

Research and Development for Hydrogen Safety, Codes and Standards

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Overview

Timeline

- Project start date Oct 2003
- Project end date Sep 2009
- Percent complete 33%

Budget

- Total project funding
 - DOE share: \$3.7M
- FY04 Funding: \$1.7M
- FY05 Funding: \$2.0M

Partners

- SRI, large scale release experiments
- University of Miami, jet flammability
- JPL, hydrogen combustion modeling
- E. McHale, ICC Ad Hoc Committee member
- IEA Contractors: R. Mauro, MRS Enterprises, W. Hoagland & Associates, and Longitude 122 West

Barriers

- MYPP Section 3.6.4.2 Barriers, N
 - Lack of Technical Data to Revise NFPA 55 Standard (storage)
- MYPP Section 3.6.4.2 Barriers, P
 - Current Large Footprint Requirements for Hydrogen Fueling Stations
- MYPP Section 3.7.5.2 Barriers, E
 - Obtaining Industry Input and Consensus
- MYPP Section 4.4.3 International
 - International partnership to advance hydrogen and fuel cell technologies



Objectives

Sandia provides a technical basis for assessing the safety of hydrogen-based systems for code and standards development.

- **Hydrogen-Compatible Materials**
 - material compatibility reference: pressure vessel steels, stainless steels, pipeline steels, nonferrous alloys, and composites
 - slow crack growth and fatigue testing in hydrogen environments
- **Scenario Analysis, Risk Assessment for Safety**
 - fluid mechanics, combustion, heat transfer, cloud dispersion
 - physical and numerical experiments, engineering models
 - large and small scale gaseous leaks, liquid leaks, metal hydrides
 - quantitative risk assessment and consequence analysis
- **Codes and Standards Advocacy and Change Process**
 - setbacks: ICC and NFPA
 - materials: ASME and CSA



Materials compatibility approach

**Materials Compatibility
Workshop Dec 2003
SNL**

- **Define material property needs to support C&S development**
- **Identify relevant operating conditions for hydrogen service**

**Industrial Collaborations
2004-2005**

- **Establish relationships with OEMs for obtaining real materials**
- **Initiate testing of production materials**

**Technical Reference
Website established
Jan 2005**

- **Develop global reach and portal for hydrogen compatibility**
- **Pressure vessel steels, stainless steels, and pipeline steels, and non-ferrous materials**

**SDO collaborations
2004-2005**

- **Engage stakeholders to provide input on materials data needs**
- **Establish forum to exchange ideas and create partnerships**

Hydrogen embrittles materials

Codes and standards groups want materials selection guidance:

- existing knowledge of hydrogen compatibility needs to be compiled and synthesized: provide a Technical Reference
- published data on hydrogen-assisted fracture of engineering alloys are incomplete: additional materials testing is required

Technical Reference

- *text* summarizing basic properties subject to internal and external hydrogen
- *tables* summarizing data relevant to hydrogen-assisted fracture
- *plots* comparing properties in hydrogen and ambient environments

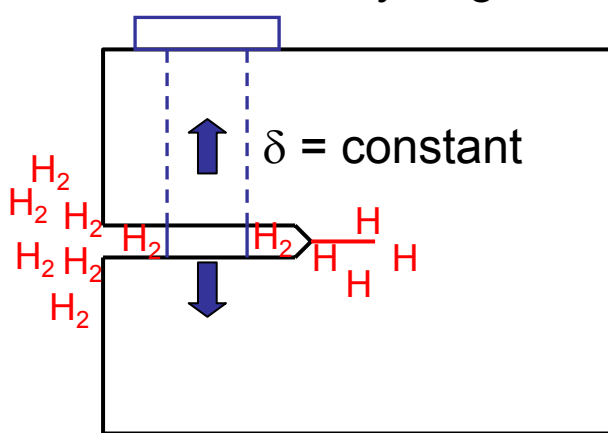
<http://www.ca.sandia.gov/matlsTechRef/>

Materials Testing

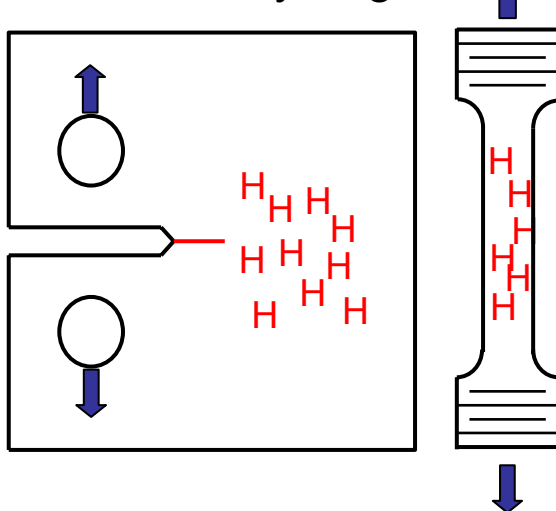


Materials testing

External Hydrogen



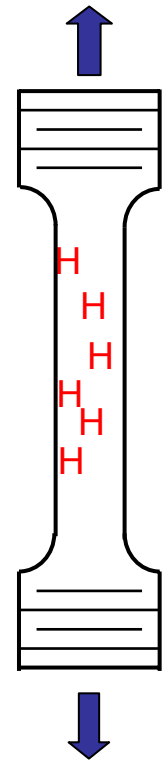
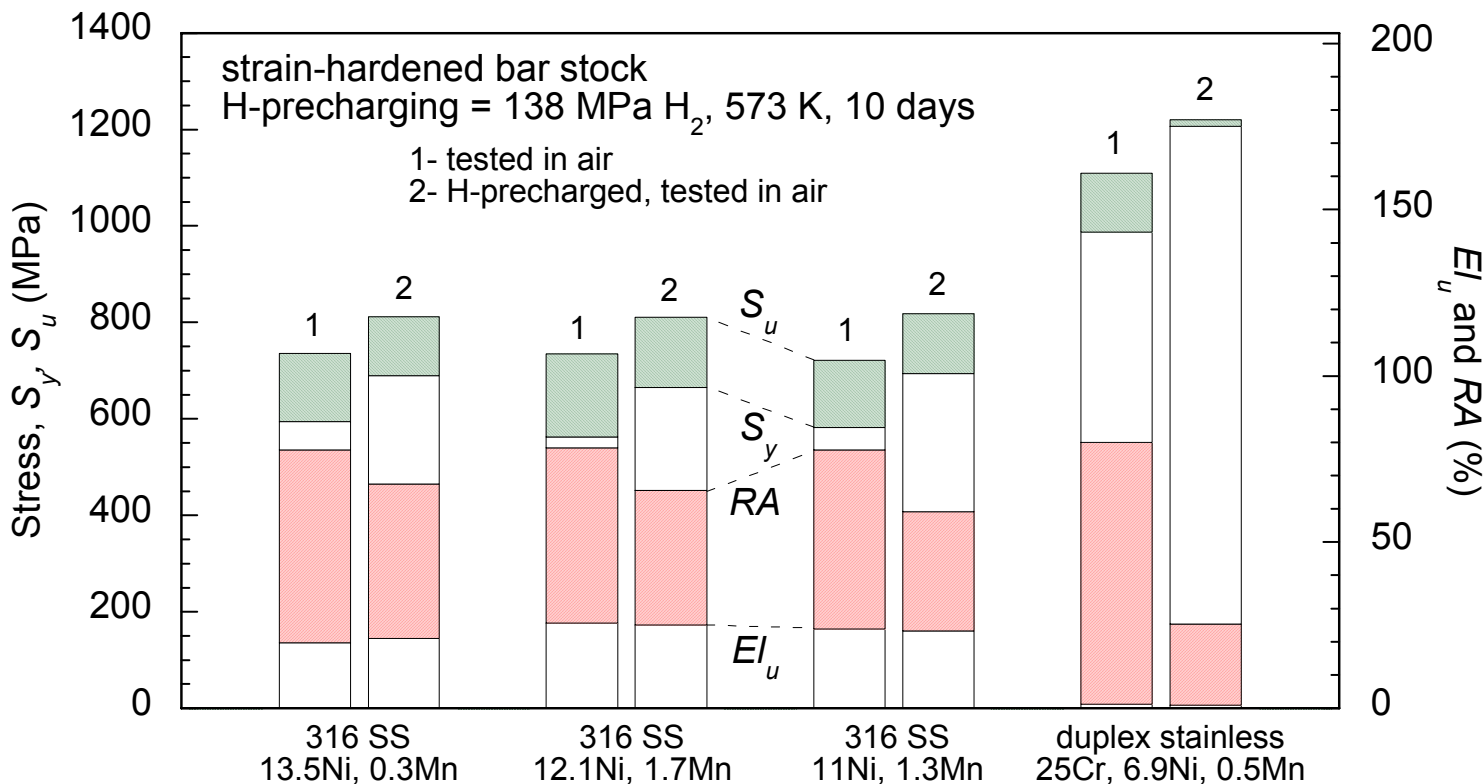
Internal Hydrogen



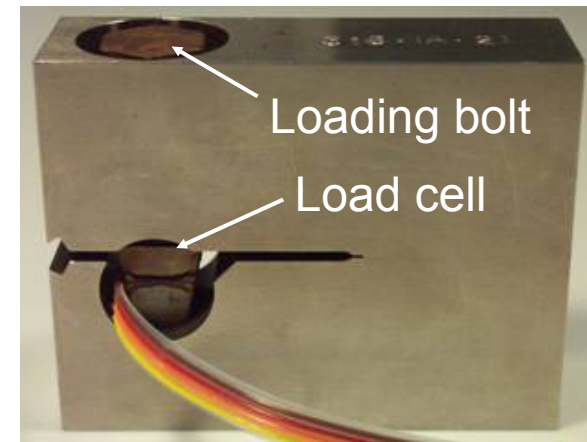
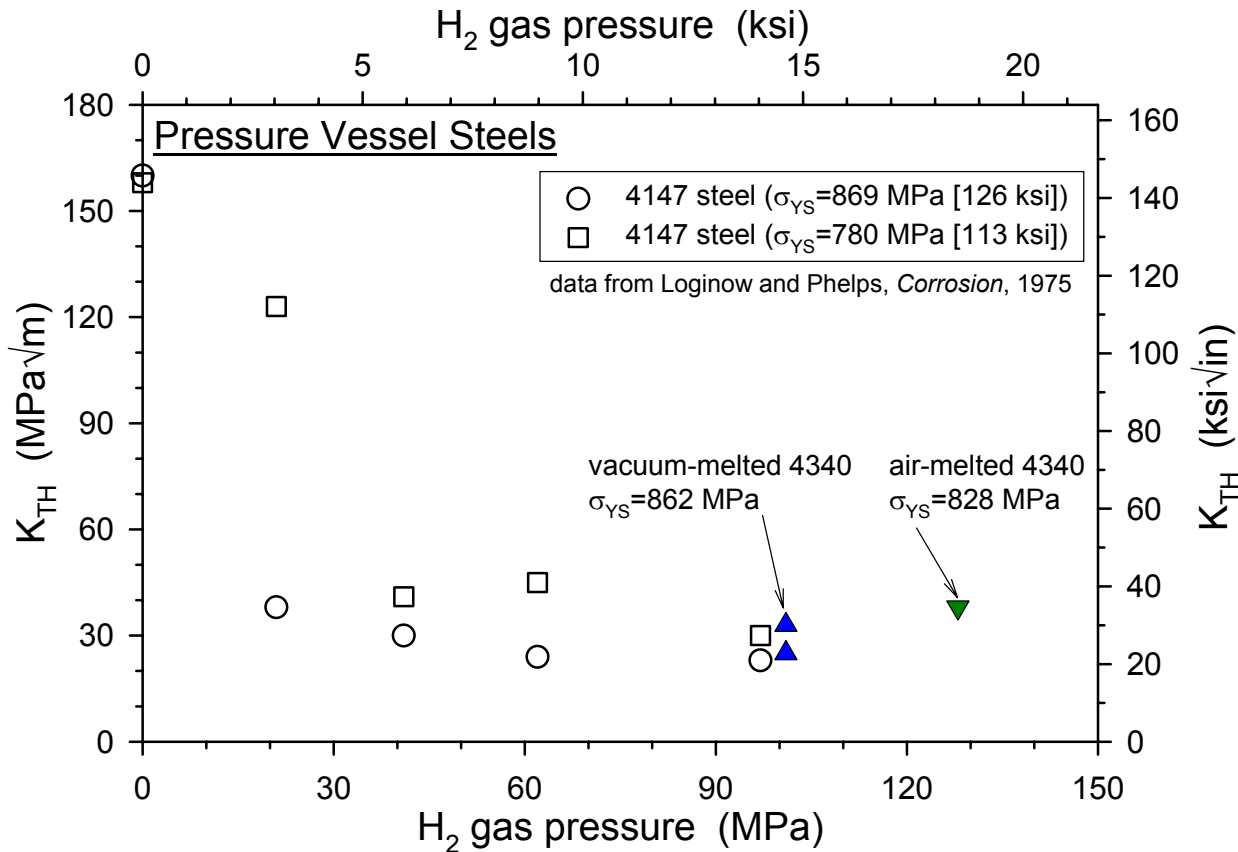
- “Strength of materials” (i.e., tensile strength) approach is not adequate for design because of hydrogen embrittlement phenomena; therefore, a fracture mechanics approach is recommended
- Slow crack-growth testing: static loading in H_2 pressures up to 28.8 ksi at 25°C, environmental chamber allows experiments at $-75^\circ\text{C} < T < 175^\circ\text{C}$
- Internal hydrogen testing: fracture experiments in air on specimens previously exposed to high-pressure hydrogen gas
- Planned experiments to measure fracture properties :
 - Pressure vessel steels
 - Pipeline steels
 - Stainless steels
 - Aluminum alloys

Composition effects in 316 steel

- Type 316 stainless steel is not strongly affected by hydrogen
- High Ni content in 316 imparts superior resistance to hydrogen-assisted fracture (higher RA when H-precharged)
- Duplex stainless steel has low resistance to hydrogen-assisted fracture in tension



Pressure affects crack threshold



Initial K_{TH} measurements for modern “clean” steels are similar to data for older steels



Summary of accomplishments

- Materials Compatibility Workshop, Dec 2003
- Technical Reference Website is Online since Jan 2005
 - six alloy specific chapters released
- Established relationships with OEMs to supply real materials for testing (two Non-Disclosure Agreements in place)
- Initiated fracture testing on pressure vessel steels and stainless steels
 - Slow crack growth testing
 - Internal hydrogen testing
- Participation in Codes and Standards activities
 - ASME: corresponding membership in BPV PT on H₂ Tanks, Hydrogen Materials Task Force, conferences and workshops
 - ASTM: workshop on materials testing for gaseous H₂ service
 - CSA: support HGV common issues working group
 - DOT: establish technical collaboration on hydrogen compatibility research



Future work

Remainder of FY05

- Compile literature (Technical Reference) on hydrogen compatibility of low-alloy steels (pressure vessels and pipelines)
- Testing of low-alloy steels and stainless steels
- Establish partnership for obtaining pipeline steel and welds for testing in hydrogen gas

FY06

- Initiate testing of pipeline steels
- Hydrogen compatibility of nonferrous alloys
- Develop facility for active loading in high-pressure hydrogen
 - no active facilities in the US
 - necessary for fatigue testing in hydrogen environments
- Investigate opportunities for testing modified low-alloy steels with the goal of improving resistance to hydrogen-assisted fracture



Scenario analysis approach

**Separation Distance
Workshop 2002**

- **Separation distance task kick-off meeting**
- **Sandia / SRI to focus on large jets, U of Miami on small jets**

**Unintended Releases
Workshop Dec 2003
NREL/SNL**

- **Define safety scenarios to drive R&D for C&S development**
- **Set priorities for research and development and analysis**

**Interact w/ ICC Ad Hoc
Committee for H2 Gas
2003-2004**

- **Define generic refueling station safety themes,**
- **Identify unintended release parameters and risk drivers**
- **Experimental jet testing and model development**
- **Quantify consequences for momentum-driven leak regime**

**Risk Assessment
Workshop Mar 2005
NREL/SNL**

- **Engage stakeholders to explore risk assessment tools**
- **Define requirements for RA in C&S development**

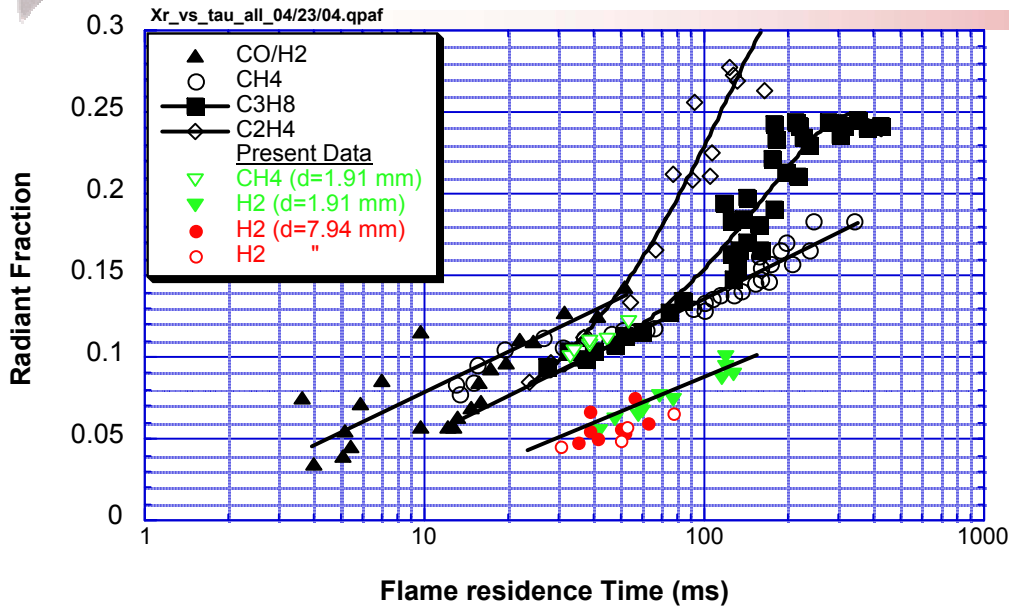
Quantify consequences



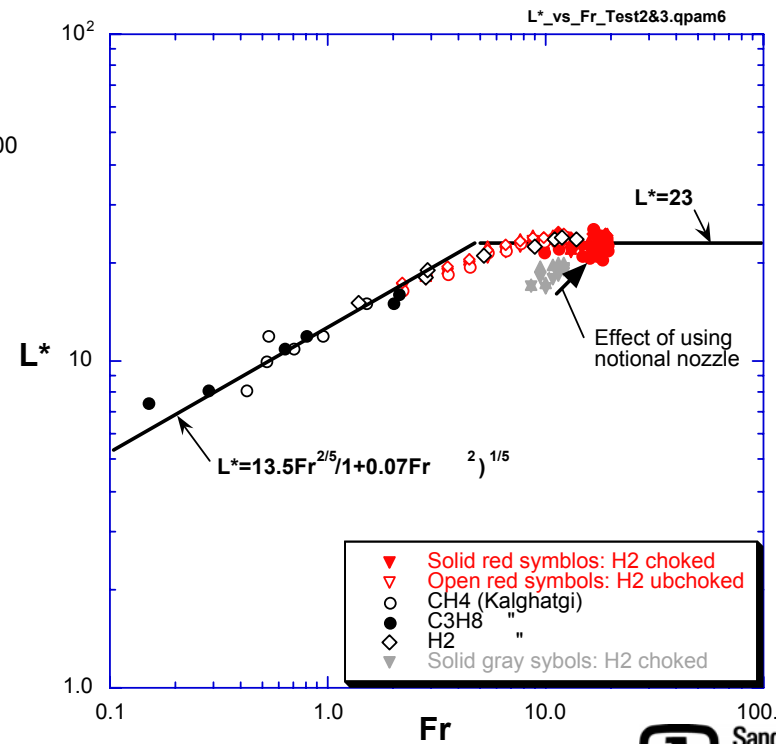
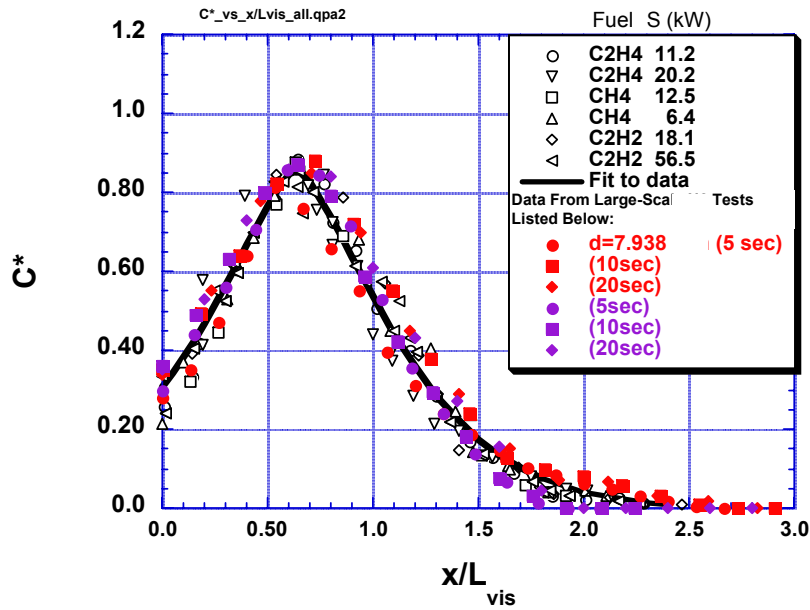
Vertical Flame
10-12 ft tall, 2-3 ft wide
(H₂ flame at SRI test site)

- With refueling station setbacks in mind...
- Objects exposed to a hydrogen release encounter:
 - Heating from thermal radiation
 - Flame impingement (flame size)
 - Combustible gas contact (footprint)Each of these items must be quantified to determine hazard length scales for separation distance
- Experimental measurements provide:
 - Flame shape and flame impingement distances for different flow rates
 - Sustainable lean ignition limits for turbulent jets
 - Hydrogen flame radiation heat flux
- Hydrogen plume behavior is then described in engineering models for parameter studies and risk assessment

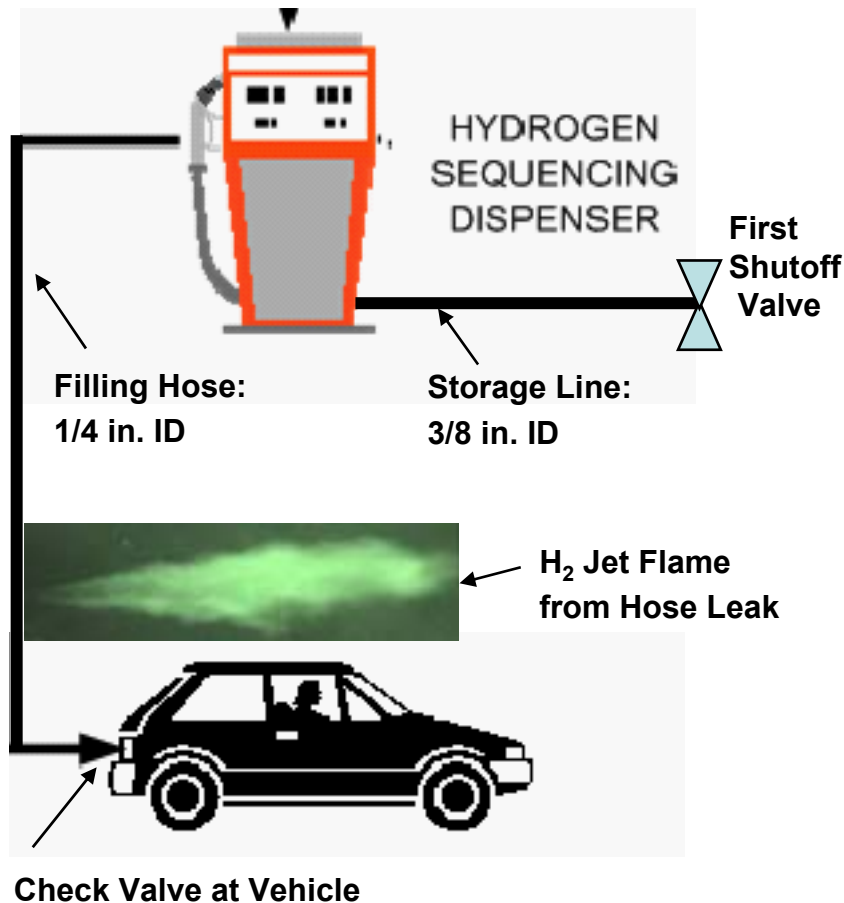
H₂ jets are similar to other jets



- fraction of chemical energy converted to thermal radiation
- radiation heat flux distribution
- jet length



Refueling station risks

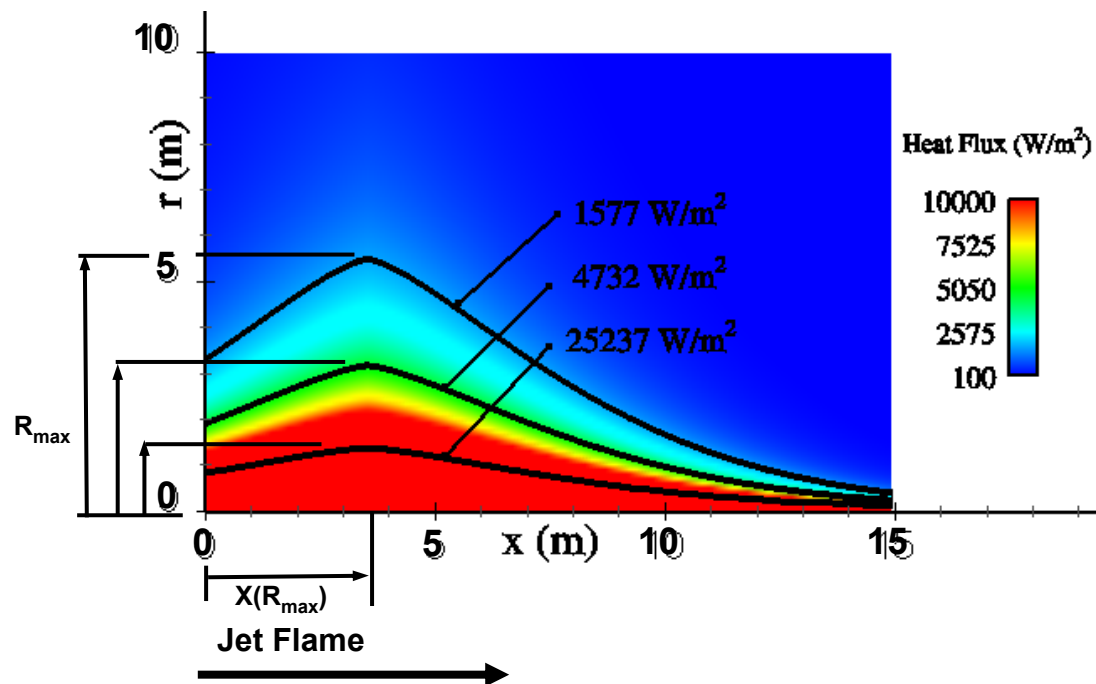


- Leak scenario parameters
 - storage pressure
 - leak orifice size
- Risk metrics define hazard length scales
 - spatial location of heat flux levels:
 - 3 min avg exposure to people
 - exposure to combustibles
 - exposure to lot line
 - the spatial envelope of ignitable gas

Thermal radiation model

Thermal radiation engineering model is defined by

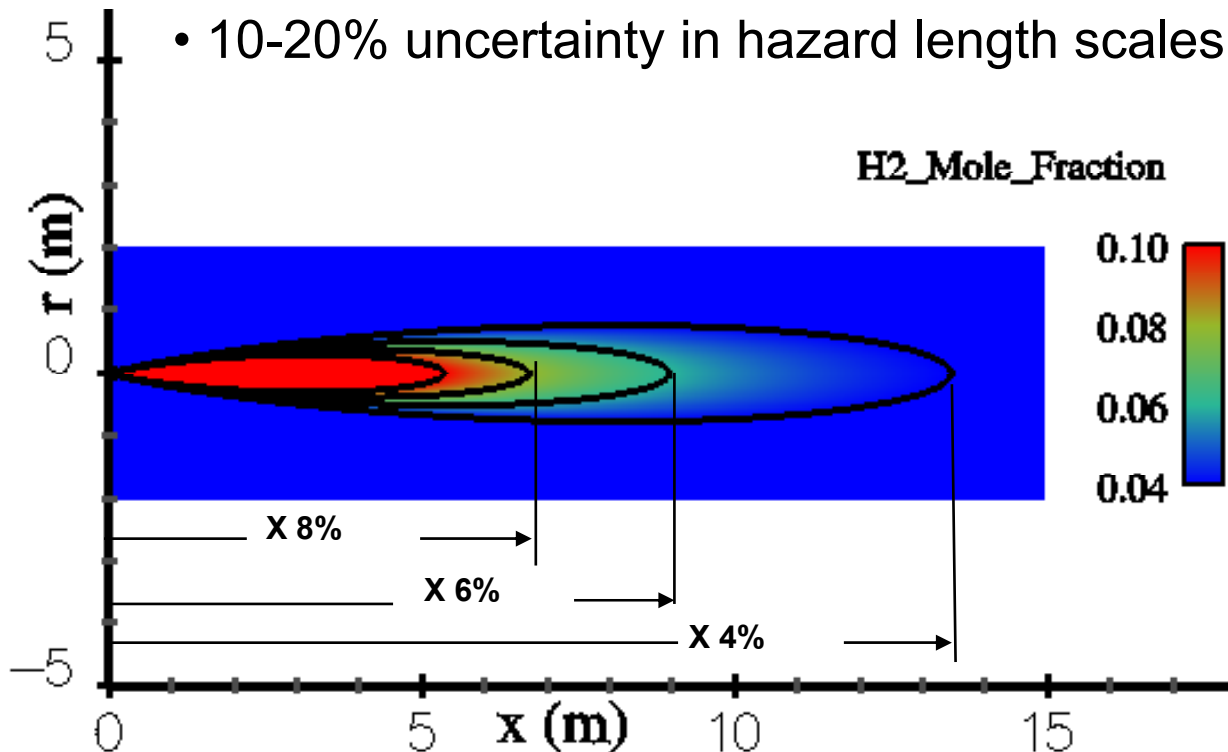
- thermodynamic expression for tank blow-down
- experimental correlations
 - flame length and width
 - fraction of chemical energy converted to thermal radiation
 - spatial distribution of thermal radiation
- 10-20% uncertainty in hazard length scales



Unignited jet model

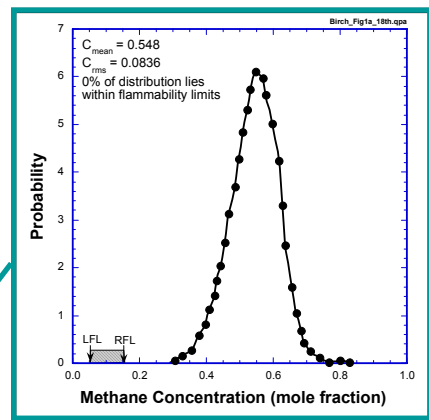
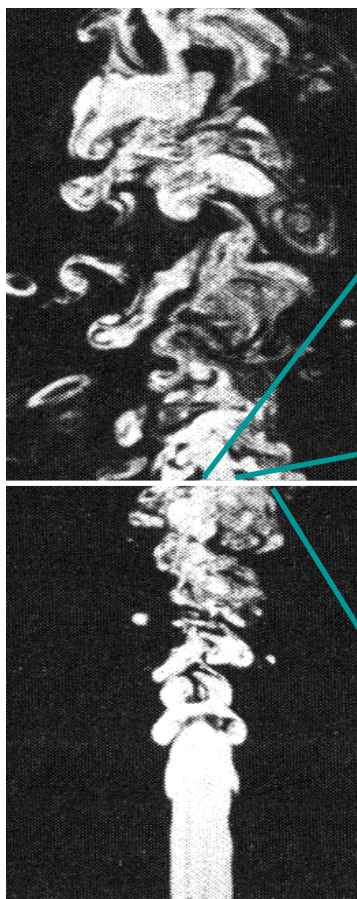
Flammable gas footprint engineering model is defined by

- thermodynamic expression for tank blow-down
- experimental correlations
 - turbulent jet decay
 - mean lower flammability limit
 - flame blow-off limits
- 10-20% uncertainty in hazard length scales

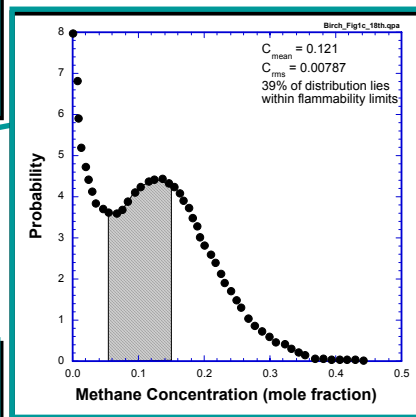


Jet ignition probability

Methane jet into ambient air (Birch et. al., 1981)

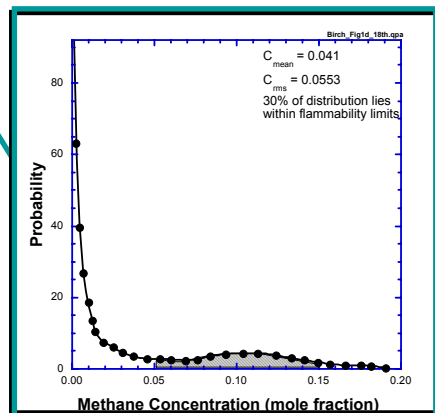


$r/D=0.0$



$r/D=1.5$

$z/D=10$



$r/D=1.8$

- Probability distributions quantify intermittent nature of turbulent flows
- There is a distribution of flamelets igniting between 4% and 8%
- Flammability limits for H_2 are well established with over 70 references in the refereed literature.

Flammability Factor is defined as the cumulative probability of a potentially flammable mixture occurring at a given point.



Summary of accomplishments

- Co-hosted workshops on Separation Distances, Unintended Releases, and Risk Assessment
- We understand the behavior of hydrogen jet flames
 - Laboratory measurements and field scale measurements for 2500 psi and 6000 psi sources
 - Fluid mechanics, combustion, and thermal radiation models
- We are providing consequence analysis for the setback problem
 - Participated in semi-annual ICC AHC technical meetings
 - Quantified consequences for refueling station accidents, working with a “working group” from the ICC AHC
- We communicate
 - 4 conference papers and reports
 - 14 meeting and conference presentations



Future work

Remainder of FY05

- Complete IJHE article on hydrogen jet flames
- Complete momentum-driven jet parameter studies and publish
- Perform probability risk assessment (PRA) of refueling station hazards
- Begin small-scale release studies for buoyant plumes

FY06

- Small-scale hydrogen release studies for confined and unconfined scenarios: experiments and models for buoyant flows
- Tube-tank trailer pressure relief device study
- Barrier wall interaction studies
- Begin scoping metal hydride storage accident scenarios

Presentation end



Publications / Presentations

Publications

- Schefer, “Combustion Basics”, in *National Fire Protection Association (NFPA) Guide to Gas Safety*, 2004.
- Schefer, Houf, Bourne, and Colton, “Turbulent hydrogen-jet flame characterization,” *International Journal for Hydrogen Engineering*, accepted for publication, Jan 2005

Conference Papers and Reports

- San Marchi, Somerday, Robinson, Moen, Keller, Leon, Chong, and Maness, “Materials workshop analysis”, *Hydrogen Codes and Standards Materials Compatibility Workshop*, Livermore, CA, Dec 2003.
- Schefer, Houf, Moen, Chan, Maness, Keller, Leon, Tam, “Unintended releases workshop analysis”, *Hydrogen Codes and Standards Unintended Release Workshop*, Livermore, CA, Dec 2003.
- Bourne, Colton, Houf, and Schefer, “Experimental measurements to characterize the thermal and radiation properties of an open-flame hydrogen plume”, *15th NHA Meeting*, Los Angeles, CA, Apr 2004.
- Somerday, Balch, Novak, and Sofronis, “Mechanisms of hydrogen-assisted fracture in austenitic stainless steel welds”, *11th International Conference on Fracture*, Mar 2005.
- Robinson, Somerday, and Moody, “Hydrogen embrittlement of stainless steels”, *11th International Conference on Fracture*, Mar 2005.
- Houf and Schefer, “Predicting radiative heat fluxes and flammability envelopes from unintended releases of hydrogen”, *16th NHA Meeting*, Washington, DC, Mar 2005.
- Chernicoff, Englom, Houf, San Marchi, and Schefer, “Characterization of leaks from compressed hydrogen dispensing systems and related components”, *16th NHA Meeting*, Washington, DC, Mar 2005.
- San Marchi, Balch, and Somerday, “Effect of high-pressure hydrogen gas on fracture of austenitic steels”, *ASME Pressure Vessels and Piping Division Conference*, Denver, CO, Jul 2005.
- Leighty, Holloway, Merer, Keith, Somerday, and San Marchi, “A 1,000 MW wind-plant delivering hydrogen fuel from the Great Plains to a distant urban market”, *ISES 2005 Solar World Congress*, Aug 2005.



Publications / Presentations

Presentations

- Moen, R&D progress and program overview, ICC Ad Hoc Meeting, Golden, CO, May 2003.
- Moen, R&D progress and program overview, ICC Ad Hoc Meeting, Golden, CO, Nov 2003.
- Houf, R&D progress and consequence analysis, ICC Ad Hoc Meeting, W. Sacramento, CA, May 2004.
- Houf and Schefer, "Model-based prediction of radiative heat fluxes from hydrogen jet flames", International Conference on Numerical Combustion, Sedona, AZ, May 2004.
- Keller, "Economizing the refueling station footprint", ICC Final Action Hearings, Overland Park, KS, May 2004.
- Keller, "Hydrogen combustion behavior", Fuel Cell Summit, Coral Gables, FL, Jun 2004.
- Moen, R&D progress and consequence analysis, ICC Ad Hoc Meeting, Coral Gables, FL, Jun 2004.
- Houf and Schefer, "Predicting radiative heat fluxes from hydrogen jet flames for use in codes and standards," NFPA 9th Fire Risk and Hazard Assessment Research Application Symposium, Jun 2004.
- San Marchi, Somerday, and Robinson, "Hydrogen pipelines and material compatibility research at Sandia", International Pipeline Conference, Forum on Challenges of Hydrogen Pipeline Transmission, Oct 2004.
- Somerday, Balch, and San Marchi, "Subcritical crack growth susceptibility of low-alloy steels in high-pressure hydrogen gas", ASM Materials Solutions Meeting, Columbus, OH, Oct 2004.
- Moen, R&D progress and program overview, NHA workshop, Fuel Cell Seminar, Austin, TX, Nov 2004.
- Moen, C&S Tech Team review of Sandia program, Washington, DC, Jan 2004.
- Keller, National Academy of Sciences Review, Feb 2005.
- Ohi, Cox, Moen, and Keller, Risk Assessment Workshop, Golden, CO, Mar 2005.
- Moen, Keller, and Ohi, "Risk assessment workshop report-out", NHA Conference, Mar 2005.
- Somerday and San Marchi, "Sandia National Laboratories perspective on hydrogen-assisted fracture: materials testing and variables governing fracture", ASTM Workshop on High Pressure Hydrogen, May 2005.
- Houf and Schefer, "Radiative heat fluxes and flammability envelopes from unintended releases of hydrogen", NFPA World Safety Conference and Exposition, Las Vegas, NV, Jun 2005.
- San Marchi, "Hydrogen compatibility of structural steels", Fall MRS 2005, Boston, MA, Nov 2005.



Hydrogen safety

This project contains two distinct research elements:

- quantify the consequences of unintended releases of hydrogen and subsequent combustion
- study the conditions for hydrogen-assisted fracture in engineering materials at very high pressures

Combustion) The most significant hydrogen hazard is the presence of large hydrogen flames from 40 MPa sources, formed during testing. A specific hazard associated with these flames is thermal radiation heat transfer, which can result in a burn hazard to personnel located close to the flame.

Fracture) The most significant hazard associated with materials testing in high-pressure hydrogen gas (up to 200 MPa) is the release of hydrogen due to failure of a pump or fitting in the laboratory plumbing system during filling of the pressure vessels.



Hydrogen safety

Combustion) During the test when a flame is present, test personnel are confined to a thick-walled concrete bunker located at a safe distance (15 m) from the flame. All operations are performed from the bunker using remotely controlled safety valves to release hydrogen gas from the storage tank and fill the plumbing leading to the jet where the flame is stabilized. Closing the storage tank valve and venting the plumbing are controlled remotely after each test. Confining test personnel to a bunker also mitigates the hazard associated with a sudden release of high pressure gas due to the failure of a system component.

Fracture) The laboratory is equipped with sensors to alert personnel of a hydrogen release. In addition, the laboratory space is continuously vented during filling of the hydrogen pressure vessels. Finally, operations are performed remotely so that personnel are outside of the laboratory during filling of the pressure vessels. We use several measures to manage slow leaks from pressure vessels. First, we inspect the pressure vessels to ensure the hardware, especially seals, are in good condition. Second, we check for potential slow leaks from each sealed vessel by filling with helium prior to filling with hydrogen. Third, the primary pressure vessels are located in secondary containers. Hydrogen that is released from the primary vessel into the secondary container is vented from the laboratory.