Project ID #ST42

Chemical and Environmental Reactivity Properties of Hydrogen Storage Materials within the Context of Systems

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Friday, June 13th, 2008

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Overview

Timeline

- Start: July 2007
- End: September 2010
- Percent complete: 30%

Barriers

On-Board Hydrogen Storage

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

Budget

- $2.1M (DOE H2 program)
- FY07 Funding: 300K
- FY08 Funding: 600K

Partners/collaborators

- SRNL - Anton
- UTRC - Mosher
- IPHE Safety
- BNL – Graetz
- PNNL – Autrey
- SNL - Ronnebro

Team members and capabilities:	
Rich Behrens - Physical Chemist **Rich Larson** – Chemical Engineer **Bob Bradshaw** – Chem Engineer	**Ken Stewart** – Laboratory systems **Mike Kanouff** – Num. analyst **Greg Evans** – Multiphase flow

Overall Objective:

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

Eventual Impact:

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

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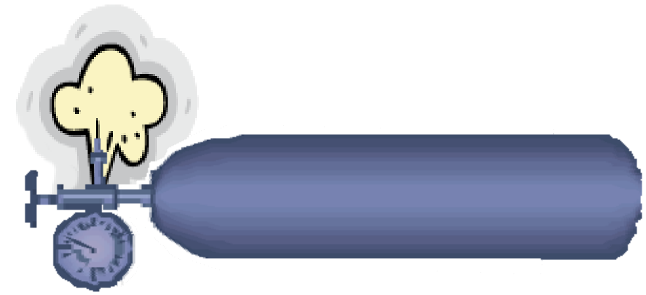
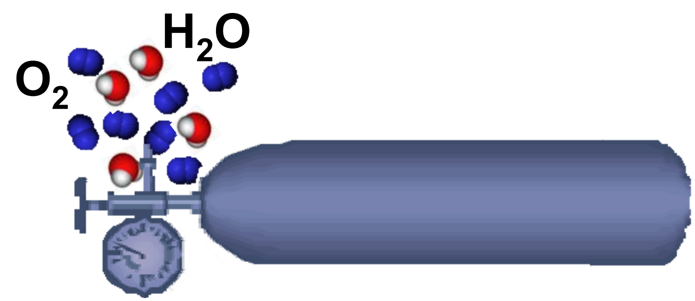
Approach: Credible contamination scenarios considered based on NFPA, ISO and SAE draft language

- Breach in tank/plumbing
  - Release of hydrogen plume
  - Entrainment of reactive powders
- Entrance of air/moisture through breach
  - Thermal run-away, fire
  - Formation of hazardous reaction products
- Contaminated refueling (ISO and SAE)
  - High concentration contamination
  - Low concentration life-cycle contamination
- Mitigation of hazard
  - Treatment of contaminated bed
  - Use of fire suppression chemicals





Plan: Project organized into four tasks to address each of these contamination scenarios

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 by developing validated multi-dimensional multi-physics models. (***UTRC***)

- Extends process predictive capability to the application scale

Task 3 - Quantify implications of low-level life-cycle contamination. (***MHCoE***)

- Identifies handling and operability hazards of reaction products formed

Task 4 - Identify and demonstrate hazard mitigation strategies that are appropriate for a broad spectrum of hydrogen storage materials. (***UTRC***)

- Identify contaminated bed treatment methods
- Assess the fundamental usefulness of fire suppressant chemicals

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

Milestones and go/no-go's

Quantify contamination chemical processes and hazards (Phase I)	
Identify materials for FY08 new materials efforts in coordination with SRNL, UTRC, IPHE partners, DOE CoEs and independent projects	11/07
Go/No-Go:Each method identified will be analyzed to verify applicability to hydrogen storage materials in general	
Predict chemical process hazards during accident scenarios	
Design/build macro-scale model validation hardware	
Identify tools required to accurately perform reactive dust cloud modeling.	6/08
Go/No-Go: Analyze modeled accident processes to determine relevance to end-use scenarios (e.g. accidents resulting in reactive dust clouds)	
Quantify low-level contamination effects on reactivity and performance	
Design, build, and procure contamination manifold	10/07
Complete parallel contamination sorption testing on sodium alanates or other appropriate complex hydride on at least 2 samples.	5/08
Go/No-Go: Determine if hazard exists due to low-level contamination exposure.	
Identify and demonstrate hazard mitigation strategies	
Quantify chemical properties changes caused by CO_2 treatment of two alkali-metal containing sorption materials technologies.	6/08
Go/No-Go: Discontinue CO_2 treatment research if method is inappropriate for new materials.	

Task 1 - Quantify fundamental processes and hazards of contamination reactions

Accomplishments:

- New methods developed to quantify reaction processes and kinetics between hydrogen storage materials and oxygen and water
- Contamination reaction processes of alane (α-AlH_3) investigated at a variety of scales
- Three new materials under investigation, amino boranes, calcium borohydride, Li-B-Mg systems (see additional slides section)
- Contamination Sieverts apparatus assembled to produce samples for analysis

The STMBMS* is an appropriate tool to help quantify complex reaction processes

* Simultaneous thermo-gravimetric modulated-beam mass spectrometer

This is an instrument used for measuring thermodynamic properties of molecules and studying reaction kinetics of complex systems

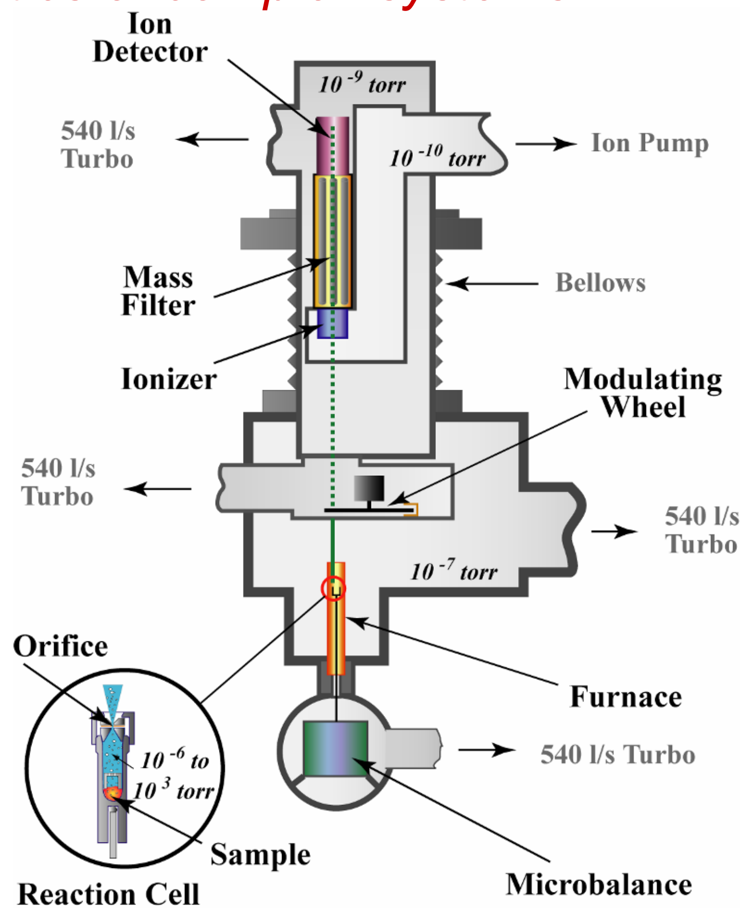
Instrument details:

- Knudsen effusion cell installed within a furnace and upon a microbalance
- Simultaneous modulated molecular beam mass spectrometer provides time-dependent species info
- High accuracy FTMS for species identification

Data from each of these components is correlated and analyzed to determine reaction processes and kinetics

Two types of experiments:

- Decomposition operation: The instrument is used to characterize content and kinetics of oxidized, un-oxidized, and treated materials
- Contamination study operation: materials that evolve oxygen or water are placed in the reaction cell in combination with the hydride materials of interest

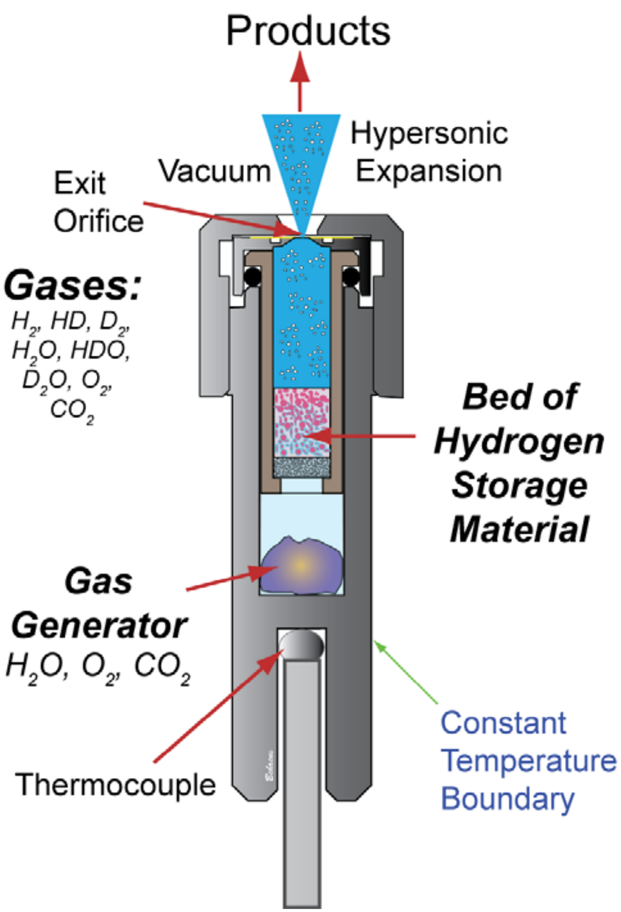


[1] Behrens, R., Jr., Review of Scientific Instruments, 1987. **58**(3): p. 451-461

[2] Lee, Y.T. et al, Review of Scientific Instruments, 1969. 40(11): P. 1402 - 1408

New methods have been developed to quantify reactions with O_2 and H_2O vapor

New Flow Cell:



Relevance: New reaction cell allows us to understand the fundamental reaction processes between materials and contaminants (Task 1)

Method: Materials that evolve oxygen or water are placed in the reaction cell in combination with the hydride materials of interest

For water vapor exposure:
3Å Mol sieve (loaded with H_2O or D_2O)

For water and CO_2 exposure:
Sodium bicarbonate (labeled with hydrogen or deuterium)
$2\ NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O\ (g) + CO_2(g)$

For O_2 exposure:
Silver (II) oxide
$2\ AgO \rightarrow Ag_2O + 1/2\ O_2$

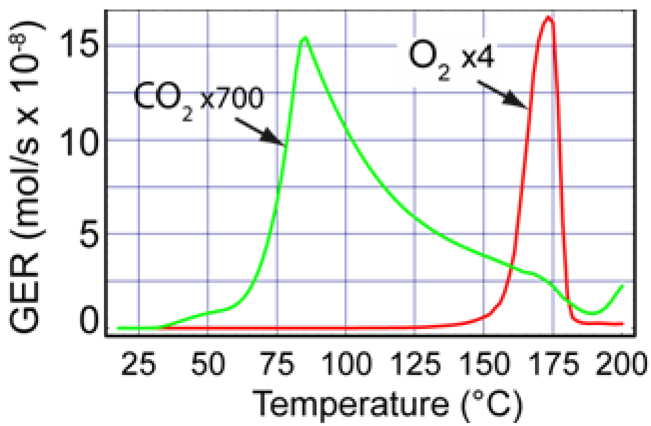
Methods validated using alanates (See additional slides!)

Silver (II) Oxide (AgO) utilized to expose sample to O_2 and quantify reactions

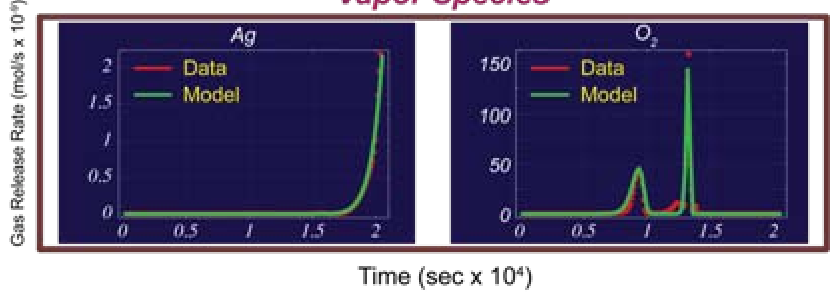
Decomposition provides source of O_2

- $2\ AgO \rightarrow Ag_2O + ½\ O_2$ 75 to 180°C.
- $Ag_2O \rightarrow 2\ Ag(s) + ½\ O_2$ 300 to 410°C
- $Ag(s) \rightarrow Ag(g)$ >700°C.

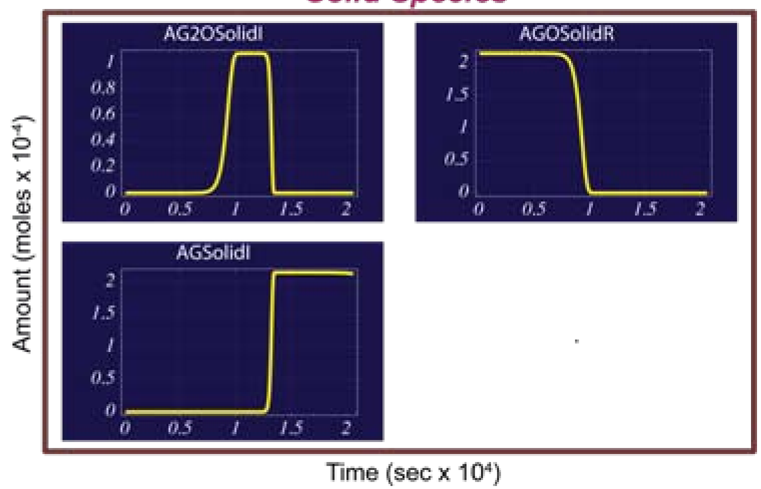
Lower temperature region



Vapor Species



Solid Species



AgO Reactions and Rate Expressions

Reaction	Rate expression	ΔH (kJ/mol)	A	Ea (kJ/mol)	A	B	ΔHs(kJ/mol)
$2AgO \rightarrow Ag_2O + 1/2\ O_2$	$dAgO/dt = -k1 * AgO$	-7.15	1.78E+22	215.2			
Ag_2O -- $2Ag + 1/2\ O_2$	$dAg_2O/dt = -k2 * Ag_2O$	30.9	2.17E+25	348.6			
Ag(s) --> Ag(g)	Log10(P) = A -B/T(K) P in Pascals (n/m²)				6.4444	9555.6	182.9

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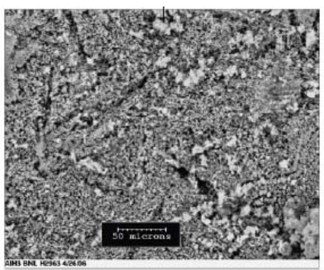
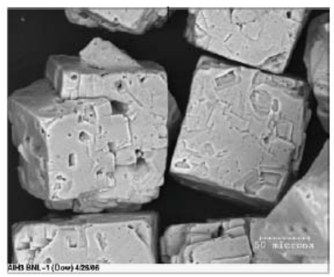
Baseline decomposition studies illuminate reaction processes in the absence of contamination

α-phase alanes (BNL) are the focus of the current contamination studies

α-AlH3→ Al + 3/2H2



α-AlH_3 (BNL) 100-200 nm



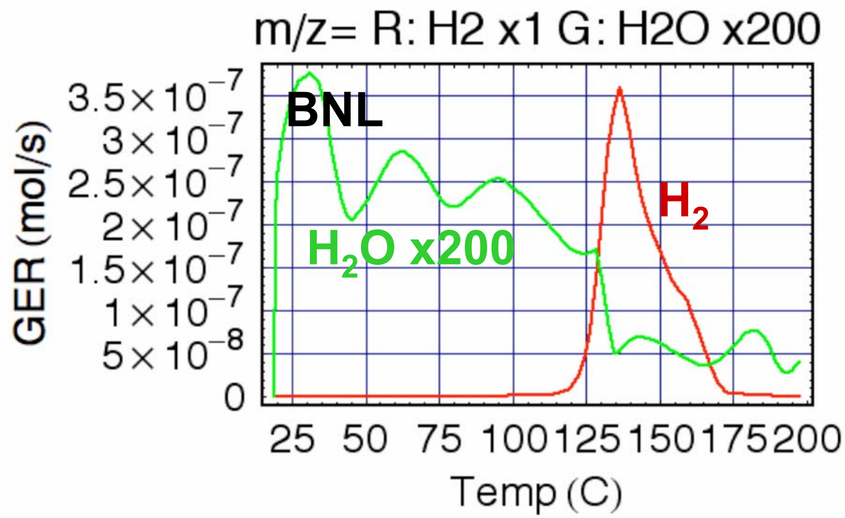
α-AlH_3 (Dow) 50-100μm

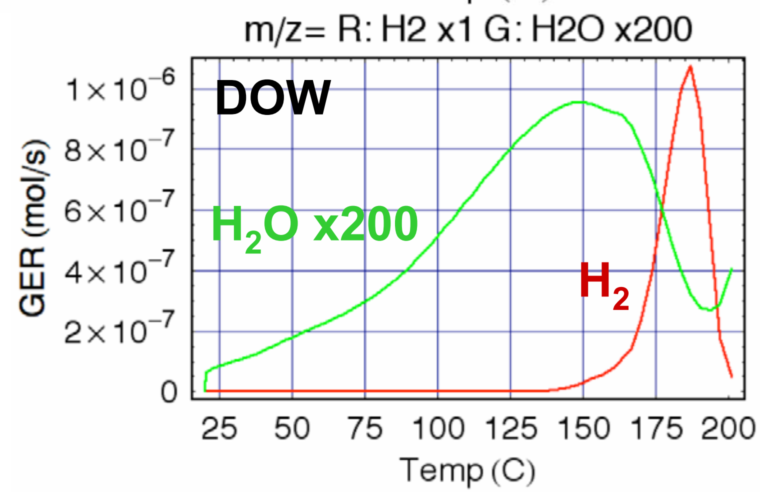
Alane testing:

- Baseline decompositions of BNL and DOW materials
- Reactions with oxygen
- Reactions with water vapor (H_2O or D_2O)

Results help define:

- kinetics models of decomposition processes (See appendix)
- kinetics models of contamination processes

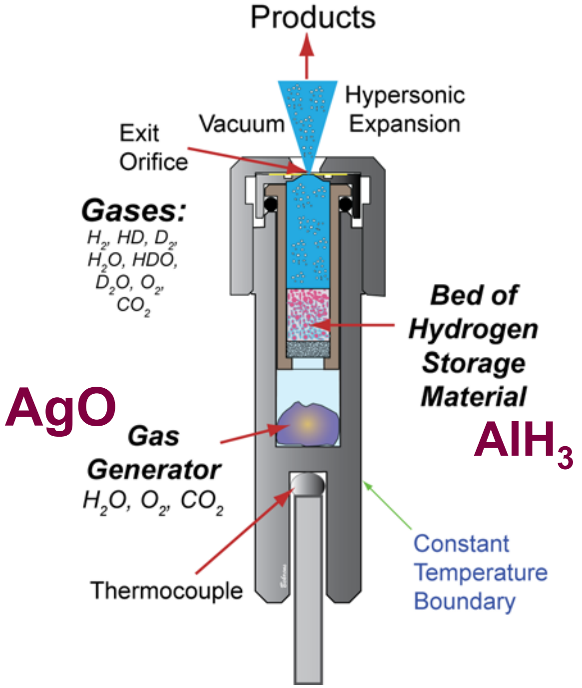




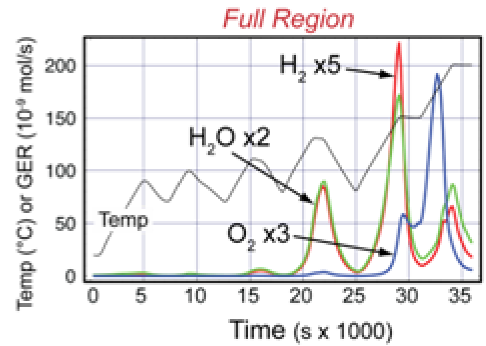
Materials supplied by BNL (Graetz)

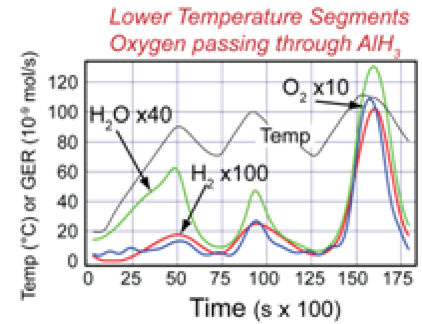
Contamination of a AlH_3 bed with O_2 at moderate temperature results in dehydrogenation, production of water and partial oxidation of the aluminum surface

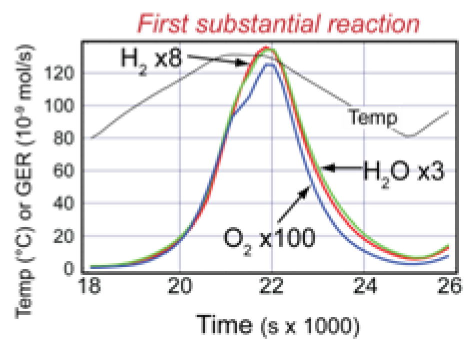
- O_2 formed from AgO passes through bed of AlH_3.
- Provides data needed to develop model of reaction kinetics.

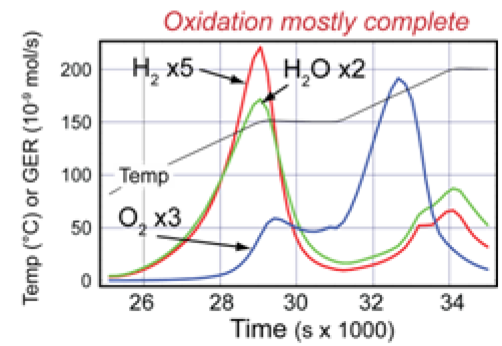


Data collected under relatively high confinement (exit orifice diameter = 40μm)









~10% of the original hydrogen remains in the sample,
2/3 as H_2O (aluminum hydroxide)
1/3 remains in the form of AlH_3

Previous work on the oxidation of alane at moderate temperatures is nonexistent, so even the reaction products were unknown.

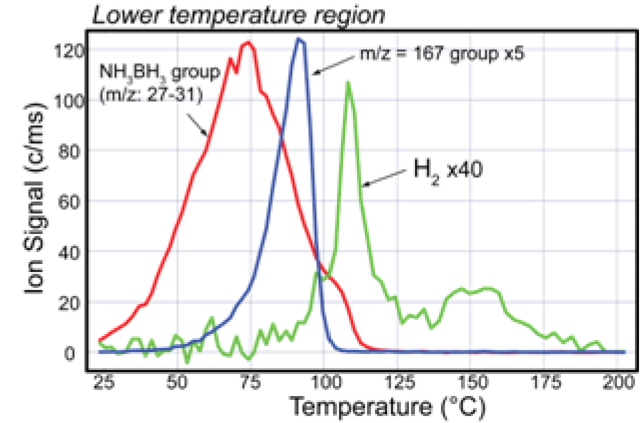
High-temperature: Weiser et al., "On the Oxidation and Combustion of AlH3 a Potential Fuel for Rocket Propellants and Gas Generators", *Propellants, Explosives, Pyrotechnics* 32, No. 3 (2007)

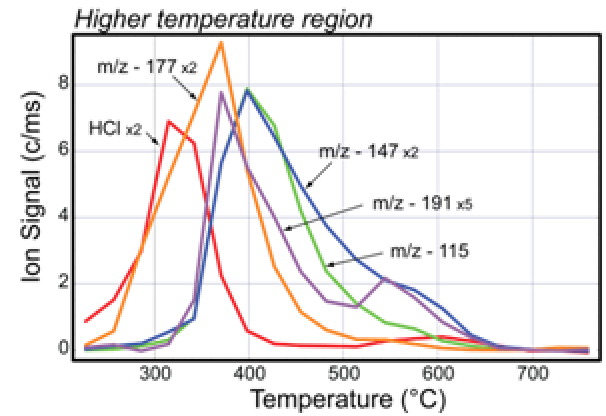
Amino borane studies demonstrate new approach to determine complex reaction processes

NH_3BH_3 procured from PNNL (Autrey)

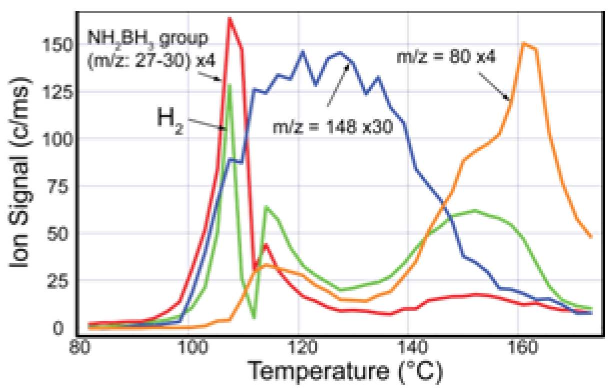
- Formation of H_2 results from set of complex reaction processes.
- The sequence of reactions leading to H_2 can be investigated in both gas and condensed phases.
- Potential to provide new insight into how to design reactors with NH_3BH_3 type compounds.
  - Can probe catalyzed reactions.

Results under lower confinement show condensed phase processes





Results under higher confinement show sequence needed to determine reaction pathways



Formulas for m/z values are currently being determined with high resolution FTICR mass spec measurements

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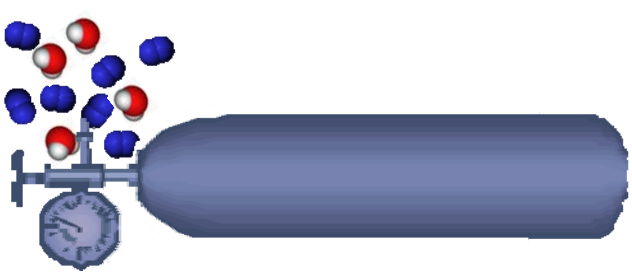
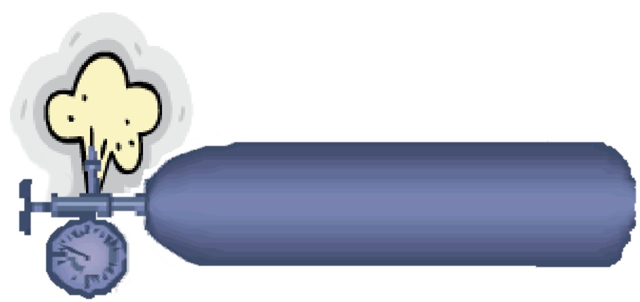
Predict processes during accident scenarios

Accomplishments:

- Assembled flow-through contamination manifold designed to validate application-scale contamination models
- Transport modeling effort coordinated with initial experiments to quantify flow field in a compacted alane bed.
- Alane bed contaminated with air and analyzed
- Multi-phase flow field prediction performed as a first step towards dust cloud combustion modeling



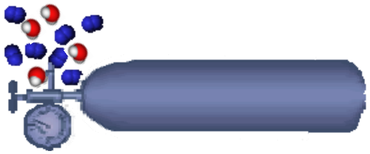


A flow through reactor has been designed to extend the reaction models to include bulk-scale contamination processes

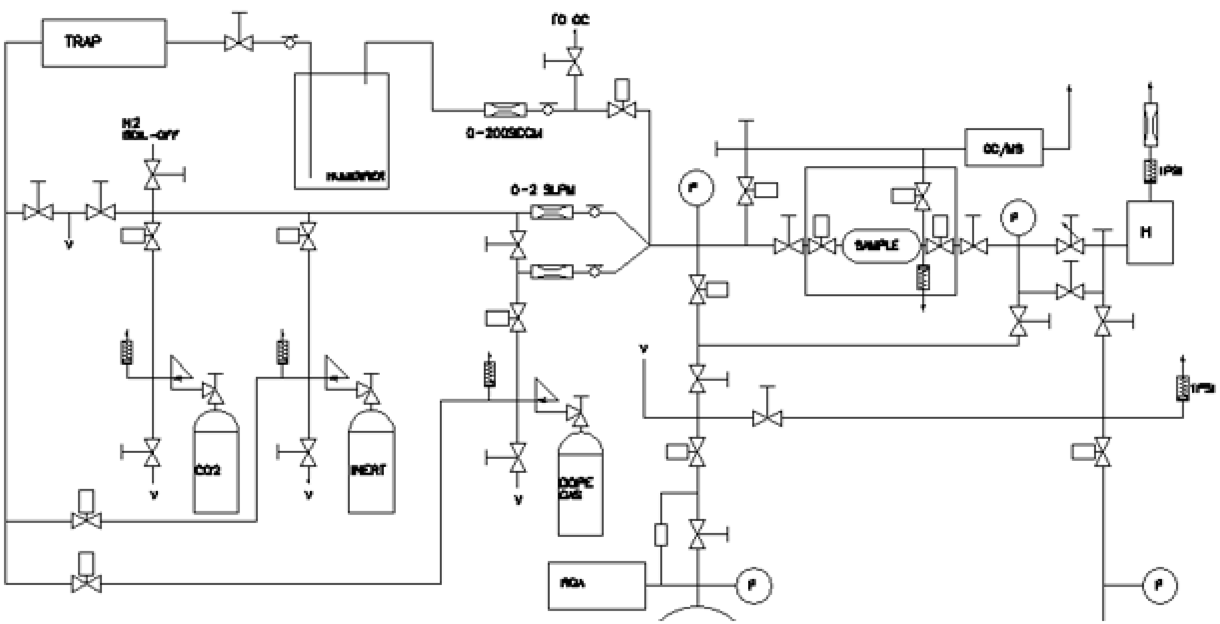
Uses:

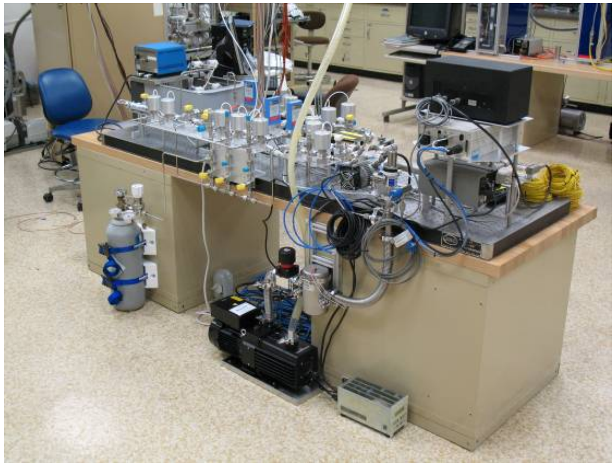
- Contamination flow-through reactions
- Controlled oxidation with water vapor and oxygen
- Data utilized to validate fully coupled numerical models

Diagnostics:



- Flow rate and pressure drop across bed
- Temperature and heat generation rate
- Gaseous reactants and products (GC and differentially pumped RGA)
- Solid product analyses (STMBMS)





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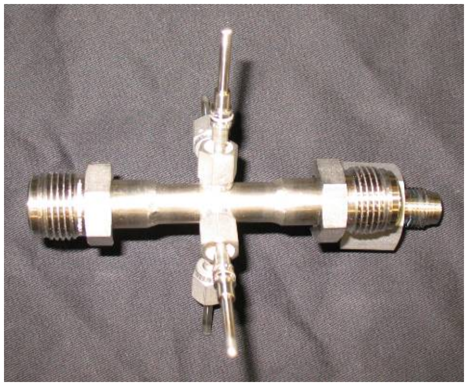
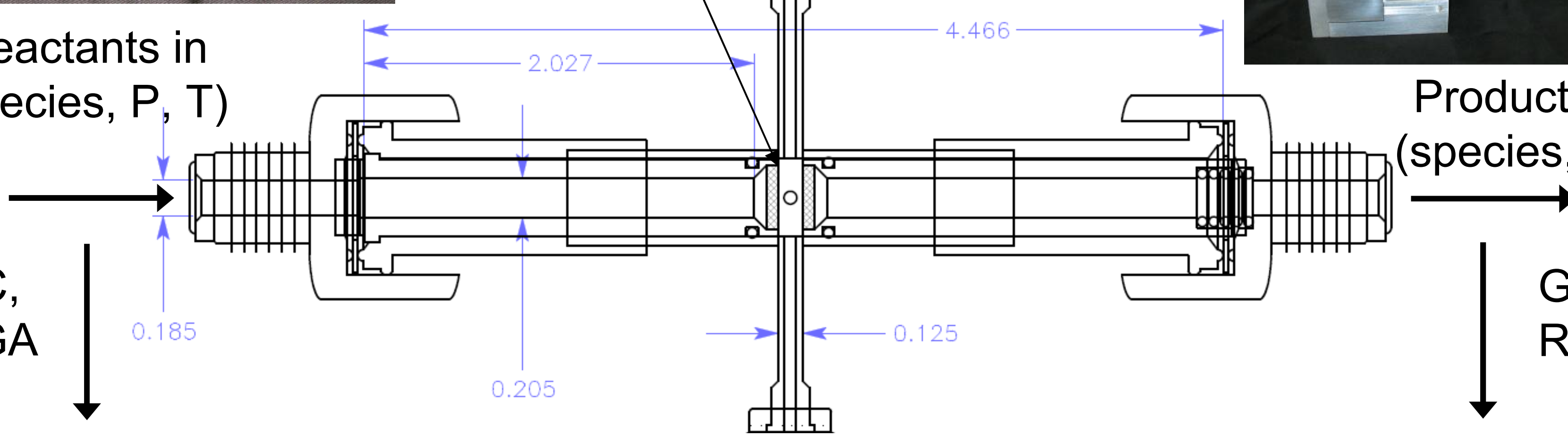
Contamination reactor allows us to assess gas/solid reactions in a porous medium





Data utilized to build and validate fully coupled heat and mass transfer and chemical kinetic models of packed bed contamination

A set of transport equations that apply to all flow regimes will be used to calculate the contamination of the hydride beds

Young & Todd Model: Capillary Pore Interpolation Method

$$\frac{\partial \phi c_i}{\partial t} = -\nabla \cdot \boldsymbol{J}_i + R_i$$

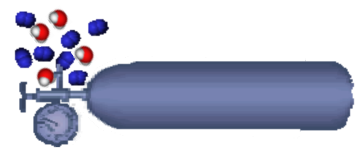
Species conservation with chemical reaction

$$\frac{\phi}{\tau^2}\nabla p = -A_A \sum_i M_i^{1/2} \boldsymbol{J}_i$$

Convective transport

$$\frac{c\phi}{\tau^2}\nabla x_i = \sum_j \left[\frac{x_i \boldsymbol{J}_j}{(\mathrm{D_A})_{ji}} - \frac{x_j \boldsymbol{J}_i}{(D_A)_{ij}} \right]$$

Multi-component diffusive transport



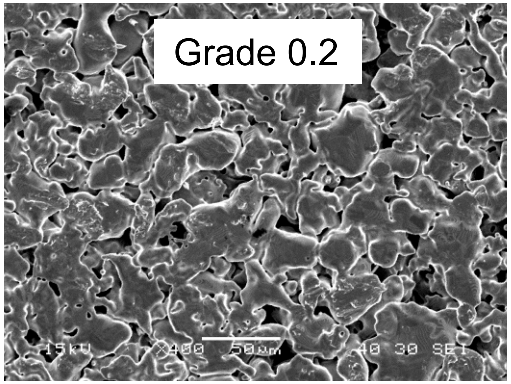
Transport coefficients

regime \ mechanism	Convective	Diffusive
Continuum (Kn < 0.01)	$A_C = \frac{32\mu}{c d_p^2 \sum_i x_i M_i^{1/2}}$	$(D_B)_{ij} = \frac{3}{16 n \sigma_{ij}^2 \Omega_{ij}} \left[\frac{2RT}{\pi} \left(\frac{1}{M_i} + \frac{1}{M_j} \right) \right]^{1/2}$
Free molecular (Kn > 1)	$A_K = \frac{3}{2d_p}\sqrt{\frac{\pi RT}{2}}$	$(D_K)_i = \frac{2-f_i}{f_i}\frac{d_p}{3}\sqrt{\frac{8RT}{\pi M_i}}$
Interpolation (All Kn)	$\frac{1}{A_A} = \frac{1}{A_C} + \frac{1}{A_K}$	$\frac{1}{(D_A)_{ij}} = \frac{1}{(D_B)_{ij}} + \frac{1}{(D_K)_i}$

Ref: JB Young and B Todd, Intl J Heat and Mass Transfer, Vol 48, 2005

Calculated results based on measured porous media (frits) properties and the Young&Todd model compare well with experimental measurements

SEM image of the frit →



An SEM image of the frit filled with epoxy, cut and polished →

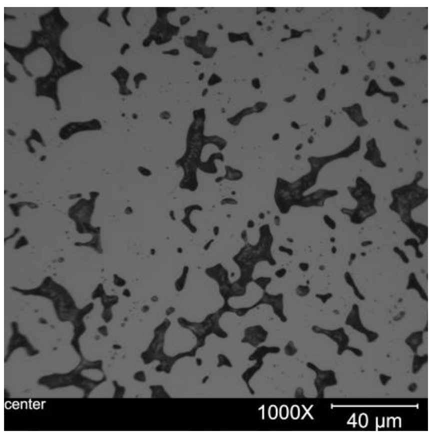
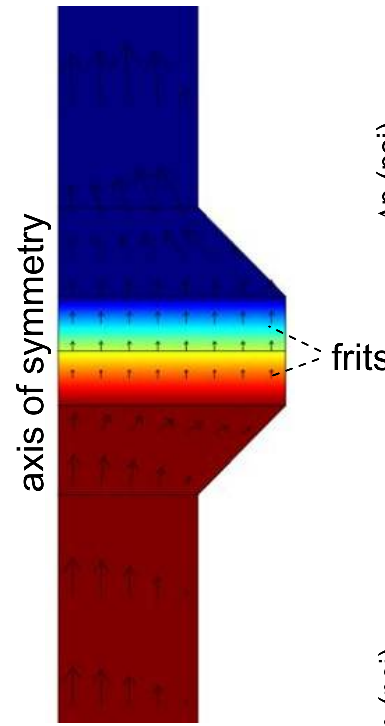


Image processing yields geometric characteristics

Grade	porosity	pore size (μm)	tortuosity
0.2	21%	10	4.9

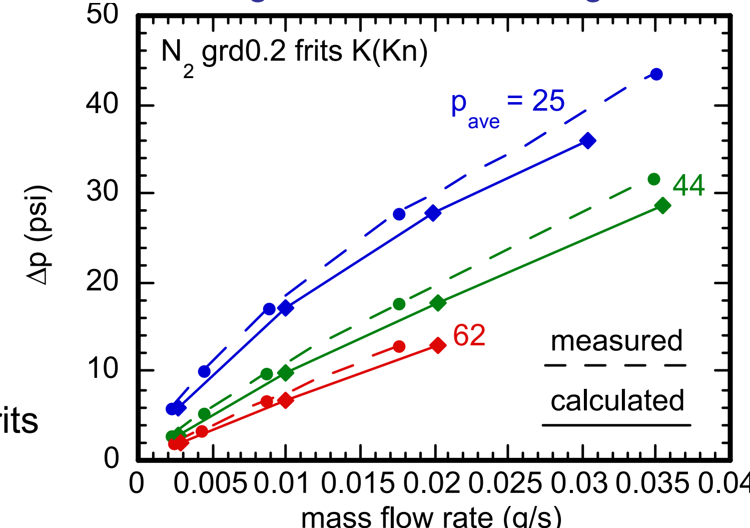
This data is used in the Young&Todd model for the permeability →

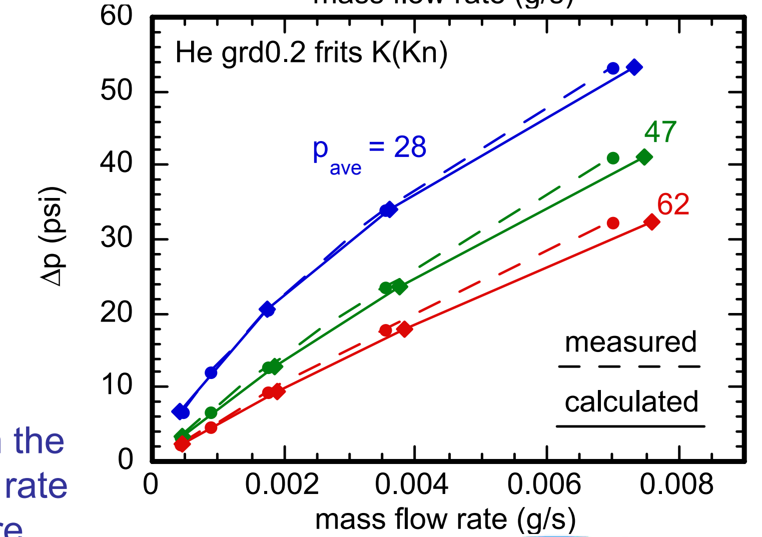
$$K = \frac{\phi}{\tau^2} d_p^2 \left[\frac{1}{32} + \frac{5}{12} Kn \right]$$



This is used in the model for flow rate and pressure calculations

Good comparisons were obtained for a range of flow rates and gases





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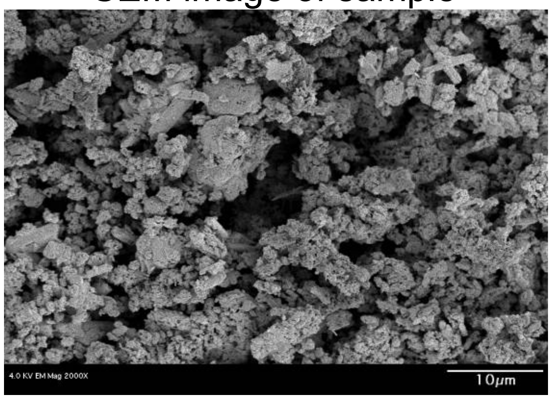
Good agreement was obtained between measured and calculated pressure drops across an alane sample

Sample holder loaded with alane

91 mg, 3.8 mm thick

SEM image of sample

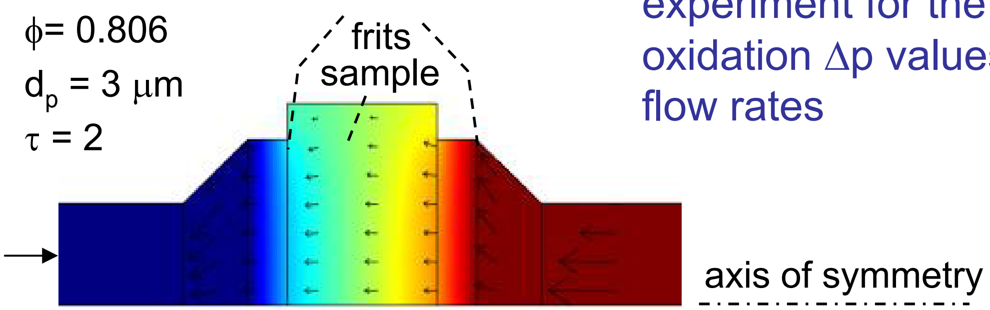


Permeability model parameters:

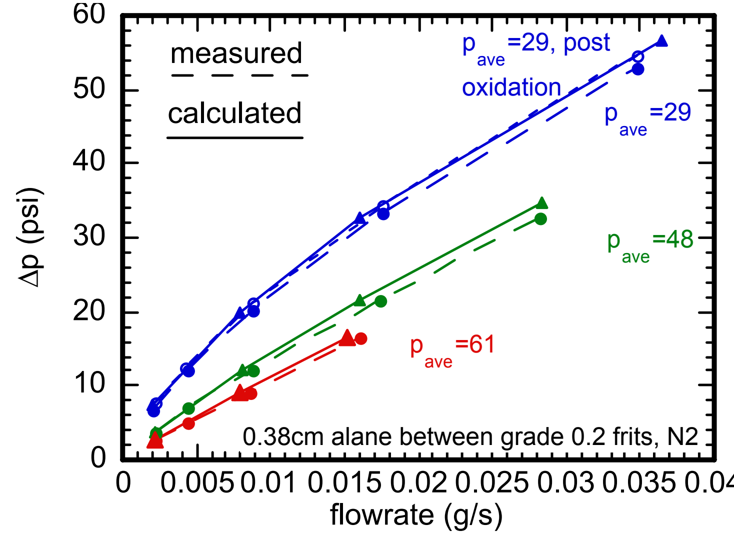
ϕ= 0.806

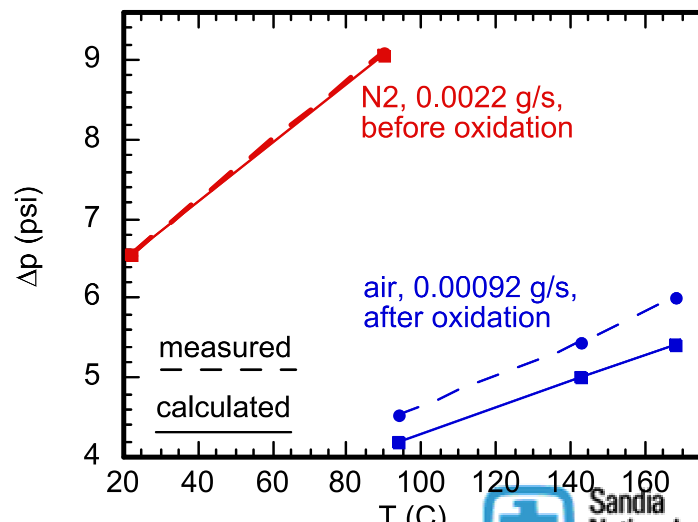
d_p = 3 μm

τ = 2



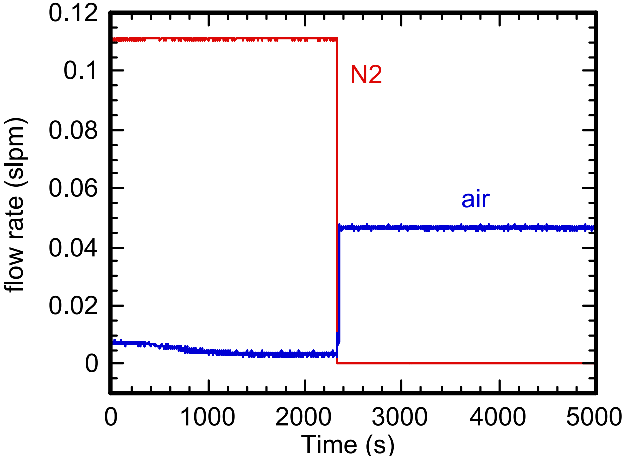
- The measured results for the pre- and post-oxidation Δp are ~equal, indicating the sample morphology does not change significantly
- The model predicts Δp well for a range of flow rates and a range of average pressures
- The model captures temperature effects on Δp
- There is some discrepancy between model and experiment for the post-oxidation Δp values at low flow rates



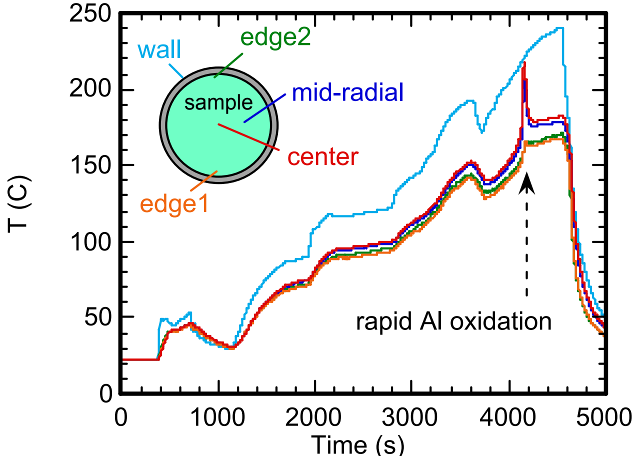


The alane sample was heated and exposed to air while its temperature and gaseous reaction products were monitored

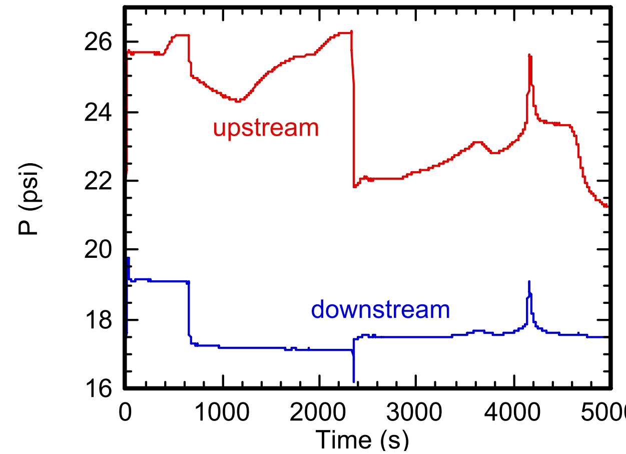
Initial heating was done under a nitrogen flow before switching to air



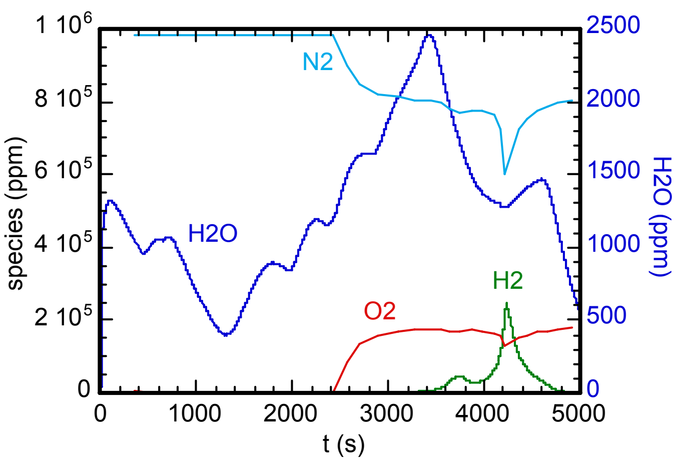
Thermocouples were positioned in 5 different locations in the sample



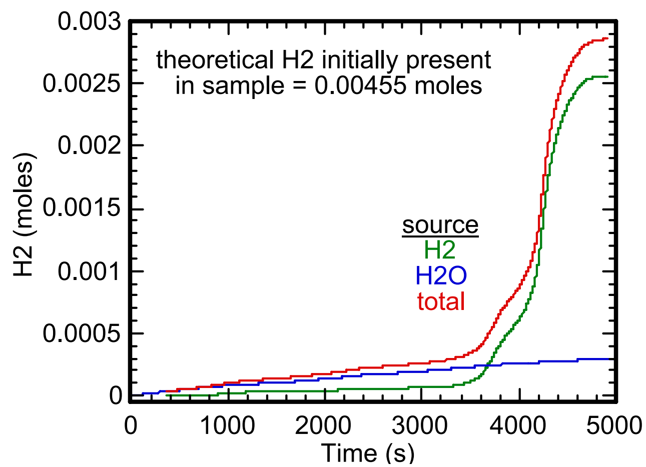
The pressure drop across the sample was recorded



At low temperatures H_2O is the primary product; at higher temperatures H_2 is evolved



- **Only the surface of the aluminum is oxidized (XRD results)**
- **A portion of the original hydrogen remains on the sample in the form of aluminum hydroxide and AlH3**
- **Results are dramatically different for a dehydrogenated alane bed**



Validation data for bulk contamination reaction models!

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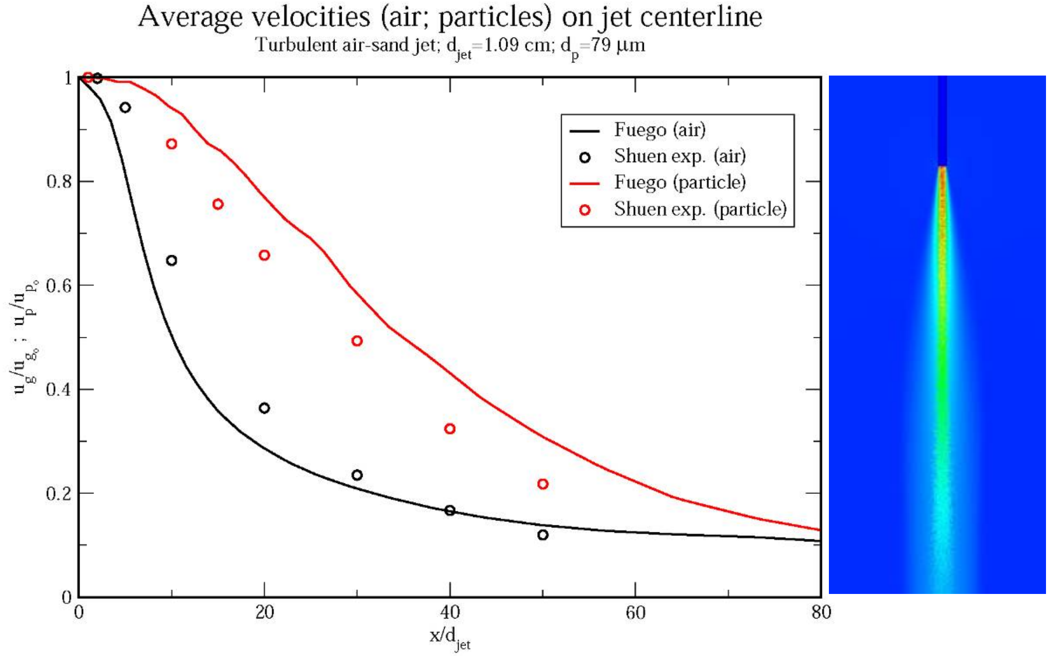
Efforts have been undertaken to quantify and predict dust cloud combustion events

Problem addressed: Currently, no developed numerical codes are able to predict the complex processes experienced during a metal dust cloud combustion event

Approach:

1. Predict gas/particle flow field from a hydride tank rupture using CFD (T, P, Conc.)
2. Utilize burning velocity data as a semi-empirical approach in lieu of detailed chemical kinetics of the reaction processes (**UTRC**)
3. Explore the use of DESC FLACS for this type of combustion event
4. Gather additional data is needed for model implementation and validation (e.g., turbulence intensity; radiation heat transfer).

Validation of Fuego capability for isothermal turbulent air-particle jet:



Jet centerline decay of particle concentration and air velocity data from: Shuen, AIAA Journal, v. 23, no. 3, pp. 396-404, March 1985.

Future Work

Task 1 – Fundamental contamination processes

- Continue alane contamination work by developing validated models for combined water and oxygen exposure
- Continue to evaluate new materials; amino boranes, Ca/Li borohydrides, etc

Task 2 – Scaling accident scenarios

- Make validated predictions of bulk-scale alane humid-air exposure scenarios
- Evaluate capability of FLACS DESC to predict metal dust cloud combustion

Task 3 – Low level contamination hazard

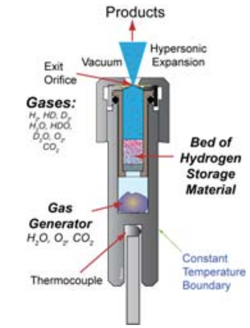
- Evaluate reversible Li-amide/alanate samples for hazardous solid product formation

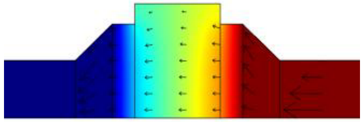
Task 4 – Hazard mitigation!!

- Investigate use of novel materials and standard fire suppression chemicals for use with various H_2 storage materials

Summary

- A suite of new methods identified to quantify contamination processes between hydrogen storage materials and O_2/H_2O
  - AgO, Ag_2O, mol sieve, $NaHCO_3$
  - Flow cell
- Contamination processes of alanes with O_2 investigated
- Three new materials analysed including amino-borane, Li-B-Mg compounds, and calcium borohydride
- Flow through contamination manifold completed and utilized during alane oxidation experiments
- Models validated for flow fields through a porous alane bed
- Validating experiments performed to quantify reaction processes between alane and O_2
- Flow field calculations of particle-entrained gas streams quantified using Fuego
- Contamination Sieverts apparatus assembled to produce appropriately hydrogenated samples





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