Project SA2

Research and Development for Hydrogen Safety, Codes and Standards

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Sandia National Laboratories

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This presentation does not contain any proprietary or confidential information

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Overview

Timeline

- Project start date Oct 2003
- Project end date Sep 2015
- Percent complete 25%

Budget

- Total project funding (from FY03)
  - DOE share: $5.4M
- FY05 Funding: $2.0M
- FY06 Funding: $1.5M

Partners

- SRI: combustion experiments
- ISO/IPHE Contractor: R. Mauro
- IEA Contractors: MRS Enterprises, W. Hoagland & Associates, and Longitude 122 West
- Interactions with CSTT, ASME, CSA, ISO, ICC, NFPA, NHA

Barriers & Targets

- MYRDDP Section 3.6.4.1 Targets:
  - Provide expertise and technical data on hydrogen behavior
  - Hydrogen storage tank standards for portable, stationary and vehicular use
  - Materials reference guide for design and installation
- MYRDDP Section 3.6.4.2 Barriers:
  - N. Insufficient Technical Data to Revise Standards
  - P. Large Footprint Requirements for Hydrogen Fueling Stations
  - J. Lack of National Consensus on Codes & Standards
  - K. Lack of Sustained Domestic Industry Support at International Technical Committees

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Objectives

- **Safe design of structures for storage and transport of high-pressure hydrogen gas requires material property data that reflects service conditions:**
  - material compatibility reference: pressure vessel steels, stainless steels, pipeline steels, nonferrous alloys, and composites
  - slow crack growth and fatigue testing in hydrogen environments
- **Development of new hydrogen codes and standards needs a traceable technical basis:**
  - fluid mechanics, combustion, heat transfer, cloud dispersion
  - physical and numerical experiments, engineering models
  - large and small-scale gaseous leaks, liquid leaks, leaks associated with advance storage materials (metal and chemical hydrides)
  - quantitative risk assessment and consequence analysis
- **Provide advocacy and technical support for the codes and standards change process:**
  - consequence and risk: ICC and NFPA
  - materials: ASME and CSA

Approach

- Compose "Technical Reference for Hydrogen Compatibility of Materials", http://www.ca.sandia.gov/matlsTechRef
- Conduct materials testing in hydrogen gas up to 100 MPa pressure supporting fracture mechanics methods for design of flaw-tolerant structures
- Conduct characterization experiments for hydrogen plumes from low-pressure sources and small leaks; validate models of buoyancy-driven flow using imaging techniques
- Introduce more risk-informed decision making in the codes and standards development process using quantitative risk assessment; provide a traceable technical basis for new codes

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Technical Reference for hydrogen compatibility of materials

- 10 chapters have been completed and posted to the website
- 4 chapters completed over this past reporting period
  - Low-alloy steels Fe-Ni-Cr-Mo and Fe-Cr-Mo (example: pressure vessels)
  - Fe-Ni-Co and Copper (example: seals)
- 1 chapter nearing completion
  - Duplex stainless steels (example: tubing and valves)
- Additional chapters scheduled for FY06
  - Ferritic carbon steels (example: piping)
  - Aluminum alloys (example: pressure vessels, ICE components)

Review of literature shows that more materials testing is needed, particularly at high H_2 gas pressures

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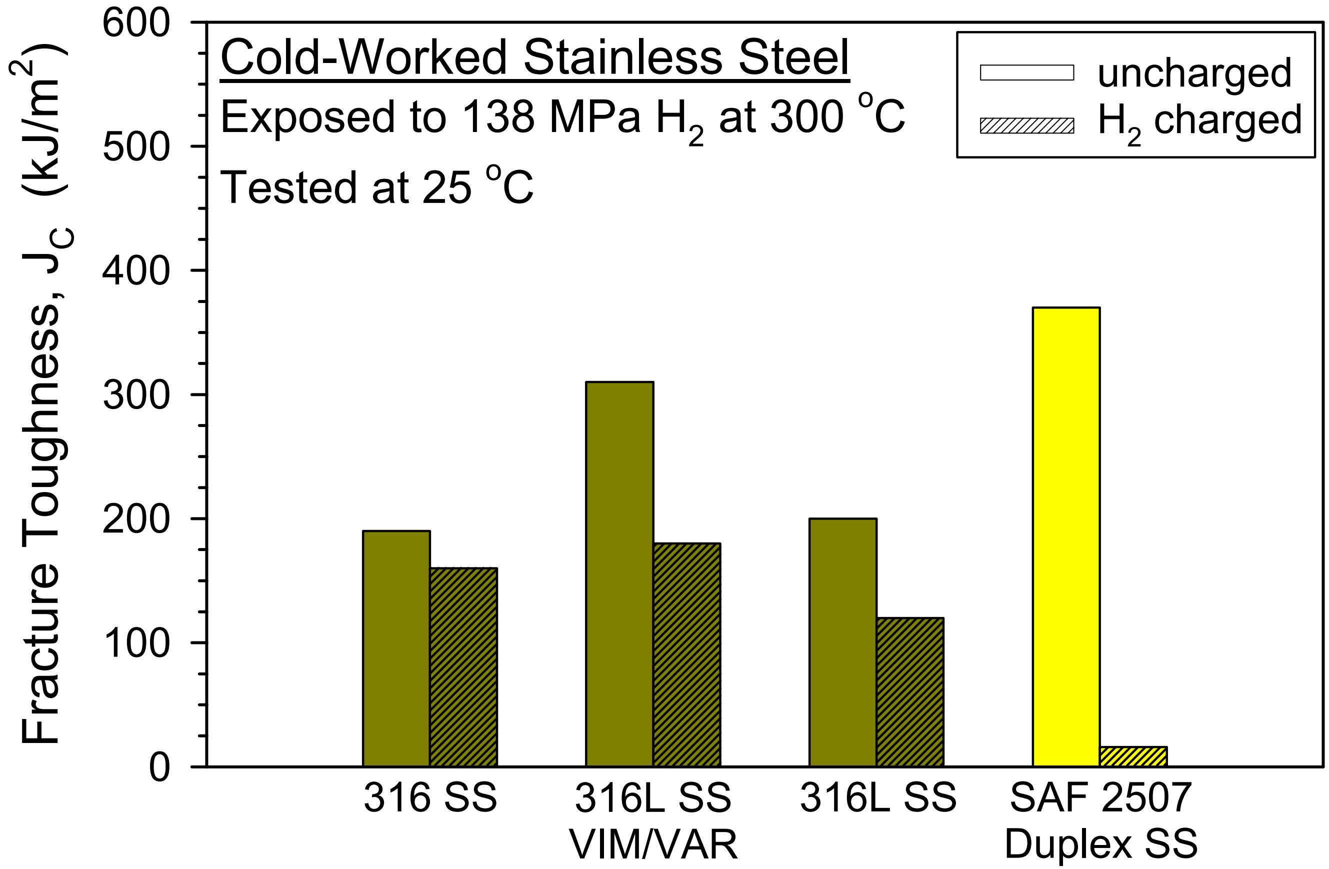
Materials testing: stainless steels for tubing applications



- Fracture-mechanics data is essential for structural design in H_2.
- Results show that both steel composition and microstructure affect hydrogen-assisted fracture.

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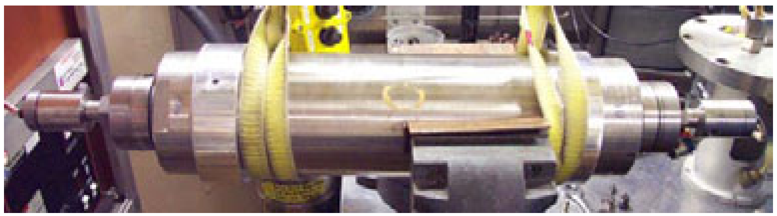
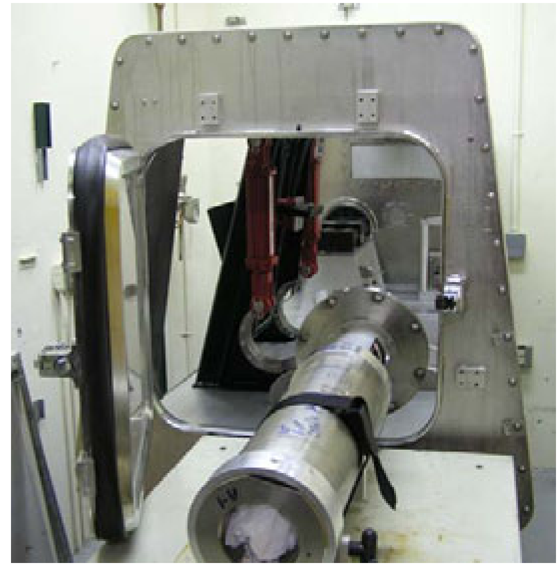
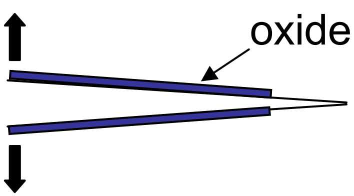
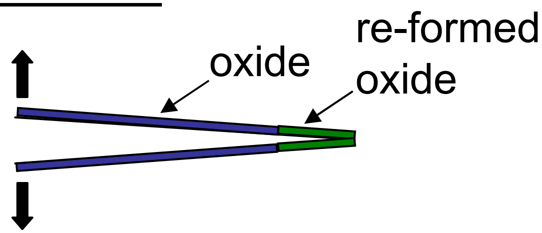
Improving the protocol for crack growth experiments



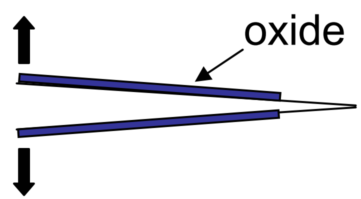


Loading crack in air

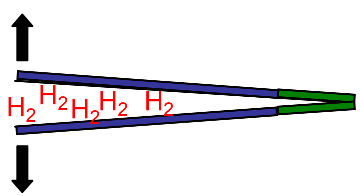




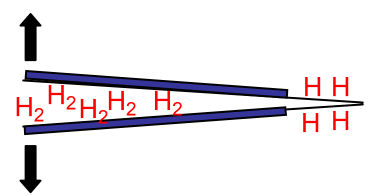
Loading crack in glovebox



Exposure to hydrogen gas



Exposure to hydrogen gas



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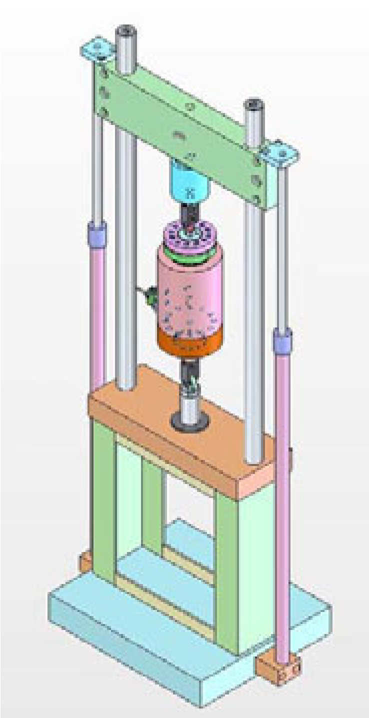
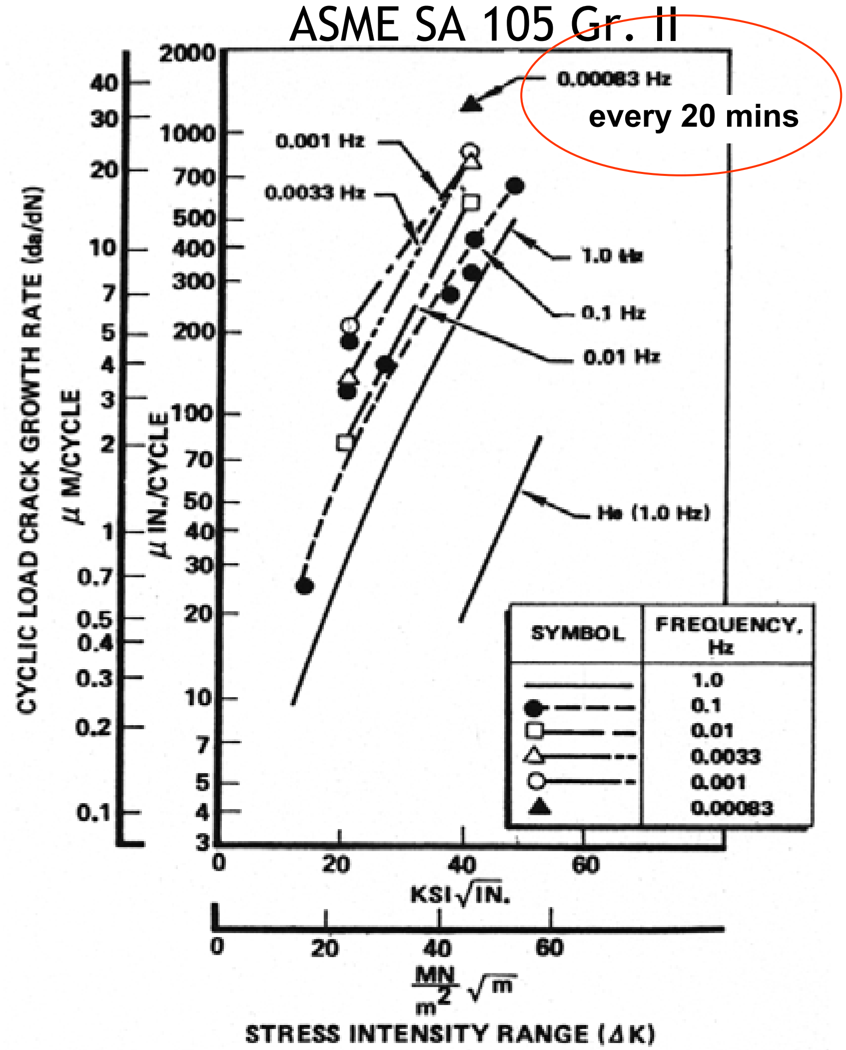
Fatigue experiments in high-pressure hydrogen gas

- ASME fracture mechanics-based design codes require fatigue crack growth rate data.
- Sandia has capital equipment funds to build a system for fatigue experiments in 100 MPa hydrogen gas.

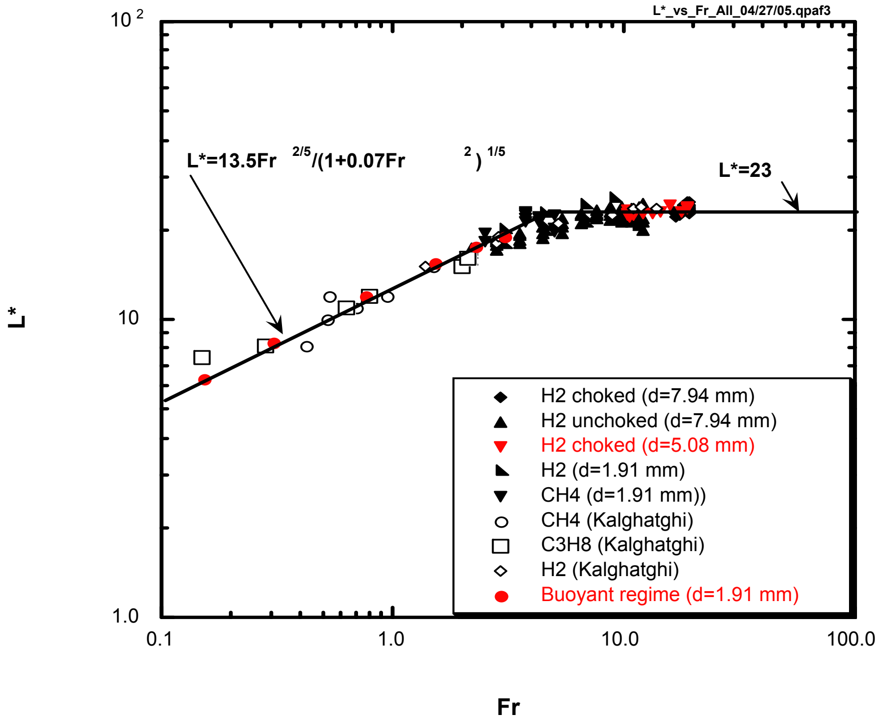


- Design of the pressure vessel, coupled to the mechanical test frame, is in progress for FY06.
- Limited test data indicates that hydrogen-assisted fatigue is more pronounced at lower cycle rates.



Data from: R.J. Walter and W.T. Chandler, *Effects of Hydrogen on Behavior of Metals*, 1975

Large-leak jet work has been published



Nondimensional flame lengths in momentum and buoyancy-dominated flows correlate well with the flame Froude number .

Definitions

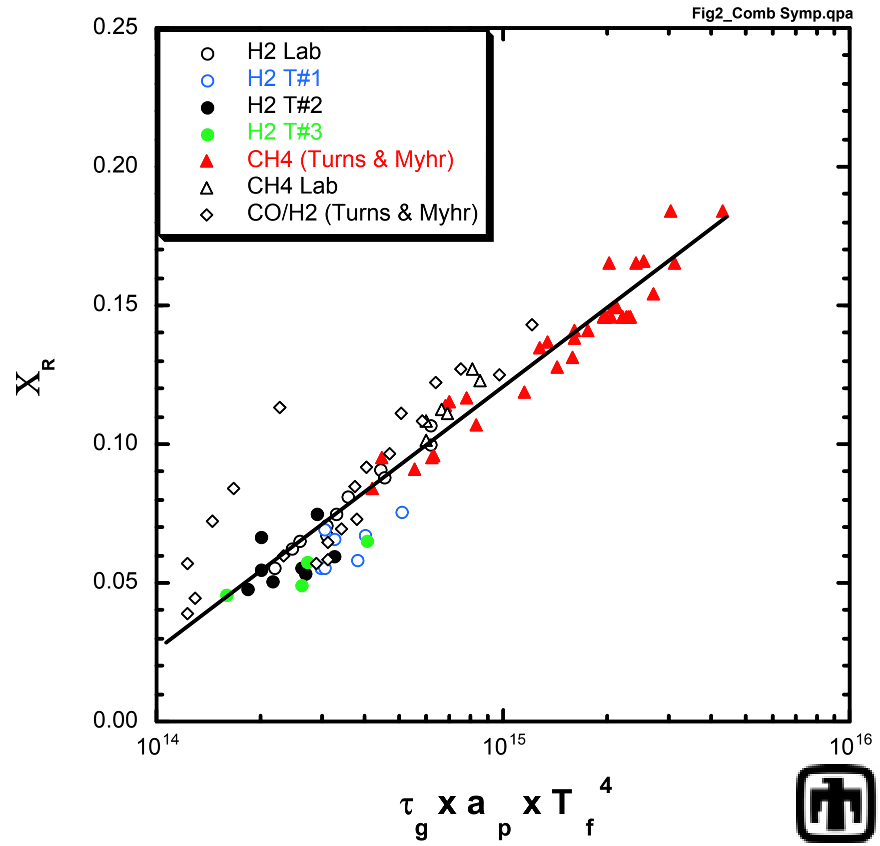
- **Dimensionless flame length**

  $L^* = L_f f_s / (r_e / r_\infty)^{1/2} d_j$

- **Flame Froude number**

  $Fr_f = u_e f_s^{3/2} / [d_j^* g(T_f - T_\infty) / T_\infty]^{1/2}$

Radiative fractions from non-sooting jet flames collapse onto a single curve when residence time (τ_g) correlation is modified to include Plank-mean absorption coefficient, a_p, and flame temperature, T_f .



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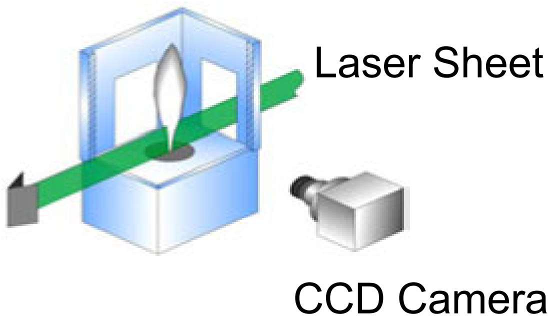
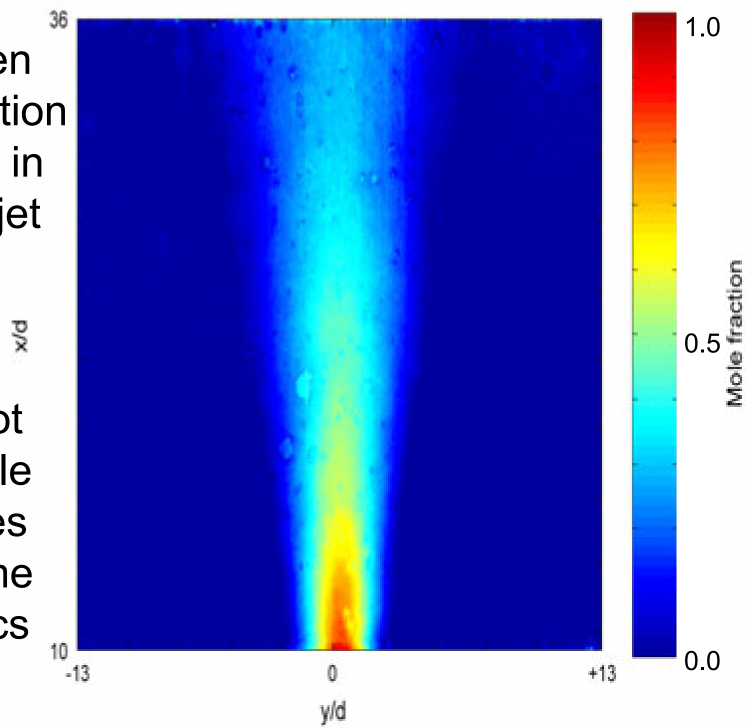
Plume imaging of small leaks is used to map mean concentration contours

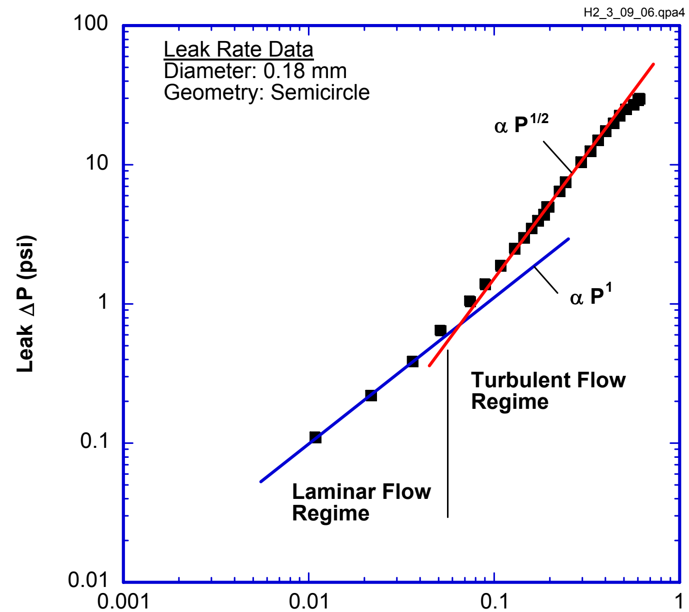
Rayleigh scattering system



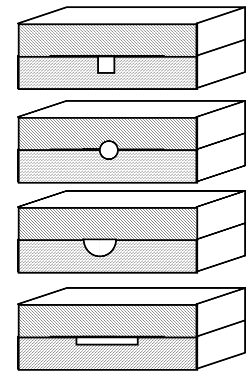
Hydrogen concentration contours in 1.9-mm jet

200-shot ensemble averages the plume dynamics

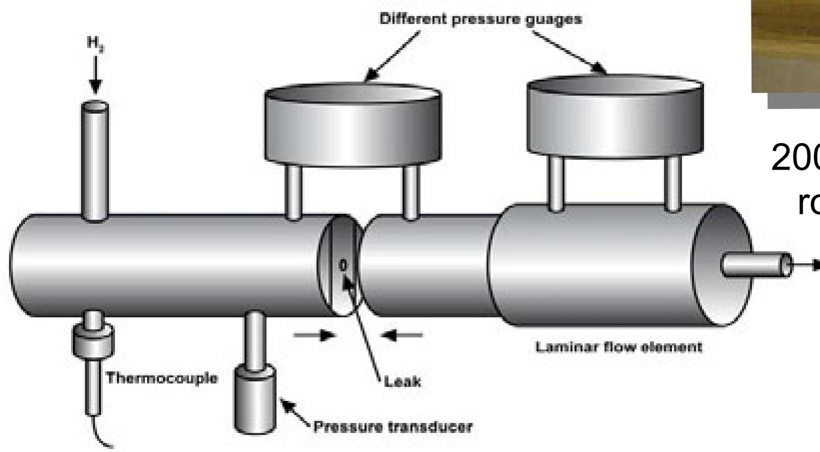




Measure flow rate for variable geometries



200 μm diam. round leak



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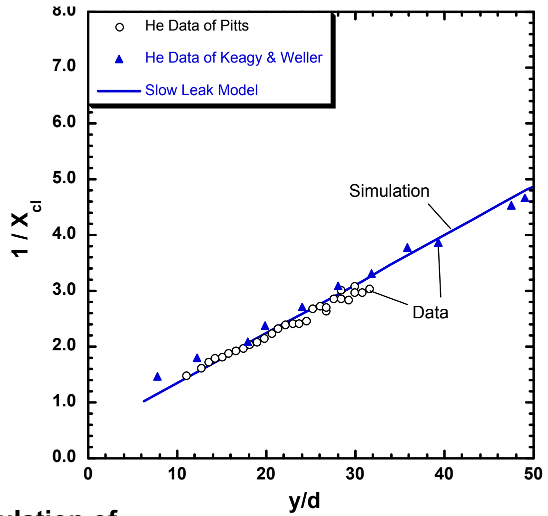
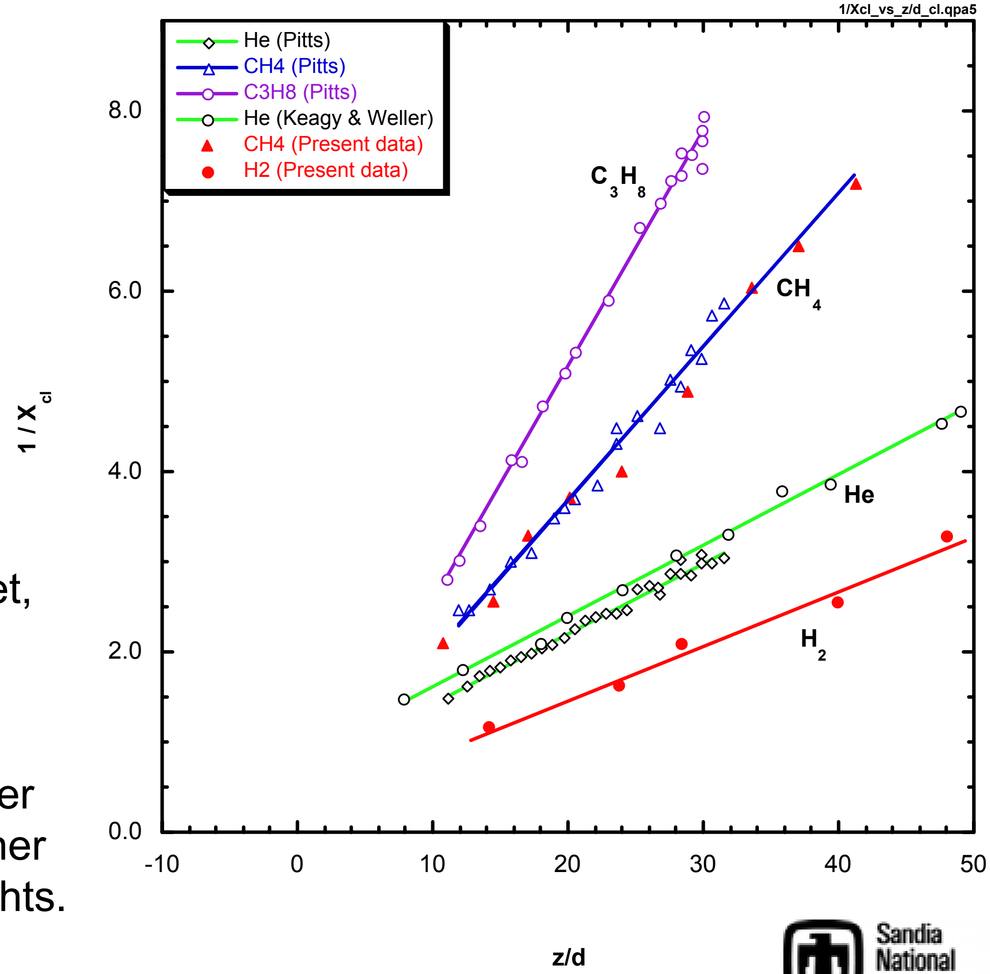
Validate engineering models for buoyantly-dominated slow leaks

Engineering model for buoyantly-driven flow is different from momentum-driven model:
- uses a different entrainment law
- integrate along the stream line to capture trajectory

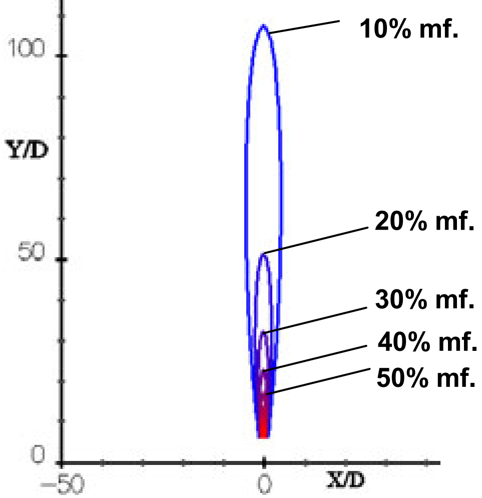
Comparison of Simulation and Data for Concentration Decay of Vertical Buoyant Helium Jet



Experimentally measured centerline concentration decay rates



Mole Fraction Contours for Simulation of Vertical Buoyant Helium Jet



Dia = 3.25 mm
Fr_{den} = 274

In a turbulent jet, hydrogen concentration decays more slowly than other gases with higher molecular weights.

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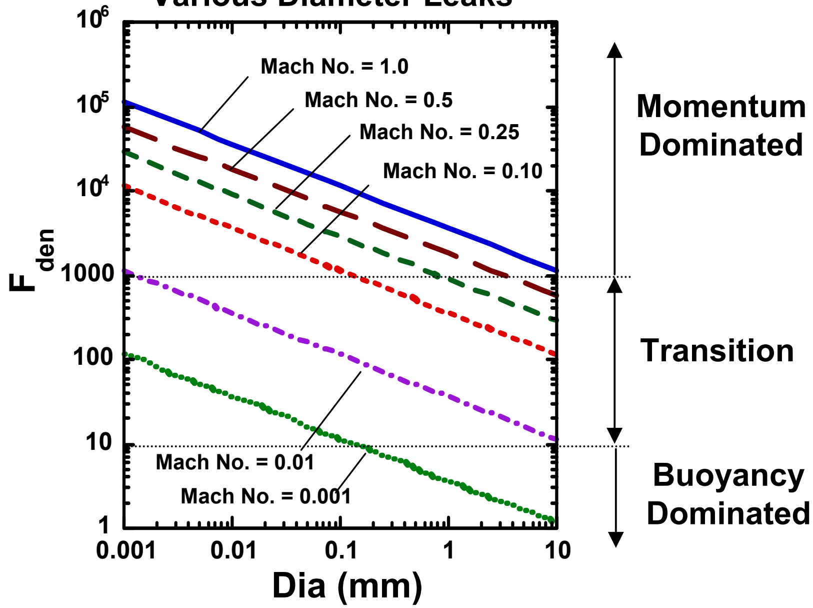
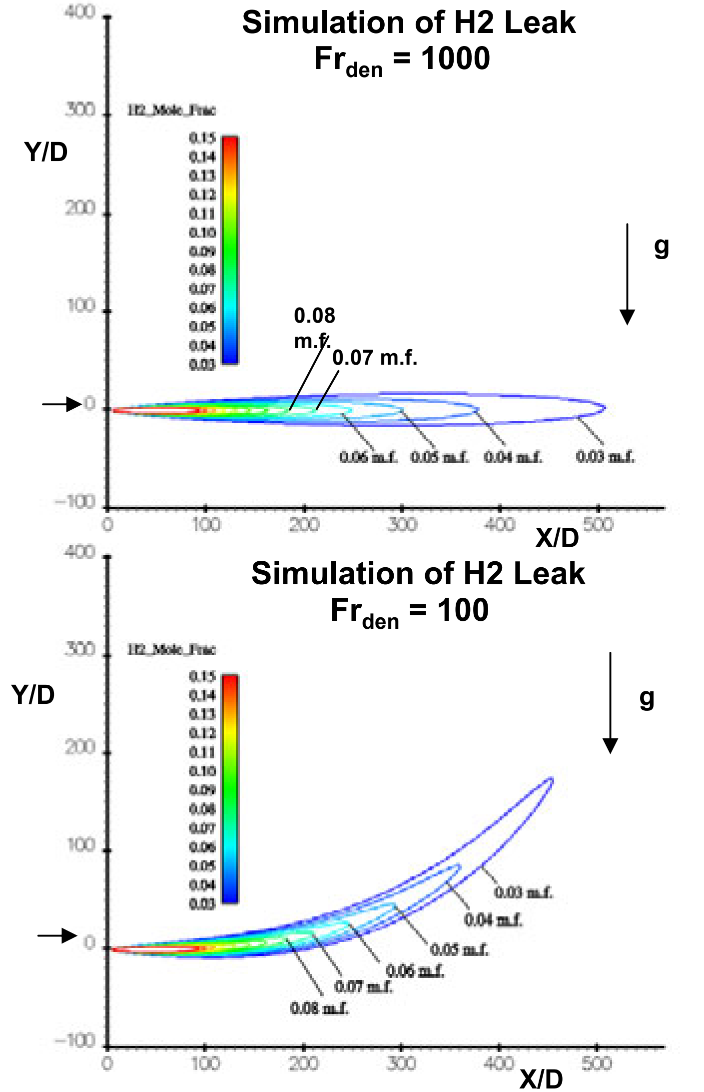
Influence of buoyant force is quantified by the dimensionless Froude number

- Jets from choked flows (Mach 1.0) are typically momentum-dominated.
- Lower source pressures or very large pressure losses through cracks lead to subsonic, buoyancy-dominated plumes.

Densimetric Froude Number for Various Diameter Leaks



$Fr_{den} = U_{exit} / (gD(rho_{amb} - rho_{exit})/rho_{exit})^{1/2}$



Ricou and Spalding entrainment law (J. Fluid Mechanics, 11, 1961)

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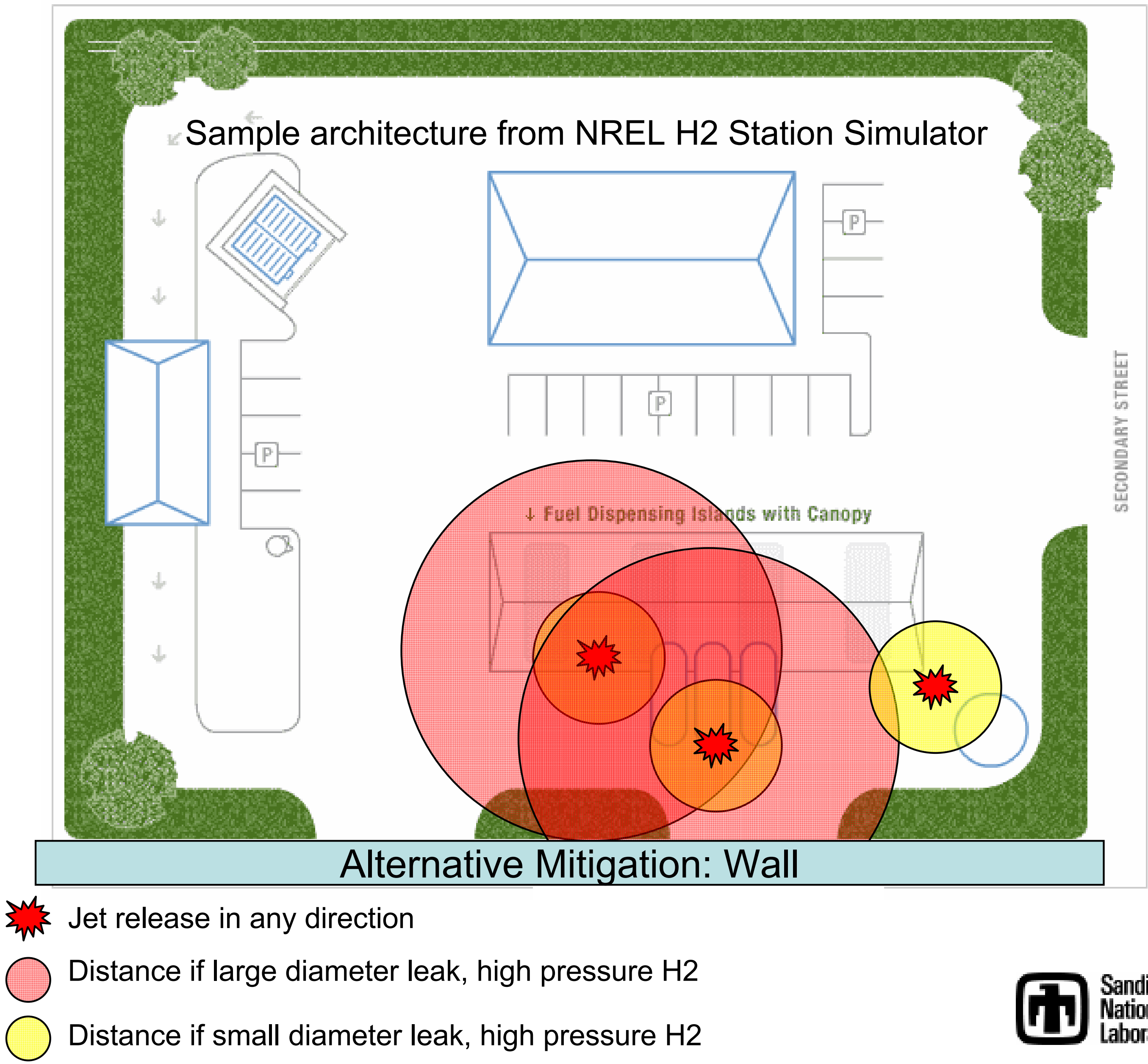
Separation distance RA approach

- Quantitative risk assessment (QRA) is a natural framework for making risk-informed decisions. We propose a general QRA approach to define refueling setbacks.
- Three risk drivers are identified for the analysis: 1) jet flame extent and thermal radiation, 2) pressure-volume work and over-pressure, and 3) combustible gas footprint.
- Likelihood of events is estimated from component reliability and architecture-based FMEA studies.
- For hazards with large length scales, site-specific mitigation strategies should be identified.



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Can separation distances for existing fuels be used for hydrogen?

5 ft	10 ft	15 ft	25 ft
fueling with barrier	fueling	storage < 6000 gal	storage > 6000 gal
storage < 125 gal above ground	fueling	venting	storage 500 – 2K gal above ground
storage commercial	fueling	storage > 6000 gal protected	storage commercial
	storage		storage
	< 2000 gal under ground		storage < 3500 gal commercial
	compressor		storage > 6000 gal protected
	remote pumping		

Gasoline

- Release of motor fuel, migration, and subsequent ignition
- Ignition of motor fuel in container
- Evaporation and ignition of fumes
- Evaporation, ignition, and explosion of fumes in contained area

Natural Gas < 200 bar

- Explosive release of compressed gas
- Release and ignition of gas
- Asphyxiation of gas displacing oxygen
- Evaporation, ignition, and explosion of gas in contained area

Liquified Petroleum < 30 bar

- Asphyxiation of evaporant gas displacing oxygen
- Explosive release of gas and liquid
- Release, migration, and ignition of gas
- Release migration, ignition, and explosion of gas in contained area

Gaseous Hydrogen < 500 bar

- Asphyxiation of hydrogen displacing oxygen
- Explosive release of compressed hydrogen
- Release, projection, and ignition of gas
- Release, ignition, and explosion of gas in contained area

Liquid Hydrogen < 10 bar

- Release, evaporation to gaseous hydrogen, and asphyxiation from displaced oxygen
- Release, evaporation to gaseous hydrogen, migration, and ignition
- Release, evaporation to gaseous hydrogen, ignition, and explosion in a confined area
- Explosive release of gas
- Release and cryogenic damage

A systems analysis of setbacks for various fuels was performed and the study considered several use cases: venting, storage, dispensing, etc.

Although there is some correlation between pressure, energy content, and setback distance, there is no strong evidence of a common approach. *Hydrogen is used differently.*

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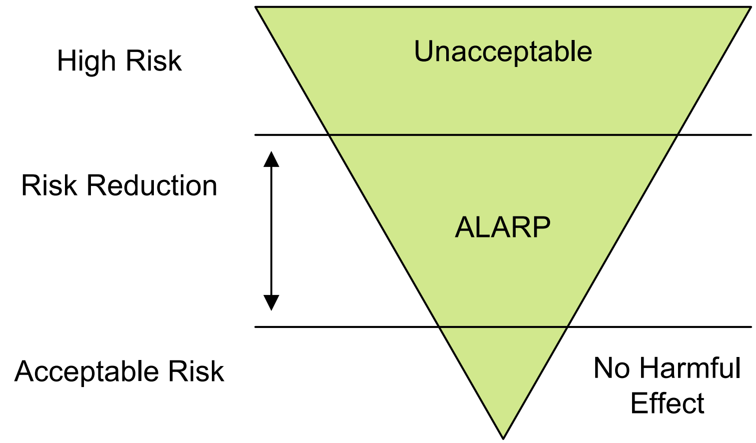
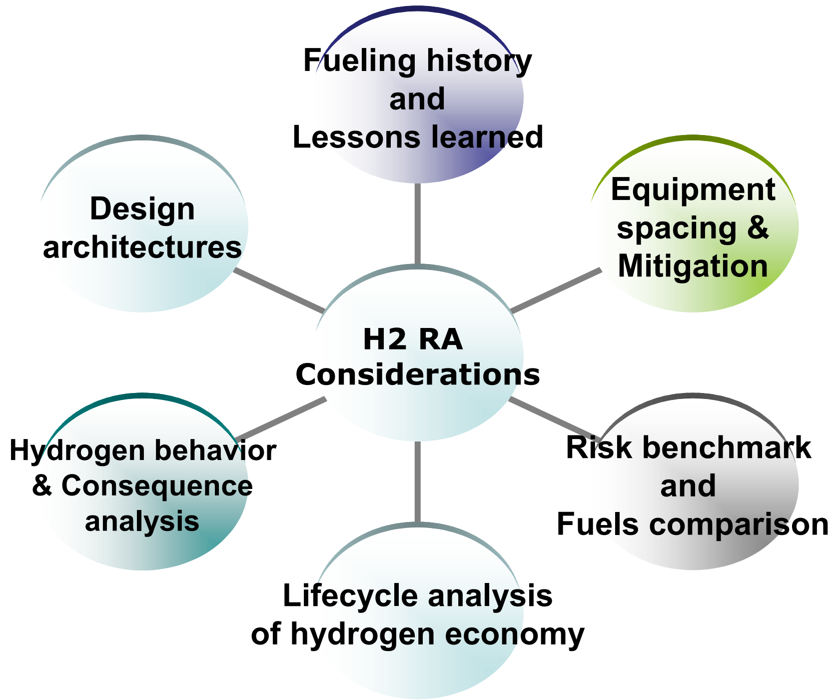
Acceptable risk for H_2 refueling

- Clearly defined risk metrics are required for QRA implementation.
- We assume a "no greater risk" principle where hydrogen fueling should be no riskier than other fuel alternatives.





- Baseline "acceptable" risk might be defined as the risk of everyday life.
- Beyond baseline, reduce risk using ALARP
  - Consequences above the risk threshold require mitigation strategies or engineering solutions to drive them below the acceptable level.
  - Consequences below the threshold can still be driven downwards by reducing exposure.

Future Work

Remainder of FY06

- Continue buoyancy-driven plume parameter studies and publish
- Perform probability risk assessment (PRA) of refueling station hazards
- Complete first draft of Materials Technical Reference

FY07

- Complete slow leak work, extend to releases in enclosed spaces
- Investigate safety aspects of barrier walls and other passive mitigation strategies
- Begin scoping advanced hydrogen storage system safety scenarios
- Extend risk analysis to identify needs for step-out technologies and study how the public perceives risk in order to develop a risk communication strategy
- Address requests for additional chapters Materials Technical Reference and begin study of composite systems
- Perform static crack growth and fatigue testing in high-pressure environments
- Develop heat transfer and flow models to optimize 70 MPa refueling

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Summary

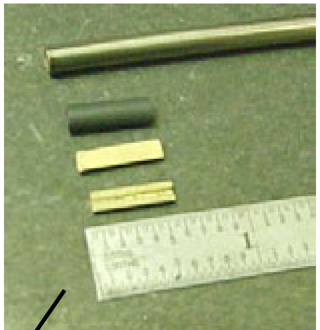
- Safe design of structures for storage and transport of high-pressure hydrogen gas require material property data that reflect service conditions.
  - Screening and documenting existing quality data in a Technical Reference
  - Creating new slow crack-growth data for fracture mechanics design
  - Leveraging Sandia plant equipment funding to develop an experimental facility to measure fatigue-assisted crack growth

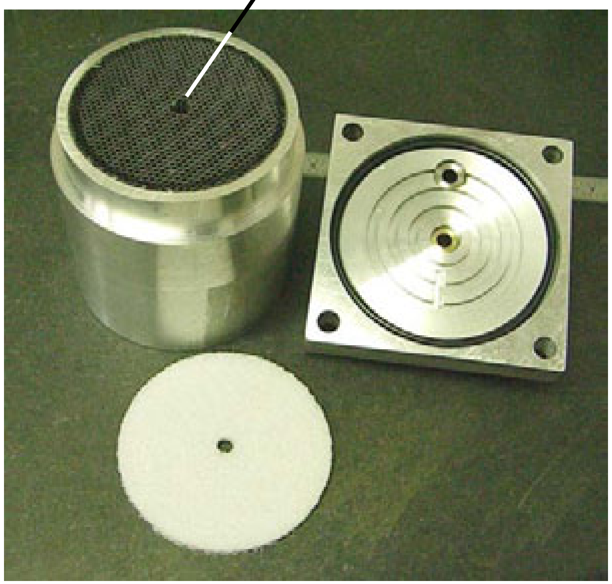
- Though hydrogen is used differently than other fuel gases, the behavior in unintended releases is similar when scaled appropriately.
  - Finished publication of large-release, momentum-dominated work
  - Performing experiments and developing models for small-release, buoyancy-dominated hydrogen flows

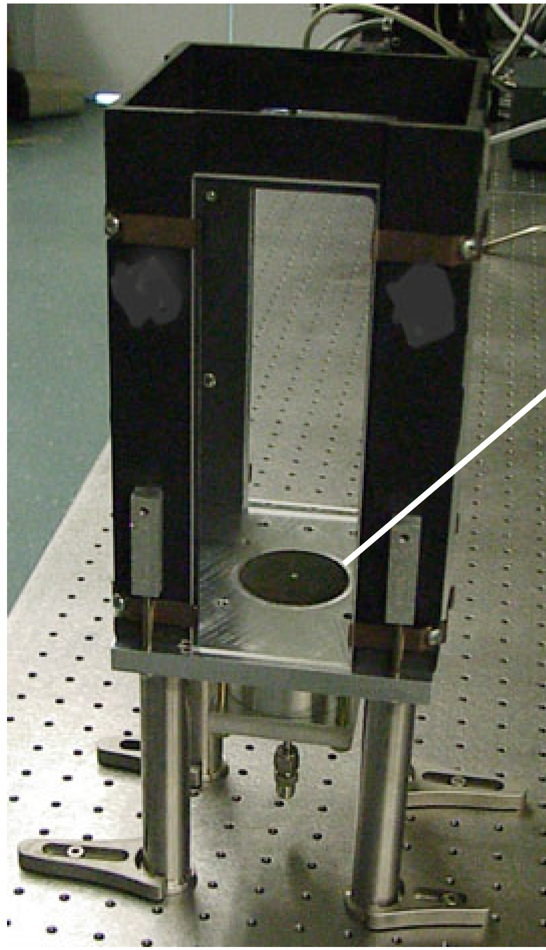
- Quantitative risk analysis should be used in the codes and standards development process to provide a traceable, technical basis.
  - Performing QRA to help understand setback requirements for refueling
  - Engaging international risk experts in this discussion

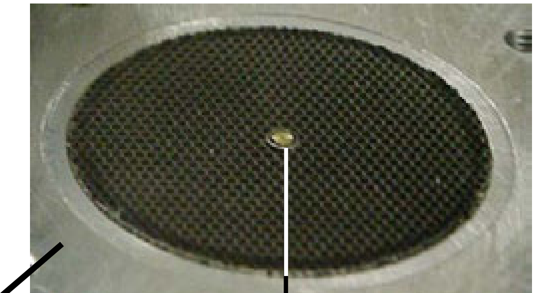
Backup Slides

Buoyant plume apparatus









- Variable leak geometries can be implemented.
- Vertical and horizontal orientations.

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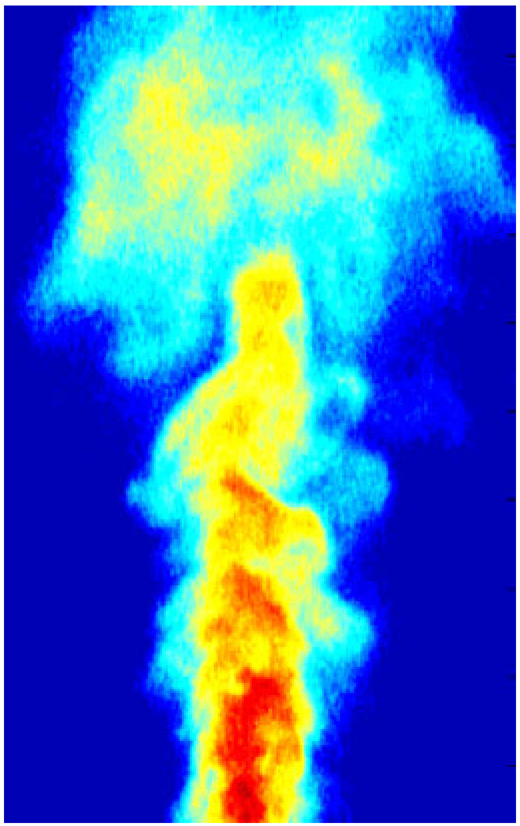
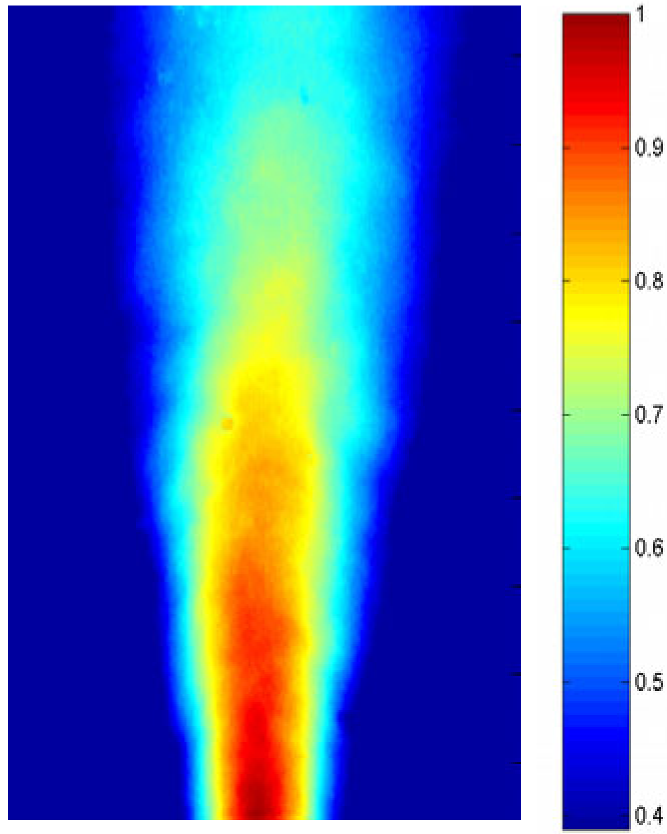
Instantaneous imaging of hydrogen concentration

Rayleigh scattering images of unignited H_2 leak

Instantaneous

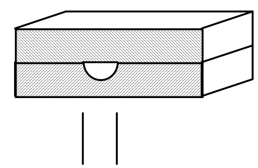


Ensemble-Averaged (50 images)



The ensemble-averaged results are used for validation of time-averaged modeling techniques. The structure of instantaneous concentration fluctuations is lost in the calculations.

Leak Geometry



d=0.18 mm
Q=10 slm
Turbulent Regime

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Responses to previous year reviewers' comments

- "*Technology transfer regarding materials compatibility with hydrogen is excellent. However, collaboration is lacking with other entities in the U.S. and internationally doing similar work.*"

  We are corresponding members of the ASME Boiler and Pressure Vessel Project Team on Hydrogen Tanks. We participate in the H2 Material Testing coordinating committee. We have collaborations with two material vendors, but the nature of the relationships is protected by Non-Disclosure Agreement. We partnered with Swagelok for a poster on 316 stainless steel at the 2006 NHA conference. We acted as reviewers for the European "HySafe Best Practices" document for the materials compatibility chapter.

- "*The flame behavior work should endeavor to tie in 'real-world' scenarios, which add considerable complexity to the behavior of a leak, hydrogen dispersion, and flames, deflagrations, and detonations.*"

  Extensions of our fundamental studies to systems that add geometric complexity have been proposed as part of our program, but we have not started due to budget constraints. We are aware of the need to characterize proposed mitigation strategies such as barriers and also deal with other obstructions and enclosures.

- "*Risk assessment should be narrowed or dropped. The project did not appear to fully incorporate many well established procedures already in use by government regulatory bodies.*"

  We are not performing risk assessments to qualify individual refueling stations. Our use of risk assessment is twofold: 1) introduce risk-informed decision making to the codes and standards development process using a quantitative approach, and 2) use quantitative risk assessment to identify and prioritize future research needs for step-out technologies. In this sense, our use of risk assessment is more theoretical and not aimed at regulating the industry or persuading specific authorities having jurisdiction.

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Publications

1. San Marchi, Somerday, and Robinson, “Permeability, Solubility and Diffusivity of Hydrogen Isotopes in Stainless Steels at High Gas Pressures”, accepted in *International Journal of Hydrogen Energy*

2. Somerday and San Marchi, “Effects of Hydrogen Gas on Steel Vessels and Pipelines”, *Materials for the Hydrogen Economy*, R.H. Jones and G.J. Thomas, eds., to be published

3. Houf and Schefer, “Predicting Radiative Heat Fluxes and Flammability Envelopes from Unintended Releases of Hydrogen,” accepted in *International Journal of Hydrogen Energy*

4. Schefer, Houf, San Marchi, Chernicoff, and Englom, “Characterization of leaks from compressed hydrogen dispensing systems and related components”, accepted in *International Journal of Hydrogen Energy*

5. Molina, Schefer, and Houf, “Radiative Fraction and Optical Thickness in Large-Scale Hydrogen-Jet Flames,” *Proceedings of the Combustion Institute*, accepted for publication, April, 2006

6. Schefer, Houf, Williams, Bourne, and Colton, "Characterization of High-Pressure, Under-expanded Hydrogen-Jet Flames”, submitted to *International Journal of Hydrogen Energy*

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Presentations

1. (invited) Somerday, San Marchi, and Balch, "Hydrogen-Assisted Fracture: Materials Testing and Variables Governing Fracture", ASME/SRNL Materials and Components for the Hydrogen Economy Workshop, Aug. 2005
2. (invited) San Marchi and Somerday, "Permeability, Solubility and Diffusivity of Hydrogen in Stainless Steels at High Gas Pressures", ASTM Hydrogen Gas Embrittlement Workshop, Nov. 2005
3. (invited) San Marchi, Somerday, and Balch, "Hydrogen Effects in Engineering Materials", MRS Symposium, The Hydrogen Cycle - Generation, Storage, and Fuel Cells, Nov. 2005
4. (poster) San Marchi, Somerday, Tang, and Schiroky, "Hydrogen Effects in Austenitic 316 and Super Duplex 2507 Stainless Steels", NHA Annual Hydrogen Conference, March 2006
5. (poster) Mendez, Moen, Ohi, Keller, and Allen, "A framework and risk principle for Hydrogen Safety Codes and Standards", NHA Annual Hydrogen Conference, March 2006
6. Mendez, "Maximum tolerable risk level for hydrogen systems/infrastructure", Joint Workshop on Hydrogen Safety and Risk Assessment, March 2006
7. Moen, "Hydrogen modeling and experimental studies", IEA Annex 19, Hydrogen Safety Experts Mtg, March 2006
8. Keller, "U.S. testing facilities and plans", IEA Annex 19, Hydrogen Safety Experts Mtg, March 2006

Critical Assumptions / Issues (1)

We apply science-based engineering to verify hydrogen behavior (fluid mechanics and unintended releases).

- Assumes that field-scale hydrogen jets and plumes (ignited and unignited) behave in a manner similar to other gases that have been studied at the laboratory scale and can be modeled with relatively simple engineering methods. Our hypothesis has proved to be true so far.

- Scope has been limited to canonical flows, but we would like to extend the project and add geometric complexity to study the effectiveness and safety of passive mitigation strategies such as barriers and releases in enclosed spaces.

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Critical Assumptions / Issues (2)

We apply science-based engineering to study hydrogen behavior in structural materials (materials compatibility).

- Assumes metallic structural materials are susceptible to hydrogen embrittlement and that crack-growth rate is a good metric for compatibility. We believe fracture-mechanics methods must be used in design for hydrogen service.

- Scope has been limited to crack-growth testing and does not allow for fundamental exploration of embrittlement mechanisms. We know the parameters that influence fracture, but there is no accepted model that can be used to the quantify behavior of new materials or of existing materials at more extreme conditions.

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Critical Assumptions / Issues (3)

We apply quantitative risk assessment for risk-informed decision making.

- Assumes we can acquire or synthesize accident frequency data for use in a quantitative risk analysis. This information, if it exists, is held closely by industry.
- Assumes we can create a general QRA methodology that provides valuable information for the development of new codes and standards and establishes a traceable technical basis.
- Assumes quantitative risk assessment can help prioritize the codes and standards research focus for new technologies.

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