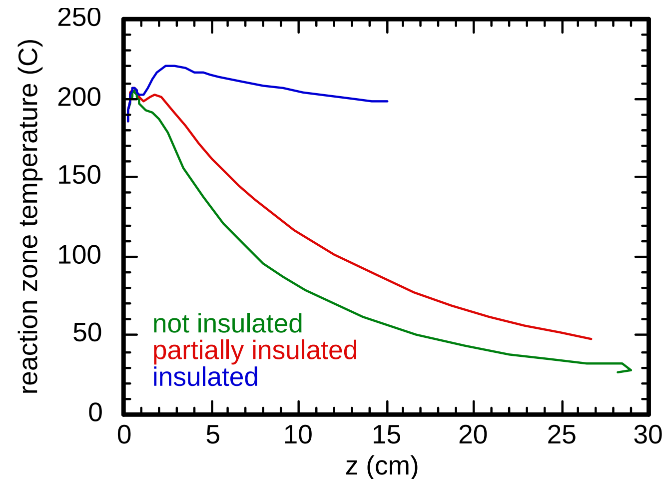
- increases the exotherm but slows the reaction front progression

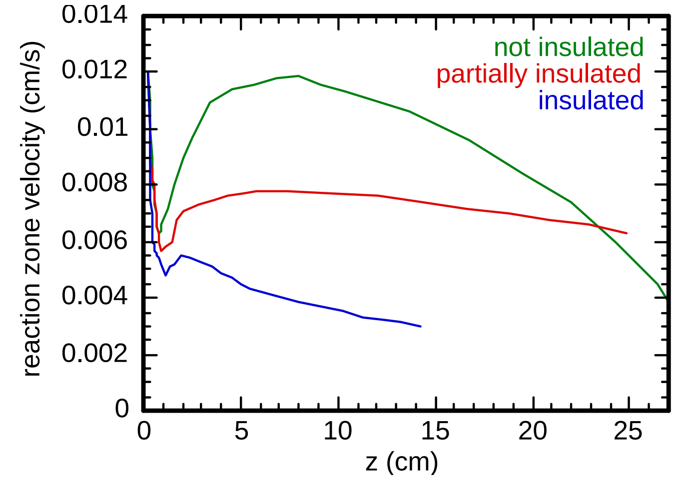
Higher metal hydride densities:

- impedes the flow of O2 and slows the reaction front progression

Other scenarios:

- Fully hydrogen charged bed
- Pool fires
- Different bed geometries

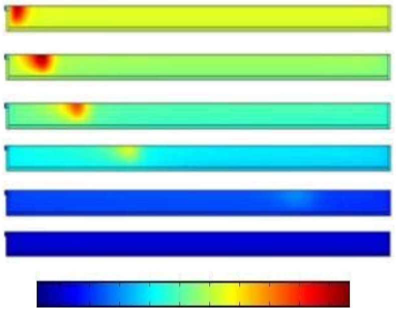




Conclusions resulting from alane system accident scenario

Outcomes to an *alane* breach in tank event:

- An oxidation reaction front propagates through the system
- Only moderate temperatures are experienced due to limitation in the oxygen diffusion



→ **Input to risk assessment process**

Additional considerations:

- We need full-scale model validation
- Alane oxidation kinetics unknown as temperatures exceed ~400 °C
- Other metal hydrides are more reactive – *mitigation may be required to avoid loss-of-containment*

***Mitigation technology development opportunity*:**

Normally inert components acting to quench the reaction front

Thank you!