

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

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DOE Hydrogen Program

Annual Peer Review

Arlington, VA

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Project ID: STP\_50\_Khalil

# Overview

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## ■ Timeline

- Start: June 2007
- End: May 2010
- Percent complete: 35% (spending)

## ■ Budget

- \$1.34M Total Program
  - \$1.07M DOE
  - \$0.27M UTRC
- FY08: \$300k
- FY09: \$400k

## ■ Barriers

- F. Codes & Standards
- A. System Weight & Volume

## ■ Target

- EH&S: “Meets or exceeds applicable standards”

## ■ Partners

- Kidde-Fenwal: dust cloud testing



- Multiple collaborators

# Collaborations

## *Other DOE Reactivity Projects*

- Savannah River National Lab
- Sandia National Labs



## *IEA HIA Task 22 / IPHE Project (with SRNL & SNL)*

- FZK (Germany, Government lab)
- AIST (Japan, Government lab)
- UQTR (Canada, University)



## *Canadian Government Project*

- HSM Systems, Inc. (Industry)



## *Additional Collaborations*

- DOE Hydrogen Program Codes & Standards
- DOE Hydrogen Program Safety Panel
- NFPA Hydrogen Technology Committee
- IEA HIA Task 19



# Project Objectives & Associated Tasks

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## High Level Objectives

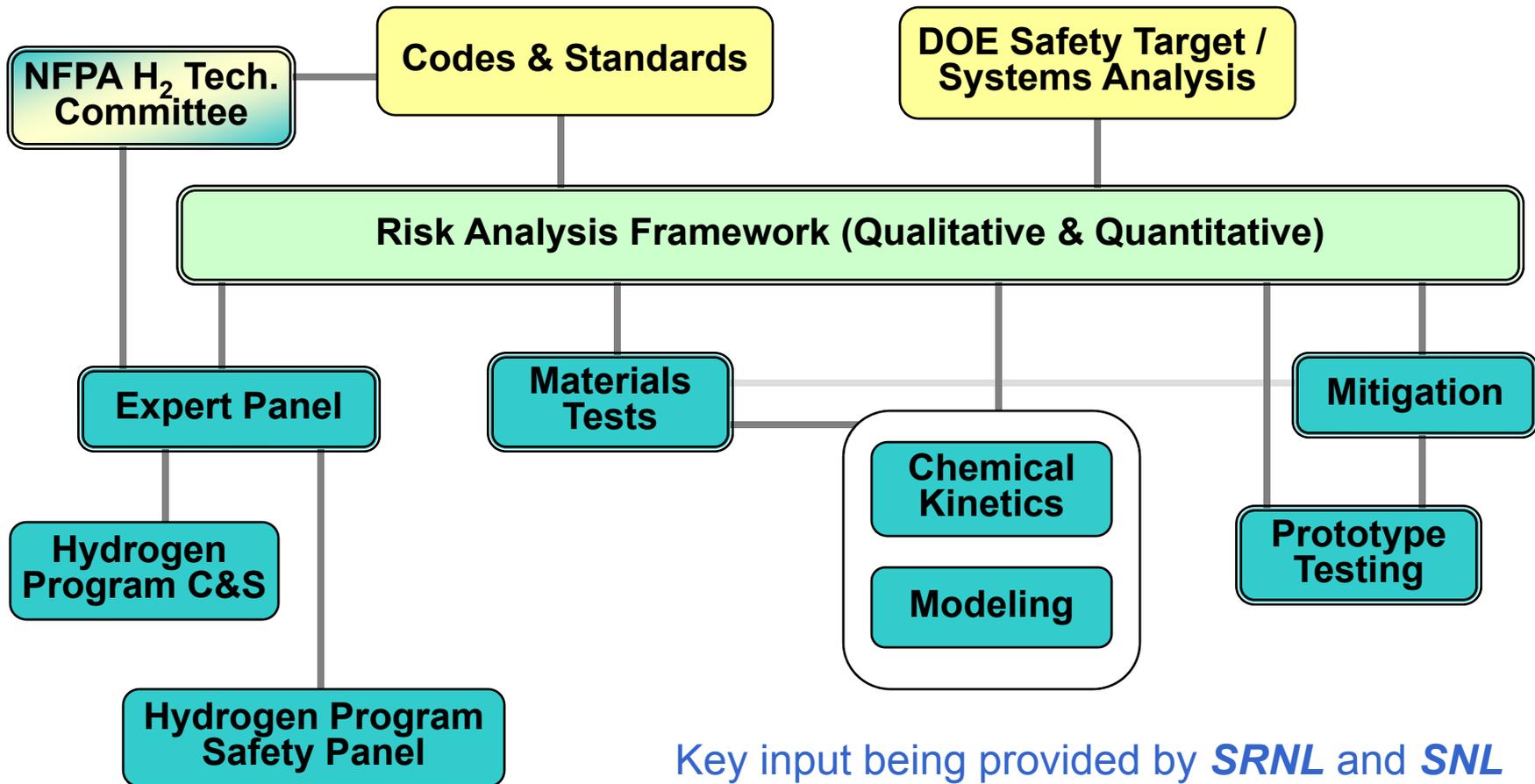
- Contribute to **quantifying** the DOE On-Board Storage **Safety Target**: “Meets or exceeds applicable standards.”
- **Evaluate** reactivity of **key materials** under development in the material Centers of Excellence.
- Develop methods to **reduce risks**.

## Primary Tasks

- Risk analysis
  - Qualitative risk analysis for a broad range of scenarios
  - Quantitative risk analysis for key scenarios
- Material testing
  - Dust cloud: standard and modified ASTM procedures
  - Reaction kinetics: air exposure / time resolved XRD
- Risk mitigation
  - Material oriented risk reduction
  - System configuration level
- Subscale prototype demonstration

# 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.



Key input being provided by *SRNL* and *SNL* for material testing & modeling.

# Collaborations

## Coordinated DOE & IEA / IPHE Task Matrix

	UTRC	SRNL	SNL	AIST	FZK	UQTR
<b>Risk Analysis</b>						
Analysis Development	X					
Expert Panel Scoring	X	X	X	X	X	X
<b>Material Testing</b>						
Standardized Bulk Tests		X		X	X	X
Dust Cloud Tests	X			X	X	
Calorimetry		X				
TR-XRD	X					
TGA-MS			X			
<b>Modeling</b>						
Reaction Kinetics		X	X			X
Dust Cloud			X			
Air & Water Infiltration / Reaction		X	X		X	
<b>Risk Mitigation</b>						
Concept Development	X	X	X			
Hazard Testing	X	X	X		X	X
<b>Prototype Demonstration</b>						
	TBD					

# Materials & Systems

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Examine hydrogen storage material candidates and related system configurations which are being developed within the DOE Hydrogen Program.

## Current Focus Materials:

- $2\text{LiBH}_4 + \text{MgH}_2$
- Activated carbon
- $\text{AlH}_3$
- $\text{NH}_3\text{BH}_3$
- Others can be added based on material development progress

## General System Classes:

- On-board reversible hydride bed systems (guided by  $\text{NaAlH}_4$  prototypes)
- On-board reversible adsorbant systems (based on activated carbon)
- Off-board regenerable based systems (variants for alane & ammonia borane)

# Overview of Technical Accomplishments

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- Qualitative Risk Analysis / design FMEA
  - Conceptual system configuration designs developed for baseline FMEAs of on-board reversible and off-board regenerable storage systems.
  - Definition of Expert Panel and preliminary opinion pooling for on-board reversible system FMEA.
- Quantitative Risk Analysis
  - Event tree model was developed, having vehicle collision as an accident initiator, which included hazard scenarios of hydrogen leakage and dust dispersion both as a cloud and deposited layer.
  - Fault tree models were developed for a range of damage categories from pressure waves produced by hydride and aluminum dust cloud events.
  - Framework for economic consequence analysis.
- Dust Clouds Testing
  - Completed testing for partially discharged  $2\text{LiBH}_4 + \text{MgH}_2$ .
  - Full matrix for AX-21 carbon in air.
  - Partial matrix for discharged alane.
- Air Reactivity / TR-XRD
  - Ammonia borane.

# Risk Analysis Overview

## Qualitative – Broad Scope

## Quantitative – Key Risks

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

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

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

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

- Consequences
- Recommendations for Engineered Safety Features

**Fault Tree Analysis (FTA)**

**Event Tree Analysis (ETA)**

Standard approach used by Nuclear Power Industry & NASA

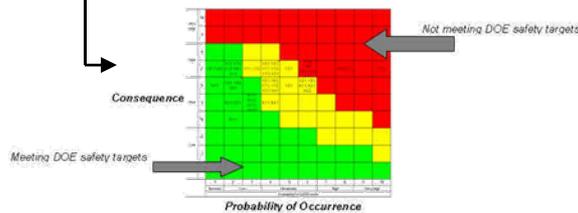
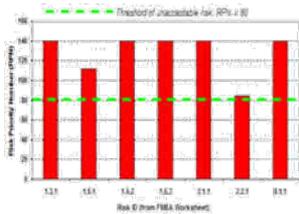
**FTA/ETA Linking**

**Quantified Accident Sequences**

**Consequence Analysis**

**Uncertainty Analysis**

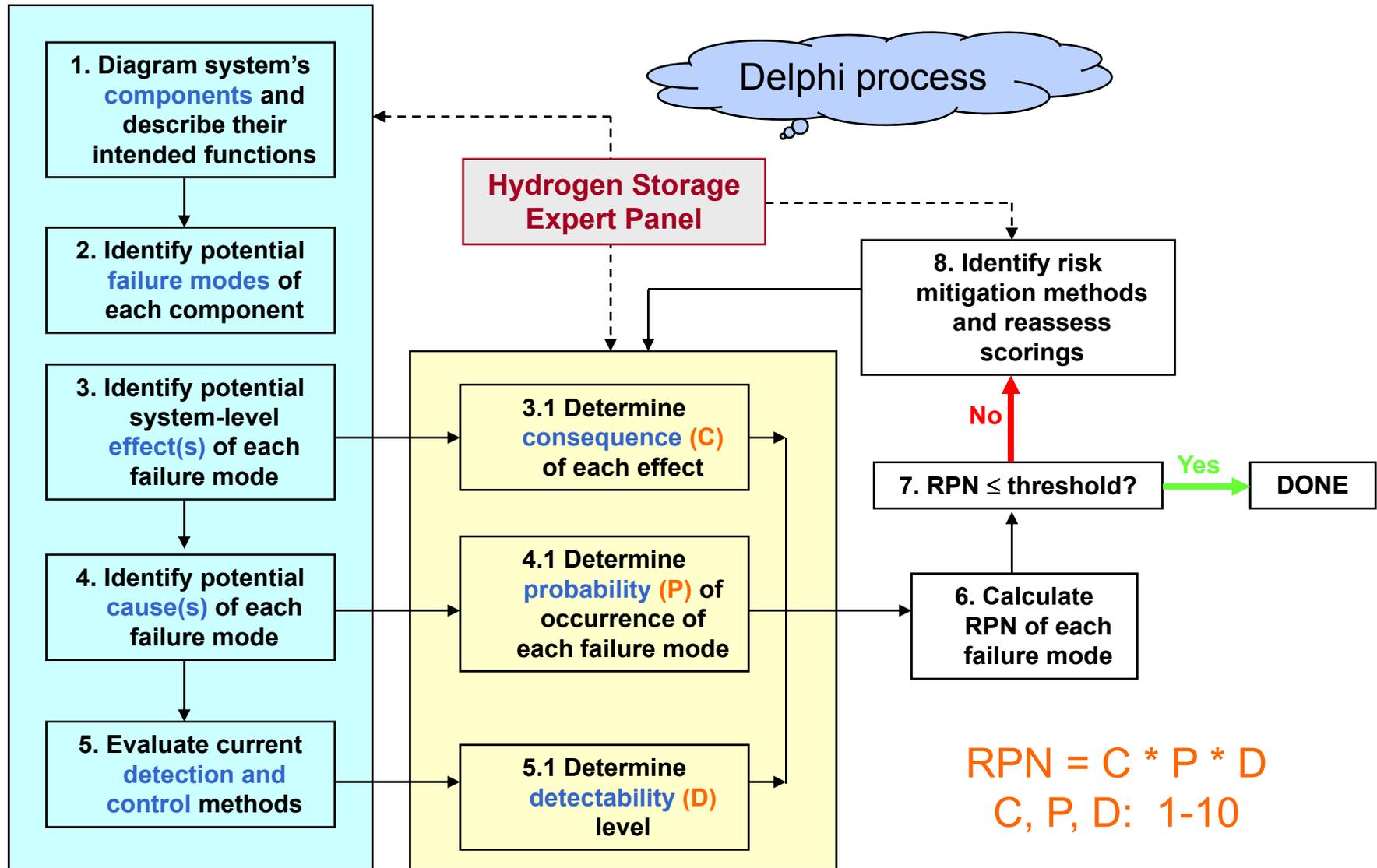
**Parameter Sensitivity Studies**



\* SAE J1739 Standard  
**SAE International**



# Qualitative Risk Analysis: FMEA Roadmap



# FMEA Spreadsheet

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	Risk Quantification Based on Existing Conditions				Ma Ha
						Consequence	Probability	Detectability	Risk Priority Number (RPN)	
Pressure vessel (containing NaAlH <sub>4</sub> )	Vessel designed to withstand H <sub>2</sub> pressure and contain hydride material	1.1 Vessel breach leading to hydride dispersion in a wet environment	Hydride rapid reaction, fire	1.1.1 Automotive accident	1. Design vessel for crashworthiness 2. Proper vessel location in vehicle to minimize vulnerability	7	3		210	Pellet to red water
				1.1.2 High g loads from vehicle absorption	1. Internal design to prevent powder separation and densification 2. Fiber optic sensor for composite		2	2	28	
				1.1.3 Ballistic impact	Damage tolerant fiber overwrap		7	1	10	70

Component

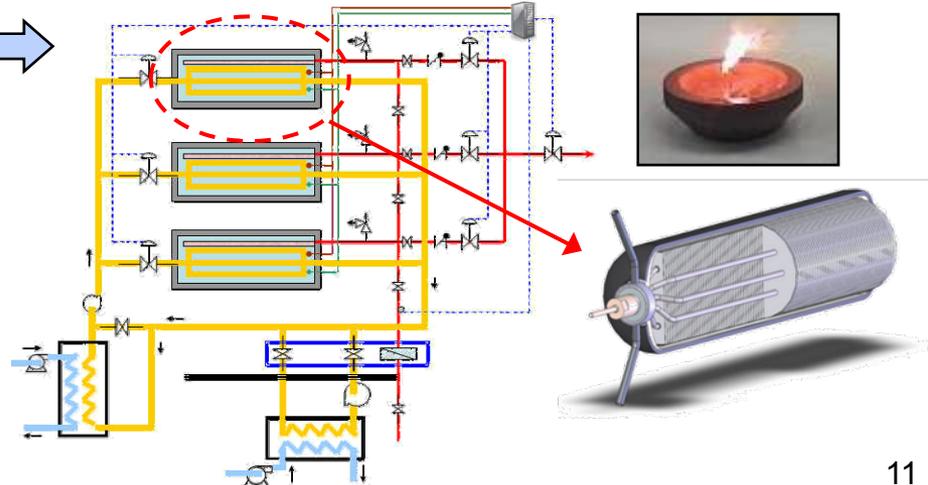
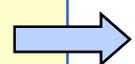
Failure Mode

Root Cause

Current Controls

Risk Scoring

- Initial assessment based on NaAlH<sub>4</sub> material and system due to existing knowledge – applicable to other on-board reversible materials.
- Risk Priority Number =  $\text{Consequence} * \text{Probability} * (\text{lack of}) \text{Detectability}$
- Acceptable / threshold risk:  $\text{RPN}_{th} = 80$



# FMEA Spreadsheet

Confidence	Risk Quantification AFTER Additional Mitigations					Threshold RPN = 80	Impact of Mitigation on DOE Non-Safety Technical Targets (Low, Medium, High)					Specific Recommended Actions		
Confidence	Additional Mitigations		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
	Material / System-Level Hazard Mitigation Strategy	Added Information to Reduce Uncertainty												
	Passivate hydride material to reduce reactivity	1. Additional testing and modeling to better understand extent and reactivity of powder 2. Sensitivity analysis modeling 3. Sensitivity analysis 4. 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 explosible concentration (MEC) b) Minimum ignition temperature (MIT) c) Minimum ignitable mixture limit (MIE) d) dP/dt and flame speed Applicable failure modes
														Obtain site vessel experience data on failure modes (applicable to all 1.1.X FM)

Additional Controls

Revised Scoring

Impact on Other Targets

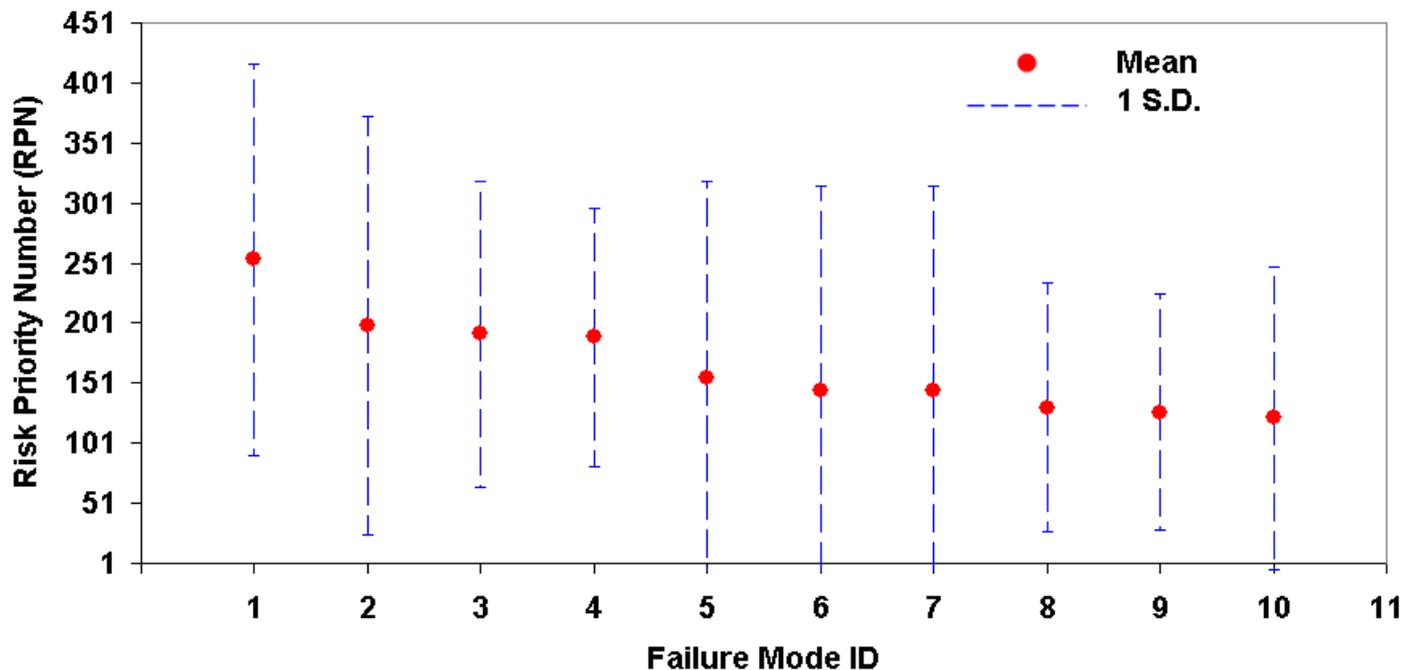
Multi-Project Actions

- 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.

# Initial FMEA / Expert Panel Risk Scoring

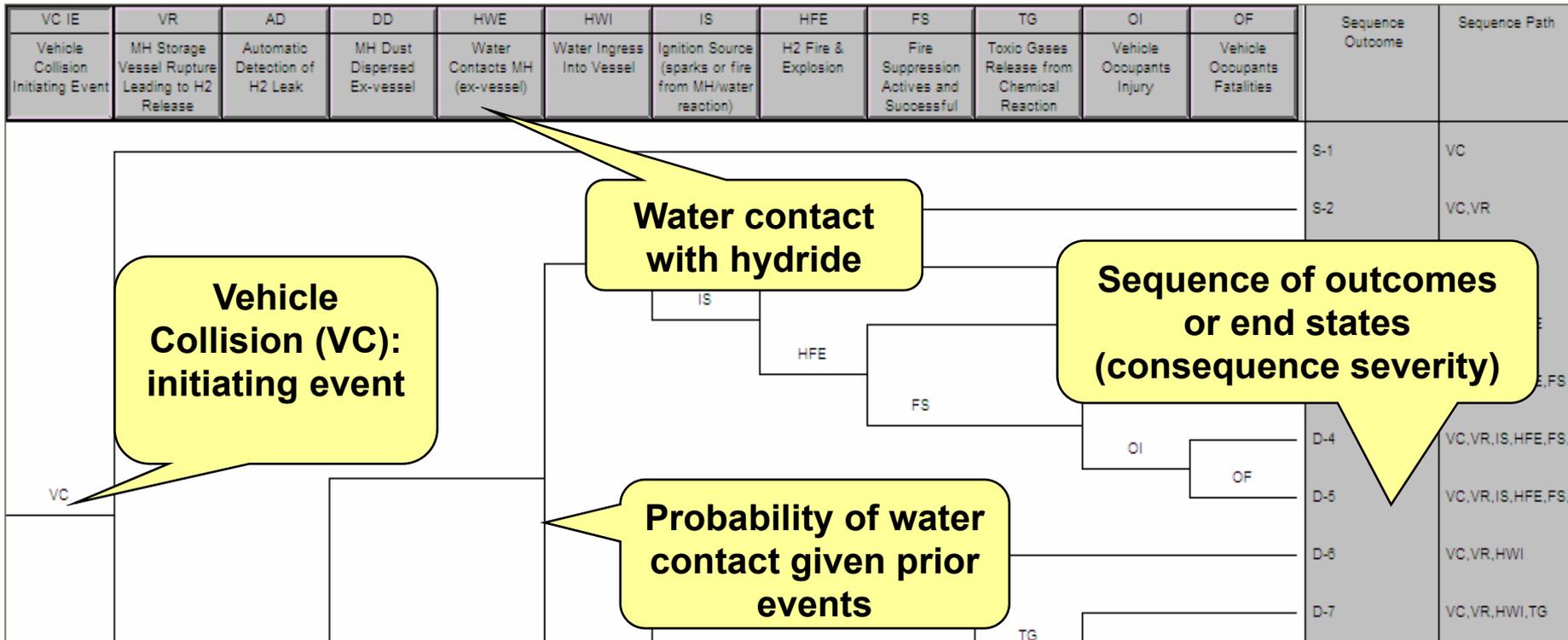
- Partial set of pooled FMEA risk scorings from the expert panel (round one elicitation).
- Three of the top failure modes are:
  - Vehicle collision leading to large break in hydride storage vessel (wet environment)
  - H<sub>2</sub> leak caused by pipe rupture resulting from impact during a vehicular collision.
  - External fire in close proximity to the vehicle, causing heating of the hydride material.
- High variability will be reduced in subsequent rounds of the Delphi iterative process.



*The Linear Opinion Pool Model was used with a weighing Factor =  $1/n$  where  $n$  is the number of experts.*

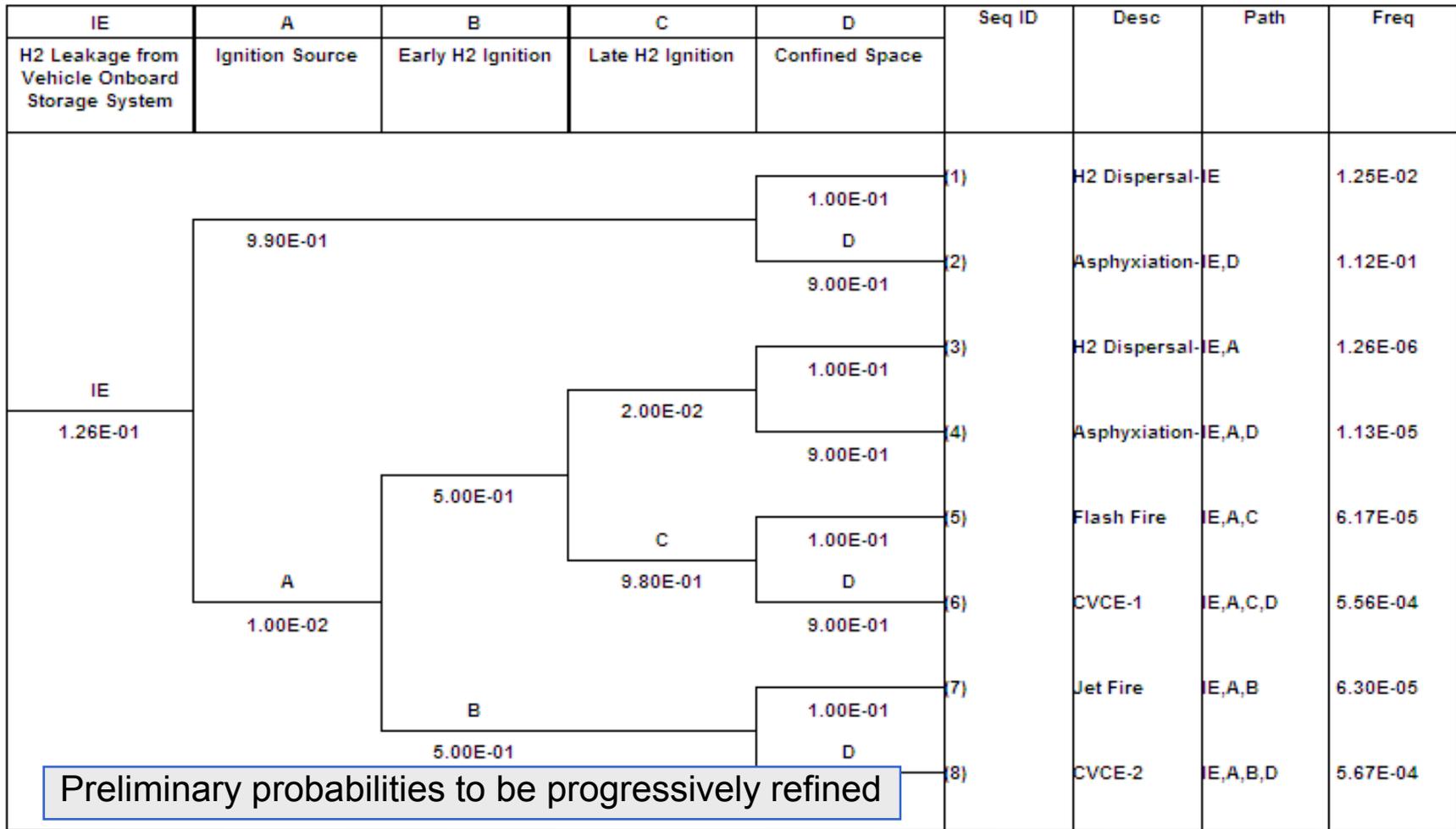
# Quantitative Analysis: ETA / FTA

- 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.



# Event Tree Analysis for Hydrogen Leakage

An Event Tree for Hydrogen Leakage (without mitigation) has been constructed and quantified.

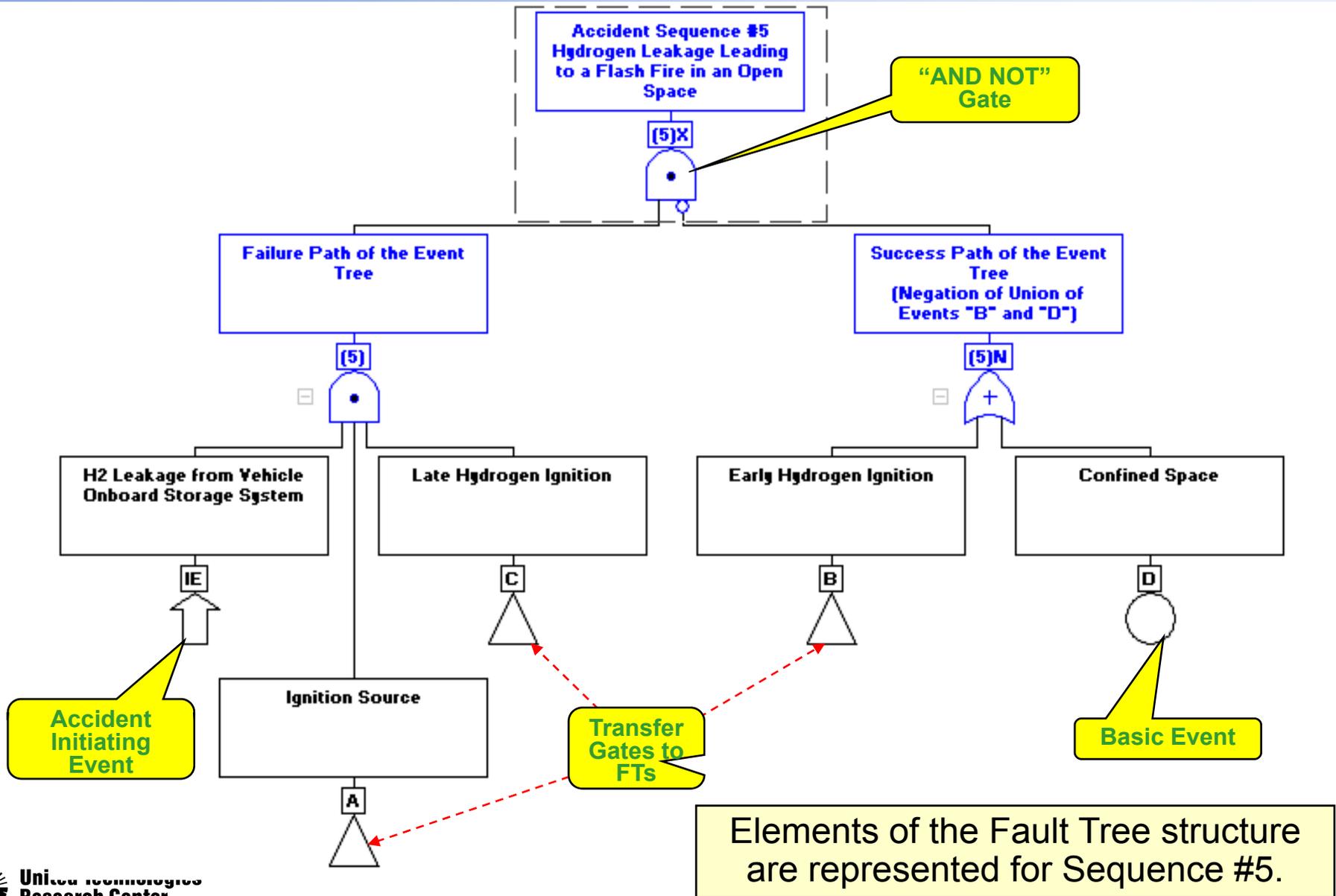


# Event Tree Analysis for Hydrogen Leakage

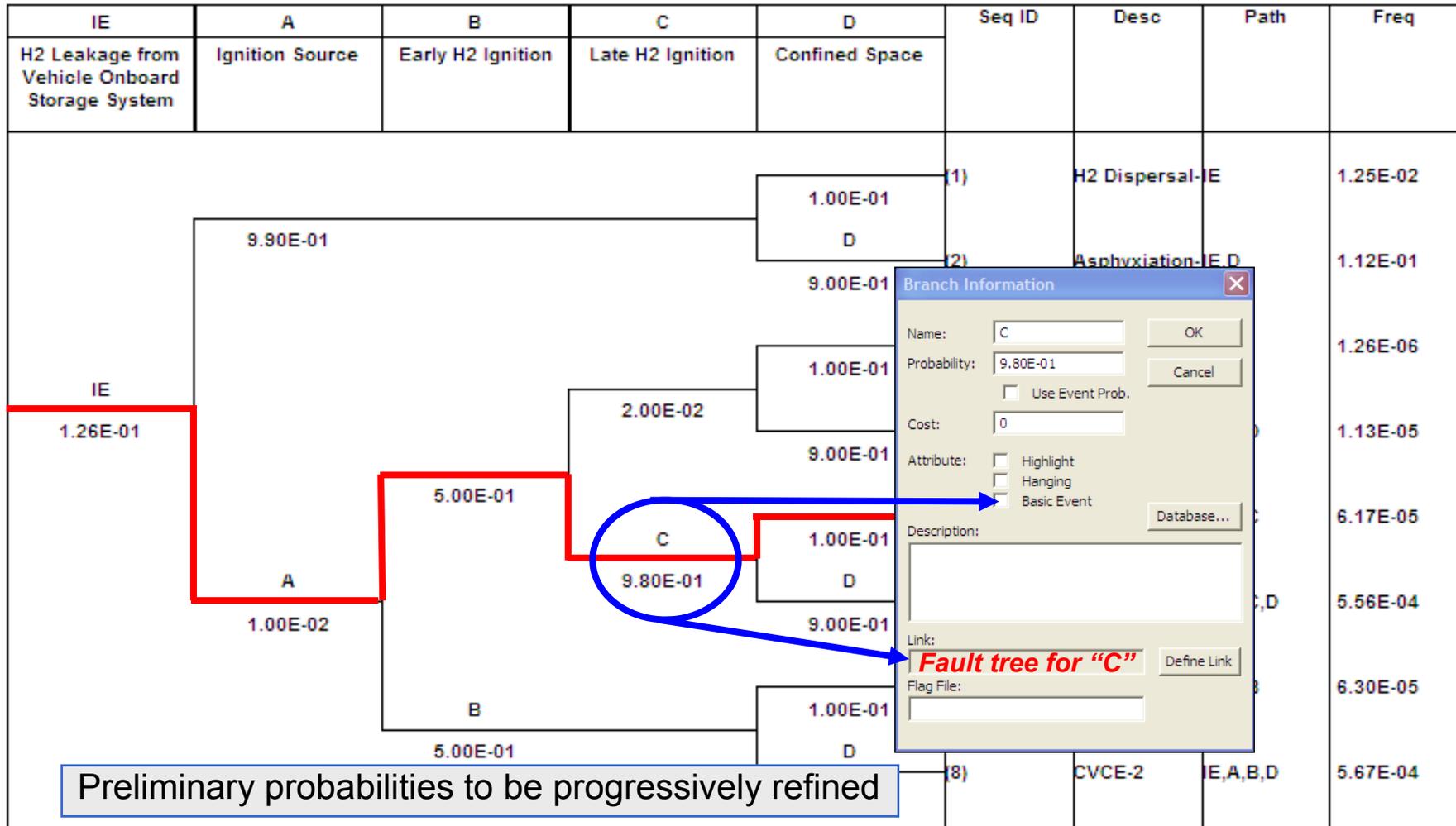
IE	A	B	C	D	Seq ID	Desc	Path	Freq
H2 Leakage from Vehicle Onboard Storage System	Ignition Source	Early H2 Ignition	Late H2 Ignition	Confined Space				
<p>IE 1.26E-01</p> <p>A 1.00E-02</p> <p>B 5.00E-01</p> <p>C 9.80E-01</p> <p>D 1.00E-01</p> <p>9.90E-01</p> <p>2.00E-02</p> <p>5.00E-01</p> <p>9.00E-01</p> <p>9.00E-01</p> <p>9.00E-01</p> <p>9.00E-01</p> <p>9.00E-01</p> <p>9.00E-01</p> <p>9.00E-01</p> <p>9.00E-01</p>	(1)	H2 Dispersal-IE	IE	1.25E-02				
	(2)	Asphyxiation-IE,D	IE,D	1.12E-01				
	(3)	H2 Dispersal-IE,A	IE,A	1.26E-06				
	(4)	Asphyxiation-IE,A,D	IE,A,D	1.13E-05				
	(5)	Flash Fire	IE,A,C	6.17E-05				
	(6)	CVCE-1	IE,A,C,D	5.56E-04				
	(7)	Jet Fire	IE,A,B	6.30E-05				
	(8)	CVCE-2	IE,A,B,D	5.67E-04				
<p>Preliminary probabilities to be progressively refined</p>								

The Event Tree represents a set of mutually exclusive sequences with different outcomes and probabilities of occurrence (ex. Sequence #5).

# Event Tree / Fault Tree Linking: Sequence #5



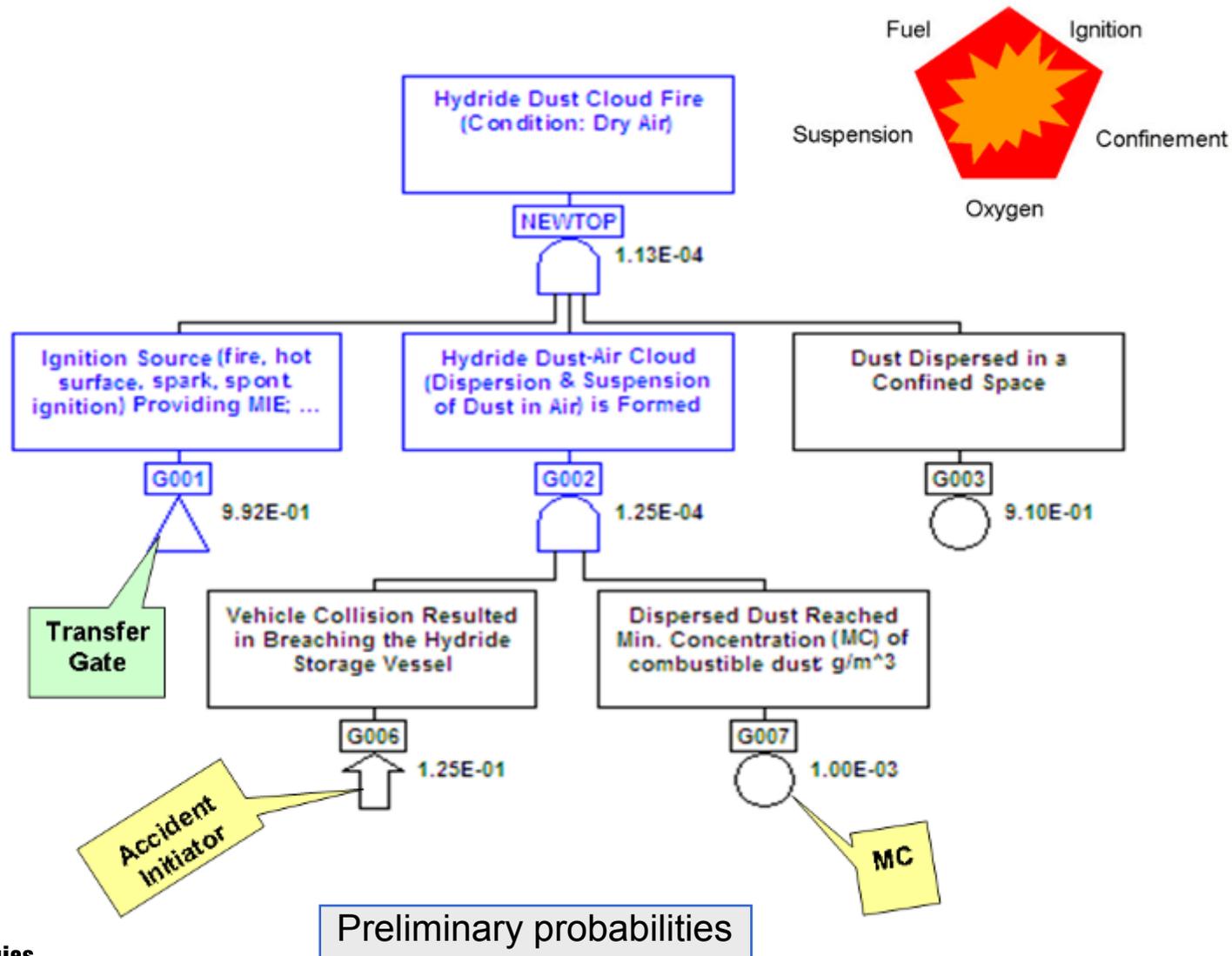
# Event Tree Analysis for Hydrogen Leakage



In CAFTA, a branch probability can be derived from a detailed Fault Tree or a Basic Event with a probability distribution to address uncertainties.

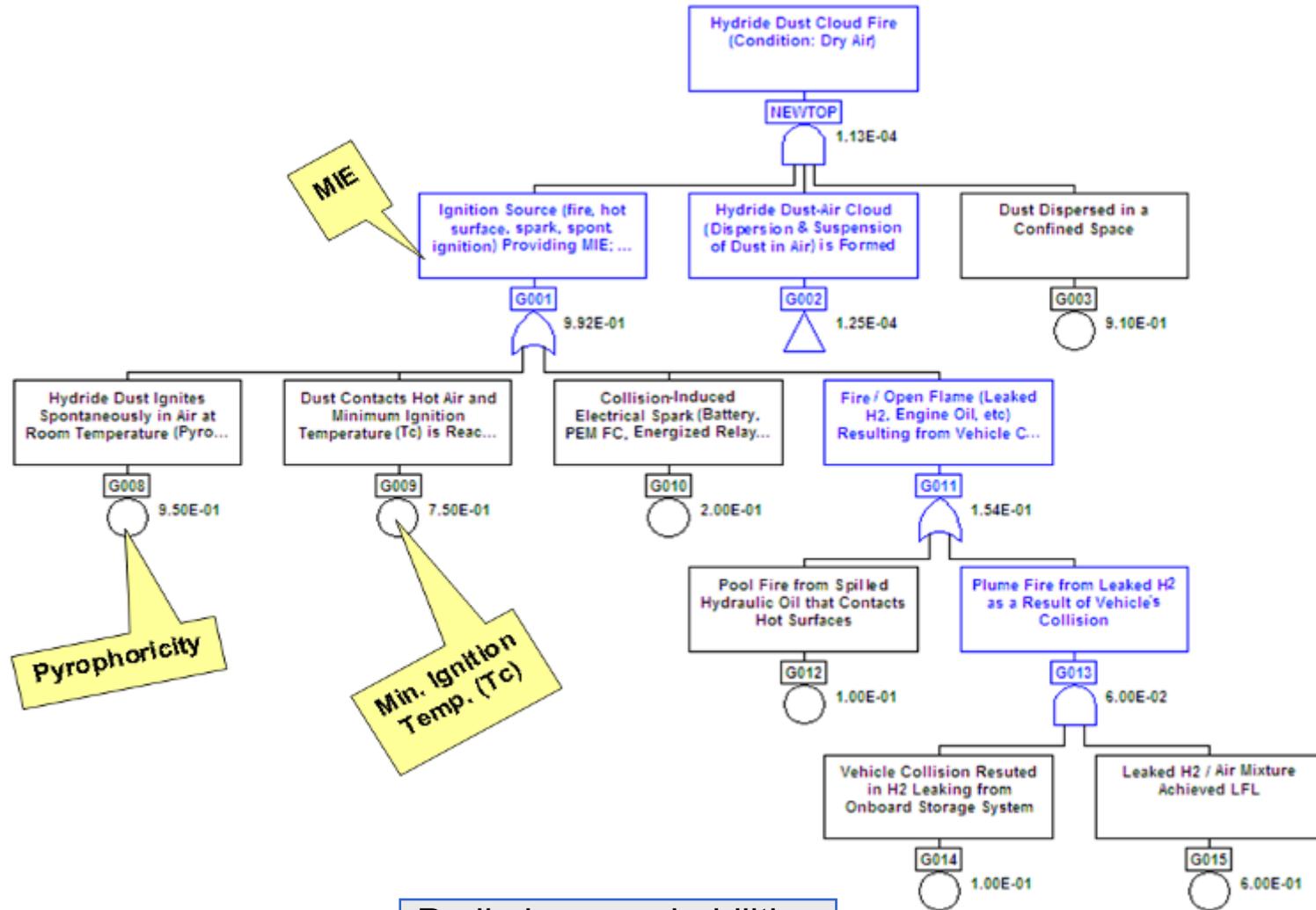
# Fault Tree Model for Dust Cloud Dispersion

Dust cloud test characterization results are incorporated into the fault tree model.



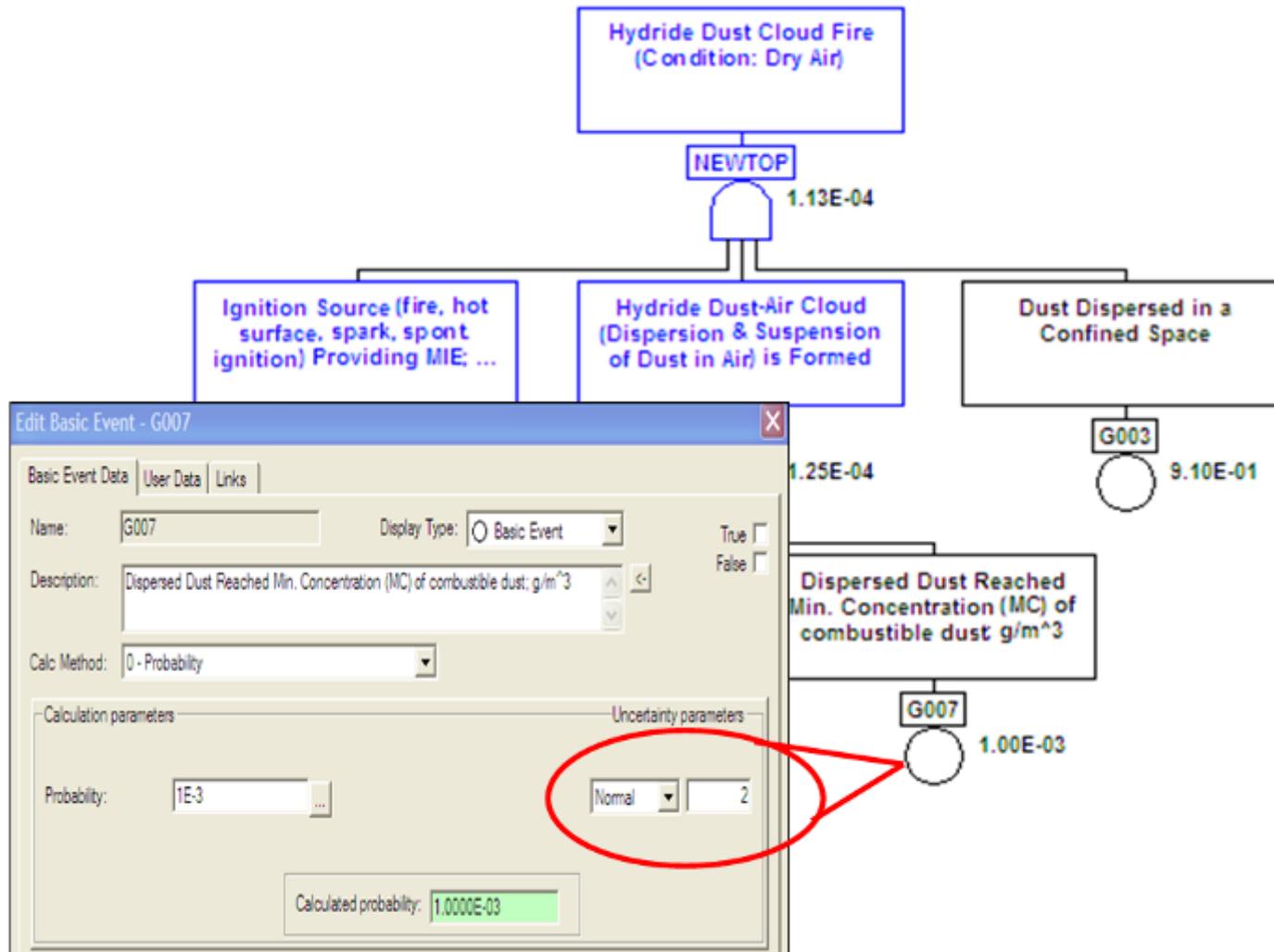
# Fault Tree Model for Dust Cloud Dispersion

Dust cloud test characterization results are incorporated in the fault tree model.



Preliminary probabilities

# Fault Tree Model - Basic Event Uncertainties



Edit Basic Event - G007

Basic Event Data | User Data | Links

Name: G007      Display Type: Basic Event      True  False

Description: Dispersed Dust Reached Min. Concentration (MC) of combustible dust: g/m<sup>3</sup>

Calc Method: 0 - Probability

Calculation parameters      Uncertainty parameters

Probability: 1E-3      Normal      2

Calculated probability: 1.0000E-03

Preliminary probabilities

# Supporting Information Sources

A wide range of information has been searched and insights implemented in the risk analyses

Information Source Category	Description / Comments
SAE J1739, Rev. August 2002	<ul style="list-style-type: none"> <li>▪ Jointly developed by Daimler Chrysler Corporation, Ford Motor Company, and General Motors Corporation.</li> <li>▪ Covers FMEA and provides general guidance in the application of this methodology.</li> </ul>
<ul style="list-style-type: none"> <li>▪ ASTM E-1226</li> <li>▪ ASTM E-1515</li> <li>▪ ASTM E-2019</li> <li>▪ ASTM E-1491</li> </ul>	<ul style="list-style-type: none"> <li>▪ Maximum pressure, rate of pressure rise and <math>K_{st}</math></li> <li>▪ Minimum concentration of combustible dusts (MC)</li> <li>▪ Minimum ignition energy of a dust cloud in air (MIE)</li> <li>▪ Minimum ignition temperature of dust clouds (<math>T_c</math>)</li> </ul>
NFPA-2: Hydrogen Technologies	Hydrogen transportation, storage, refueling stations, leakage in road tunnels and fire.
ISO TC-197  ISO / FDIS 16111	<p>Several working groups on hydrogen generation, storage, transportation, refueling stations, and detection.</p> <p>Reversible metal hydrides – portable applications.</p>

# Supporting Information Sources

Information Source Category	Description / Comments
ANSI / CSA NGV2	Requirements for compressed natural gas vehicles.
International Codes Council (ICC)	Numerous topics related to hydrogen safety and infrastructures.
Road Safety Improvement Programs and Benefit-Cost Analyses	Insights for economic sequence analysis such as costs associated with risk avoidance of injuries due to motor vehicle crashes.
Literature on Thermodynamics and Reaction Kinetics of Hydride Materials	Relevant thermodynamic and kinetics information on hydride materials are utilized in discussion of FMEA.
Publications on Dust Dispersion	Insights on dust cloud characteristics and consequences such as aluminum dust dispersion studies.
EPRI Software Packages: CAFTA and ETA-II	<ul style="list-style-type: none"> <li>▪ Part of EPRI's risk and reliability (R&amp;R) workstation.</li> <li>▪ Used by the nuclear industry, NASA, Boeing and others.</li> </ul>
ASME	Risk standards; Boiler and pressure vessel code.

# Materials Testing: Dust Cloud

## Measurements (ASTM tests)

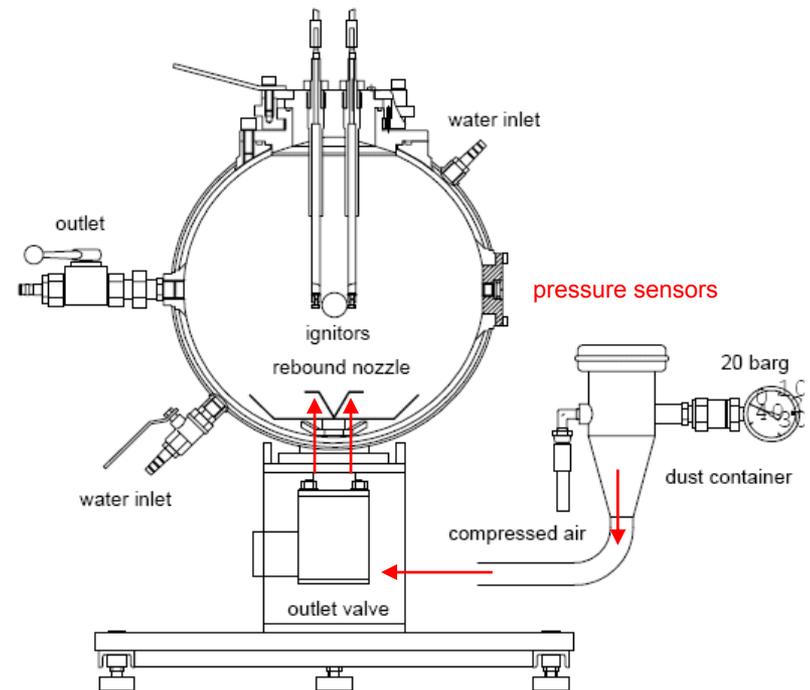
- $P_{max}$ ,  $(dP/Dt)_{max}$ ,  $K_{st}$  (E1226)
- Minimum Concentration (E1515)
- Minimum Ignition Energy (E2019)
- Minimum Ignition Temperature (E1491)



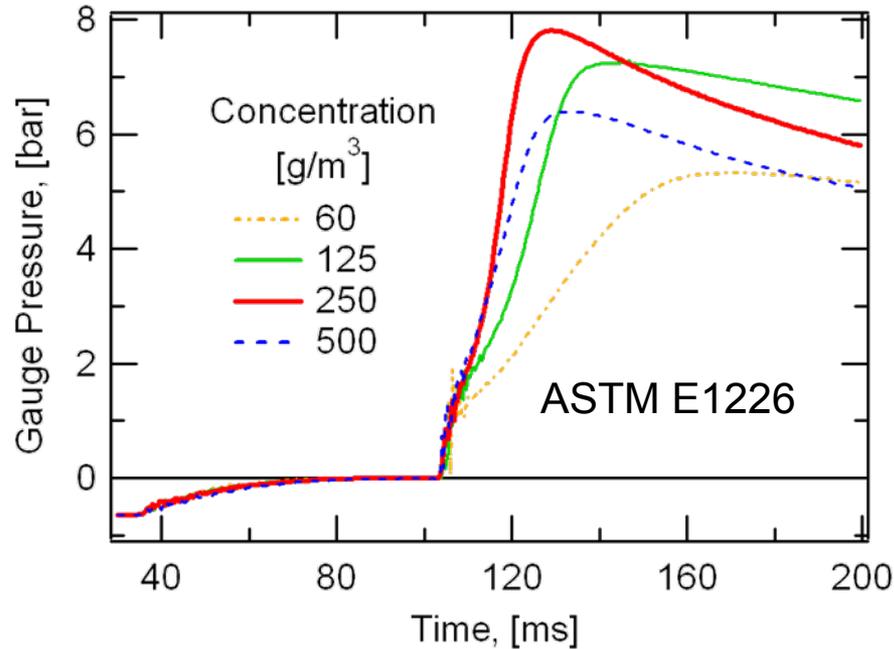
$$K_{ST} \equiv \left( \frac{dP}{dt} \right)_{max} * V^{1/3}$$

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

## Standard 20 L Kühner apparatus (E1226 & E1515)



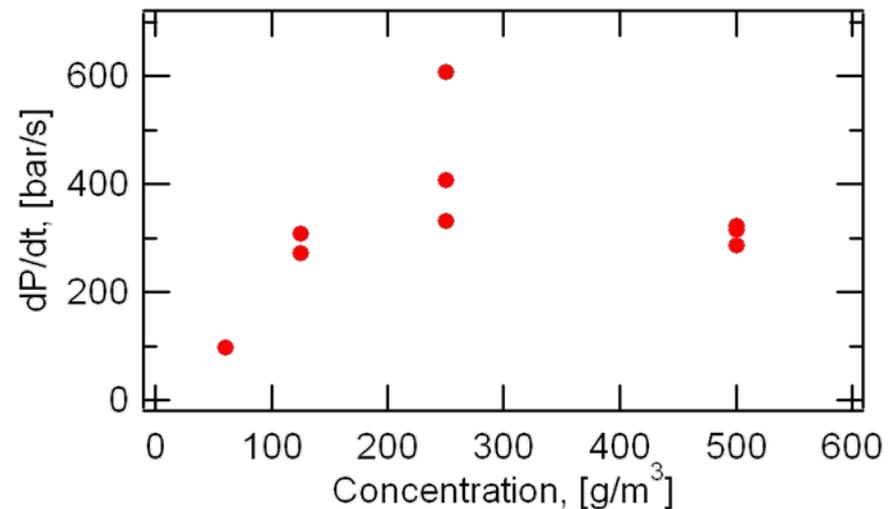
# AX-21 Carbon



	Reference Materials		
	AX-21	Pittsburgh Seam Coal	Lycopodium Spores
$P_{max}$ , bar-g	8.0	7.3	7.4
$(dP/dt)_{max}$ , bar/s	449	426	511
$K_{ST}$ , bar-m/s	122	124	139
Dust Class	St-1	St-1	St-1
MC, g/m <sup>3</sup>	100	65	30
$T_C$ , °C	760	585	430
MIE, mJ	> 10,000	110	17

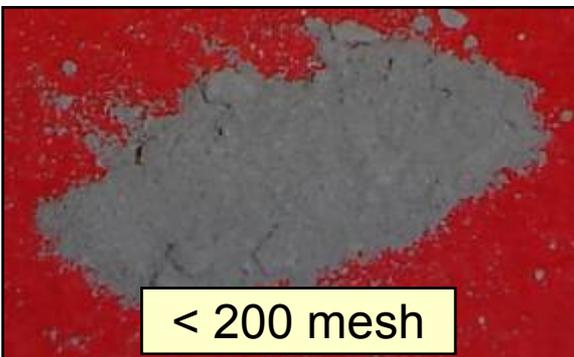
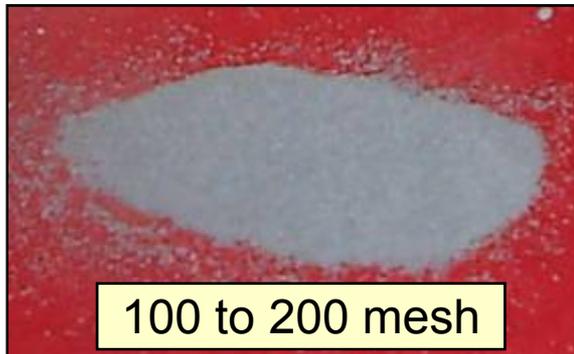
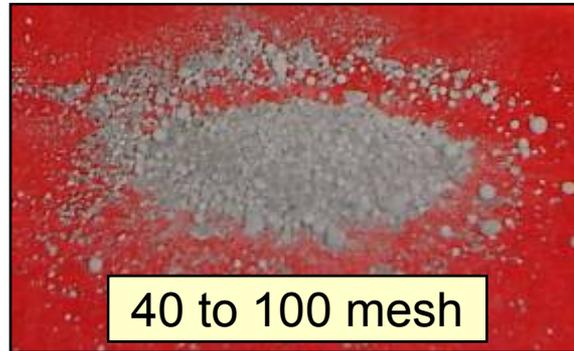
AX-21 has similar characteristics to standard reference materials except for the MIE.

Future testing to be conducted with hydrogen additions.



# Partially Discharged $2\text{LiBH}_4 + \text{MgH}_2$

Completion of dust cloud testing:  
40 to 100 mesh material.



	Hydrided	Partially Dehydrided		
	As-milled	< 200 mesh	100 to 200 mesh	40 to 100 mesh
$P_{\max}$ , bar-g	10.7	9.9	6.2	6.0
$(dP/dt)_{\max}$ , bar/s	2036	1225	153	118
$K_{ST}$ , bar-m/s	553	333	42	32
Dust Class	St-3	St-3	St-1	St-1
MC, $\text{g/m}^3$	30	30	60	30
$T_C$ , $^{\circ}\text{C}$	150	230	310	270
MIE, mJ	< 9	< 9	$22 < \text{MIE} < 47$	20

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

Quantification of particle size influence on dust cloud characteristics.

# Discharged Alane

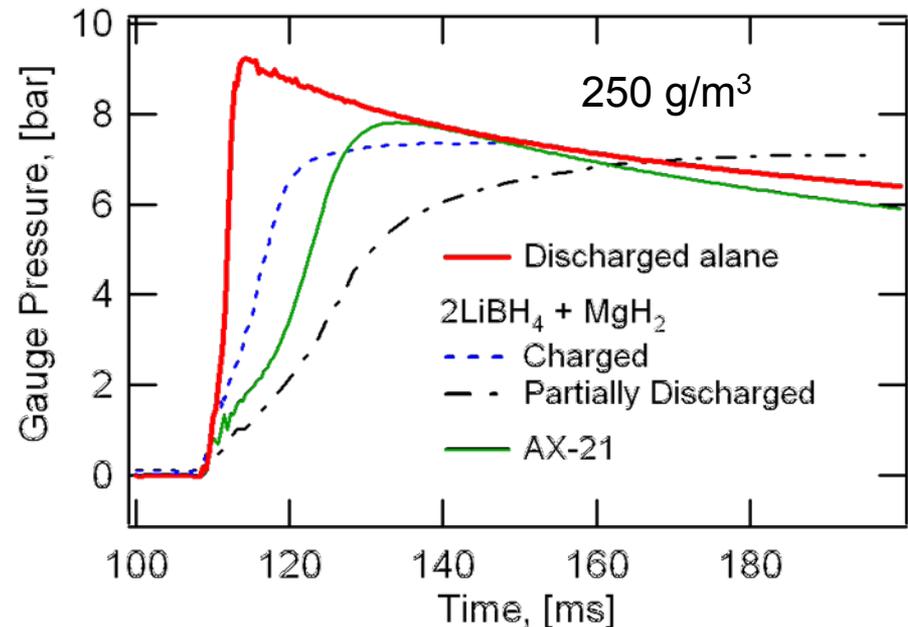
## Semi-quantitative XRD

- Al: 97.8 wt%  
(100 nm crystallite size)
- LiCl: 1.4 wt%
- AlOCl: 0.7 wt%
- NaCl: 0.1 wt%

	Reference Materials		
	Discharged Alane	Pittsburgh Seam Coal	Lycopodium Spores
MC, g/m <sup>3</sup>	125 to 250	65	30
T <sub>C</sub> , °C	710	585	430
MIE, mJ	< 10	110	17
Sieve Analysis			
> 200 mesh (75 μm)	6%	16%	0%
< 200 mesh (75 μm)	94%	85%	100%

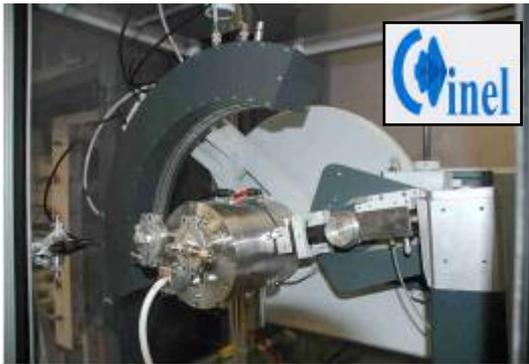
Due to current limited material quantities, full K<sub>st</sub> & MC determinations could not be made. This will be addressed in future efforts.

For 250 g/m<sup>3</sup>, dP/dt is the largest of materials tested to date.



# Air Exposure: Ammonia Borane

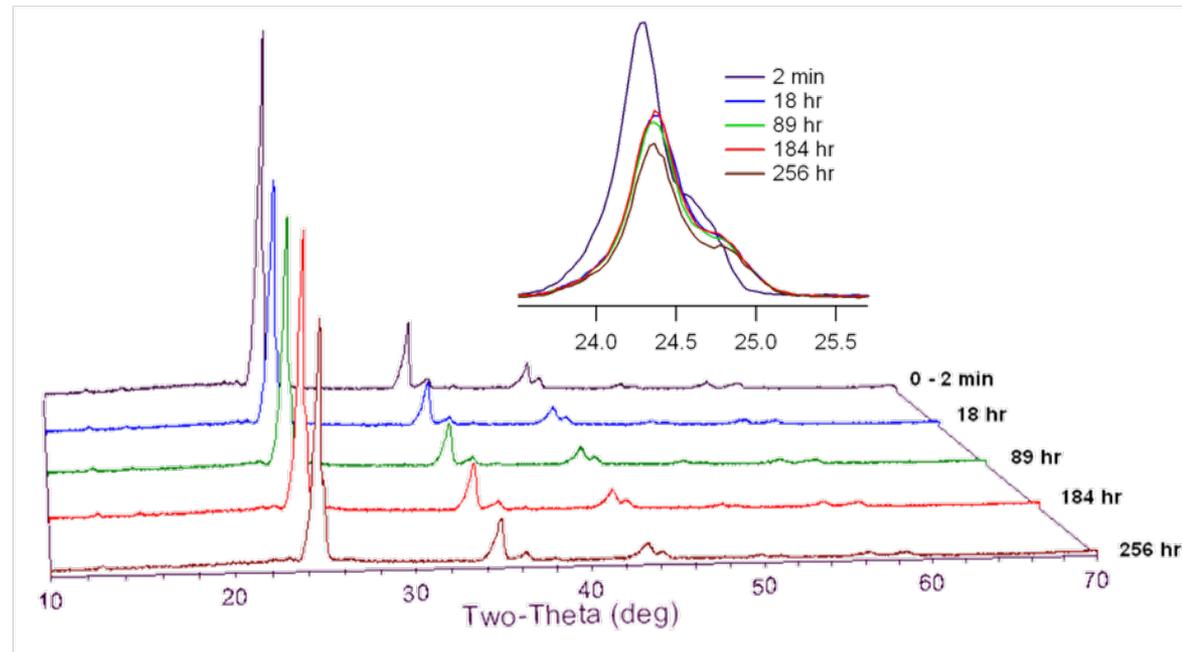
Real time measurement of composition evolution to complement SRNL calorimetry and SNL flow-through reactor efforts.



## Starting Material

Source: Sigma-Aldrich

Preliminary XRD indicates nearly all tetragonal  $\text{NH}_3\text{BH}_3$  with trace levels of  $(\text{BH}_2\text{NH}_2)_4$ .



TR-XRD of ammonia borane at  $\approx 50\%$  relative humidity and  $23^\circ\text{C}$ .

Reactivity with ambient air is very slow relative to some of the other hydrogen storage material candidates ( $\text{NaAlH}_4$ ,  $2\text{LiBH}_4 + \text{MgH}_2$ , ...).

# Future Work

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## *FY09*

### Risk Analysis

- Complete compilation of input from Expert Panel for multiple rounds of scoring regarding the on-board reversible risk assessment.
- Refine quantitative ETA / FTA risk analyses for key hazards of the on-board reversible system.

### Material Testing & Mitigation

- Complete AX-21 and AlH<sub>3</sub> testing.
- Develop and test risk mitigation methods.
- Design and construct powder cycling and dispersion apparatus to subject material to cyclic / vibratory conditions and simulate vessel breach.

### Go / No Go decision

## *FY10*

### Risk Analysis

- Develop quantitative ETA / FTA risk analysis for an off-board regenerated system.
- Pending Go / No-Go decision, determine subscale prototype configuration and conduct related risk analysis.

### Material / System Testing & Mitigation

- Refine risk mitigation methods.
- Pending Go / No-Go, develop and test representative subscale prototype.

# Summary

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**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

- $2\text{LiBH}_4 + \text{MgH}_2$
- $\text{AlH}_3$
- $\text{NH}_3\text{BH}_3$
- 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.