VI.5 Hydrogen Safety, Codes and Standards Research and Development

Jay Keller (Primary Contact), Chris Moen, Robert Schefer, Bill Houf, Brian Somerday, Chris San Marchi
Sandia National Laboratories
P.O. Box 969
Livermore, CA 94551
Phone: (925) 294-3316; Fax: (925) 294-2276; E-mail: jokelle@sandia.gov

DOE Technology Development Manager: Patrick Davis
Phone: (202) 586-8061; Fax: (202) 586-9811; E-mail: Patrick.Davis@ee.doe.gov

Objectives

- Provide technical program management and support for Safety, Codes and Standards within the Hydrogen, Fuel Cells and Infrastructure Technologies Program.
- Identify critical safety scenarios and gather the technical data required to support codes and standards decisions.
- Develop a scientific basis for evaluating credible safety scenarios, providing technical data for codes and standards decisions.
- Analyze hydrogen-related engineered systems and components for safety issues and identify probable hazards.
- Develop benchmark experiments and a defensible analysis strategy for risk assessment of hydrogen systems.
- Develop engineering models that can be used for rapid assessment of different scenarios and risk analysis.
- Participate in the hydrogen codes and standards development/change process.
- Identify and collect data from journals and reports for inclusion in Technical Reference for Hydrogen Compatibility of Materials.
- Execute materials testing to generate data for inclusion in Technical Reference for Hydrogen Compatibility of Materials.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research Development and Demonstration Plan:

- Hydrogen Production
  - E. Control and Safety
  - M. Material Durability
- Technology Validation
  - E. Codes and Standards
  - B. Storage

Approach

- Provide technical direction and technical management for the Safety, Codes and Standards within the Hydrogen, Fuel Cells and Infrastructure Technologies Program.
- Participate as a member of the FreedomCAR/Fuel Codes and Standards Tech Team (CSTT).
- Participate as a member of the Safety Panel.

- Maintain the interactive web site for the DOE management team, the CSTT, and the Safety Panel.
- Develop benchmark datasets and a defensible analysis for risk assessment of hydrogen systems.
- Provide defensible science as basis for codes and standards development.
- Participate in codes and standards development.
- Identify the materials of construction and operating conditions of components proposed for the hydrogen economy infrastructure.
- Search journals and reports for materials data that are pertinent to the proposed operating conditions for components in the hydrogen economy infrastructure.
- Compile data in an evolving document, which is entitled the Technical Reference for Hydrogen Compatibility of Materials.
- Conduct materials testing to generate data that is absent from the existing body of materials data contained in journals and reports.

Accomplishments

- Completed the analysis of the findings for the Hydrogen Codes and Standards Unintended Release Workshop held December 5, 2003 at Sandia National Laboratories (SNL). The goal of this workshop was to identify safety scenarios that define experiments and models required to support the development of credible standards.
- Completed the development and analysis of benchmark dataset for large-scale hydrogen jet flames. The data will provide the benchmark dataset needed for model validation of unintended large-scale hydrogen releases.
- Developed a predictive capability for radiative heat transfer based on engineering models and experimentally verified correlations for large-scale hydrogen jet flames.
- Developed an engineering model to determine the concentration decay of high-momentum high pressure hydrogen jets. This capability is important to determine how quickly an unintended hydrogen release mixes with air to a point where it is no longer flammable.
- Participated in the code change process with the International Code Council Ad Hoc Committee for Hydrogen Gas. Applied models to characterize refueling station hazards, reporting results at committee meetings. Held monthly teleconferences to develop new separation distances approach based on pressure ranges.
- Completed a draft of a book chapter for the National Fire Protection Association (NFPA) on basic combustion principles.
- Organized a workshop at SNL/California in December 2003 to identify and prioritize materials data needs for the Technical Reference for Hydrogen Compatibility of Materials. The workshop was attended by individuals from codes and standards agencies, national laboratories, and private industries.
- Prioritized data review and materials testing. The following materials classes were identified as high priorities for inclusion in the Technical Reference for Hydrogen Compatibility of Materials: pressure vessel steels, pipeline steels, and stainless steels.
- Identified and reviewed 40 journal publications and reports pertaining to effects of gaseous hydrogen on fracture of stainless steels and pressure vessel steels.
- Drafted two sections on stainless steel data to establish preliminary format for Technical Reference for Hydrogen Compatibility of Materials.
- Initiated materials testing to measure hydrogen-assisted fracture thresholds under static loading at gas pressures up to 150 Megapascals (MPa) for the pressure vessel steel 4340.

Future Directions

- Continue work to provide scientific basis for high pressure release scenarios by extending pressure range to expected future storage pressures of 5,000 pounds per square inch (psi) from current 2,500 psi data base.
- Walled storage at refueling stations is being considered as a means of reducing separation distances. Experimentally investigate and characterize heat transfer and barrier integrity in release scenarios involving flame impingement on walls. Obtain benchmark data to support model development and validation.
- Continue to develop and validate model to predict behavior of ignitable gas contours in release scenarios that result in combustible jet flows.
- Experimentally investigate the behavior of full-size hydrogen transport cylinders subjected to fuel fires similar to those expected in vehicle accident scenarios. Determine the minimum size requirements for a pressure relief device to safely vent hydrogen before pressure vessel failure.
- Identify critical safety scenarios and develop defensible models for small-scale hydrogen release scenarios. The engineering models will provide the technical basis needed to establish ventilation requirements.
- Continue to compose Technical Reference for Hydrogen Compatibility of Materials. The content of this living document will evolve as data is collected from the literature and generated from materials testing. Expand literature review to include data for other metals (i.e., pipeline steels and aluminum alloys) and non-metals (i.e., polymers and composites).
- Complete literature review for materials data on stainless steels and pressure vessel steels.
- Execute testing to fill gaps in the existing database for hydrogen compatibility of materials. Testing to measure thresholds for hydrogen-assisted fracture under static and fatigue loading is planned for pressure vessel steels, pipeline steels, stainless steels, and aluminum alloys.
- Develop new hydrogen detection and leak mitigation strategies. Develop and demonstrate new hydrogen senor technology based on combined palladium-based metal-insulator-semiconductor (Pd-MIS) and chemical resistor (Pd-CR) devices.
- Develop thin catalytic coating technology as a cost-effective mitigation strategy for small hydrogen leaks.
- Begin development of an optical sensor technology for standoff detection of hydrogen leaks. Standoff distances would range from several to tens of meters.
- Develop hydrogen fire suppression techniques through experiment and modeling.

Introduction

A major barrier to the development of a hydrogen economy and the deployment of hydrogen technologies is the lack of tested codes and standards. Such codes and standards are necessary to assure that related products and systems are safe and perform as designed. A well-developed set of codes and standards governs most components related to our current hydrocarbon-based energy infrastructure. The use of hydrogen as an energy carrier on a large-scale commercial basis, while integral to the future hydrogen economy, is currently untested and underdeveloped. The development of an infrastructure for the future hydrogen economy will require the simultaneous development of an analogous set of safety codes and standards to establish guidelines for building this structure. Because some of the properties of hydrogen are unique, existing energy-related codes and standards may not be applicable. The applicability of current codes must be evaluated to determine if they must be modified or replaced. The purpose of this project is to provide the technical basis for assessing the safety of hydrogen-based systems and using the assessment findings to modify relevant codes and standards. The project impacts areas of hydrogen utilization, including bulk transportation and distribution, storage, production and utilization.

The materials effort focuses on developing a materials guide resource titled, Technical Reference for the Hydrogen Compatibility of Materials. This effort is identified in the draft Multi-Year Research, Development and Demonstration Plan (Table 3.6.5) issued in June 2003. The content of the Technical Reference for Hydrogen Compatibility of Materials is being developed by reviewing journals and reports for materials data and by conducting materials testing to fill gaps in the existing database.

Approach

Efforts during this year were directed toward the following program components: 1) Scenario Analysis, Risk Assessments for Safety, 2) Hydrogen-Compatible Materials, and 3) Codes and Standards Advocacy. The purpose of the hydrogen Safety Scenario Analysis is to develop a scientific basis for evaluating credible safety scenarios and providing technical data for codes and standards decisions. Sandia National Laboratories is developing benchmark experiments and a defensible analysis strategy for risk assessment of hydrogen systems. This work includes experimentation and modeling to understand the fluid mechanics and dispersion of hydrogen for different leak scenarios. It includes investigations of hydrogen ignition and combustion processes and subsequent heat transfer from hydrogen flames. Technical information is contained in simple engineering models that are used for rapid assessment of different scenarios and risk analyses.

The purpose of the Hydrogen-Compatible Materials component is to address the materials and methods of construction in the hydrogen economy infrastructure. Identifying the materials of construction and operating conditions of components in the hydrogen economy infrastructure defined the proposed content and structure of the Technical Reference for Hydrogen Compatibility of Materials. Two parallel paths are established for composing the content: data collection from existing journals and reports, and data generation through a materials testing program.

As part of the Codes and Standards Advocacy, SNL is an active participant in the codes and standards development process through groups such as the International Code Council (ICC) ad hoc committee on hydrogen gas. This participation ensures that the codes that are put into place are based on defensible science and that the correct scientific knowledge base is developed in the most expedient way possible.

Results

Scenario Analysis, Risk Assessment: Unintended Releases. We completed the analysis of the findings for the Hydrogen Codes and Standards Unintended Release Workshop held December 5, 2003. The goal of this workshop was to identify safety scenarios that define experiments and models required to support the development of credible standards. The workshop findings provide the guidance to define and prioritize research and technical activities on the needs of the standards development organizations. The discussion first focused on the hydrogen systems expected to evolve during future hydrogen infrastructure development. These included storage, bulk transportation and distribution, production, and utilization. Once these hydrogen systems were identified, release scenarios were identified. Of the 68 release scenarios identified, the majority were leaks that resulted in combustible cloud formation. The leak size, its origin and surroundings were all used to further categorize the scenarios and resulting hazards. Additional scenarios included liquid hydrogen releases, interactions between hydrogen and hydrocarbon fuels, hydrogen originating from fuel-cell anode off-gas bleeds, electrolyzer leaks, and metal hydride storage. Based on the identified scenarios several areas for future research have been defined. These include turbulent open-jet flames, flames impinging on surfaces, combustible cloud dynamics, dispersion, and ignition, the effect of external fires on hydrogen storage vessels and liquid hydrogen spill dynamics. The results of the workshop and the subsequent analysis have been written into a report that was disseminated to interested individuals and organizations.

Scenario Analysis, Risk Assessment: Experimental Validation of Large-Scale Releases. Reduction and analysis of the data obtained in large-scale hydrogen jet flame tests during FY 2003 was completed. Applying a network flow model of the gas bottles and piping to compute jet exit velocities, densities, and pressures for the experiments reduced uncertainties in the experimental jet exit conditions. The data analysis showed that additional measurements were needed to provide a more complete benchmark data set for model validation. A test plan was formulated to perform additional large-scale hydrogen jet flame experiments at the SRI test site and the new tests were completed in April and May 2004. The visible flame characteristics were measured to determine visible flame lengths for vertical and horizontal jets. The flame radiation measurements were repeated with more closely spaced, higher sensitivity radiometers. Finally, a combination of pressure probes and thermocouples was used to quantify the jet exit conditions (velocity, gas density and temperature) and validate the model calculations.

Scenario Analysis, Risk Assessment: Modeling of Large-Scale Releases. When accidental releases of hydrogen gas occur from high-pressure sources they may become ignited to form turbulent hydrogen jet flames. Codes and standards safety issues related to such jet flames are concerned with the length and diameter of the flame, the duration of the flame, potential impingement heat transfer from the flame, and amount of thermal radiation emitted from the flame and its variation with distance. Sandia National Laboratories developed a capability to predict hydrogen flame safety information based on engineering models and experimentally verified correlations for large-scale hydrogen jet flames.

For example, in most potential accident scenarios the probable size of the high-pressure tank rupture and the initial pressure and temperature of the hydrogen in the tank are known. Assuming that a tank rupture behaves similar to a high-pressure source with a small effective-diameter outlet nozzle, the model can be used with the known initial conditions to calculate the temporal history of the tank blow-down and nozzle exit conditions. Knowing the nozzle exit conditions, empirical correlations are used within the simulation to determine the transient variation of flame length, total radiative power from the flame, and the radiative heat flux at a distance from the flame. Figure 1 shows the radiative heat flux normal to the axis of a hydrogen jet flame issuing from a 7.9 millimeter (mm) hole in a hydrogen tank at a pressure of 1.37×10^7 Nt/m^2.

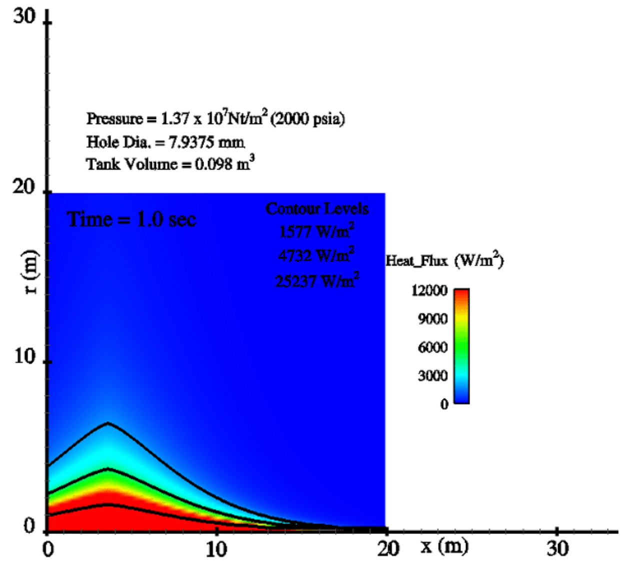

Figure 1. Simulation of Radiative Heat Flux Contours from a Hydrogen Jet Flame 1 Second into the Blow-Down of a Hydrogen Tank (Hole Dia. = 7.9 mm, Tank Pressure = 1.37×10^7 Nt/m^2).

For instances where the high-pressure hydrogen release is unignited it is important to determine how quickly the hydrogen jet mixes with air and dilutes to a point where it is no longer flammable (approximately 4% by volume or mole fraction of 0.04). Sandia National Laboratories developed an engineering model for determining the concentration decay of high-momentum, high-pressure hydrogen jets based on the approach followed by Birch et al (1984) for high-pressure natural gas jets. The model is based on classic empirical entrainment laws for turbulent jets and was experimentally verified by Birch et al for natural gas jets up to tank pressures of 76 bars and for an ethylene jet at a tank pressure of 8 bars. Figure 2 shows a simulation of hydrogen concentration contours for a hydrogen jet issuing into still air from a hydrogen tank at a pressure of 1.37×10^7 Nt/m^2 through a 7.9 mm diameter hole.

Hydrogen Compatible Materials. The first objective for composing the Technical Reference for Hydrogen Compatibility of Materials was to define and prioritize the content. This was accomplished primarily through a workshop held at SNL, where attendees from codes and standards agencies, national laboratories, and private industries provided input. Further definition of content and priorities for

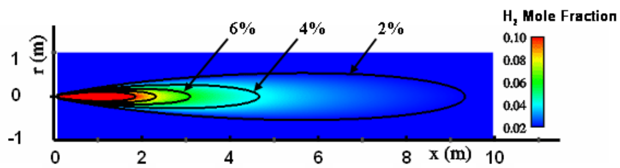

Figure 2. Simulation of Hydrogen Concentration Contours from a High-Momentum Turbulent Jet into Still Air (Hole Dia. = 7.9 mm, Tank Pressure = 1.37×10^7 Nt/m^2).

the Technical Reference for Hydrogen Compatibility of Materials was established through follow-up discussions with the American Society of Mechanical Engineers (ASME). Based on input provided at the workshop and by ASME, high priority was assigned to identifying and generating materials data for pressure vessel steels, pipeline steels, and stainless steels. An initial search was conducted for existing materials data on stainless steels and pressure vessel steels. This search led to the review of 40 journal articles and reports on hydrogen-assisted fracture of stainless steels and pressure vessel steels. Based on data gathered from these sources, two preliminary sections on materials data for stainless steels were drafted for the Technical Reference for Hydrogen Compatibility of Materials.

Based on input provided at the workshop and through interactions with ASME an initial materials testing program was defined for pressure vessel steels and stainless steels. The test program for pressure vessel steels begins with measuring hydrogen-assisted fracture thresholds under static loading for 4340 steel. The testing program will examine the effects of material strength and chemical composition on fracture thresholds in hydrogen gas pressures up to 150 MPa. Two heats of 4340 steel (i.e., air-melted and vacuum-melted) were procured, and heat treatment procedures are being explored to provide material yield strengths between 620 MPa and 900 MPa. The test program for stainless steels begins with measuring deformation and fracture properties for several steels, including 22Cr-13Ni-5Mn, 21Cr-6Ni-9Mn, and 316. Initial experiments were conducted to measure the tensile deformation properties of forged 22Cr-13Ni-9Mn and forged 21Cr-6Ni-9Mn after exposure to 140 MPa gaseous hydrogen at 300^{o}C.

It has become clear that the scope of the materials testing programs requires collaboration with industrial partners that have a stake in the hydrogen economy. Such collaborations have been initiated, although the nature of these relationships is protected by non-disclosure agreements. The vendors will supply initial material data which will be protected. Subsequent data generated by SNL will be publicly available.

Code Change Process. We have continued working with the International Code Council (ICC) ad hoc committee on hydrogen gas to define separation distances for a hydrogen fueling station. As part of this work, the group has identified credible operating conditions and accident scenarios for the station. We have continued development of the hydrogen jet flame model and have applied the model to predict hydrogen jet flame lengths and radiation heat flux exposure levels for the fueling station. The results of the studies were presented to the ICC working group during teleconferences and meetings held between February and June 2004, and provide the basis for revised setback distances for hydrogen infrastructure.

We are collaborating with the Canadian Transportation Fuel Cell Alliance, particularly Stuart Energy, on safety issues related to unintended releases of hydrogen. At the request of Stuart Energy, SNL performed transient simulations of the blow-down of a 700 bar hydrogen storage tank for two different leak scenarios. Results of the work were documented in a memo and sent to Stuart Energy along with data files of the simulation. Stuart Energy used results of the work in a three-dimensional simulation to assess the effectiveness of a small wall to protect against the high-pressure release.

Conclusion

- Solid progress is being made on the development of a technical database for Hydrogen Codes and Standards development.
- Preliminary definitions of the scope, structure, and priorities for the Technical Reference for Hydrogen Compatibility of Materials were accomplished.
- An initial review of existing materials data for stainless steels and pressure vessel steels

indicates that substantially more data is needed for high-pressure hydrogen environments.

References

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FY 2004 Publications/Presentations

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2. Termaath, C. Y., Skolnik, E. G., Schefer, R. W. and Keller, J. O., "Emissions reduction Benefits from Hydrogen Addition to Midsize Gas Turbine Feedstocks", International Journal of Hydrogen Energy, submitted, 2004
3. Houf, W. G. and Schefer, R. W. (2004), "Model-Based Prediction of Radiative Heat Fluxes from Hydrogen Jet Flames", Tenth International Conference on Numerical Combustion, May 9-12, 2004, Sedona, AZ.
4. Schefer, R. W., Houf, W. G., Bourne, B. and Colton, J., "Experimental Measurements to Characterize the Thermal and Radiation Properties of an Open-flame Hydrogen Plume", 15th Annual U. S. Hydrogen Conference and Hydrogen Expo USA, April 26-30, 2004, Los Angeles, CA.
5. Keller, J. O., "Economizing the Footprint of the refueling Station", ICC Final Action Hearings, Overland Park, KS, May, 2004.
6. Keller, J. O., "Fundamentals of Hydrogen Behavior", HAMMER Training Facility Planning Meeting, Richland, WA, May, 2004.
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8. Keller, J. O., "Separation Distances", Coral Gables, FL, June 15, 2004.
9. Houf, W. G. and Schefer, R. W., "Determination of Separation Distances from Large-Scale Hydrogen Flames", International Code Council (ICC) Hydrogen Ad Hoc Committee Meeting, Boulder, CO., Nov. 19, 2003.
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13. Schefer, R. W., Houf, W. G., Moen, C. D., Chan, J. P., Maness, M. A., Keller, J. O., Leon, M. V. and Tam, R., "Hydrogen Codes and Standards Unintended Release Workshop", Sandia National Laboratories, Livermore CA, 2004.

Special Recognitions & Awards/Patents Issued

1. Invited to write a book chapter for the NFPA on the basic combustion behavior of hydrogen flames.