IX.6 Hydrogen Release Behavior

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Start Date: Fiscal Year 2002
End Date: Project continuation and direction determined annually by DOE

Objectives

(1) Scenario Analysis, Risk Assessments for Safety
  – Develop a scientific basis and the associated technical data for modifying or developing new codes and standards for the commercial use of hydrogen.
  – Develop benchmark experiments and a defensible analysis strategy for risk assessment of hydrogen systems.
  – Develop and apply risk-informed decision-making tools in the codes and standards development process.

(2) Hazards Mitigation Technologies for Hydrogen Applications
  – Determine stability and compatibility of candidate odorants with fuel cell components.

(3) Codes and Standards Advocacy
  – Provide technical program management and support for the Safety, Codes and Standards Program element.
  – Participate in the hydrogen codes and standards development/change process.

Technical Barriers

This project addresses technical barriers from the Codes and Standards section of the Hydrogen, Fuel Cells and Infrastructure Technologies 2007 Multi-Year Research Plan:

(F) Limited DOE Role in the Development of International Standards
(I) Conflicts Between Domestic and International Standards
(N) Insufficient Technical Data to Revise Standards
(P) Large Footprint Requirements for Hydrogen Fueling Stations
(Q) Parking and Other Access Restrictions

Contribution to Achievement of DOE Safety, Codes & Standards Milestones

This project contributes to achievement of the following milestones from the Codes and Standards section of the Hydrogen, Fuel Cells and Infrastructure Technologies 2007 Multi-Year Research Development and Demonstration Plan:

- **Milestone 3**: Complete detailed scenario analysis risk assessments. (4Q, 2007)
- **Milestone 4**: Complete analytical experiments and data collection for hydrogen release scenarios as needed to support code development. (2Q, 2008)
- **Milestone 7**: Perform tests of walled hydrogen storage systems. (3Q, 2007)
- **Milestone 21**: Completion of necessary codes and standards needed for the early commercialization and market entry of hydrogen energy technologies (4Q, 2012)

Accomplishments

- Experiments and simulations were completed to characterize the effect of ignition delay time, ignition location, and confinement configuration on the overpressure produced during the ignition of hydrogen leaks near barrier walls.
- A new gaseous hydrogen separation distance table was approved and incorporated into National Fire Protection Association (NPFA) 55. The new table was created by NFPA 2 Task Group 6 based on risk analysis, leak frequency data analysis, and hazard models developed by Sandia.
- Harmonization of consequence models has been achieved for separation distances in International Organization for Standardization (ISO) 20100 and NFPA 55, working through TC197/WG11. Discussions on risk analysis methodology continue.
- The European Union HYdrogen PERmitting (HYPER) project completed the Installation Permitting Guidance for stationary hydrogen and fuel cell systems with contributions by Sandia on barrier wall experiments and models.
- Simulations of pressure relief device (PRD) releases from fuel cell vehicles in tunnels were performed to

determine the evolution of the flammable volume of hydrogen in the tunnel and the over-pressure produced by delayed ignition at different locations.

- Turbulent hydrogen jet ignition and light-up experiments showed that the time-averaged fuel concentration and conventional flammability limits established for quiescent fuel/air mixtures do not correspond to the flammable boundaries of a turbulent hydrogen jet. A predictive model of ignition (flammability factor) of turbulent hydrogen jets was developed and validated with the ignition experiments.
- Princeton University research indicates that auto-ignition is enhanced by blunt-body obstructions due to increases in gas temperature and the promotion of fuel-air mixing.
- Experiments were conducted at the SRI Corral Hollow test site to investigate the effect of electrically charged particles as a source of hydrogen auto-ignition.
- Liquid hydrogen discharge and dispersion models were developed for small (fittings and cracks) and large (choked flow through vents and PRDs) releases.
- Risk assessment tools to support the permitting of hydrogen refueling stations have been developed and will be incorporated on the National Renewable Energy Laboratory (NREL) hydrogen permitting Web site.
- Two candidate odorant molecules were evaluated for fuel cell membrane compatibility and dosing stability by the team of Enersol and the Pennsylvania State University.
- Sandia organized and hosted the spring International Energy Agency (IEA) Task 19 meeting in San Francisco (April 21-23rd). As participants in IEA Task 19 hydrogen safety, we have generated written guidance on risk criteria and harm criteria.

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Introduction

The purpose of this comprehensive project is to enable risk-informed development of codes and standards for hydrogen fuel cell technology that is based on a traceable, scientific foundation. Our scenario analysis and risk assessment efforts focus on defining scenarios for the unintended release of hydrogen and quantifying the consequences through scientific experimentation and modeling. Quantitative risk assessment (QRA) is used to identify risk drivers and risk mitigation strategies for the commercial use of hydrogen. We combine our validated models with QRA to support risk-informed decision-making in the code development process.

Approach

A significant number of tasks are focused on combustion behavior and thermal effects from the unintended release of hydrogen in the built environment, namely barrier wall interactions, ignition characteristics, partially confined spaces (tunnels, garages, warehouses), and liquid hydrogen handling. Technical information is used by codes and standards developers writing for International Code Council and NFPA, also through the Hydrogen Industry Panel on Codes. International partnerships for vetting technical data and analysis methods occur through activities such as IEA Task 19 on Hydrogen Safety and the European HYPER project. Recent work has focused on harmonizing separation distance approaches for ISO 20100, hydrogen fueling.

Results

Risk Assessment: QRA was used to help establish risk-informed separation distances in ISO 20100 for gaseous hydrogen refueling stations through TC197/WG11. To support the ISO and IEA Task 19 (hydrogen safety) efforts, risk criteria and harm criteria were surveyed and adopted values were documented. Additional QRA analyses continued this year focusing on the risk tradeoffs associated with the use of barriers to protect the public and facilities from hydrogen jet fires. A joint effort with NREL to establish Web-based risk assessment tools also continued this year.

Barrier Wall Design: Experiments and simulations were completed to characterize the effect of ignition delay time, ignition location, and barrier wall configuration on the over-pressure produced during the ignition of hydrogen leaks. In addition to single-wall and three-sided wall (135° wall angles) barriers, a new configuration consisting of three-walls with a 90° wall angle was evaluated, shown in Figure 1. The experimental ignition delay time was varied between 67 msec and 6 seconds after leak initiation. The over-pressure remains nearly constant over the range of delay times with all three-wall configurations. This general behavior agrees with our models. Numerical simulations with FLACS (FLame ACceleration Simulator) show that barrier walls reduce the lateral and vertical extent of hazard distances by approximately 50% as compared to a free jet. Because safety distances in the new NFPA 55 table are based on these same pressures and leak diameters of our simulations, model results indicate that use of a barrier wall would allow the reduction of safety distances by approximately half.

Partially Enclosed Spaces: Simulations of releases from hydrogen fuel cell vehicle tanks in tunnels were performed to understand potential over-pressures from delayed ignition of a PRD release, most likely due to a vehicle fire. Dispersion of ignitable clouds of hydrogen following the blow-down of 70 MPa gaseous tanks through a PRD was determined for transversely and longitudinally ventilated tunnels over a range of operating conditions. Transient simulation of the ignition of the flammable cloud was used to estimate deflagration overpressure. Results indicate that ignition overpressure is sensitive to ignition delay time and position, with the lower overpressures occurring for short ignition delay times (approximately <2 sec) when the flammable volume is rich or for longer ignition delay times (approximately >10 sec) where the flammable volume has dispersed to a lean concentration. These delays are the most likely ignition scenarios because the mixture will ignite early near the fire that actuates the PRD or away from the vehicle at some other ignition source.

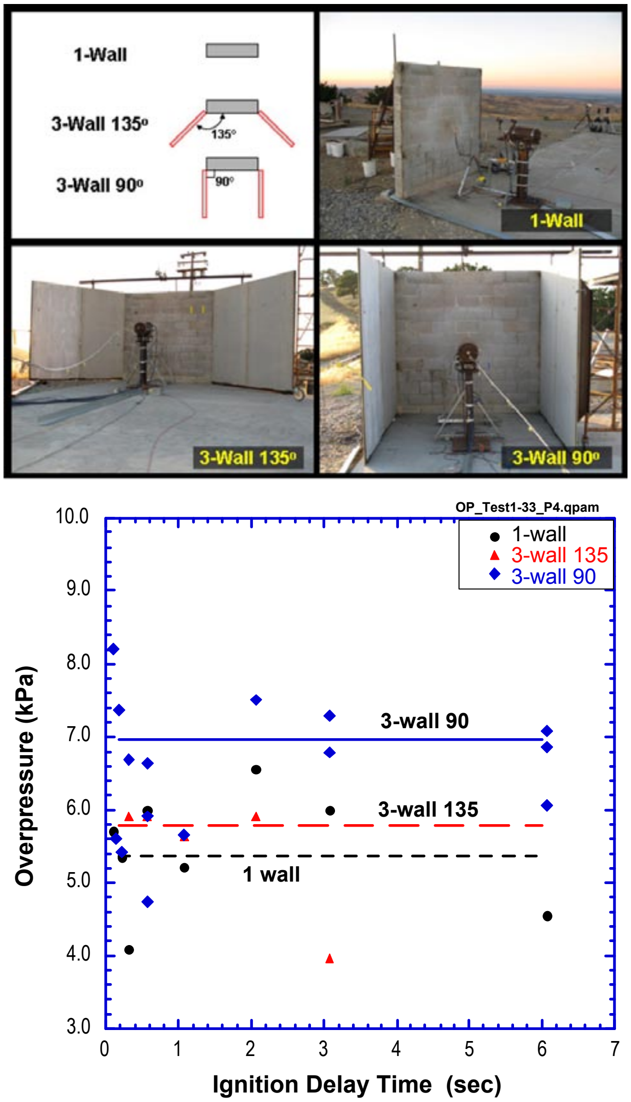

FIGURE 1. Variation in overpressure with ignition delay time for single-wall, three-sided wall with 135° angle, and three-sided wall with 90° angle (pressure transducer located in front of wall).

Lean Ignition Limits in Turbulent Jets: Previous experience shows that the lower flammability limits for a quiescent hydrogen mixture do not match mean values for highly fluctuating, turbulent jets. The probability of ignition (P_I) of turbulent hydrogen jets into air was determined using a pulsed Nd:YAG laser, focused to generate an ignition spark that served as the ignition source. Laser Rayleigh scattering was used to characterize the fuel concentration throughout the jet. The dramatic differences between the time-averaged hydrogen concentration field and the instantaneous field give clues to why the average concentration and conventional flammability limits established for quiescent fuel/air mixtures do not correspond to the flammable boundaries of turbulent fuel jets. The measured hydrogen jet light-up contour is shown in Figure 2. Local ignition could only be obtained if the instantaneous composition at the ignition point was within the static flammability limits. In addition to the direct measurement of P_I, the measured probability distribution functions of local fuel concentration were integrated over the static flammability limits to obtain the measured flammability factor, which provides a good representation of P_I. Models of P_I were developed and validated by comparing with measured flammability

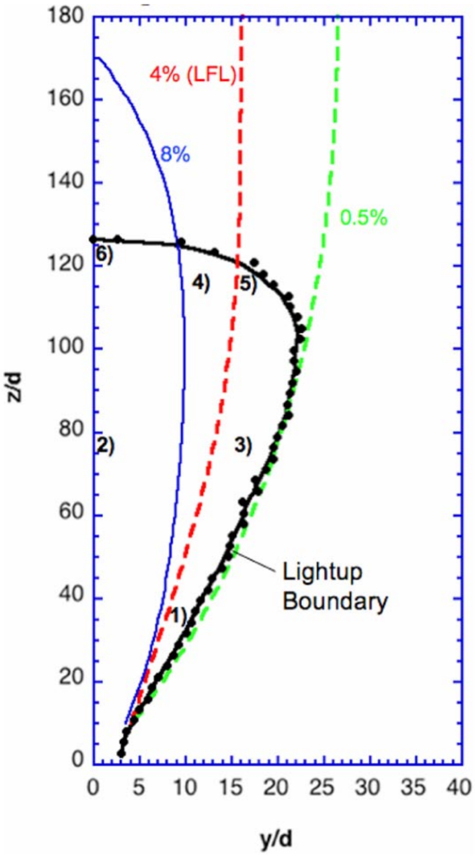

FIGURE 2. Jet light-up contours for the H_2 jet. Each point is the mean of five tests.

factors. Validated models can be used to provide a technical basis for the determination of safety distances in codes and standards regulations for flammable gases.

Auto-Ignition Mechanisms: The ignition source in many reported incidents has not been identified, often referred to as an auto-ignition event. Two of the most likely ignition sources for these events include shock heating of the resulting hydrogen/air mixture and ignition due to electrostatically charged particles. In collaboration with Princeton University, we implemented a combined experimental and modeling program to identify the potential role of shock heating as an auto-ignition source. Princeton research indicates that auto-ignition is enhanced by blunt-body obstructions due to increases in gas temperature and the promotion of fuel-air mixing. We worked with SRI to study electrically charged particles as a source of auto-ignition. Experiments conducted at the Corral Hollow test site focused on determining what factors create the highest particle charges in hydrogen flow through pipes and an investigation of whether a static discharge in such a flow can cause auto-ignition. It was found that the highest charge was detected when the particles passed through a 10-foot steel pipe prior to exiting the nozzle. A grounded probe was placed in the charged particle stream in an attempt to achieve auto-ignition. Five attempts were made to ignite the hydrogen jet by discharging the charge particle cloud to the grounded probe, but no successful ignitions were achieved.

Liquid Hydrogen: A series of computer models were developed to describe the behavior of hydrogen as it is being discharged from a liquid hydrogen storage system. The models account for discharge from both the saturated liquid and saturated vapor portions of the hydrogen storage system. Models were developed for slow leaks with large pressure drops like those typically occurring from fittings or small cracks. Models were also developed for larger choked flow discharges like those that might occur from pressure relief devices, vent stacks, or the intentional discharge of hydrogen during fuel transfer. Validation for high-momentum cold hydrogen jets was accomplished by comparing predictions for centerline hydrogen concentration with those measured by Forschungszentrum Karlsruhe.

Odorants: Two candidate molecules were investigated as odorants for hydrogen gas by the team of Enersol and the Pennsylvania State University. It was found that molecule A had no adverse effect on the polarization and long term (16 hr) degradation up to 40 ppm in concentration. At higher concentrations of molecule A (400 ppm), fuel cell performance degraded. For molecule B, the extent of degradation in the long-term fuel cell performance depended on the concentration with no negative impacts on performance at concentrations up to 30 ppm. The performance degradation was found to be completely reversible by feeding pure hydrogen.

Conclusions and Future Directions

- Barrier walls can be used to reduce setbacks by factor of two.
- No ignition-timing versus over-pressure sensitivities were observed for jet flow obstructed by barrier walls.
- The cryogenic vapor cloud model indicates hazard length scales exceed the room-temperature release; validation experiments are required to confirm.
- Light-up maps have been developed for lean-limit ignition; flammability factor model provides a good indication of ignition probability.
- (future) Hydrogen ignition experiments will be conducted in turbulent jet flows that interact with surfaces to provide data for ignition model validation in more complex flow environments. Risk-informed separation distances will be updated with new ignition probabilities.
- (future) Lab-scale cryogenic vapor experiments will be conducted for low-momentum jets to provide validation data. Validated cryogenic leak models will be used to predict flammability envelopes for credible release scenarios
- (future) Validation experiments for hydrogen releases in partially-confined enclosures such as tunnels and parking structures will be performed. The risk associated with accidental releases of hydrogen in tunnels, parking structures, and storage sheds will be evaluated.

FY 2009 Publications/Presentations

1. Ruggles, et al., "Ignition Limits for Sustainable Combustion of Hydrogen in Turbulent Flows," 32nd Int. Symposium on Combustion, August 2008.

2. Houf, et al., HYPER Rep. 4.3, Chap. 6: "Effect of Barriers and Walls," August 2008.

3. Schefer, et al., "Investigation of Small-Scale Unintended Releases of Hydrogen: Buoyancy Effects", *Int. J. Hydrogen Energy*, Vol. 33, September 2008.

4. Schefer, et al, "HYPER Report 5.4 – Report on Experimental Evaluation of Barrier Walls for Risk Reduction of Unintended Releases of Hydrogen," September 2008.

5. Schefer, Groethe, Houf, and Evans, "Experimental Evaluation of Barrier Walls for Risk Reduction of Unintended Hydrogen Releases," SAND2008-41411, 2008.

6. Schefer and Houf, "Investigation of Small-Scale Unintended Releases of Hydrogen: Momentum–Dominated Regime", *Int. J. Hydrogen Energy*, Vol. 33, November 2008.

7. Winters, "Modeling Leaks from Liquid Hydrogen Storage," SAND 2009-0035.

8. Winters, "Modeling Vessel Fillup and Blowdown," SAND 2009-0100.

9. Diop, et al., “A Parametric Study of Jet-Wall Interactions for Compressed Hydrogen Gas Leak Scenarios,” 42nd AIAA Aerospace Sciences Meeting, January 2009.

10. Houf, Evans, and Schefer, “Analysis of Jet Flames and Unignited Jets from Unintended Releases of Hydrogen,” *Int. J. Hydrogen Energy*, February 2009.

11. Schefer, et al., “Experimental Evaluation of Barrier Walls for Risk Reduction of Unintended Hydrogen Releases”, *Int. J. Hydrogen Energy*, Vol. 34, February 2009.

12. LaChance, Houf, Middleton and Fluer, “Analyses to support development of risk-informed separation distances for hydrogen codes and standards,” SAND2009-0874.

13. Houf, et al. “Evaluation of Barrier Walls for Mitigation of Unintended Releases of Hydrogen,” 2009 NHA Conference.

14. LaChance, et al. “Development of Uniform Harm Criteria for Use in the Quantitative Risk Analysis of the Hydrogen Infrastructure,” 2009 NHA Conference

15. Winters and Houf, “Results from an Analytical Investigation of Small-Scale Releases from Liquid Hydrogen Storage Systems,” 2009 NHA Conference.

16. Sprague, et al., “Odorization of Hydrogen for Fuel Leak Detection,” 2009 NHA.

17. Zhang, Ruggles, and Schefer, “Ignitability limits for combustion of hydrogen in turbulent flows,” Sixth U.S. National Combustion Mtg., Ann Arbor, MI, May 2009.

18. Winters and Houf, NHA Fuel Cell Safety Report, May 2009.

19. Lee, et al., “Impact of Hydrogen Odorants on PEMFC Performance,” 215th Electro. Chem. Soc Mtg, San Francisco, CA, May 2009.

20. Houf, et al., “Evaluation of Barrier Walls for Mitigation of Unintended Releases of Hydrogen,” NHA Online Fuel Cell Safety Report, May 2009.

21. Twelve stakeholder briefings throughout FY 2009.