Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company,
for the United States Department of Energy's National Nuclear Security Administration
under contract DE-AC04-94AL85000.

The reactivity properties of hydrogen storage materials in the context of systems

2009 DOE H_2 Program Annual Merit Review

May 20th, 2009

Daniel E. Dedrick
Sandia National Laboratories

Mike Kanouff, Rich Larson, Bob Bradshaw, George Sartor, Richard Behrens, LeRoy Whinnery, Joe Cordaro, Aaron Highley

stp_51_dedrick

Overview

Timeline

- Start: July 2007
- End: September 2010
- Percent complete: 60%

Budget

- $2.1M

  (100% DOE H_2 program)
- 630K in FY08
- 750K for FY09

Barriers

On-Board Hydrogen Storage

- –Durability/Operability (D)
- –Codes and Standards (F)
- –Reproducibility of Performance (Q)

Partners

SRNL - Anton
UTRC – Mosher
IPHE

AIST
SRNL™
SAVANNAH RIVER NATIONAL LABORATORY
Kidde Fenwal
Forschungszentrum Karlsruhe
in der Helmholtz-Gemeinschaft
IRH
Institut de recherche sur l'hydrogène
Université du Québec à Trois-Rivières
United Technologies
Research Center

Relevance: Overall Objective

Develop generalized methods and procedures required to quantify the effects of hydrogen storage material contamination in an automotive environment

Eventual Impact:

- Enable the design, handling and operation of effective hydrogen storage systems for automotive applications.
- Provide technical basis for C&S efforts when appropriate technology maturity has been attained.

Approach: Project organized into three inter-dependent and collaborative tasks

Task 1 - Quantify fundamental processes and hazards of material contamination (*SRNL, UTRC, IPHE*)

- Illuminates the fundamental contamination mechanisms
- Results in chemical-kinetic reaction models

Task 2 - Predict processes during accident scenarios (*UTRC, SRNL*)

- Extends process predictive capability to the application scale

Task 3 - Identify and demonstrate hazard mitigation strategies (*UTRC*)

- Identify contaminated bed treatment methods
- Assess methods for controlling contamination reactions

All hydrogen materials are sourced from collaborators (DOE programs, IPHE) to ensure relevance and continuity!

Credible contamination scenarios considered based on NFPA, ISO and SAE draft language

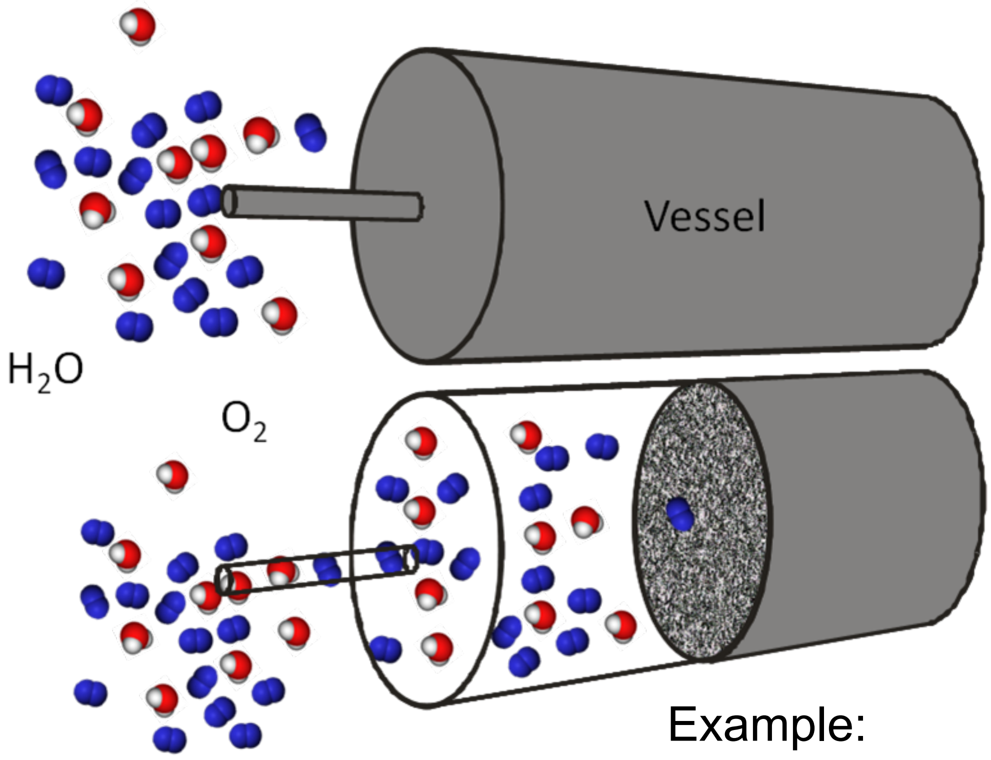
Scenarios:

Breach in plumbing/tank

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

Contaminated refueling stream

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



Example:
Alane, α-AlH_3

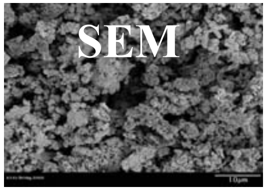
Outcomes:
- Thermal run-away/fire
- Loss of containment
- Formation of hazardous products

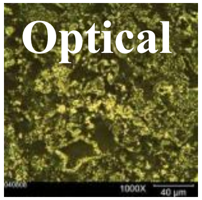
Mitigation:
- Reaction quenching
- Ignition suppression
- Product treatment

Relevant predictive simulation requires model parameter characterization and validation

Characterize **physical properties**

Parameters:
- **particle size**
- **porosity**
- **tortuosity**
- **surface area**





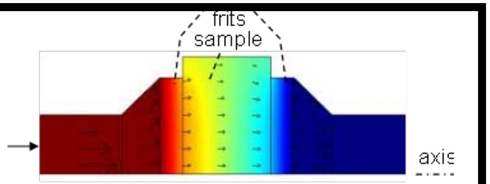
Other tools:
- BET
- XRD, etc

Other properties:
- Densities
- Thermal
- Interface effects

Assemble **permeability** models

Young and Todd* model:

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



Transport FEM

Assemble **chemical-kinetic** models

Alane hydrogen release:

AlH_3 --> Al + $3/2$ H_2

$dAlH_3/dt = - k1 * AlH_3$

$k1 = A * Exp[-Ea/RT]$

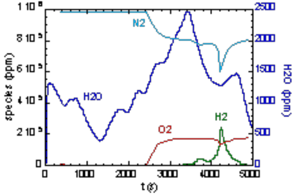
$A = 4.4*10^{22}$

Ea = 200.7 kJ/mole

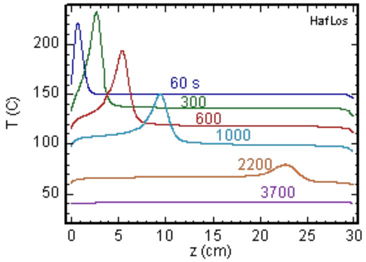
Oxidation of alane:

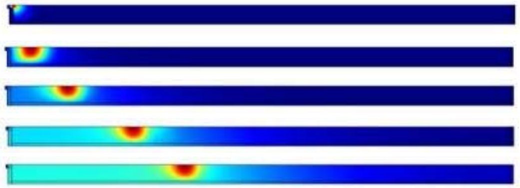
$$\frac{3}{2} O_2 + AlH_3 \rightarrow \frac{1}{2} Al_2O_3 + \frac{3}{2} H_2O$$

$$\frac{d[AlH_3]}{dt} = -3.85e7[O_2][AlH_3]\sqrt{T}\, e^{-1000/T}$$



Couple heat,
mass transfer,
and chemical-kinetic
models





Governing equations of heat and mass transport

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): $\boldsymbol{v} = \phi\boldsymbol{u}$

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

K is the permeability

ϕ is porosity

Energy transport:

$$\left(\rho c_{p}\right)_{m}\frac{\partial T}{\partial t}+\left(\rho c_{p}\right)_{g}\boldsymbol{v}\cdot\nabla T=k_{m}\nabla^{2}T+R\Delta H$$

Species transport:

$$\frac{\partial c_{i}}{\partial t}+\nabla\cdot\left(v_{i}c_{i}\right)=R_{i}$$

Exchange of mass between gas and solid phases

Mass continuity:

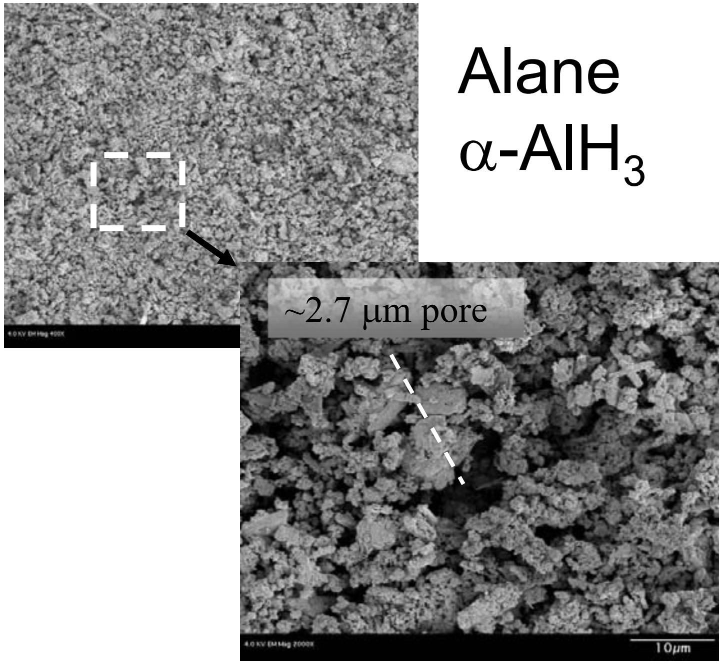
$$\frac{\partial\rho}{\partial t}+\nabla\cdot\left(\rho v\right)=MR$$

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

- Permeability definition: $$K = \frac{\mu v}{dp/dx}$$
- The ‘Ergun’ model is frequently used: $$K = \frac{\phi^3 d_{particle}^2}{150(1-\phi)^2}$$
- We use a model by Young&Todd that includes **Knudsen number** effects due to the small particle and pore sizes that characterize some materials:

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

- Caveats:
  - Hydride beds have a distribution of pore sizes, d_p
  - Tortuosity, τ, is very difficult to measure

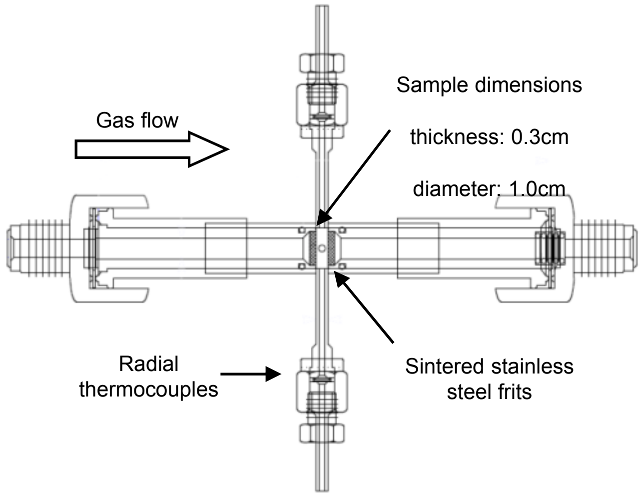


Alane
α-AlH_3

Material	ϕ	d_p(µm)
Alane	0 .68-0.81	1.6 - 3
Activated Carbon	0.5	3.1
Amino Borane	0.389	3.8

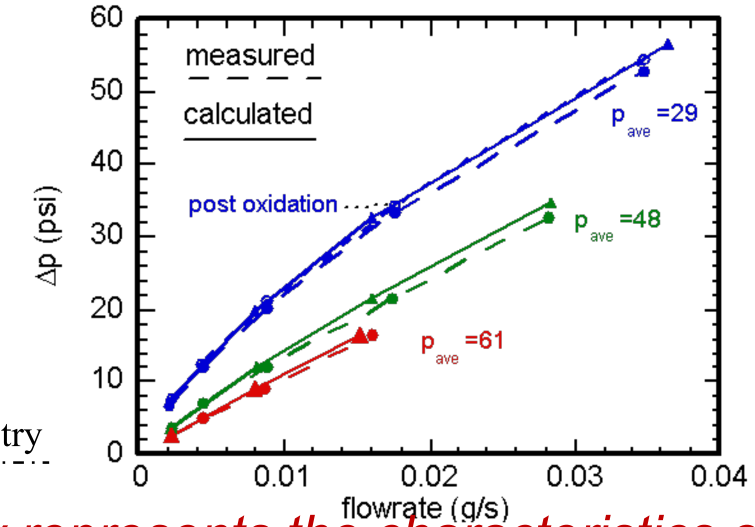
Permeability model parameter determination

Flow-through sample holder



End view of 100mg alane bed

Comparison of data to simulation

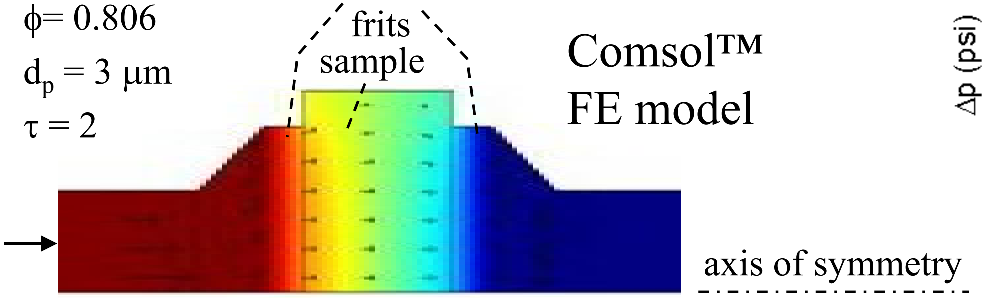


Permeability model parameters:

$\phi = 0.806$

$d_p = 3\ \mu m$

$\tau = 2$



Comsol™ FE model

The Young and Todd model accurately represents the characteristics of flow through metal hydride beds.

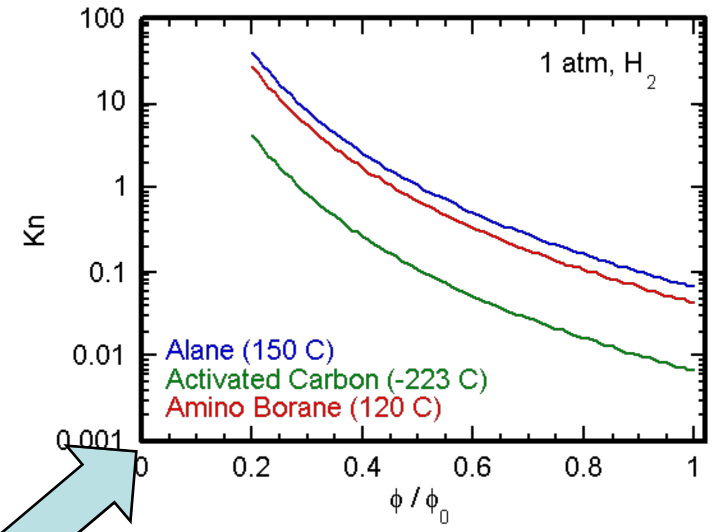
Permeability model is generally applicable to a variety of hydrogen materials

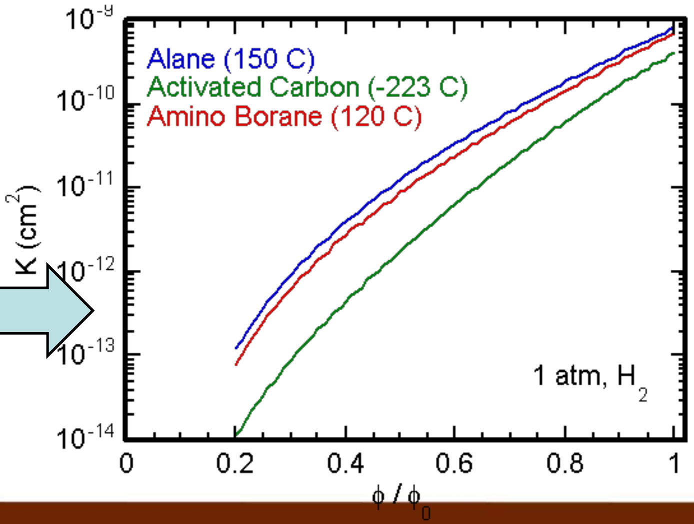
Permeability models were assembled for 3 different packed beds:

1. Alane (BNL)
2. Ammonia borane (PNNL)
3. Activated carbon (Caltech/UTRQ)

Models were extended to other bed densities:

- The relationship of pore size to porosity was empirically derived:
  $d_p = d_{p0}(\phi/\phi_0)^4$
- Wide range of Knudsen numbers represent flow for all relevant porosities and temperatures
- A high solid fraction can lead to a *several* orders of magnitude reduction in permeability





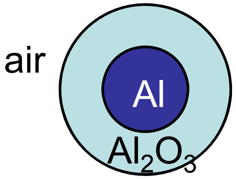
Alane oxidation *chemical kinetics* and *thermal conductivity* models

***Chemical kinetics** (presented at AMR and August Tech Team meeting)*

Modified shrinking-core model (Larson)

O_2 dissociates and dissolves at outer surface:

$$O_2 \Leftrightarrow 2\,O(s)$$



Dissolved oxygen diffuses through oxide layer

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

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

Al is the bulk Al concentration and β and *k* are temperature-dependent constants.

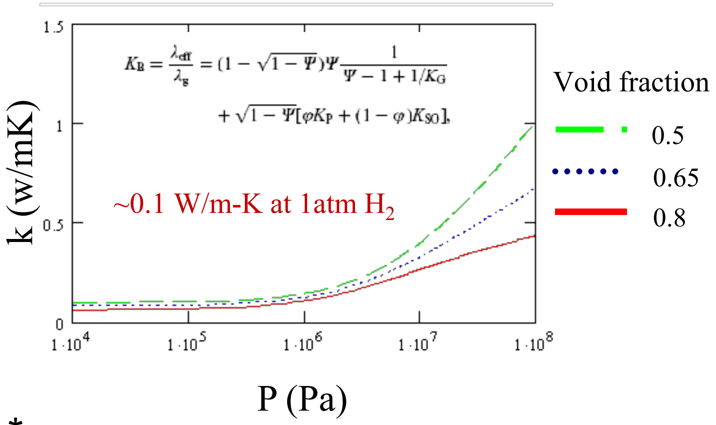
Thermal Conductivity

Model developed by Zehner, Bauer, and Schlünder and adapted by Rodriquez-Sanchez)*

Thermal conductivity is a function of:

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

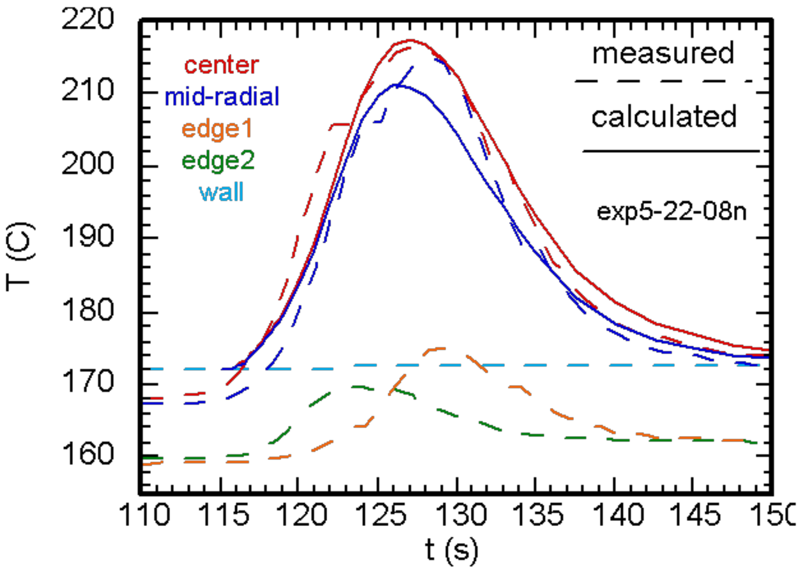
Direct thermal properties measurement of alane is in progress (collaboration with Purdue)

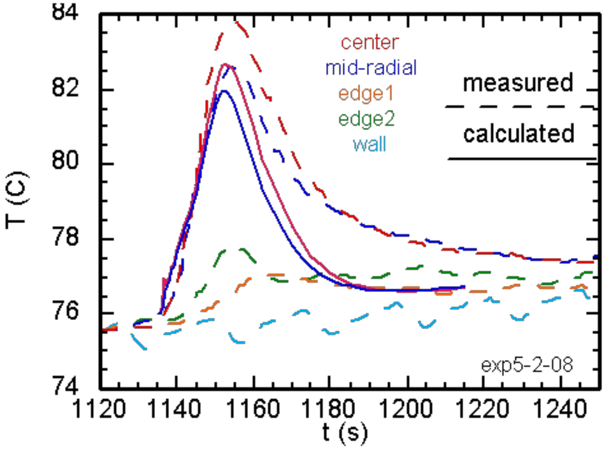


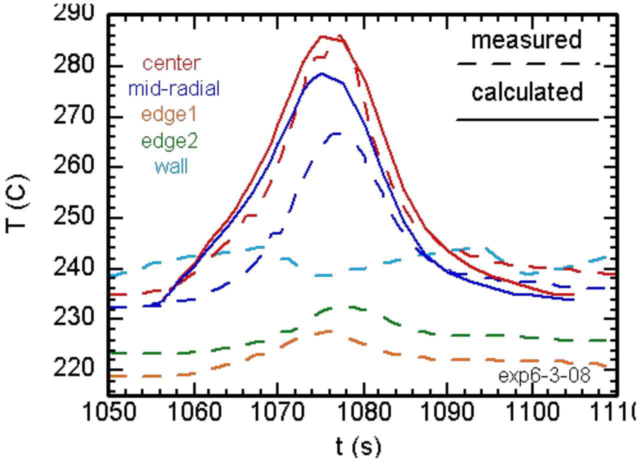
* Rodriguez Sanchez et al. International Journal of Hydrogen Energy 28 (2003) 515 – 527

A robust set of chemical kinetics parameters determined experimentally

Exotherms resulting from exposure of 100mg beds to dry air







Larson kinetics model:

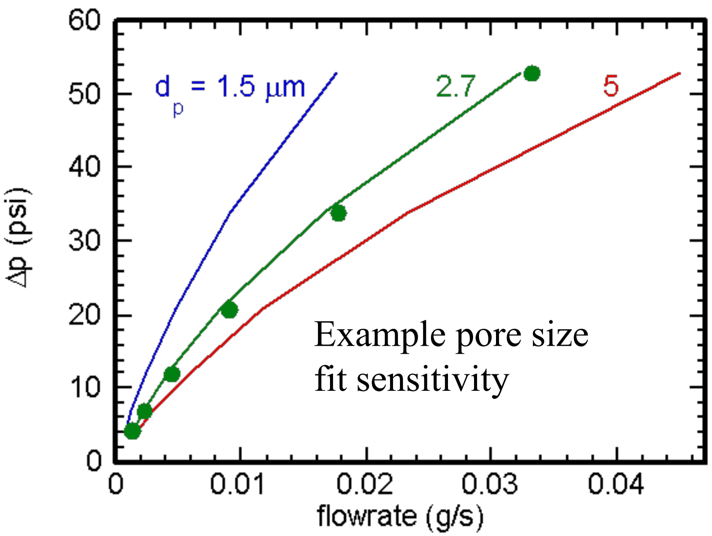
$$\frac{d[Al]}{dt} = -\frac{6(1-\phi)\sqrt{Kp}\,k_0 e^{-Q/RT}}{D}\left[1-\frac{2+\alpha D k_1 e^{Q1/RT}}{6}\left(1-\frac{[Al]}{[Al]_0}\right)\right]$$

Parameters:

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

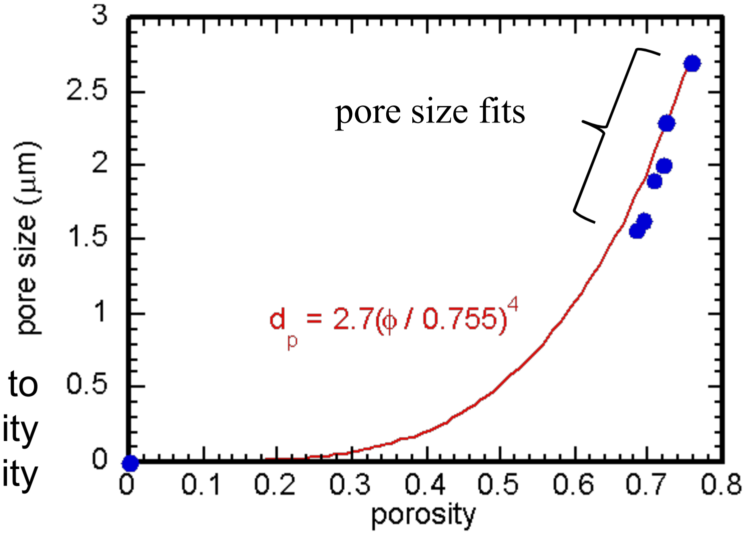
$$Q1 = 1.66e11, \quad \alpha = 1, \quad D = 150nm, \quad R = 8.315e7$$

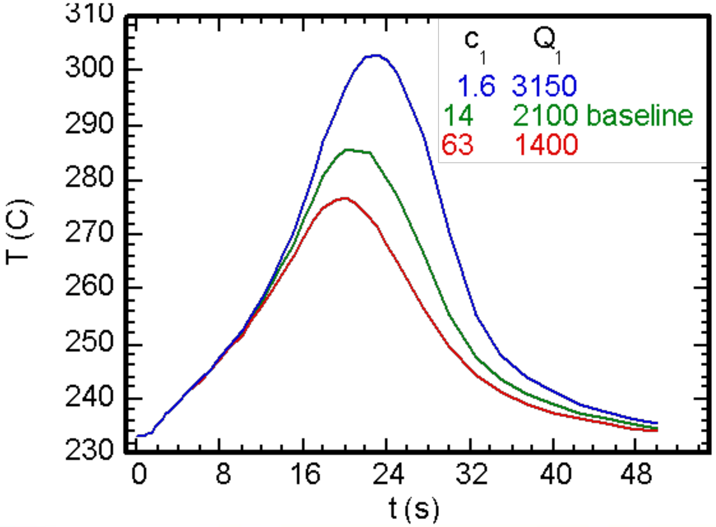
Model sensitivity studies indicate that thermal conductivity uncertainty is highly influential



Pore size fit shows good sensitivity…

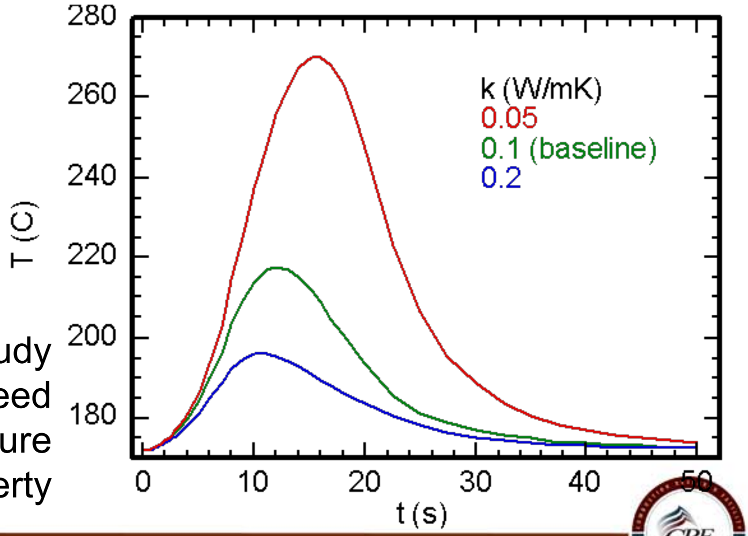
…and correlates well to experimental variability in porosity





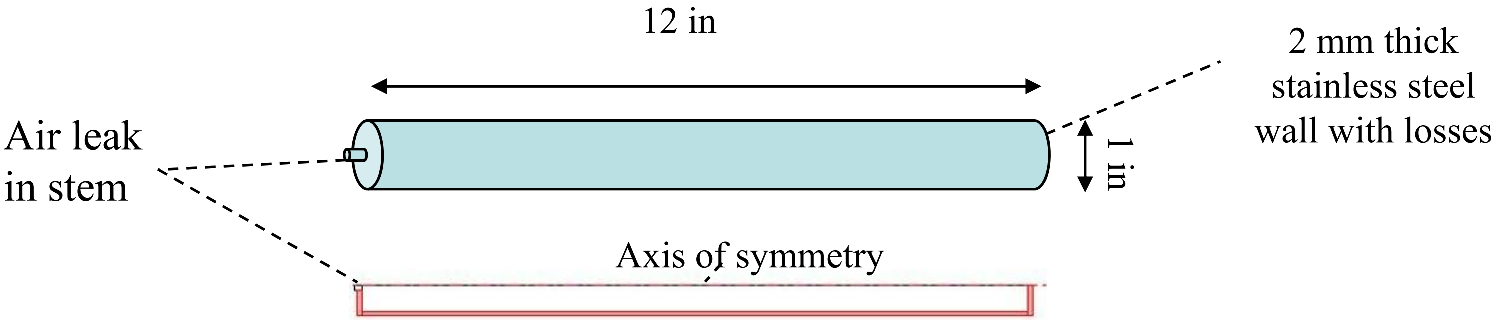
Chemical kinetics fit results in a set of parameters with sensitivity to both the *amplitude* and *shape* of the exotherm…

…Kth sensitivity study indicates that we need to accurately measure this property



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

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



Model description:
- Axisymmetric (Comsol™ framework)
- R. Larson chemical kinetics
- Young and Todd permeability model
- Advection and diffusion

Breach in tank (worst case):
- Empty bed – no H_2 evolution
- Bed at 150 °C and $\Delta P = 0$
- Air leak at stem
- Diffusion/advection of air into bed
- Oxidation reaction processes
- Heat loss to the environment

Simulation cases:

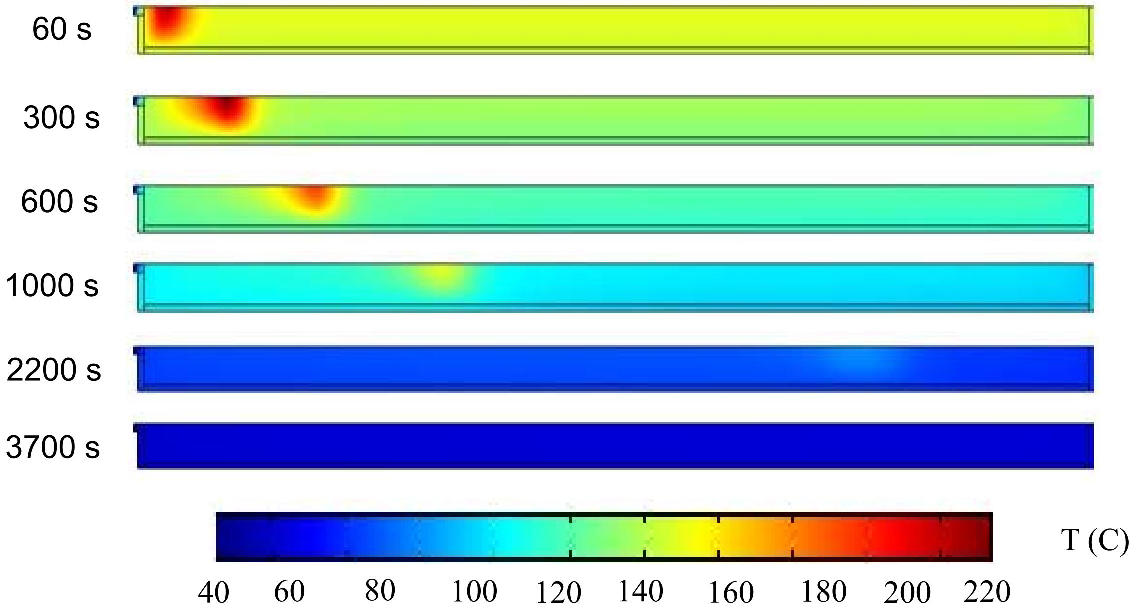
Name	Porosity	Natural convection (W/m2-K)	Radiation ε	Initial Temp. (°C)	Advection
Insulated	0.755	0	0	150	On
Partially Insulated	0.755, 0.5	5.5	0	150	On/Off
Not Insulated	0.755	11	0.3	150	On

Prediction of scaled up contamination event indicate a propagating reaction front

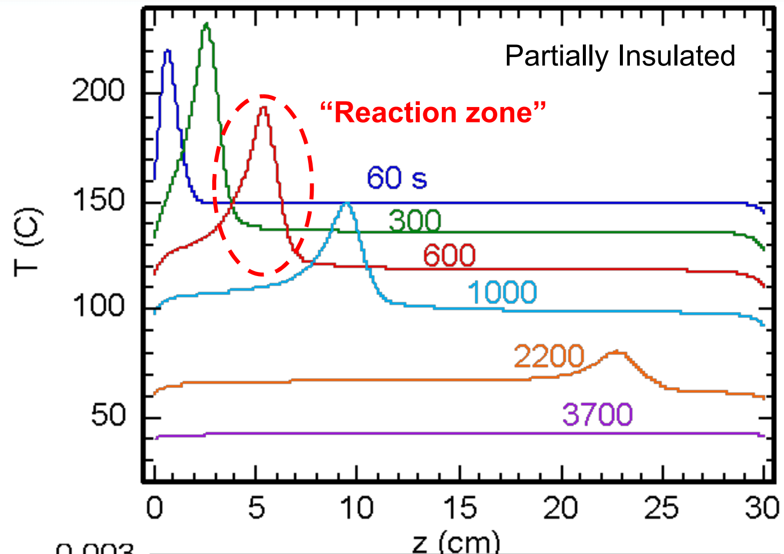
Partially Insulated case:

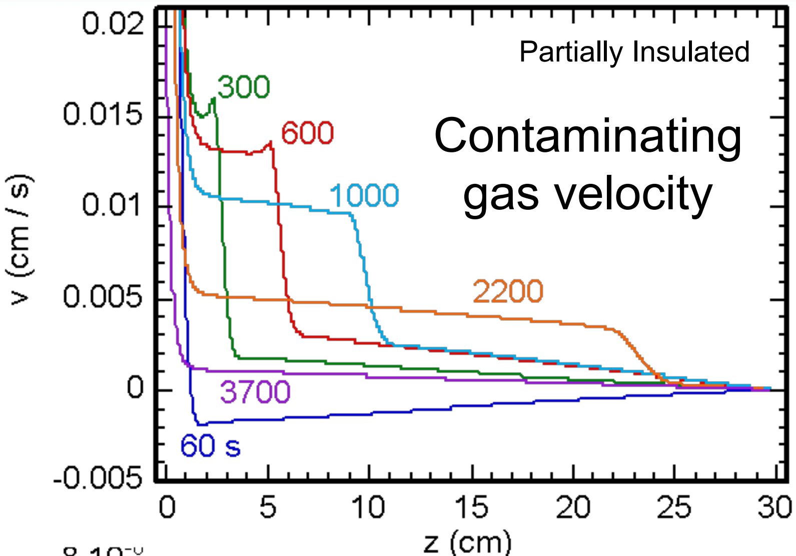
- Bed cools by natural convection (5.5 W/m^2-K)
- A reaction front propagates for over 1 hour

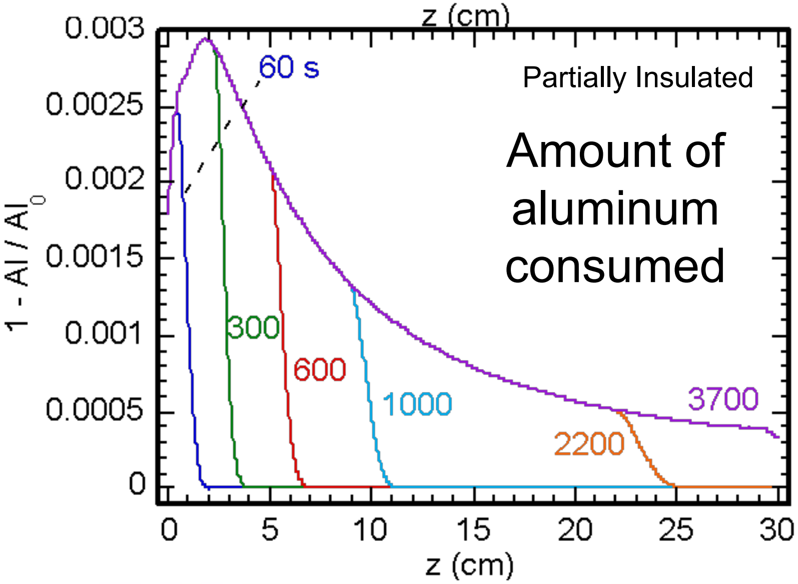
Time-lapse of reaction front propagation:

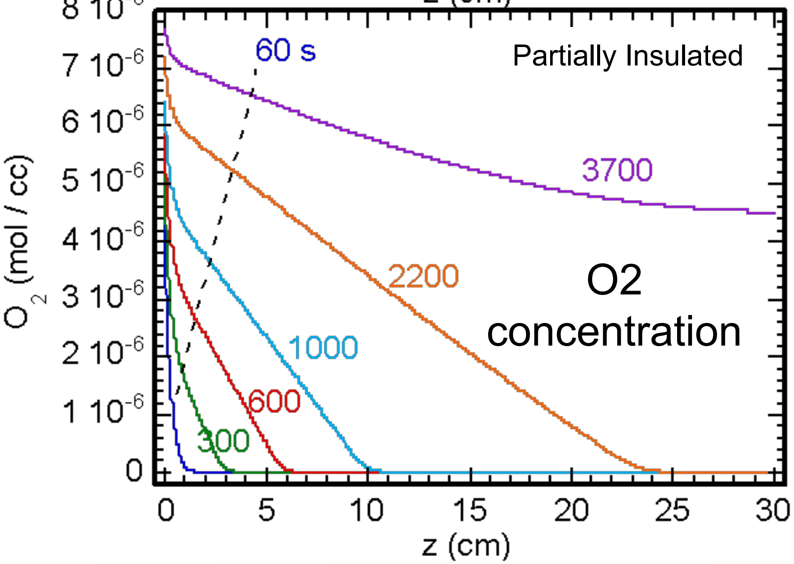


Simulation results indicate self-quenching due to limited oxygen diffusion

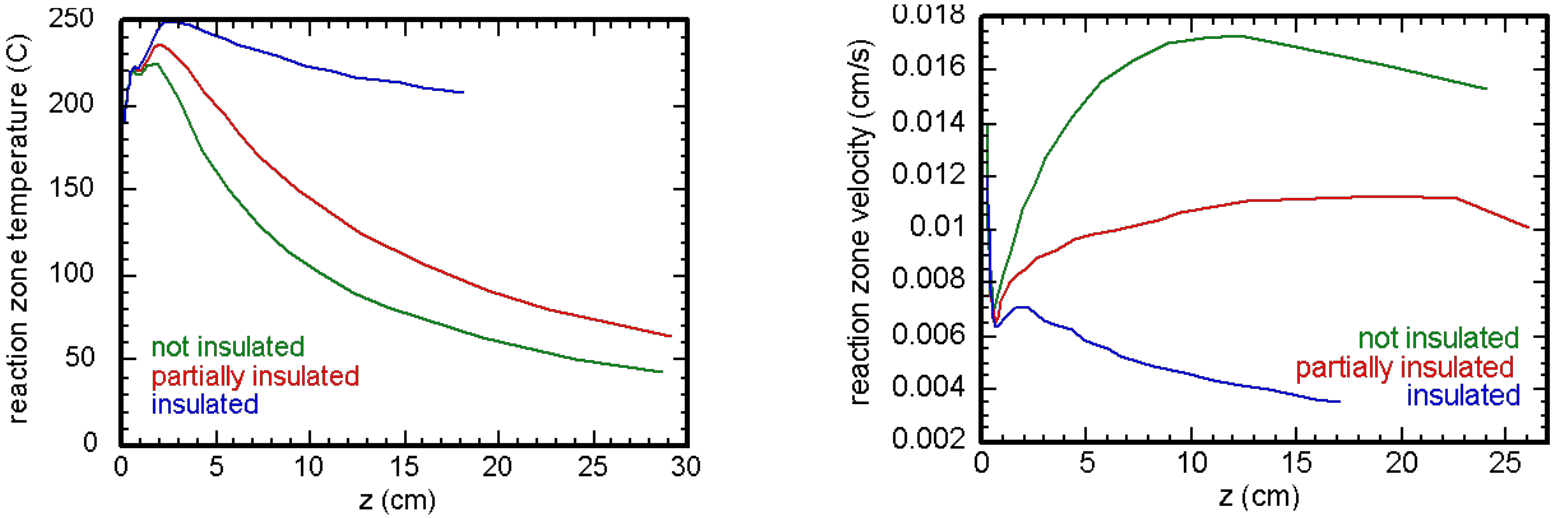




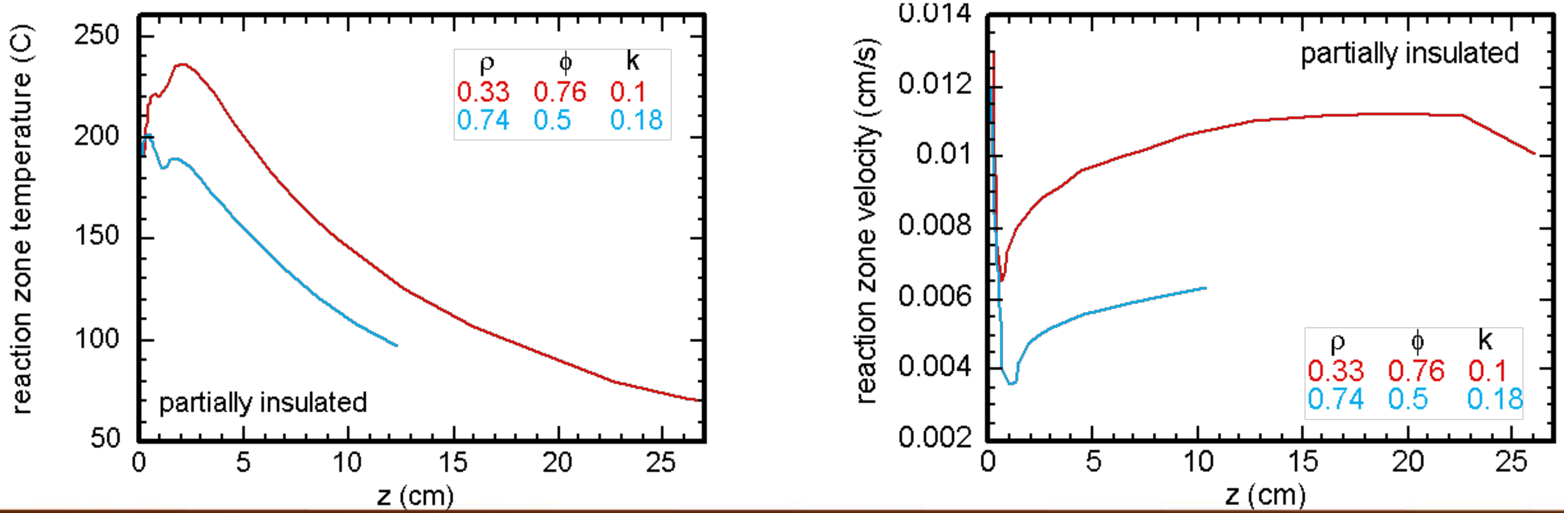




The insulating the system increases the exotherm but slows the reaction front progression



Additionally, higher density impedes the flow of O_2 and slows the reaction front progression



Conclusions resulting from alane system contamination effort

Outcomes to a breach in tank event:

- A propagating reaction front is the result of a breach in tank scenario
- Only moderate temperatures are experienced due to limitation in the oxygen diffusion – situation improves with increasing density!
- Predicted exotherms fall within the relevant range for kinetic parameters
- Little difference is seen between the oxidation of Al vs $AlH_{3.}$ Most likely due to the outer shell of Al only participating in the reaction.
- The introduction of humidity does not impact the reaction processes.

Caveats:

- A de-hydrogenating bed will compete with the contamination process and will be considered in future calculations
- Kinetics unknown as temperatures exceed ~400 °C
- Maximum temperature is highly influenced by thermal conductivity

Mitigation:

- Normally inert components acting to quench reaction front as a fail safe

Approach for hazard *Mitigation* (Task 3) of tank over temperature and failure during contamination

Hazard addressed:

A contamination reaction front propagating though a bed of metal hydride leading to over temperature, fire, vessel failure, release of hydride.

Requirements for mitigation technology:

- *Must* contribute less than 10% to the overall weight and volume of the hydrogen storage system
- *Must not* inhibit hydrogen uptake/release rates or capacity during normal operation
- *Must be* low cost

Approach:

Normally inert components that fail-safe the system by reaction suffocation, and/or fire suppressant deployment

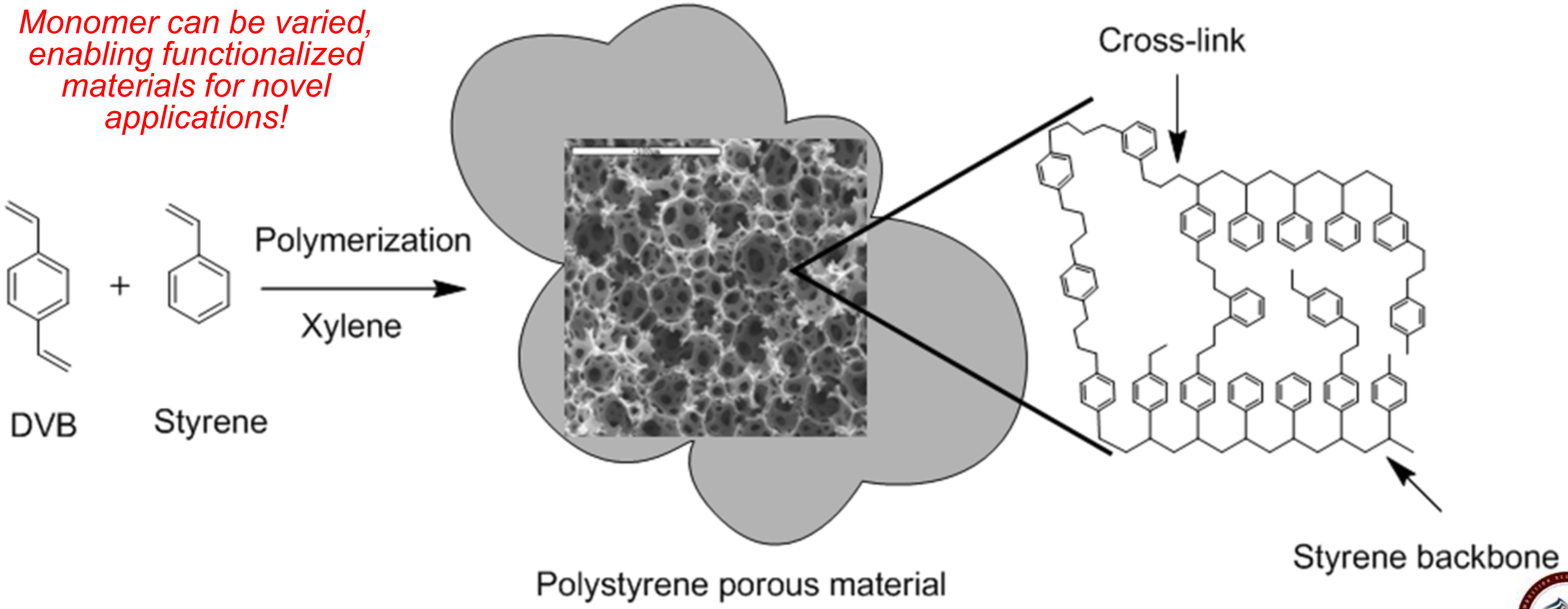
1. Integrated functionalized porous polymers as hydride supports
2. Non-integrated liner or encapsulant

Proof of concept materials:

Sodium alanates, ammonia boranes

Approach #1: Integrated porous polymeric materials as mitigation components

- SNL has developed IP for particle immobilization within a polymer matrix (US Patent 5,866,623)
  - Matrix made via polymerization of an inverse emulsion to furnishes a microporous scaffold
  - Reduction of ionic salts incorporated within pores gave well defined metal hydride particles
- SNL has developed polymer aerogels and xerogels for gas absorption (SAND96-8240)
  - Polymerization of organic gels gives highly cross-linked nanoporous scaffolds
  - Various monomers were selected for mechanical and chemical properties.
  - Density and pore size can be adjusted by changing the concentration of monomers

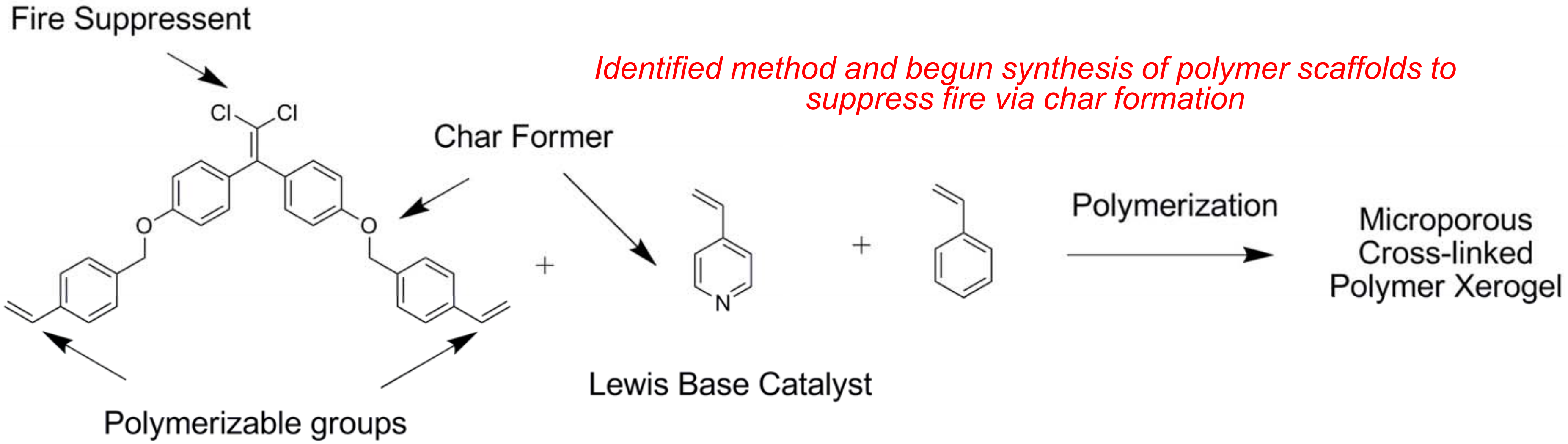


Monomer can be varied, enabling functionalized materials for novel applications!

Proposed tri-functional micro/nano porous polymer (*Challenges*)

- Hazard mitigation via fire suppression
  - Engineered polymer scaffold can suppress fire via char formation - *must select or synthesize new monomers*
- Scaffolding to immobilize bed and inhibit particle sintering
  - Low density/high surface area polymer xero/areo-gels – *must demonstrate structural rigidity to withstand extreme environments*
- Modification of hydrogen release/uptake via surface catalysis
  - Lewis basic monomer used in polymer formulation – *select polymers with reactive functional groups that are compatible to polymerization step*

Preliminary work to make xerogels has been initiated in order to prove viability of hydride incorporation and set base-line for hazard mitigate (TGA and high resolution microscopy)



Identified method and begun synthesis of polymer scaffolds to suppress fire via char formation

Approach #2: Mitigation using high melting organics as a liner or bed encapsulant

Contamination reaction quenching using high melting organics that flow when heated above 200 °C to surround the bed

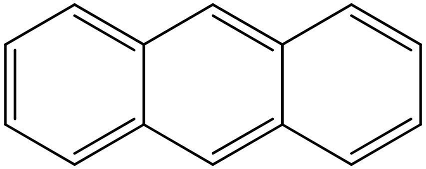
Classes of organics include:

- small molecules
- oligomers
- polymers

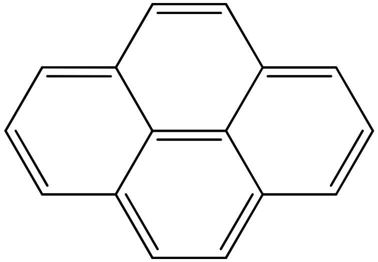
Implementation:

- Single layer between tank containment and bed.
- Plumbing constriction
- Exotherm will melt organic material and allow flow to cut off air access to bed.
- Option to functionalize:
  - halogenated hydrocarbons may be incorporated as fire retardants
  - char forming intumescent materials may be used to form a thick char

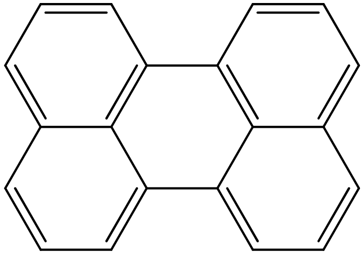
Several possible organics are appropriate for Approach #2



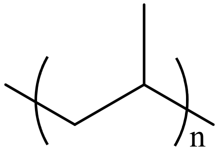
anthracene
Chemical Formula: $C_{14}H_{10}$
Molecular Weight: 178
Melting Point: 210C



pyrene
Chemical Formula: $C_{16}H_{10}$
Molecular Weight: 202
Melting Point: 145C



perylene
Chemical Formula: $C_{20}H_{12}$
Molecular Weight: 252
Melting Point: 276C



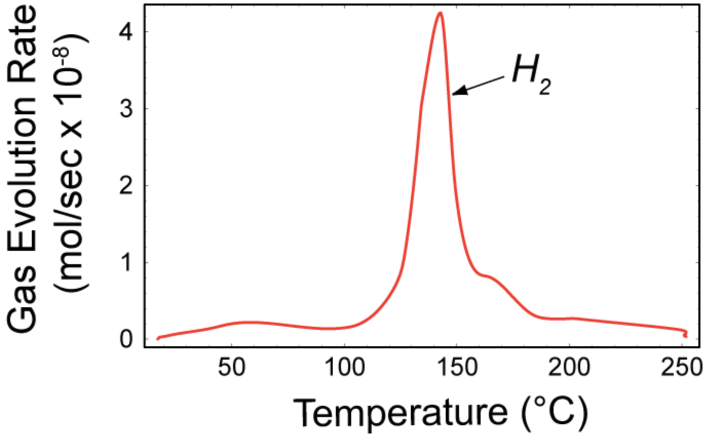
polypropylene
Chemical Formula: C_3H_6
Molecular Weight: 5,000-12,000
Melting Point: 157C

Other options:

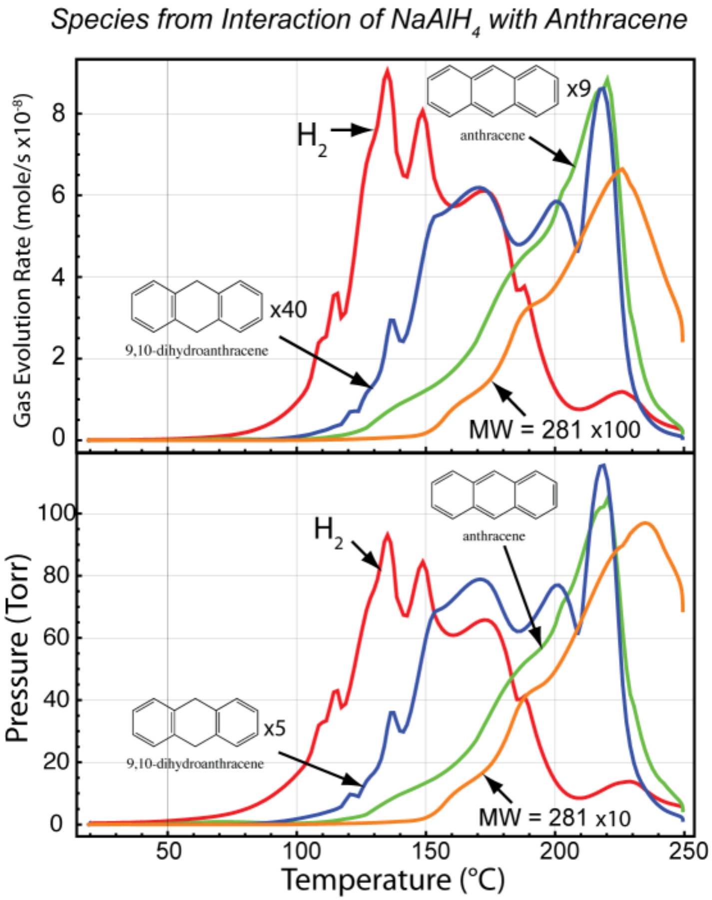
- Polymers are much less expensive (intrinsic value vs market price…)
- Unfortunately, the polymer viscosities will not be as low in the liquid phase
- Fire retardant polypropylene is available with no decrease in melting point

Reaction between anthracene and $NaAlH_4$ shows hydrogenation & change in H_2 evolution

$NaAlH_4$ by itself



Mixture of $NaAlH_4$ with

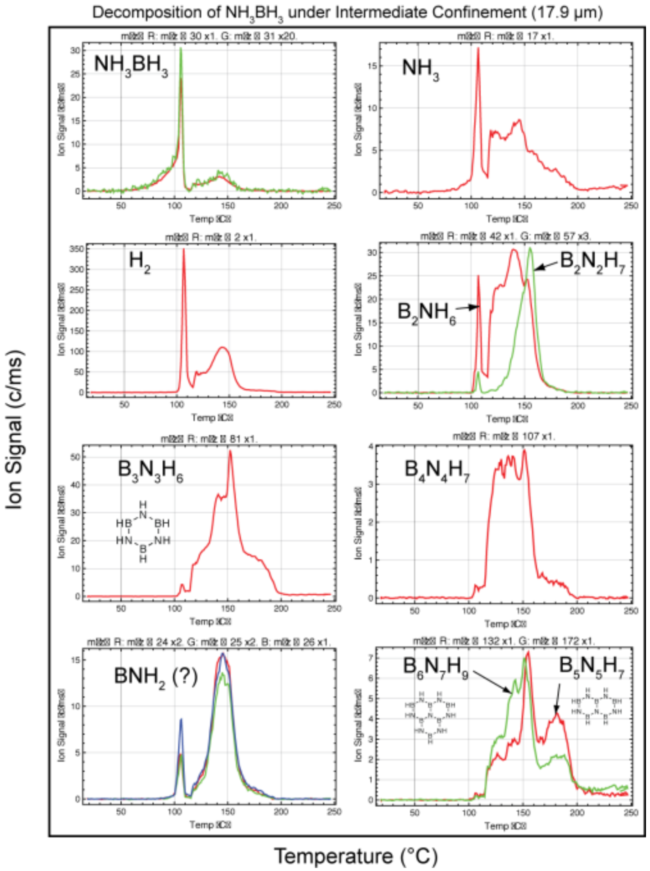

Species from Interaction of $NaAlH_4$ with Anthracene

- Start of H_2 evolution is similar but duration is longer with anthracene
- Hydrogenates anthracene and leads to formation of higher MW products in mixture

Shows promise, but may interact significantly with alanates

New materials: AB decomposition processes illuminated – mobility of reactive species

Ion signals of species evolving from the Knudsen cell mounted in a TG (STMBMS)



Decomposition of NH_3BH_3 under Intermediate Confinement (17.9 μm)

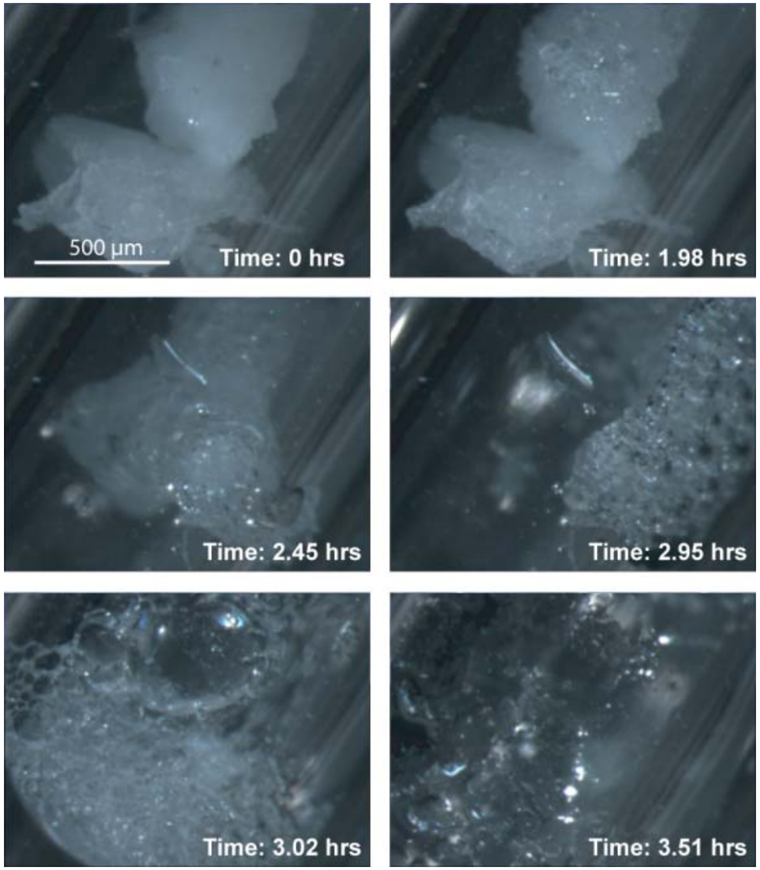
Decomposition process observed at intermediate pressure

1. NH_3BH_3 evolves from the sample
2. Rapid evolution of H_2 from the sample starting at approximately 100°C, accompanied by:
   - A rapid release of NH_3
   - B_2NH_6 species
   - BNH_2 species
     The B_2NH_6 species is consistent with the formation of the –$(NH_2{=}BH_2)_x$- type of polymer formed by the elimination of one mole of H_2 from NH$_3$BH3.
3. Slower evolution of
   - borazine ($B_3N_3H_6$)
   - $B_4N_4H_7$

Evolution of reactive species is highly pressure dependent – at low pressure nearly 50% of the AB sublimes

Indicates a complex reaction mechanism that is dominated by the mobility of reactive species – must be understood to be controlled

Time-lapse images of AB decomposition at 90 °C corroborate the complexity of the process



90 °C Decomposition characteristics:

- Two hour induction period
- Initially, a clear liquid forms and grows on the surface of the particles (t=1.98)
- During the next ~30 minutes, liquid grows and consumes the AB particles (t= 2.45)
- The clear liquid then adheres to the wall of the glass tube and bubbles
- Eventually, gas trapped in the closed end of the tube moves the viscous liquid past the field of view (t= 3.02)

Engineering methods may be useful in inhibiting the transport of boron-containing molecules during decomposition

Work plan for FY09 - FY10

Task 1 – Reaction processes

- Characterization of oxidation reaction processes and chemical kinetics of $2LiH+Mg(NH_2)_2$
- Investigate effectiveness of PNNL additives on controlling release of boron-containing species during AB decomposition
- Quantification of hazards presented by contaminated cycling of sodium alanates

Task 2 – Scaled up predictions

- Scaled up alane breach-in-tank validation (dependent on material availability)
- Determination of transport characteristics of $2LiH+Mg(NH_2)_2$ and couple to chemical kinetics
- Preparation for automotive scale system testing (breach-in-tank and contaminated refueling)

Task 3 – Mitigation

- Identification and synthesis of appropriate functionalized polymer foams for integrated fail-safe and transport engineering
- Identification and synthesis of normally-inert encapsulants for liner fail-safe applications
- Validation of mitigation methods

Continued vision enables eventual technology commercialization

1 year vision (included in deliverables from this project):

- Provide a set of tools to analyze the behavior of new materials within systems, along with developed mitigation approaches.

5 - 10 year vision

- Work closely with the HSECoE to enable design-for-safety
- Validate contamination scenarios and hazard mitigation methods at application appropriate scales.
- Collaborate strongly with the new H_2 materials CoE(s) to develop materials with highly controlled reaction characteristics.
- Provide SDOs with validated science-based analysis to enable the development of functional code and standards

Collaborations

Program made relevant with the help and support of:

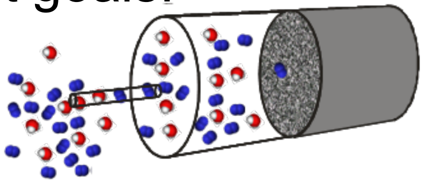
Reactivity Project Partners:	Savannah River NL – D. Anton
	UTRC – D. Mosher
Alanes:	Brookhaven NL – J. Graetz
Ammonia boranes:	Pacific Northwest NL – T. Autrey
Activated carbons:	Caltech – C. Anh
	UTRQ – R. Chanine
$2LiH+Mg(NH_2)_2$:	IPHE Partners
Borohydrides:	Sandia NL – J. Cordaro
	HRL – J. Vajo
Properties Measurement:	Purdue – T. Pourpoint

Summary

The following progress has been made towards our project goals:

- We have **identified hazards** associated with the utilization of reactive H2 materials in systems

  breach in tank, oxidation reaction process

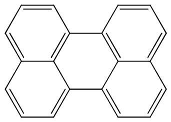


- Using alane as a demonstration, we have assembled **validated models** and have made scaled-up **predictions** of the breach in tank process

  contamination reaction front propagating though a bed

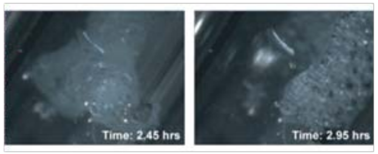
- We have identified **mitigation approaches** that will be developed to enable inerting of the hazard

  fail-safe foams and liners



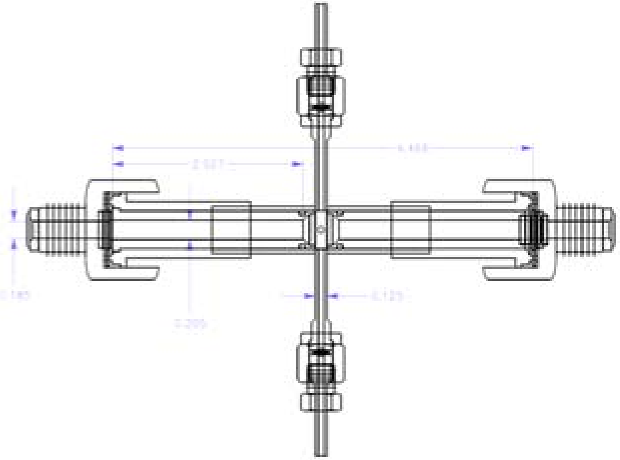
perylene
Chemical Formula: $C_{20}H_{12}$
Molecular Weight: 252
Melting Point: 276C
$2,000/Kg

- We continue to form **new partnerships** with developers of H2 storage materials, and look forward to an enduring contribution to the commercialization path.

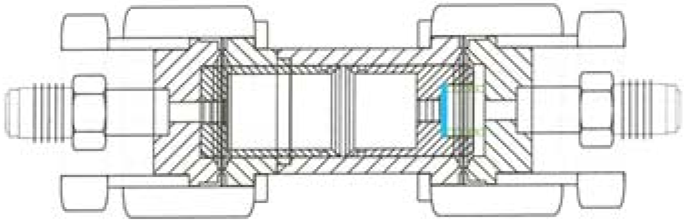


SUPPLEMENTAL SLIDES

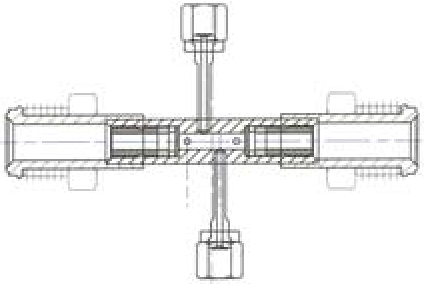
A variety of bed geometries have been assembled to ensure robustness of model parameters



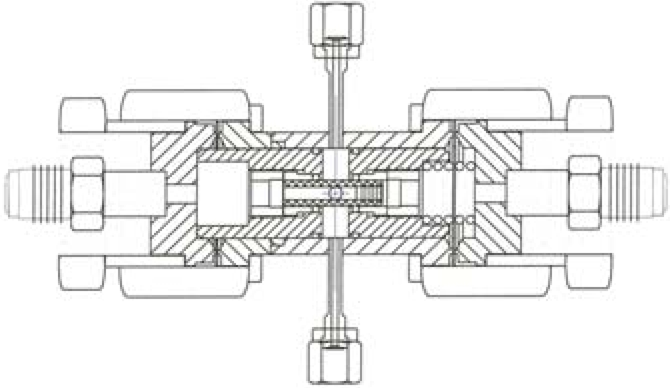
Standard sample: 3mm by 10mm



Short aspect: 2mm by 20mm



Long aspect: 12mm by 3mm

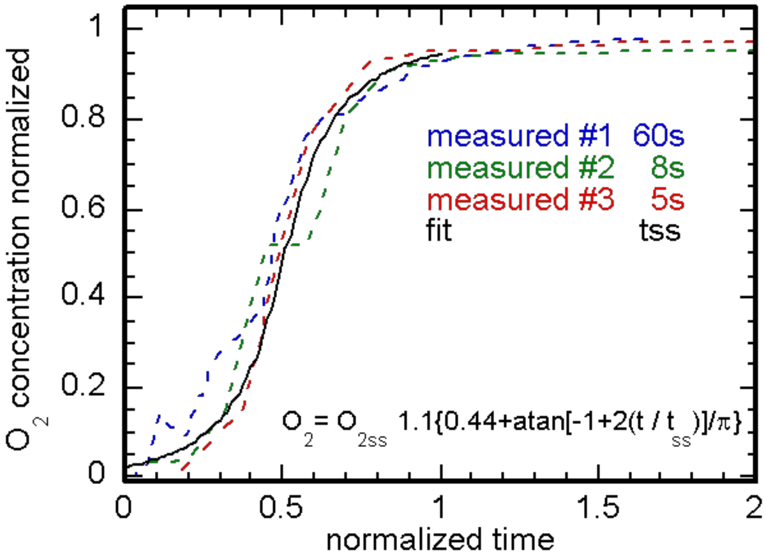


Diffusion only: dead-end annulus

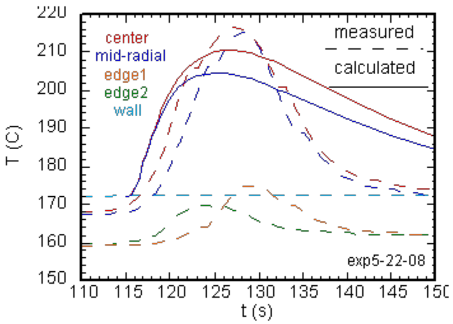
Gradual oxygen rise lead to a poor parameter fit in previous results

Measurements show that the oxygen concentration can rises slowly – rather than a step-function as modeled previously

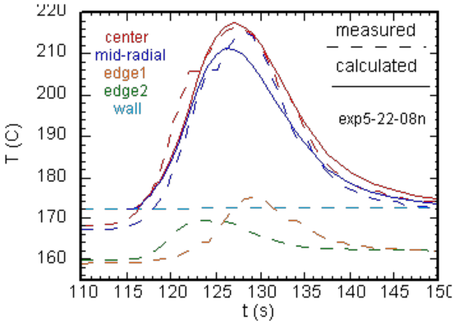
- This shape is well fitted by an ArcTan function that parameterizes the rise rate and steady oxygen concentration
- This function was used in the model to accurately simulate the oxygen conditions to which the alane samples were exposed



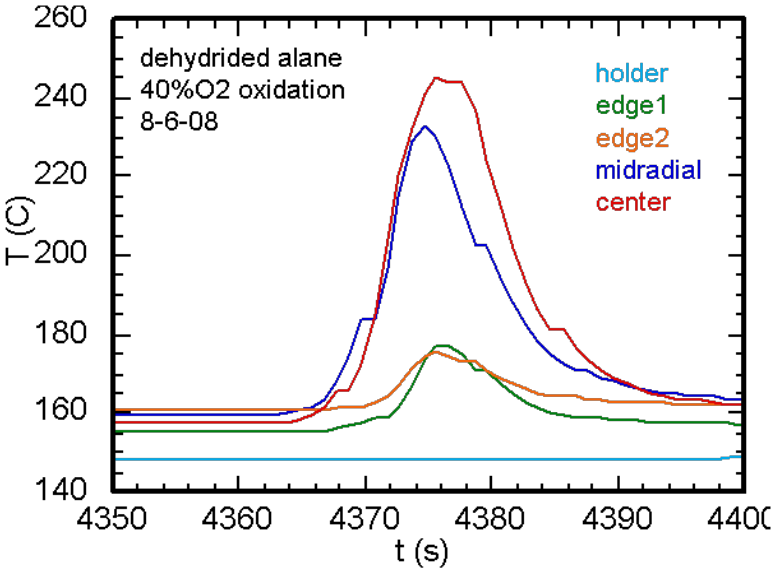
Step-function

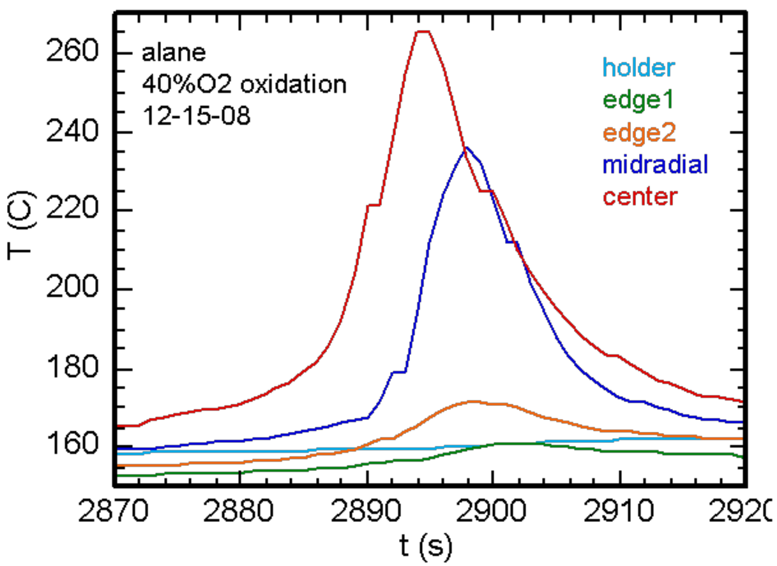


ArcTan function



Comparison of oxidation of Al vs AlH_3





Details on the kinetic parameter study