Quantifying & Addressing the DOE Material Reactivity Requirements with Analysis & Testing of Hydrogen Storage Materials & Systems

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Project ID ST41

Overview

- **Timeline**
  - Official Start: June 2007
  - Contract Signed: August 2007
  - End: May 2010
  - Percent complete: 25%
- **Budget**
  - $1.34M Total Program
    - $1.07M DOE
    - $0.27M UTRC
  - FY07: $60k
  - FY08: $410k
- **Barriers**
  - F. Codes & Standards
  - A. System Weight & Volume
- **Target**
  - EH&S: "Meets or exceeds applicable standards"

- **Partners & Collaborators**

  Project
  - UTRC
  - Kidde-Fenwal

  DOE Core Team
  - Savannah River NL
  - Sandia NL

  IEA / IPHE Additional Team Members
  - FZK (Germany)
  - AIST (Japan)
  - UQTR (Canada)

  Canadian SDTC Project
  - HSM, Inc. led alane system development
  - UTRC - alane system reactivity evaluation

  Additional Collaborations
  - DOE refueling station risk assessment
  - IEA Task 19
  - NFPA Hydrogen Technology Committee, C&S activities

Broad Objectives

- Quantify the DOE On-Board Storage Safety Target: "Meets or exceeds applicable standards."
- Evaluate reactivity of key materials under development in the materials Centers of Excellence.
- Establish generalized and specific risk analyses between reaction characteristics and satisfaction of acceptance criteria.
- Reduce reactivity consequences of candidate materials and systems through development of mitigation methods.
- Determine the trade-offs between performance and residual risk.
- Support *risk informed* choices for Codes & Standards activities.

Approach: Tasks & Materials

Underlined items are covered in the current presentation

Primary Tasks

- *Risk Analysis Framework*
- Material testing – *Dust Explosion*
- Reaction kinetics experiments – Air Exposure: *Time Resolved XRD*
- Risk mitigation
- Prototype implementation

Four Material Candidates:

- *$2LiBH_4 + MgH_2$*
- AlH_3
- NH_3BH_3
- Activated carbon

Conditions:

- *Charged & discharged*
- As-synthesized and after reaction cycling
- Without and with hydrogen
- Pure & after exposure to contaminants
- Before and after mitigation

Coordination of Multi-project Partners

Current DOE & IEA/IPHE Task Matrix

	AIST	FZK	SNL	SRNL	UQTR	UTRC
1.0 Risk Assessment						
1.1 Formal Risk Assessment						x
1.2 Std. Bulk Tests	x	x	x	x	x	
1.3 Std. Dust Cloud Tests	x	x				x
2.0 Thermodynamics & Chemical Kinetics						
2.1 Calorimetry				x		
2.2 RT-XRD						x
2.3 TGA MS			x			
2.4 Kinetics Modeling			x	x	x	x
3.0 Risk Mitigation						
3.1 Risk Mitigation Concept Generation			x	x		x
3.2 Calorimetry				x		
3.3 TGA/MS			x			
3.4 Hazards Tests		x		x	x	x
3.5 Surface Analysis		x				
4.0 Prototype System						
4.1 System Design		x				
4.2 System Reaction			x		x	x
4.3 Subscale prototype					x	x
4.4 System Design Strategy		x			x	
4.5 Materials Preparation	x	x		x	x	
4.6 Sytem Evaluation		x				
5.0 Communication						
Meetings	x	x	x	xx	x	x
QuickPlace	x	x	x	xx	x	x
WEB Sight				xx		

UTRC Task #

1.0

2.0

3.0

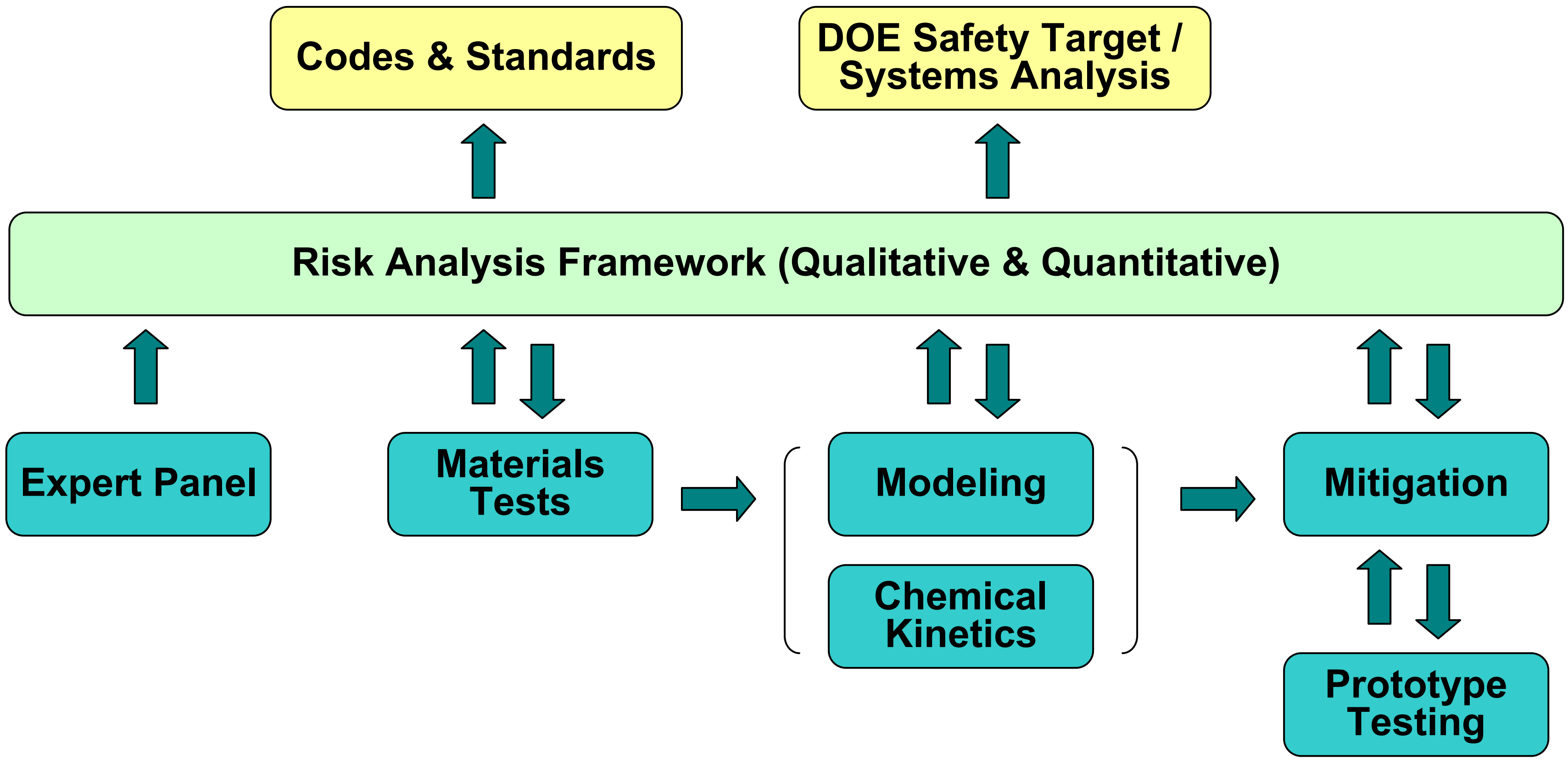
4.0

5.0

6.0

Approach: Activity Relationships

Detailed Testing and Modeling will supplement the Risk Analysis Framework to serve as the basis for risk informed reactivity and C&S decisions.



FY07 & FY08 Milestones

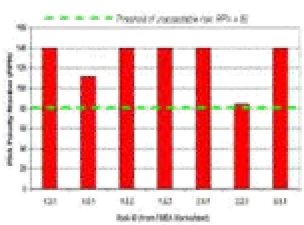
	Milestones
FY08 Q1	Develop qualitative risk analysis to select highest risks for Material #1.
FY08 Q2	Perform dust explosion tests for Material #1.
FY08 Q2	Conduct time resolved XRD for air exposure of Material #1.
FY08 Q3	Implement enhancements to dust explosion and gas exposure reactivity testing.
FY08 Q4	Perform qualitative risk analysis for top three materials.
FY08 Q4	Complete enhanced gas reactivity testing for Material #1.
FY08 Q4	Complete dust explosion tests for Material #2.

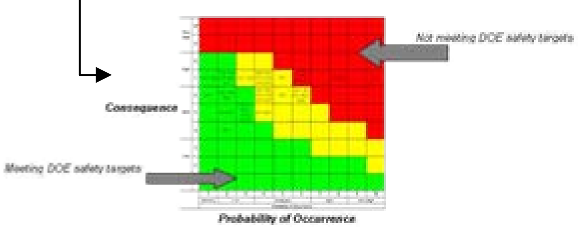
Risk Analysis Overview

Qualitative – Broad Scope

- Expert panel
- Material test data
- Modeling
- Mitigation strategies

Failure Modes and Effects Analysis (FMEA)
Standard approach for Automotive Industry and Consumer Products





Potential deviations from *normal operating conditions* (ex. vehicle operation)

Hazard and Operability Analysis (HAZOP)
Standard approach for the Chemical Industry

- Consequences
- Recommendations for Engineered Safety Features

Quantitative – Key Risks

Fault Tree Analysis (FTA)

Event Tree Analysis (ETA)

Standard approach used by Nuclear Power Industry & NASA

FTA/ETA Linking

Quantified Accident Sequences

- Accident scenario development
- Uncertainty analysis
- Parameter sensitivity studies

SAPHIRE
U.S. NRC / INL

CAFTA
EPRI

FMEA Spreadsheet

						Risk Quantification Based on Existing Conditions				
Name of Component or Subsystem	Function(s) of Component or Subsystem	Potential Failure Mode (Operational Risk)	Potential Effect(s) of Failure Mode	Potential Root Cause(s) of Identified Failure Mode	Current Detection and Control Methods	Consequence	Probability	Detectability	Risk Priority Number (RPN)	Ma Ha
Pressure vessel (containing $NaAlH_4$)	Vessel designed to withstand H2 pressure and contain hydride material	1.1 Vessel breach leading to hydride dispersion in a wet environment	Hydride rapid reaction, fire, and potential H2 explosion	1.1.1 Automotive accident	1. Design vessel for crashworthiness 2. Proper vessel lo tion in vehicle to minim vulnerability	7	3		210	Pelleti to rec water
				1.1.2 H al loads from absc esorption	1. Intern nent design ze powd ion and den 2. per optic s composite uct certification		2	2	28	
				1.1.3 Ballistic impact	Damage tolerant fiber overwrap	7	1	10	70	

Component

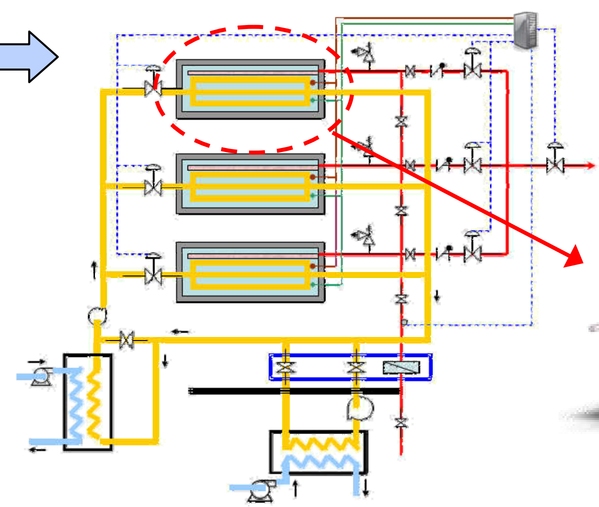
Failure Mode

Root Cause

Current Controls

Risk Scoring

- Initial assessment based on $NaAlH_4$ material and system due to existing knowledge – applicable to other on-board reversible materials.
- Risk Priority Number = Consequence * Probability * (lack of) Detectability
- Acceptable / threshold risk: RPN_{th} = 80



FMEA Spreadsheet

ons	Risk Quantification AFTER Additional Mitigations						Threshold RPN = 80		Impact of Mitigation on DOE Non-Safety Technical Targets (Low, Medium, High)					
	Additional Mitigations													
Confidence	Material / System-Level Hazard Mitigation Strategy	Added Information to Reduce Uncertainty	Consequence	Probability	Detectability	New Risk Priority Number (RPN)	Safety / DID	TRL of Mitigation Approach	Gravimetric Capacity	Volumetric Capacity	Kinetics	Cost	Operability and Durability	Specific Recommended Actions
	Passivate hydride material to reduce reactivity	1. Additional testing and mod[illegible] to better unders[illegible]tent and [illegible]wder rel[illegible] 2[illegible]sion [illegible] modeling [illegible]ysis [illegible]try and [illegible]ng [illegible]dditional [illegible]ormation on crashworthiness design criteria 5. Wet vs. dry probabilities for different geographic locations	4	2		80	0.0							Kidde Fenwal dust cloud explosion tests could provide useful insights for: a) Minimum explosi[illegible] concentration (ME[illegible] b) Minimum ignit[illegible] (MIT) c) Minimum i[illegible] MIE) d) dP/dt an[illegible] Applicabl[illegible] failure modes
														Obta[illegible]site vessel experience [illegible]ata on failure modes (applicable to all 1.1.X FM)

Additional Controls

Revised Scoring

Impact on Other Targets

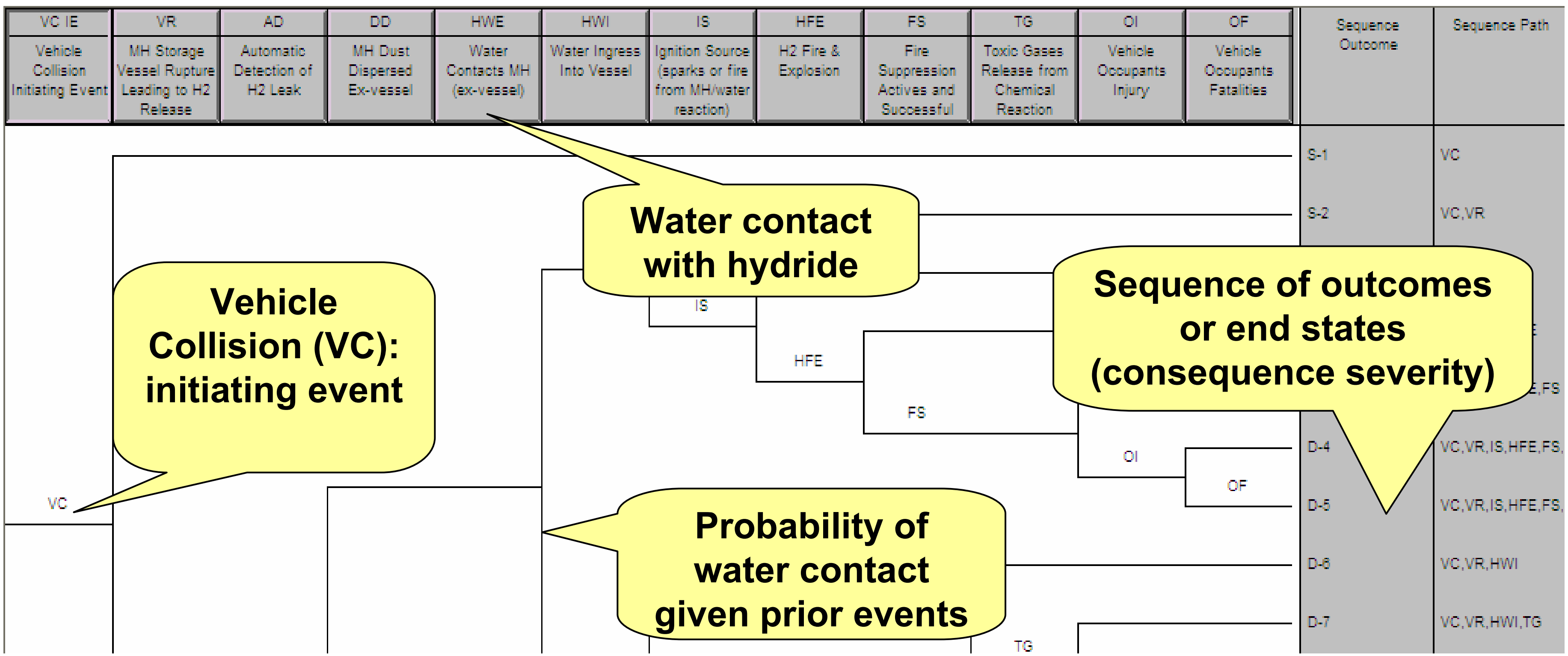
Multi-Project Actions

- If RPN > RPN_{th}, develop recommended actions which include Mitigation Development and Uncertainty Reduction (additional testing/modeling).
- Interpret mitigation Feasibility not as cost, but Technology Readiness Level (TRL).
- Examine impact on non-safety Technical Targets (weight, volume, …).

Customized FMEA framework developed for on-board reversible hydrides.
Population of entries by the multi-project team will be on-going.

Quantitative Analysis: ETA / FTA

- Event Tree (ET) describes accident progression from initiating event to end states.
- The CAFTA computer program is being employed; can be exported to SAPHIRE.
- The probability assigned to each node will be estimated from a fault tree analysis (FTA), experiments / modeling, or expert judgment.

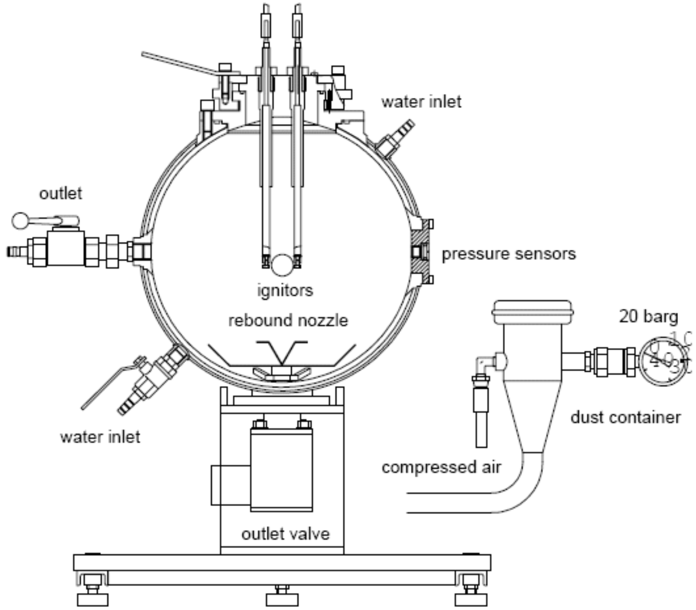


Materials Testing: Dust Explosion

Measurements (ASTM test)

- P_{max}, $(dP/Dt)_{max}$, K_{st} (E1226)
- Minimum Explosive Concentration (E1515)
- Minimum Ignition Energy (E2019)
- Minimum Ignition Temperature (E1491)

Standard 20 L
Kühner apparatus
(E1226 & E1515)



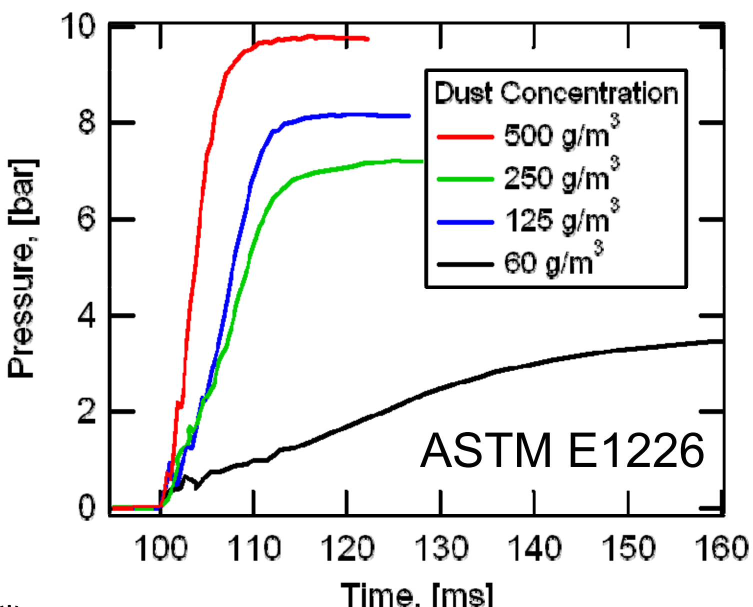
Future variation from conventional ASTM procedures

- Relative humidity monitored only ⇒ control RH.
- Perform tests with hydrogen / oxygen gas mixtures.
- Vary ignition delay – affect turbulence level.
- Additional diagnostics for heat flux, turbulence, ...

$2LiBH_4 + MgH_2$: Hydrided State

Sieve Analysis

> 40 mesh (425 μm)	5.9%
> 70 mesh (212 μm)	20.8%
> 100 mesh (150 μm)	12.6%
> 200 mesh (75 μm)	21.8%
> 400 mesh (37 μm)	9.6%
< 400 mesh (37 μm)	29.3%



Ball Milled, Hydrided State

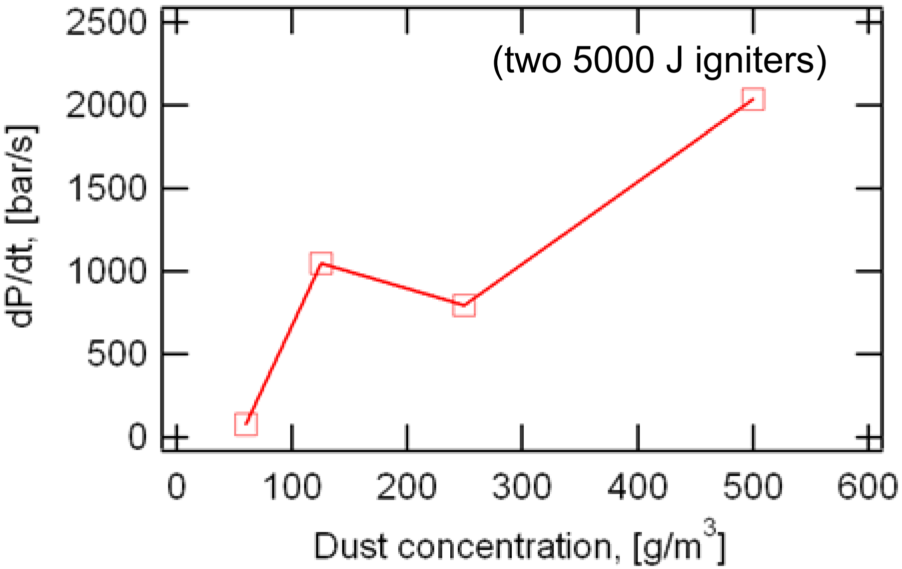
	$2LiBH_4$ + MgH_2	$NaAlH_4$ [2]	Lyco. Spores
P_{MAX}, bar-g	10.7	11.9	7.4
$(dP/dt)_{MAX}$, bar/s	2036	3202	511
K_{ST}, bar-m/s	553 [1]	869	139
Dust Class	St-3	St-3	St-1
Min. Explosive Conc. (MEC), g/m^3	30	140	30
T_C, °C	150	137	430
Min. Ignition Energy (MIE), mJ	<9	<9	17

[1] K_{ST} tests were inconclusive since $(dP/dt)_{max}$ was still increasing with dust concentration.
[2] From prior DOE contract DE-FC36-02AL67610.

When finely divided, the material is highly reactive and comparable to $NaAlH_4$.

Hydrided $2LiBH_4 + MgH_2$: dP/dt, K_{ST} & MEC

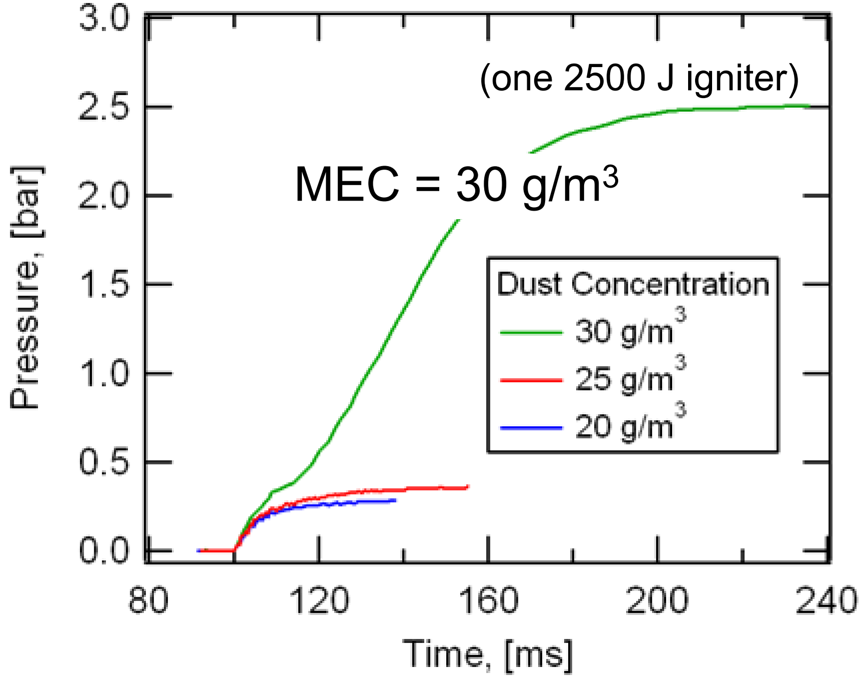
dP/Dt & K_{ST}



$$K_{ST} = \left(\frac{dP}{dt}\right)_{max} * V^{1/3} > 500 \text{ bar - m/s}$$

Dust Class	Kst bar-m/s
St-1	Up to 200
St-2	201-300
St-3	301 +

Minimum Explosive Concentration



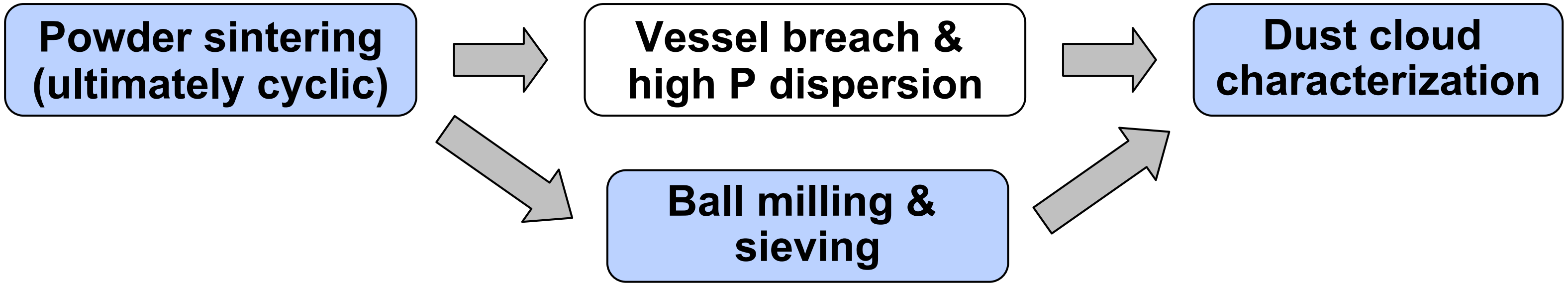
K_{ST} not saturated but still above St-3 criterion.

MEC comparatively low.

Partially Discharged $2LiBH_4 + MgH_2$

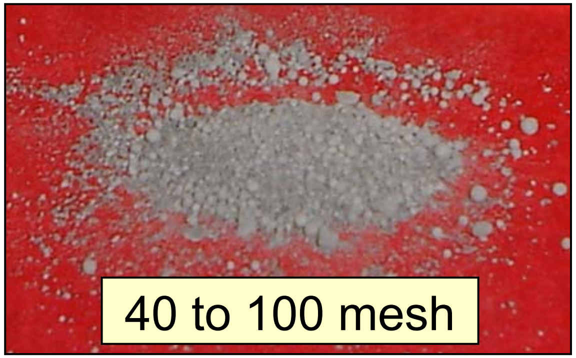
As-desorbed

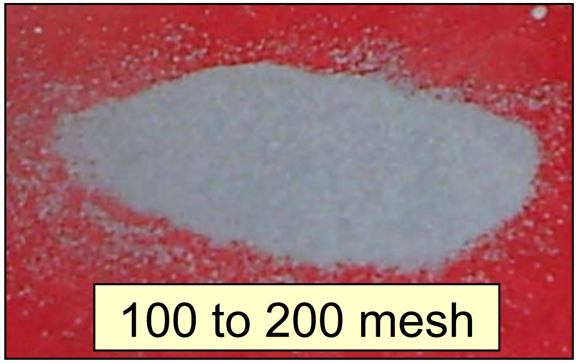
- 330°C for 2 hrs under vacuum.
- Material is in a coarse state resembling ash.

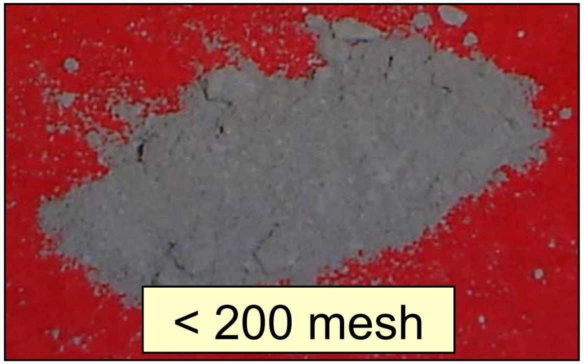


Hydride powders can sinter to various degrees. Facilitate characterization by employing mild ball milling (2.5 minutes) to mimic high pressure dispersion.

Partially Discharged $2LiBH_4 + MgH_2$



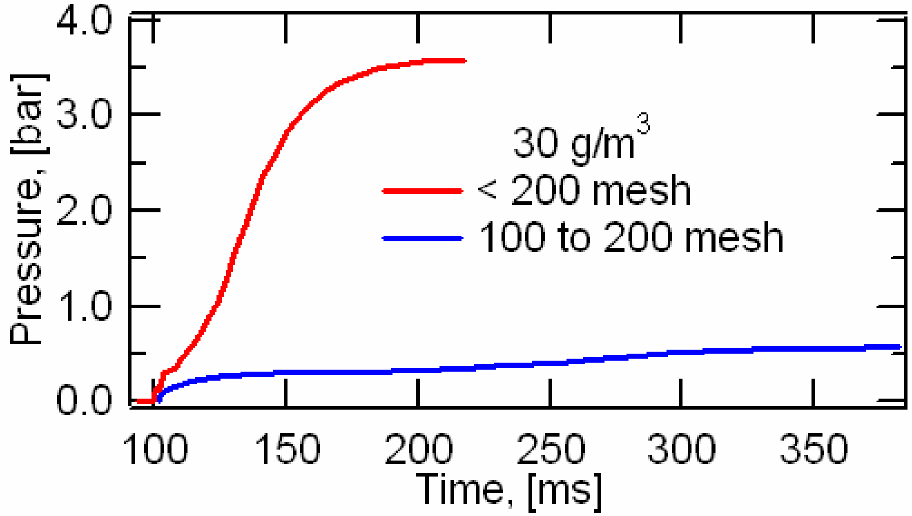




Material was SPEX ball milled for 2.5 min. & sieved.

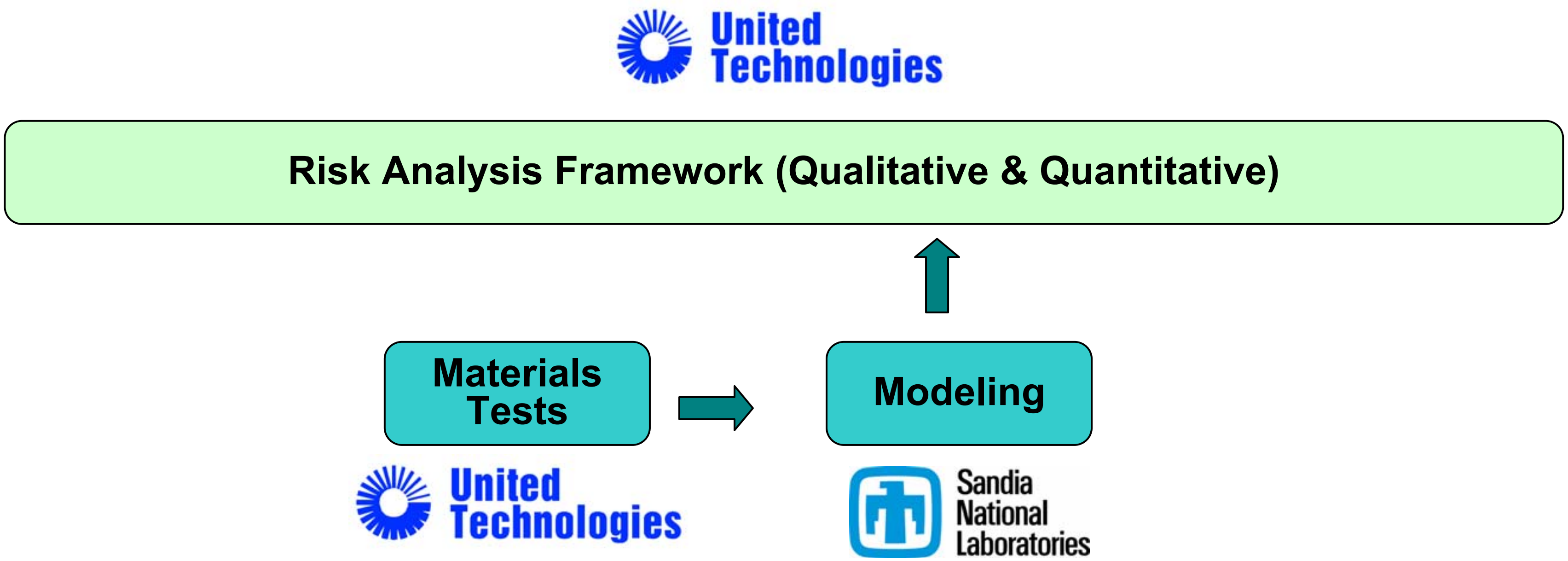
	Hydrided	Partially Dehydrided	
	As-milled	**< 200 mesh**	**100 to 200 mesh**
Min. Expl. Conc. (MEC), g/m^3	30	30	60
T_C, °C	150	230	310
Min. Ign. Energy (MIE), mJ	< 9	< 9	22 < MIE < 47

Coarser powder results in lower reactivity.



Dust Explosion Modeling / Collaboration

Results to be incorporated into dust explosion modeling by Sandia NL and ultimately provide input into the Risk Analysis Framework

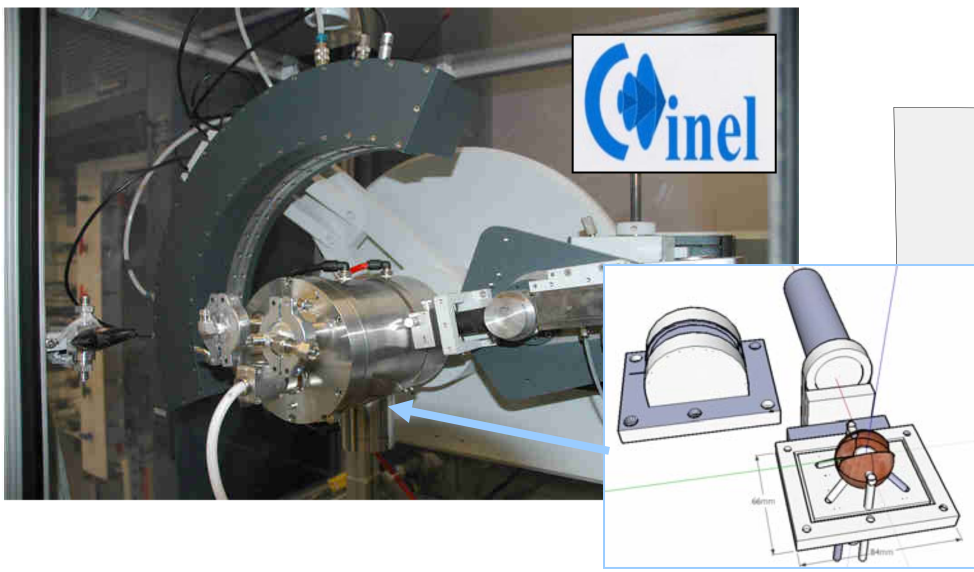


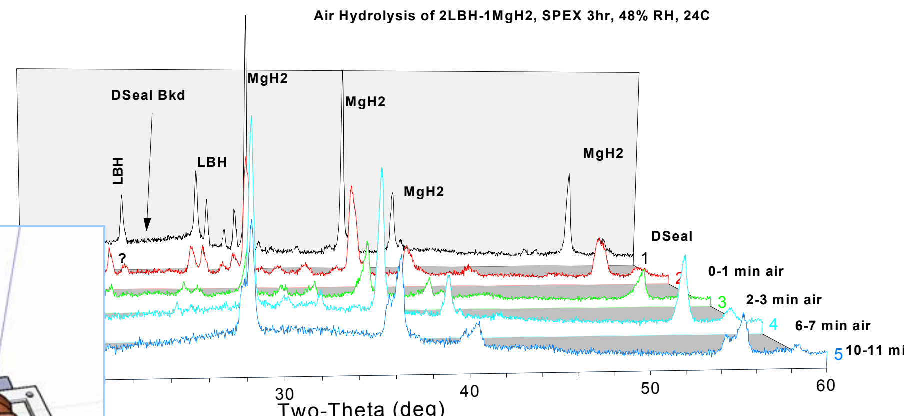
Potential integration with higher level UTC Fire & Security Industrial Explosion Protection models.

Chemical Kinetics Testing: Air Exposure

Time Resolved X-Ray Diffraction (TR-XRD)

- *Ambient air exposure*
- Conventional environmental chamber
- Design of chamber with capability for gas flow *through the powder* as well as across its surface for sufficient Mass Spec time resolution





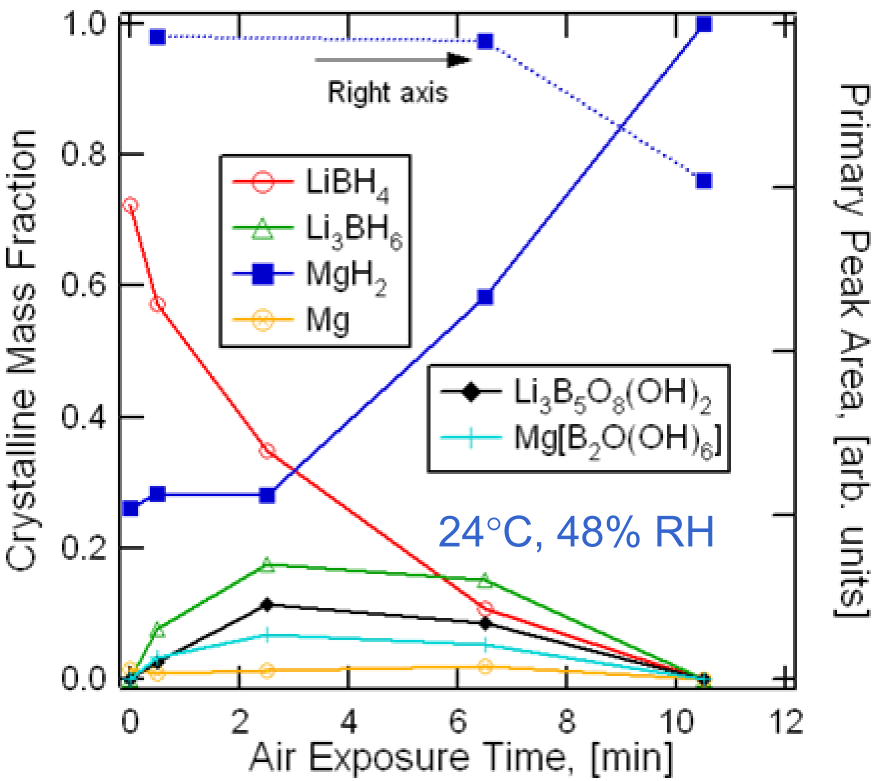
Real time measurement of composition evolution to complement SRNL calorimetry and SNL flow-through reactor.

$2LiBH_4 + MgH_2$: Hydrided State

- $LiBH_4$, MgH_2, $2LiBH_4 + MgH_2$ (hydrided & partially dehydrided)
- Complex process of water absorption & reaction
- Hydrolysis for mixture predominantly followed that of $LiBH_4$

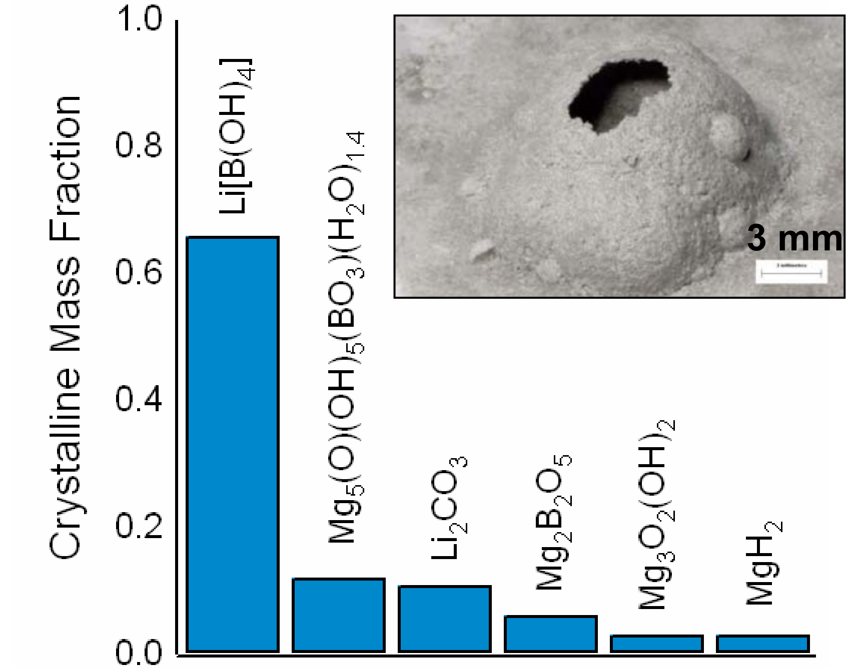
Real Time

Deliquescent / amorphous phases



21 days

Dried bubble



Future Work

FY08

Risk Analysis

- Compile input from Expert Panel for on-board reversible risk assessment.
- Initiate quantitative ETA / FTA risk analysis for key hazards of on-board reversible system.
- Define AlH_3 and NH_3BH_3 based system configurations and perform qualitative risk analysis.

Material Testing & Modeling

- Implement enhancements to dust explosion and air reactivity test methods.
- Complete $2LiBH_4 + MgH_2$ testing. Collaborate with SNL & SRNL modeling efforts.
- Initiate testing of AlH_3. Sources include Brookhaven NL, Dow and UTC “Russian” alane. Larger quantities will be produced through coordination with Canadian SDTC project.

FY09

Risk Analysis

- Conduct qualitative analysis for activated carbon and update prior configurations.
- Develop quantitative ETA / FTA risk analysis for an off-board regenerative system and refine the on-board reversible analysis.

Material Testing & Modeling

- Conduct dust explosion and air reactivity testing for AlH_3, NH_3BH_3 and activated carbon.
- Develop identified risk mitigation methods.

Go / No Go decision on prototype demonstration

Summary

Objective: Develop a greater understanding of the relationships between material reactivities and the acceptance of automotive systems.

Approach: Due to the objective complexity and scope, establish a multi-organization, multi-national collaborative team.

Scope: *Materials:* metal hydrides, chemical hydrides, adsorbants

- $2LiBH_4 + MgH_2$
- AlH_3
- NH_3BH_3
- Activated carbon

Methods:

- Qualitative & quantitative risk analyses
- Materials testing ranging from mechanistic to combined effects. Integration into reactivity & spatial / scaling modeling.
- Development of mitigation methods & demonstrations.