

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

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Annual Peer Review
Washington, DC
June 8, 2010

Project ID: ST012

Overview

■ Timeline

- Start: June 2007
- End: May 2011
- Percent complete: 64% (spending)

■ Budget

- \$1.34M Total Program
 - \$1.07M DOE
 - \$0.27M UTRC
- FT07: \$120K
- FY08: \$300K
- FY09: \$400K
- FY10: \$250K

■ Barriers

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

■ Target

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

■ Partners

- Kidde-Fenwal: dust cloud testing

■ Collaborators

- DOE reactivity projects: SNL and SRNL
- IEA HIA Task 22 / IPHE Project (with SRNL & SNL): FZK, AIST, UQTR
- DOE H2 C&S and Safety Panel
- NFPA-2 H2 Technologies Committee
- Lincoln Composites
- IEA HIA Task 19

Project Objectives & Associated Tasks

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 materials Centers of Excellence.
- Develop methods to **assess and reduce risks**.

Primary Tasks

- Risk analysis (**Task 1.0**)
 - Qualitative risk analysis (QLRA) to develop a broad range of scenarios
 - Quantitative risk analysis (QRA) for key scenarios
- Material testing
 - Dust cloud: standard and modified ASTM procedures (**Task 2.0**)
 - Reaction kinetics: air exposure / time resolved XRD (**Task 3.0**)
- Risk mitigation
 - Material-based risk mitigation (**Task 4.0**)
 - Subscale prototypes (**Task 5.0**)

Milestones

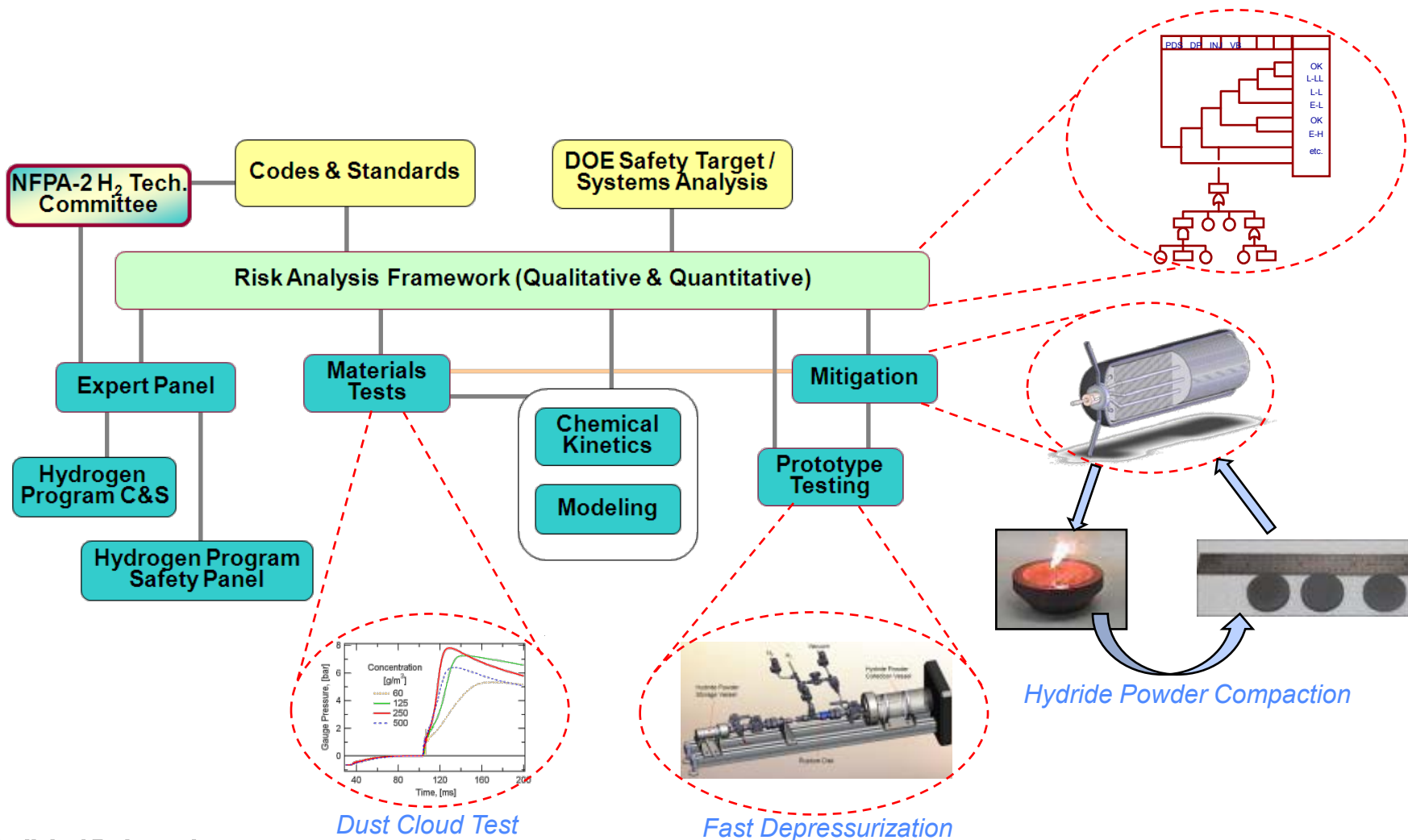
	Milestone or Go/No-Go Decision
FY07 Q4	<ul style="list-style-type: none"> • Identify risk analysis framework including qualitative and quantitative methods and tools. • Perform dust cloud characterization tests for Material #1 (2LiB₄ + MgH₂ mixture).
FY08 Q1	<ul style="list-style-type: none"> • Develop qualitative risk analysis for one on-board reversible storage system (using NaAlH₄). • Identify the dominant risks and failure modes for this system.
FY08 Q2	<ul style="list-style-type: none"> • Perform dust cloud characterization tests for Material #2 (discharged AlH₃). • Conduct time-resolved XRD for air exposure of Material #1.
FY08 Q3	Implement enhancements to dust explosion and gas exposure reactivity testing.
FY08 Q4	<ul style="list-style-type: none"> • Perform qualitative risk analysis for top two materials. • Perform dust cloud characterization tests for Material #3 (charged AlH₃). • Complete enhanced gas reactivity testing for Materials #2 and #3.
FY09 Q1	Develop quantitative risk analysis for dominant hazards (accident initiating events) based the insights generated from the design failure mode and effects analysis (d-FMEA).
FY09 Q2	<ul style="list-style-type: none"> • Perform dust cloud characterization tests for Material #4 (Maxsorb activated carbon). Test conditions: air only and air-hydrogen mixtures. • Go / No-Go decision.
FY09 Q3	Design and construct a fast blowdown (depressurization) test rig to mimic dispersion of hydride powder during a vehicular collision leading to storage vessel failure.
FY09 Q4	<ul style="list-style-type: none"> • Develop a material reactivity based test plan to demonstrate how key risks can be mitigated. • Perform reactivity tests on unmitigated and mitigated materials.

Milestones

	Milestone or Go/No-Go Decision
FY10 Q1	<ul style="list-style-type: none"> • Identify two additional safety-critical failure modes for the on-board reversible storage system. • Develop risk models for each of the identified safety-critical failure modes. • Develop an approach for converting experimental results into probability inputs to the risk models.
FY10 Q2	<ul style="list-style-type: none"> • Complete qualitative risk analysis (d-FMEA) for the off-board regenerable (alane) system. • Develop a test plan (including expected benefits) for conducting experiments on NaAlH₄ prototype system(s) fabricated in contract DE-FC36-02AL67610 to assess hazards, mitigation and neutralization methods.
FY10 Q3	Complete XRD characterization tests for at least one mitigated material structure (including those planned and coordinated by SNL material reactivity project).
FY10 Q4	<ul style="list-style-type: none"> • Conduct fast blowdown tests on selected unmitigated and mitigated materials. • Perform material reactivity tests for selected mitigated and unmitigated materials(including those planned and coordinated by SNL material reactivity project).

Approach

Materials testing and modeling results are used to supplement the Risk Analysis (RA) Framework which serves as the basis for risk-informed safety Codes & Standards (C&S).



Overview of Technical Accomplishments

Accomplishments from last year's review to date:

- **Quantitative Risk Analysis (QRA)**

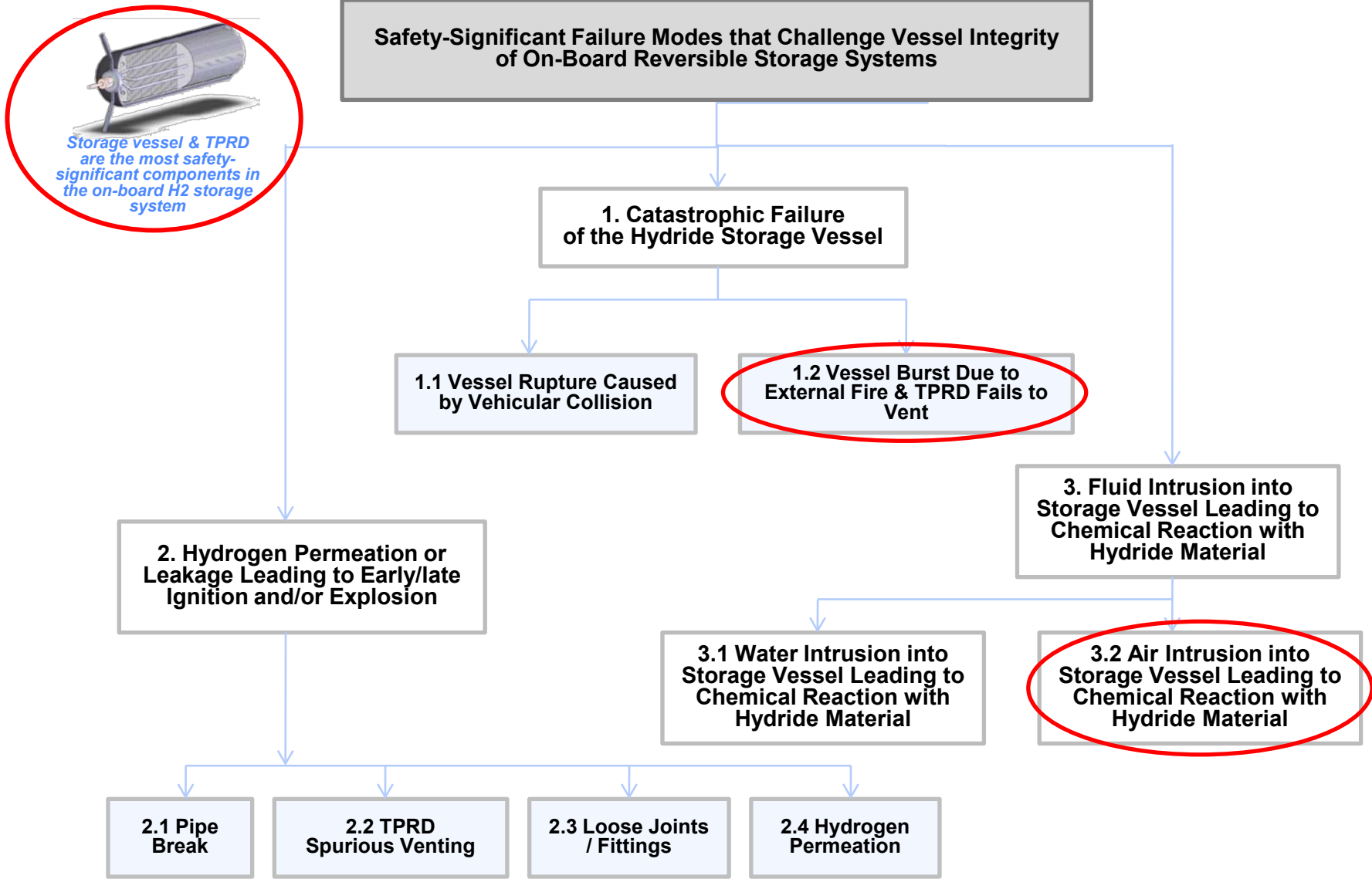
- Event tree model for external fire as an accident initiator.
- Fault tree model for in-vessel air inleakage.
- Approaches for managing uncertain inputs in risk analysis.

} Without Risk Mitigation

- **Experimental Studies**

- Material reactivity risk mitigation tests.
- Design and fabrication of a fast blowdown (depressurization) test rig.
- Hydrogen absorption / desorption cyclical tests for sodium alanate.
- XRD tests of cycled sodium alanate.

QRA: Safety-Significant Failure Modes of On-Board Reversible Storage Systems



QRA: External Fire as an Initiating Event

External Fire: a credible accident initiator based on field experience for CNGV; required bonfire test for CNGV vessels (FMVSS 304 – 20 min).

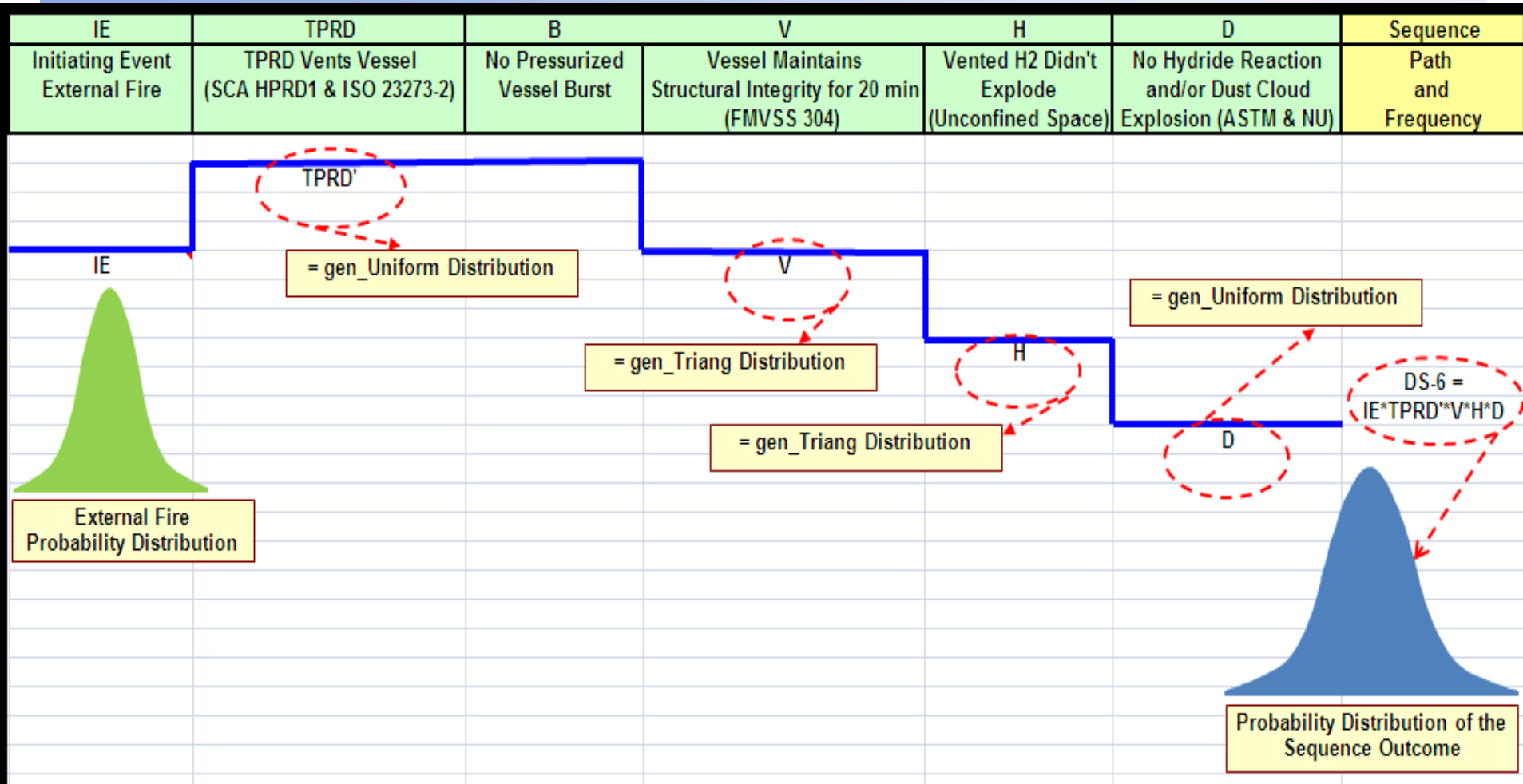
IE Normalized Initiating Event: External	TPRD TPRD Vents Vessel(SCA HPRD1 & ISO 23273-2)	B No Pressurized Vessel Burst	V Vessel Maintains Struct. Integrity	H No H2 Explosion(□ Open Space)	D No Hydride Rx and/or Dust□Cloud Explosion	Description	Sequence Path	Conditional Seq Freq
<div style="border: 1px solid red; border-radius: 50%; padding: 5px; display: inline-block;"> IE 1.00E+00 </div>	TPRD 2.22E-05	B 9.90E-01	V 6.00E-01	H 1.00E-01	D 9.90E-01	DS-1	IE	7.20E-01
						DS-2	IE,H	8.00E-02
						DS-3	IE,V	1.53E-01
						DS-4	IE,V,D	2.70E-02
						DS-5	IE,V,H	1.70E-02
						DS-6	IE,V,H,D	3.00E-03
						DS-7	IE,TPRD	8.89E-08
						DS-8	IE,TPRD,V	1.20E-09
						DS-9	IE,TPRD,V,D	1.19E-07
						DS-10	IE,TPRD,V,H	1.33E-10
						DS-11	IE,TPRD,V,H,D	1.32E-08
						DS-12	IE,TPRD,B	1.98E-07
						DS-13	IE,TPRD,B,D	1.96E-05
						DS-14	IE,TPRD,B,H	2.20E-08
						DS-15	IE,TPRD,B,H,D	2.18E-06

Normalized Fire IE Frequency

All assigned branch probabilities are preliminary

Conditional Outcome

Accident Sequence DS-15: Outcome frequency distribution using Monte Carlo Simulation



Flaw of Averages (Jensen's Inequality): $F(E\{X\}) \neq E\{F(X)\}$

Where 'X' is an uncertain variable and F(X) is a non-linear function of 'X'

A Two-Way Sensitivity Analysis of Accident Sequence DS-6

IF(DS-6 freq < 1.0E-6, "S", "K")

S = screen out seq.

K = keep seq.

- A user defined risk acceptance threshold (decision variable) = 1.0E-6/yr (a preliminary estimate)
- Each cell in the matrix contains a quantified outcome of accident sequence DS-6
- 'S' means screen sequence out as it doesn't warrant risk mitigation
- 'K' means keep sequence as it warrants risk mitigation

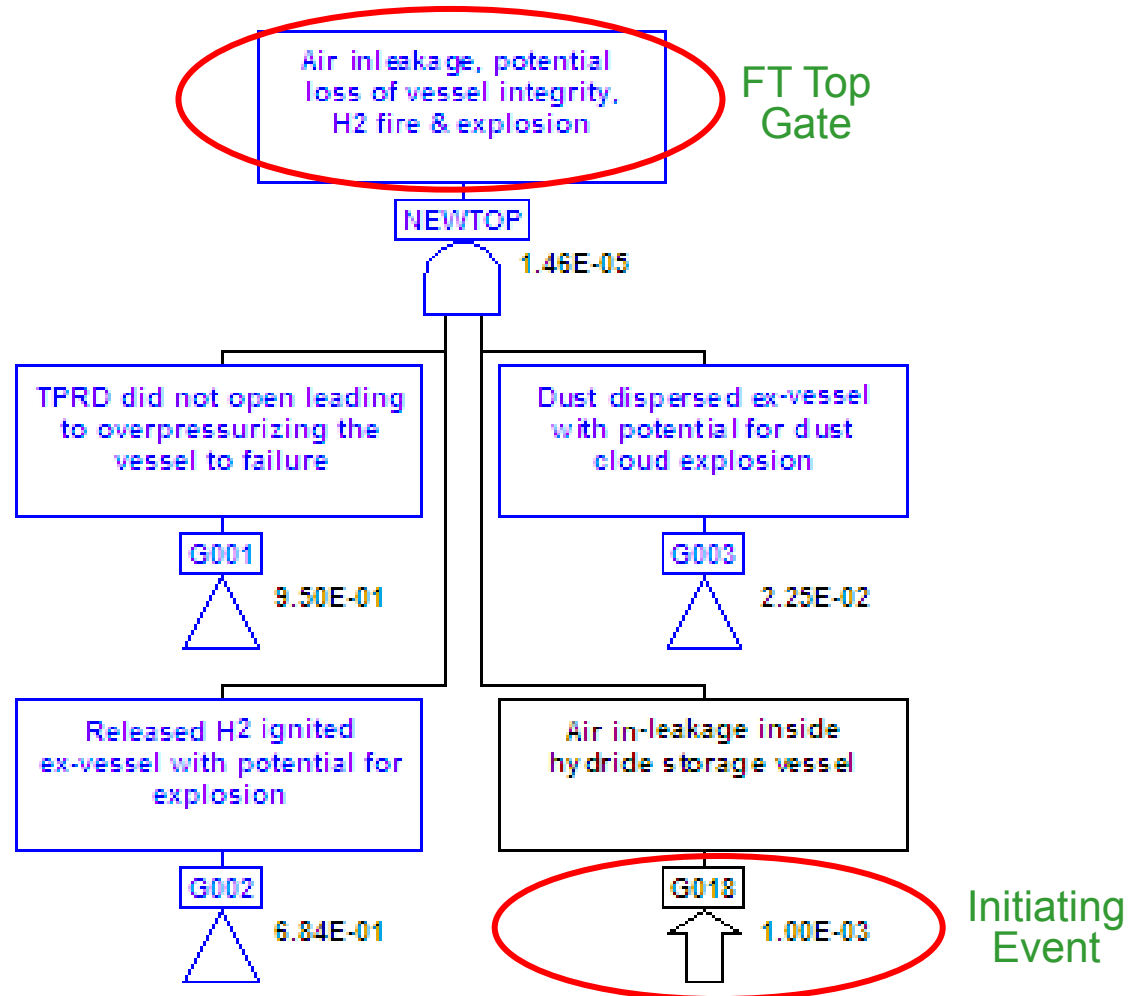
		E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U
		A Two-Way Sensitivity Analysis for Accident Sequence DS-6																
		ET Top Event H: Prob. that vented H2 explodes (given a confined space)																
		K	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10	0.11	0.12	0.13	0.14	0.15	
ET Top Event Y: Prob. that vessel lost structural integrity	0.05	S	S	S	S	S	K	K	K	K	K	K	K	K	K	K	K	K
	0.06	S	S	S	S	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.07	S	S	S	S	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.08	S	S	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.09	S	S	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.10	S	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.11	S	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.12	S	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.13	S	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.14	S	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.15	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.16	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.17	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.18	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.19	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.20	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.21	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.22	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.23	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.24	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.25	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.26	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.27	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.28	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.29	S	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K
	0.30	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K	K

Interactive Stochastic Simulation for Accident Sequence DS-6



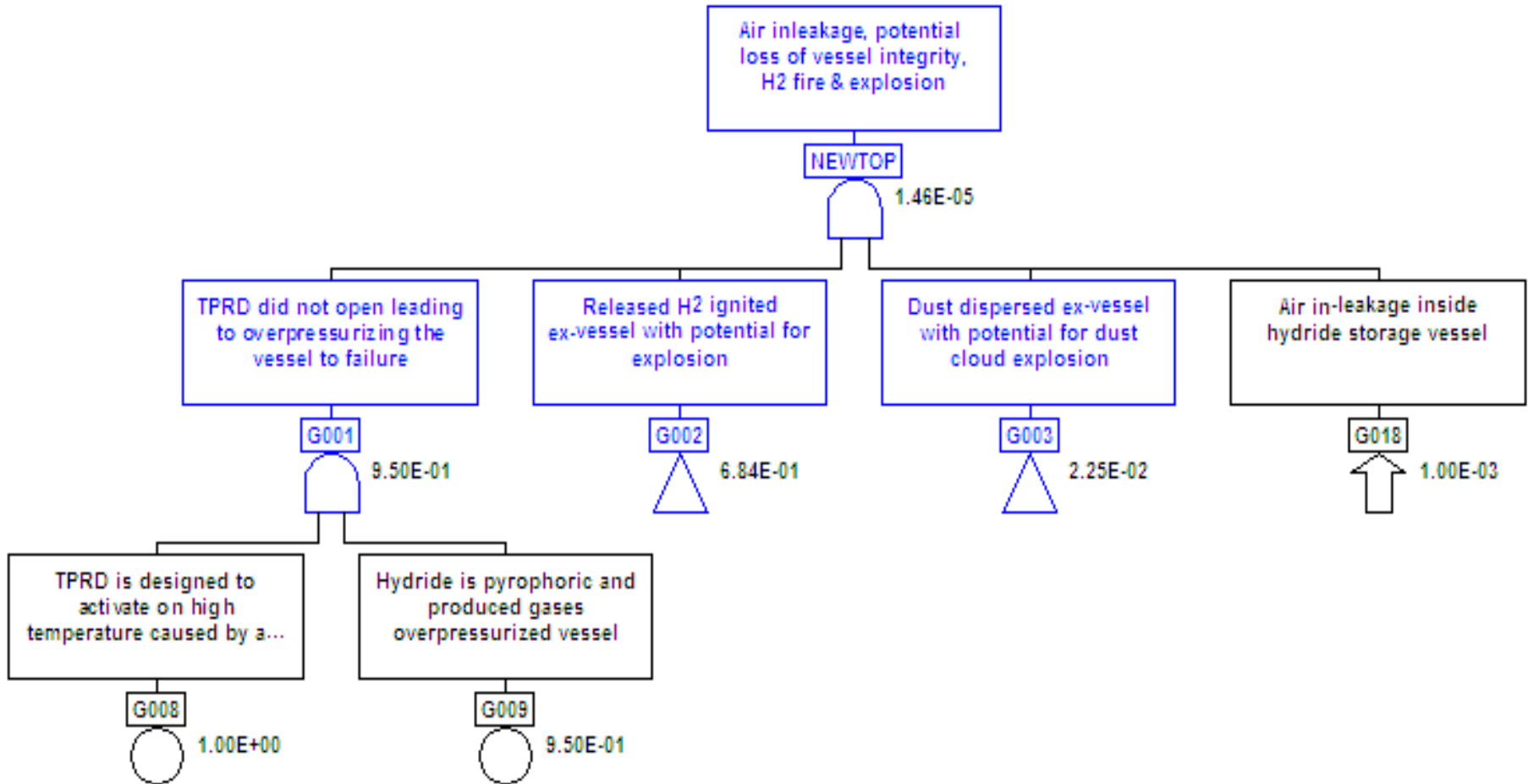
Using interactive simulation, the user can evaluate what-if scenarios using the sliding bars and observe the impact on the outcome's frequency distribution.

Fault Tree Model for In-Vessel Air Inleakage



All assigned probabilities are preliminary

Fault Tree Model for In-Vessel Air Inleakage

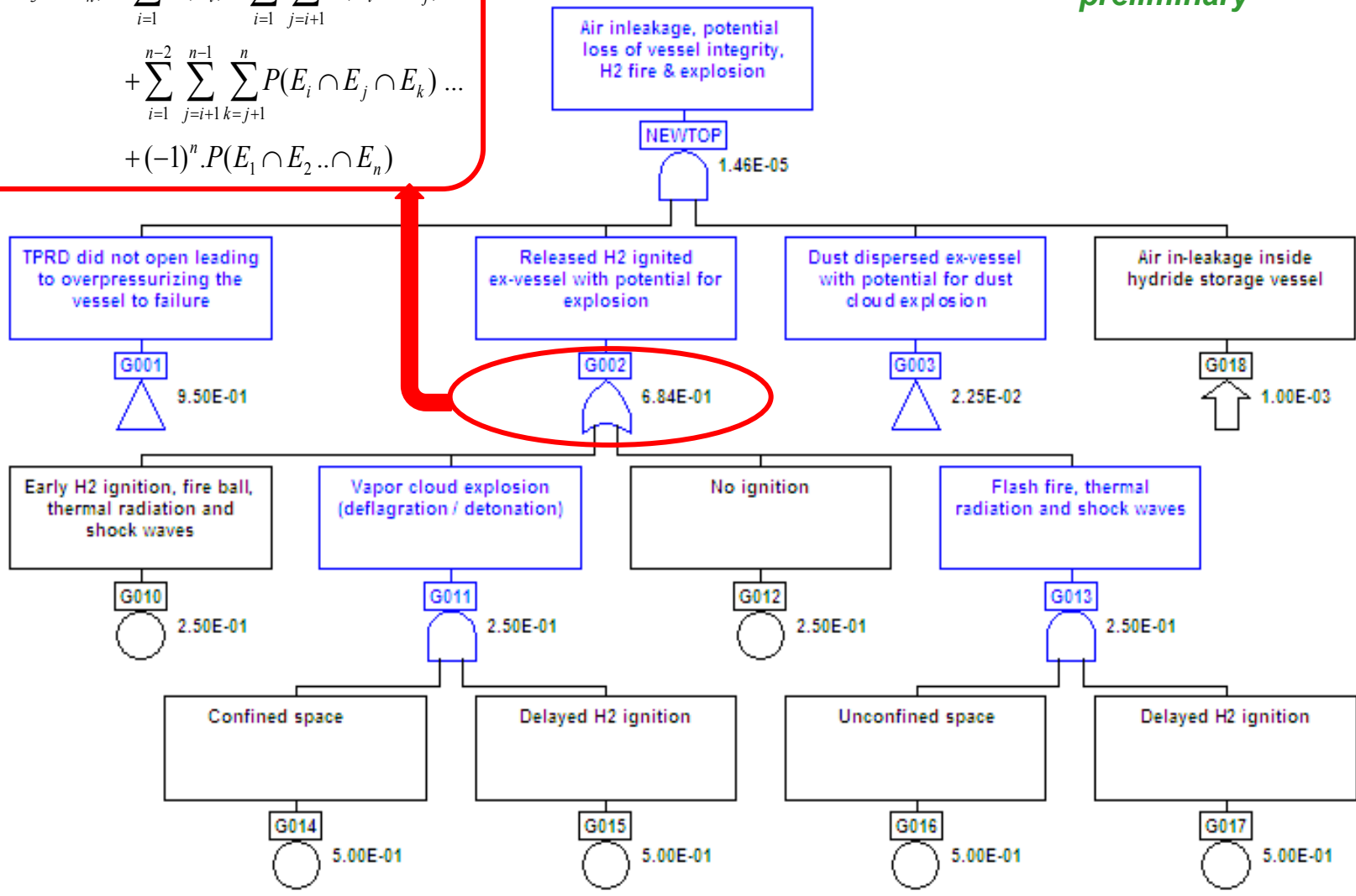


All assigned probabilities are preliminary

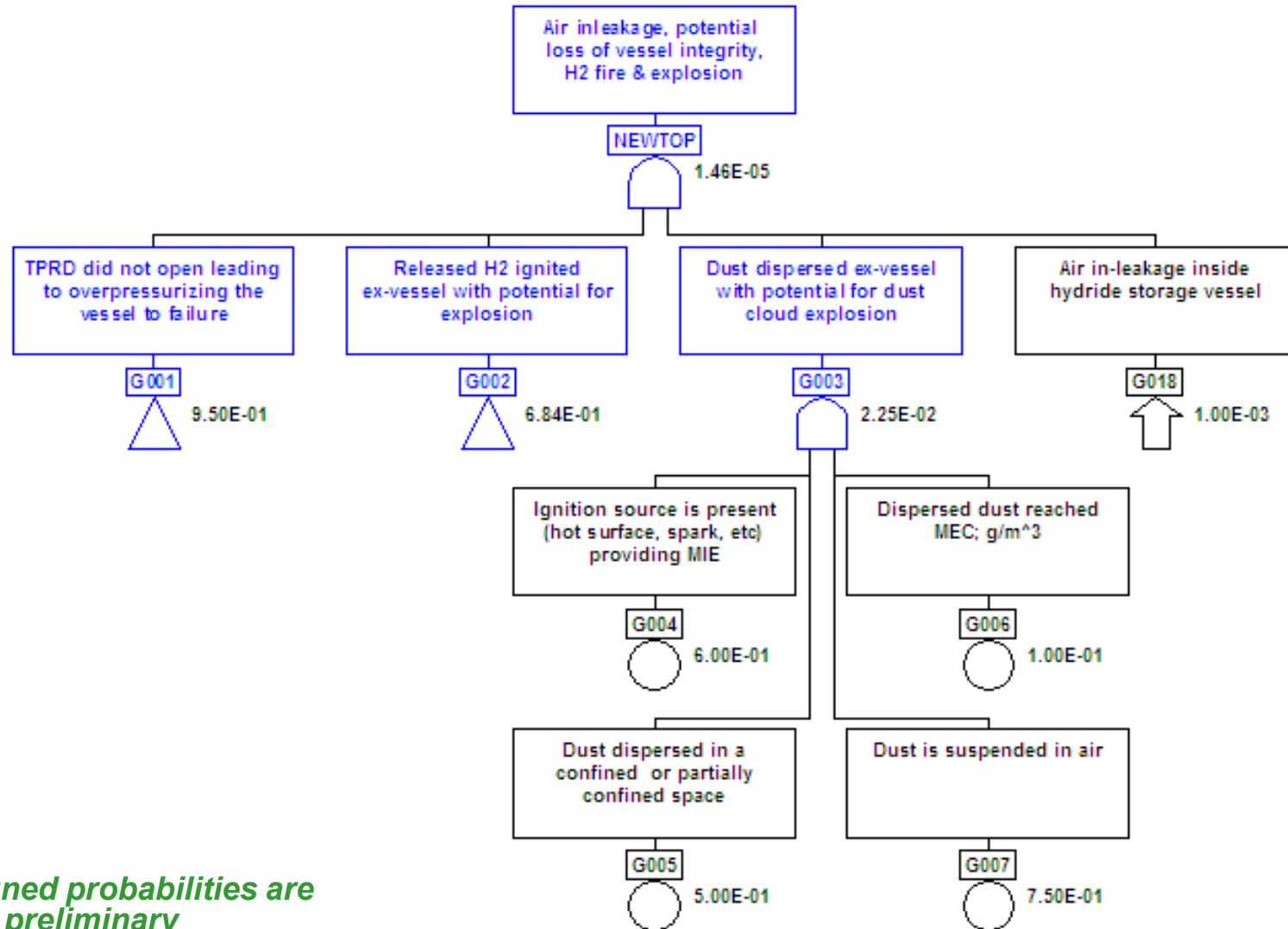
Fault Tree Model for In-Vessel Air Inleakage

$$\begin{aligned}
 P(E_1 \cup E_2 \cup E_3 \dots E_n) &= \sum_{i=1}^n P(E_i) - \sum_{i=1}^{n-1} \sum_{j=i+1}^n P(E_i \cap E_j) \\
 &+ \sum_{i=1}^{n-2} \sum_{j=i+1}^{n-1} \sum_{k=j+1}^n P(E_i \cap E_j \cap E_k) \dots \\
 &+ (-1)^n \cdot P(E_1 \cap E_2 \dots \cap E_n)
 \end{aligned}$$

All assigned probabilities are preliminary



Fault Tree Model for In-Vessel Air Inleakage



All assigned probabilities are preliminary

Use of Risk Reduction Worth (RRW) Importance Measure to Identify the Most Effective Mitigation Methods

- *RRW* is a measure of risk mitigation that would be achieved by reducing the probability of occurrence of a basic event “BE” in the system fault tree model from its baseline value to zero.
- *RRW* of a basic event ‘BE’ is expressed as follows:

$$RRW_{BE} = \frac{P(FT\ Top\ with\ P_{BE} = baseline\ value)}{P(FT\ Top\ with\ P_{BE} = 0)} \quad \text{Eq. (1)}$$

$$RRW_{BE} \geq 1.0 \quad \text{Eq. (2)}$$

- The greater the value of RRW_{BE} , the greater the importance of the component (or event) from a risk mitigation standpoint.

In a given Fault Tree model, the calculated Basic Events’ RRWs should be analyzed on a relative scale as opposed to their absolute values.

Use of Risk Reduction Worth (RRW) Importance Measure to Identify the Most Effective Mitigation Methods

Relative ranking of the calculated RRWs for the FT BEs show that the top three BEs (G008, G009 and G018) are best candidates for system safety improvement.

Basic Event (BE)	Basic Event Description	Proposed Risk Mitigation Method	
		Hardware or inspection	Chemistry
G008	TPRD is designed to activate on high temperature caused by an external fire.	Install a parallel combination relief device that activates either by high P or high T with the two activation modes acting independently	
G009	Hydride is pyrophoric (air reactive) leading to overpressurizing the storage vessel by evolved reaction gases.		Reduce material /air reactivity by: <ul style="list-style-type: none"> • Adding polymeric coating to powder. • Powder compaction.
G018	Air in-leakage inside the hydride storage vessel.	<ul style="list-style-type: none"> • Apply rigorous QA/QC during vessel manufacturing to ensure leak tight vessel. • Perform leak testing on manufactured vessels. • Periodic visual inspection during use. 	

Interactive Fault Tree Model for In-Vessel Air Inleakage

- Using scroll bars, the impact of uncertainties of basic events G008, G009 and G018 on system risk can be assessed in an interactive manner.
- The calculated risk is compared to a user defined risk acceptance threshold (the decision variable).

Gate / Basic Event	Prob / Freq	Units
→ G008	0.05	
→ G009	0.95	
G010	0.25	
G004	0.6	
G005	0.5	
G006	0.1	
G007	0.75	
G003	0.0225	
G012	0.25	
G014	0.5	
G015	0.5	
G016	0.5	
G017	0.5	
→ G018	1.00E-03	per year
G003	2.25E-02	
G011	2.50E-01	
G013	2.50E-01	
Frequency threshold below which risk sequence / cutset does not warrant risk mitigation	1.00E-06	Scroll Bar Counter
		10
System Risk	7.39E-07	per year

Scroll Bar for
BE G009: Hydride is pyrophoric and produced gases overpressurized storage vessel

G009 Counter 19

Scroll Bar for
BE G008: TPRD failed to vent

G008 Counter 1

Scroll Bar for
BE G018: Air in-leakage inside storage vessel

G018 Counter 2

Boolean Polynomials that Describe the Risk Sequences of the In-Vessel Air Inleakage Fault Tree Model

Seq #1 : G004 ∩ G005 ∩ G006 ∩ G007 ∩ G008 ∩ G009 ∩ G010 ∩ G018
 Seq #2 : G004 ∩ G005 ∩ G006 ∩ G007 ∩ G008 ∩ G009 ∩ G012 ∩ G018
 Seq #3 : G004 ∩ G005 ∩ G006 ∩ G007 ∩ G008 ∩ G009 ∩ G014 ∩ G015 ∩ G018
 Seq #4 : G004 ∩ G005 ∩ G006 ∩ G007 ∩ G008 ∩ G009 ∩ G016 ∩ G017 ∩ G018
 R = Seq #1 ∪ Seq #2 ∪ Seq #3 ∪ Seq #4

'OR' Gate G002 is calculated according to the following formula to prevent double Counting

$$P(E_1 \cup E_2 \cup E_3 \dots E_n) = \sum_{i=1}^n P(E_i) - \sum_{i=1}^{n-1} \sum_{j=i+1}^n P(E_i \cap E_j) + \sum_{i=1}^{n-2} \sum_{j=i+1}^{n-1} \sum_{k=j+1}^n P(E_i \cap E_j \cap E_k) \dots + (-1)^{n+1} P(E_1 \cap E_2 \cap \dots \cap E_n)$$

Material Reactivity Risk Mitigation: $\text{NaAlH}_4 + 4 \text{ mole\% TiCl}_3$



Fig.1: Water Dropped on a Pile (0.25-gram) of [Loose Powder](#) (Vigorous Reaction with Flame Production)



Fig.2: Windshield Washing Fluid Dropped on a Pile (0.25-gram) of [Loose Powder](#) (Vigorous Reaction with Flame Production)

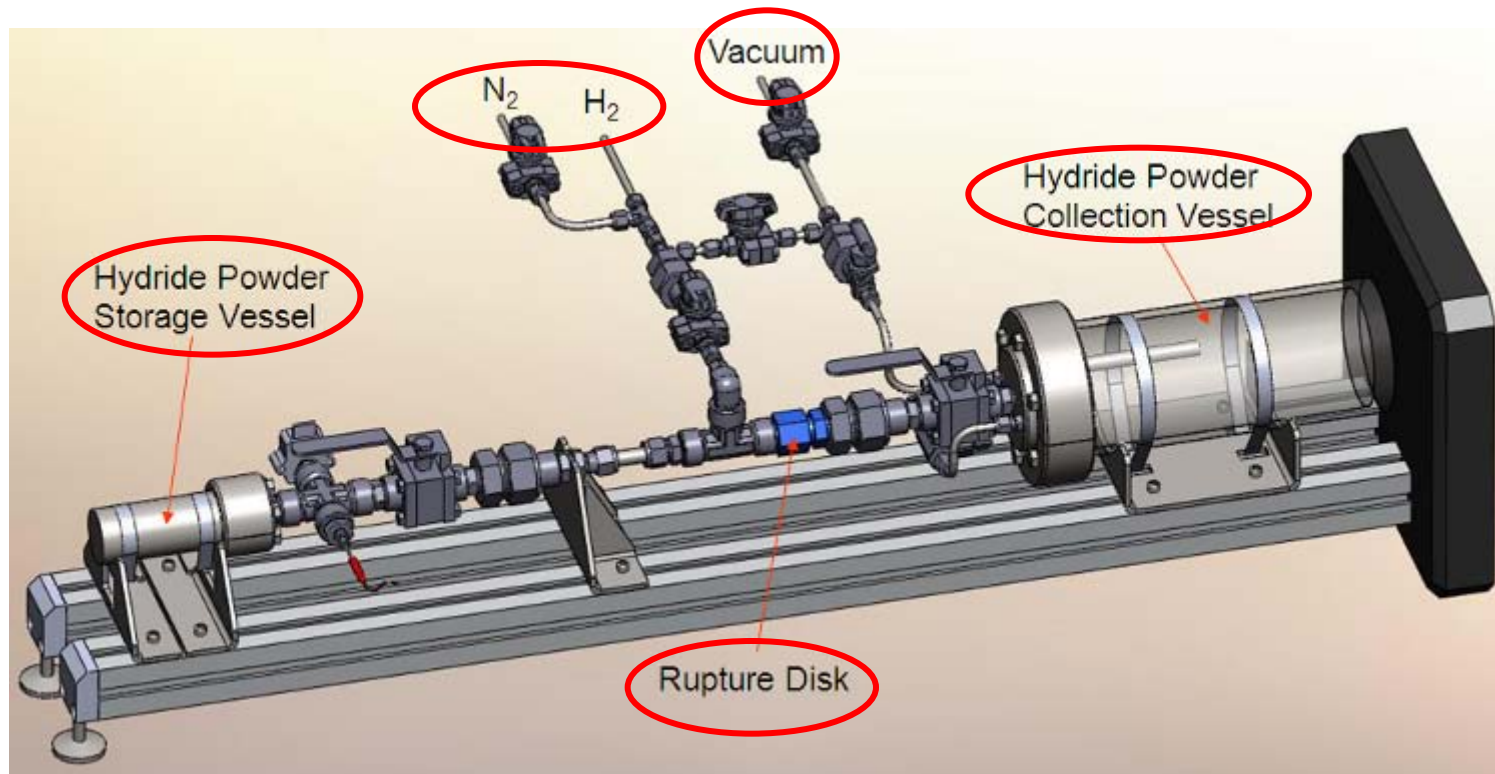


Fig.3: [Powder Compact](#): Hydride Wafer (1-gram) Dropped in 25 ml Windshield Washing Fluid (Mild Reaction without Flame Production)

Risk Mitigation Insights

Hydride powder compaction has the potential to reduce risk by suppressing material reactivity (in air as well as in each of the liquids tested) and preventing consequential hydrogen fires.

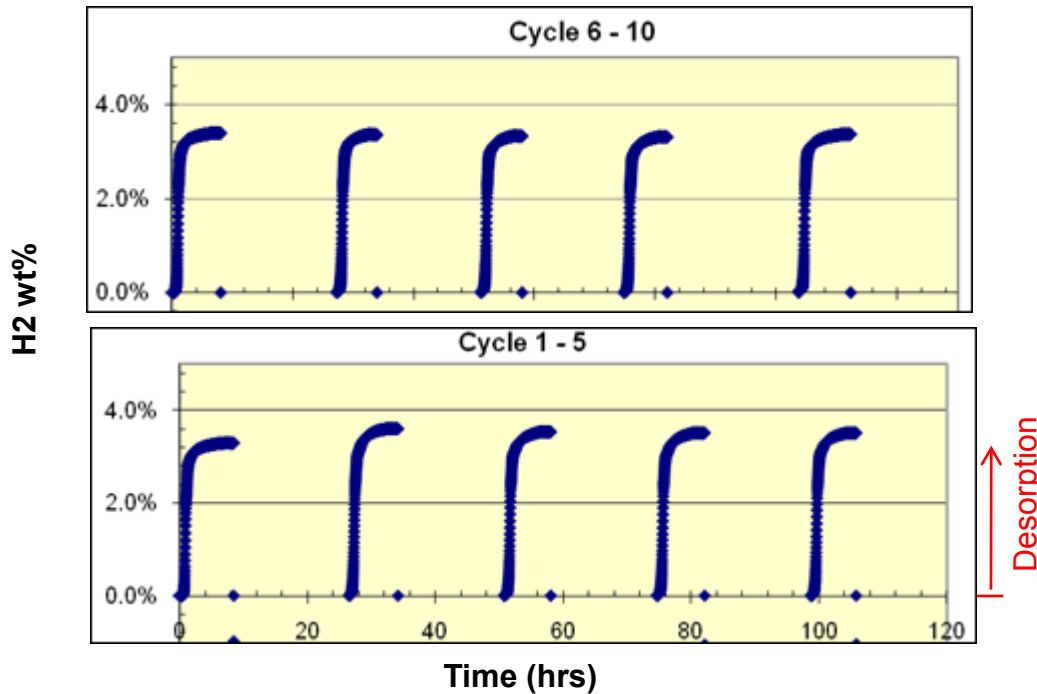
Fast Blowdown (Depressurization) Test Rig



- The test rig experimentally mimics accidental hydride storage vessel breach and its influence on powder particle size as well as durability of powder compactions as a risk mitigation method.
- Key components of the test rig: hydride powder storage vessel (**125 ml**), rupture disk, hydrogen gas supply line (**1500 psi**), nitrogen purge line, vacuum line and the hydride powder collection vessel (**2000 ml**).

Cycling Tests of $\text{NaAlH}_4 + 4\% \text{TiCl}_3$

$\text{NaAlH}_4 + 4\text{m}\% \text{TiCl}_3$; 3 hrs SPEX mill
 150°C/1 bar/6.5 hr desorption; 120°C/ 110 bar/13 hr absorption

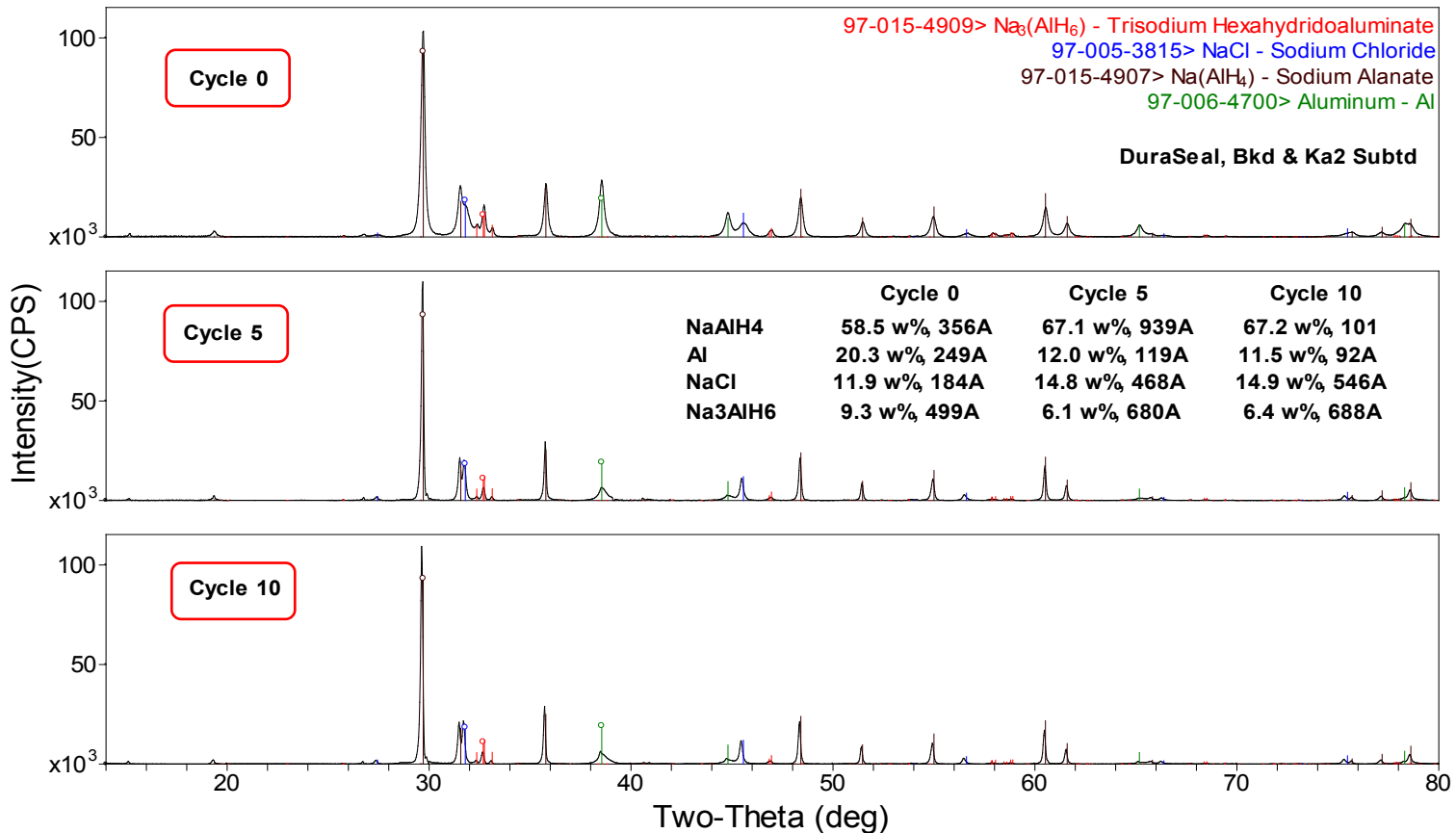


Cycle #	H ₂ capacity (wt%)	Cycle #	H ₂ capacity (wt%)
1	3.30	6	3.39
2	3.60	7	3.35
3	3.53	8	3.34
4	3.50	9	3.31
5	3.50	10	3.37

H₂ Desorption Capacity

Material cycles consistently. No significant H₂ capacity loss for 10 cycles.

XRD of Cycled $\text{NaAlH}_4 + 4\% \text{TiCl}_3$



Concentration of NaAlH_4 increased with cycling.
 Concentration of Na_3AlH_6 & Al decreased with cycling.
 Crystallite size of NaAlH_4 & Na_3AlH_6 increased with cycling.
 Crystallite size of Al decreased with cycling.

Future Work

2010 Activities

Qualitative Risk Analysis (QLRA)

- Continue QLRA efforts by completing design FMEA of the off-board regenerable (using alane) system

Quantitative Risk Analysis (QRA)

- Continue to develop accident sequences for an on-board reversible storage system.
- Develop quantitative ETA / FTA risk analysis for an off-board regenerated system.
- Develop a statistical framework for converting test data into probabilistic inputs for QRA.
- Incorporate results from the experimental and modeling activities at SNL and SRNL into UTRC QRA models.

Material and System Testing & Mitigation

- Develop and test risk mitigation methods.
- Conduct additional dust cloud characterization testing for new candidate materials.
- Experimentally investigate influence of fast blowdown (depressurization) on powder particle size as well as durability of powder compactions as a risk mitigation method.
- Develop test plan for NaAlH_4 based prototype system(s) to assess hazards mitigation and neutralization methods.

Go / No Go decision

Summary

- QLRA (d-FMEA) results showed that the **hydride storage vessel is the most safety-critical component** whose rupture could lead to high-severity consequences.
- The **storage vessel represents a single-point failure** should it catastrophically fail (burst) during postulated scenarios initiated by:
 - External fire in conjunction with TPRD failure to activate and vent as intended by design.
 - Vessel overpressurization failure mode due to causes, other than external fires, such as **air or moisture ingress** inside the vessel.
 - Should this scenario occur, TPRD will not activate since it is designed only for venting compressed gas storage vessels when exposed to direct external fires.
 - To address this vulnerability, we propose installation of a **parallel combination relief device** that activates either by high pressure or high temperature with the two activation modes acting independently.
- Currently, **bonfire and crashworthiness tests** (FMVSS 303 & 304, respectively) are designed for CNG and CHG cylinders. These tests may need to be modified to be applicable for H2 storage in hydride materials.
- Hydride **powder compaction has the potential to reduce risk** by suppressing material reactivity (in air as well as in each of the liquids tested) and preventing consequential hydrogen fires.

Additional Slides

Expert Panel Members

- Provide expert opinion on system configurations, failure modes, effects, causes, risk scoring & mitigation
- Follow Delphi iterative process based on surveys for unbiased input

Participants

Specialty / Expertise	Organization(s)	Individual(s)
DOE hydrogen storage materials & systems	DOE, SRNL, SNL, UTRC	N. Stetson, D. Anton, D. Dedrick, Y. Khalil, D. Mosher
IPHE: materials & systems	FZK, AIST, UQTR	M. Fitchner, N. Kuriyama, R. Chahine
Reliability and risk analysis	University of Maryland	Professor M. Modarres
Fire risk analysis	Consultant, FIREXPLO	Robert Zalosh
Automotive OEM	Ford	TBD
Storage system design	SNL	Terry Johnson
Insurance	Factory Mutual	Glenn Mahnken
Hydrogen risk analysis	SNL	Jeffrey LeChance
Storage vessel Manufacturer	Lincoln Composites, Inc.	Norm Newhouse
Other	CoEs, Tech Team, ...	

Materials & Systems

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

Current Focus Materials:

- NaAlH_4
 - Activated carbon
 - AlH_3
 - NH_3BH_3
 - $2\text{LiBH}_4 + \text{MgH}_2$
 - Others – refer to HSCoE
“Candidate Materials Matrix”
- } Tier 1

General System Classes:

- On-board reversible hydride bed systems (guided by NaAlH_4 prototypes)
- On-board reversible adsorbant systems (activated carbon)
- Off-board regenerable based systems (alane & ammonia borane)