IX.3 Hydrogen Safety, Codes and Standards R&D

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Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- Provide technical program management and support for the Safety, Codes and Standards program element within the Hydrogen, Fuel Cells and Infrastructure Technologies Program.
- Develop a scientific basis for evaluating credible safety scenarios, providing technical data for codes and standards decisions.
- Identify critical safety scenarios and gather the technical data required to support codes and standards decisions.
- Analyze hydrogen-related engineered systems and components for safety issues and identify probable hazards.
- Develop benchmark experiments, engineering models, and a defensible analysis strategy for risk assessment of hydrogen systems.
- Participate in the hydrogen codes and standards development/change process.
- Collect and assess data from journals and reports, and execute materials testing for the 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:

- F. Control and Safety (Section 3.1.4.2)
- L. Durability (Section 3.1.4.2)
- D. High Capital Cost and Embrittlement of Pipelines (Section 3.2.4.2)
- E. Codes and Standards (Section 3.5.4.2)
- B. Storage (Section 3.5.4.2)
- N. Insufficient Technical Data to Revise Standards (Section 3.6.4.2)

Technical Targets

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

- Develop a hydrogen materials reference guide (Section 3.6.4.1)

- Develop hydrogen storage tank standards (Section 3.6.4.1)
- Provide expertise and technical data to facilitate the development of hydrogen codes and standards (Section 3.6.4.1)
- Work directly with standards development organizations to provide technical support to facilitate and identify new codes and standards for hydrogen (Section 3.6.4.1)

Approach

- Provide technical direction and technical management for the Safety, Codes, and Standards DOE program element.
- Participate as a member of the FreedomCAR/Fuel Codes and Standards Tech Team (CSTT) and the DOE Safety Panel.
- Develop benchmark datasets and provide defensible science as a basis for codes and standards development.
- Develop a probabilistic risk assessment (PRA) of a hydrogen fueling station to identify key risk drivers and to help prioritize hydrogen safety research and development efforts related to fueling station safety, codes, and standards. Perform PRAs on remaining elements of hydrogen infrastructure.
- Participate in the codes and standards development process.
- Identify the materials of construction and operating conditions of components proposed for the hydrogen economy infrastructure.
- Perform materials R&D and literature searches to compile data in an evolving Technical Reference for Hydrogen Compatibility of Materials.

Accomplishments

- Co-hosted a Risk Assessment Workshop on March 10, 2005, at the National Renewable Energy Laboratory (NREL).
- Initiated a risk assessment analysis for a hydrogen fueling station. The preliminary focus is on assessing appropriate setbacks for hydrogen fueling stations.
- Completed a benchmark dataset for large-scale hydrogen jet flames at tank pressures of 17 MPa (2,500 psi). The new data reveal that the radiant fraction for hydrogen jet flames is approximately 50% less than that published for methane flames at the same residence time.
- Redesigned large-scale jet flame experimental apparatus and performed benchmark tests at tank pressures of 41 MPa (6,000 psi).
- Improved predictive capability for hydrogen flame radiative heat transfer analysis with improved models and experimentally measured correlations. Correlations to the new radiant fraction data from the Sandia/SRI large-scale tests were incorporated into the model.
- Completed development of a high-momentum unignited jet concentration decay model for determination of lower flammability limit contours.
- Completed hazards parameters study for small-diameter, high-momentum hydrogen leaks.
- Completed a comparative hazard study for natural gas and hydrogen leaks indicating the unignited jet decay distance to a lower flammability concentration for the hydrogen jet is about 3.5 times greater than that of the natural gas jet.
- Completed uncertainty analysis of hydrogen jet flame radiation model and high-momentum unignited jet concentration decay model, including comparison with experimental data.
- Completed a literature survey on the flammability limits for mixtures of hydrogen and air. Results of the study indicate that the flammability limits for hydrogen are well established with over 70 refereed references in the literature.

- Collaborated with U.S. Department of Transportation (DOT) staff in preparing a document for Canadian Standards Association (CSA) in support of standards for leak-testing pressure vessels.
- 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.
- Completed a chapter on Combustion Fundamentals for an upcoming book entitled National Fire Protection Association (NFPA) Guide to Gas Safety.
- Served on the Implementation Team for State of California Hydrogen Highway Blueprint document.
- A public website for distribution of chapters from the Technical Reference for Hydrogen Compatibility of Materials was established in January 2005. Six chapters have been completed.
- Relationships have been established with original equipment manufacturers to supply materials as part of the testing program to provide data for the Technical Reference.
- Fracture mechanics testing on pressure vessel steels has shown that initiation of subcritical crack growth in hydrogen gas environment can take many thousands of hours. Completed tests on modern, high-purity 4340 steel show that thresholds for subcritical crack growth in high-pressure hydrogen gas are similar to those measured for older steels.
- Fracture mechanics testing on hydrogen-exposed stainless steels has shown that base materials have high resistance to hydrogen-assisted fracture. Similar tests show that stainless steel welds are more susceptible, indicating that material microstructure is an important variable in hydrogen-assisted fracture.
- Participated in codes and standards activities related to hydrogen compatibility of materials, including DOT, the American Society of Mechanical Engineers (ASME), the American Society for Testing and Materials (ASTM) and CSA.

Future Directions

- Complete PRA of hydrogen fueling station. Perform PRAs on remaining elements of hydrogen infrastructure.
- Complete the work on high-momentum jets in FY 2005. A decision about the need to pursue large-scale release tests at storage pressures of 10,000 psi in FY 2006 will be made after examination of the 6,000-psi data in FY 2005.
- Experimentally investigate and characterize barrier walls at refueling stations being considered as a means of reducing separation distances.
- Experimentally investigate the behavior of full-size hydrogen transport cylinders subjected to fuel fires similar to those expected in vehicle accident scenarios.
- Identify critical safety scenarios and develop defensible models for small-scale hydrogen release scenarios.
- Add sections on pressure vessel steels, pipeline steels and aluminum alloys to the Technical Reference for Hydrogen Compatibility of Materials document.
- Execute testing to fill gaps in the existing database for hydrogen compatibility of materials.
- Develop infrastructure for dynamic load testing, such as fatigue testing.
- Develop new hydrogen detection and leak mitigation strategies.
- 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.

Introduction

A major barrier to the development of a hydrogen economy and the deployment of hydrogen technologies is the lack of tested safety codes and standards. Such codes and standards are necessary to assure that related products and systems are safe and perform as designed. Indeed, 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. Thus, 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 the properties of hydrogen are somewhat unique, while some energy-related codes and standards may be applicable to hydrogen usage, it is clear that the applicability of current codes must be individually evaluated and, if not applicable, the codes must be modified or replaced. The purpose of this project is to provide the technical basis for assessing the safety of hydrogen-based systems, with the accumulation of knowledge feeding into the modification of relevant codes and standards. The project impacts most areas of hydrogen infrastructure, including bulk transportation and distribution, storage, production and utilization.

The scenario analysis and risk assessment effort focuses on defining scenarios for the unintended release of hydrogen and quantifying the consequences through scientific experimentation and modeling. Quantitative risk assessment is used to identify risk drivers for the commercial use of hydrogen. The risk is based on the probability of occurrence and the magnitude of the event. We have identified general hydrogen release modes and are developing models to quantify the behavior in engineered systems.

The materials effort focuses on developing a resource entitled the Technical Reference for the Hydrogen Compatibility of Materials. This effort is driven by the need for a materials guide, as 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 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: (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, providing technical data for codes and standards decisions. Sandia is developing benchmark experiments and a defensible analysis strategy for risk and consequence assessment of unintended releases from hydrogen systems. This work includes experimentation and modeling to understand the fluid mechanics and dispersion of hydrogen for different release scenarios, including investigations of hydrogen ignition, combustion, 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 analysis. A quantitative risk assessment approach is used to identify and grade risk drivers to help focus decision making. The quantitative assessment makes use of scientific information developed in other elements of the codes and standards project.

The purpose of the Hydrogen-Compatible Materials component is to address the materials and methods of construction in the hydrogen economy infrastructure and provide a science-based resource for the development of new codes and standards. The Technical Reference for Hydrogen Compatibility of Materials is the focal point of the effort and is based on the materials of construction and operating conditions of components. Two parallel paths are established for composing the content of the Technical Reference: data collection from existing journals and reports, and data generation through a materials testing program. As data is identified or produced by following these parallel paths, the content of the Technical Reference will evolve.

As part of Codes and Standards Advocacy, Sandia 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 Ad Hoc Committee has the most current technical information on hydrogen behavior and that the correct scientific knowledge base is developed in the most expedient way possible.

Results

Scenario Analysis, Risk Assessment: Hydrogen Fueling Station Risk Assessment

We have initiated a formal quantitative risk assessment of a hydrogen fueling station. While we are in a position to quantify the consequences of unintended releases of hydrogen with our models, we need to define the level of risk associated with these consequences for codes and standards developers.

As a first step, we co-hosted the Risk Assessment Workshop on March 10, 2005, at NREL to establish buy-in from key stakeholders on the value and use of quantitative risk assessment in codes and standards development. In collaboration with our colleagues at NREL, we organized the workshop, led several of the sessions, and solicited risk assessment requirements from stakeholders. Explicit risk standards are not used in the United States, but there was support for the use of petroleum and natural gas design and operations as a baseline standard for acceptable risks for the hydrogen-fueling infrastructure. The workshop concluded with the formation of three working groups to continue the progress made. The first group will identify and compile relevant data on accident frequencies and histories; the second group will work within the code development organizations to encourage more risk-informed decision making; and the third group will iterate on philosophical issues around the use of risk assessment such a defining non-restrictive generic scenarios, defining acceptable risk limits or implicit risk standards, and assessing the cost versus benefit of introducing risk assessment into the code development process. A report from the workshop was provided to the Codes and Standards Tech Team during a teleconference and at a coordinating meeting at the National Hydrogen Association (NHA) Annual Hydrogen Conference 2005 on March 29th.

The most rigorous approach to risk-informed regulation of engineered systems is probability risk assessment (PRA), driven by a quantitative risk standard. Our working definition for that risk standard for a hydrogen fueling station is that hydrogen fueling must impose no greater risk than those risks imposed by other motor fuels: gasoline, compressed natural gas (CNG) or liquefied petroleum gas (LPG). To that end, we are developing a PRA for a generic hydrogen fueling station, working from a design basis of a "practicably failsafe" fueling station. Our analysis will initially focus on estimating the probability of hydrogen release based upon estimates of the likelihoods of various initiating events. From the PRA, we will develop an estimate of the normal operating risks of a hydrogen fueling station. This risk assessment will be parameterized by setback distances in the physical design of the fueling station – setbacks from lot lines, buildings, roadways or other fuel storage to various elements of the fueling station such as storage, dispensing and generation. The PRA will also support the evaluation of step-outs from that failsafe design.

In parallel, we are applying the same methodology to existing fueling options such as conventional gasoline stations to determine the "acceptable" risk levels. We are documenting existing setbacks required by national and international fire codes for various motor fuels as well as estimating the implicit risk standard. After completing these tasks, we will be in a position to evaluate from a quantitative risk perspective, for example, how hydrogen can be fit into gasoline stations that are designed to meet contemporary domestic and international fire codes.

Scenario Analysis, Risk Assessment: Experimental Study of Large-Scale Releases

Reduction of the data obtained in the most recent 17 MPa (2,500 psi) jet flame experiments (April 2004) was completed. The flame length data obtained showed excellent agreement with the correlations previously developed. Estimated error bars in the flame length were established from

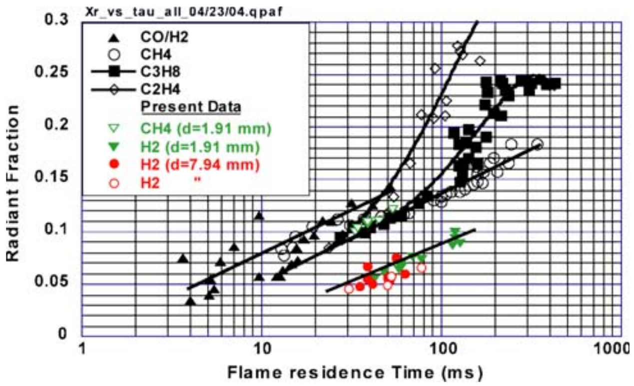

Figure 1. Radiant Fraction as a Function of Flame Residence Time (Lab H_2 and CH_4 flame data for a diameter of 1.91 mm, large-scale H_2 flame test data at a diameter of 7.94 mm)

multiple data sets as ±10 percent. The fraction of radiant energy emitted from the hydrogen flames from these tests was found to fall a factor of two below that emitted from non-sooting hydrocarbon flames for the same flame residence time, as shown in Figure 1. These results differ from earlier measurements that showed similar radiant fraction values from hydrogen and non-sooting hydrocarbon flames. This difference is attributed to a more accurate calculation of the flame residence time based on better estimates of the hydrogen jet exit conditions using the Sandia Topaz code to model the tank blow-down. Experiments in a smaller-scale laboratory flame at the Sandia Combustion Research Facility, using hydrogen and methane jets, confirm these results.

Tests were completed for large-scale hydrogen jet flames using a tank pressure of 41 MPa (6,000 psi). The tests were performed by SRI at their Corral Hollow Experimental Station (CHES). SRI worked with Air Products to deliver 6,000-psi hydrogen gas at CHES. SRI built the 40-foot instrumentation tower and executed the hydrogen release experiments. This pressure is a significant increase over previous tests carried out at a tank pressure of 17 MPa (2,500 psi) and is representative of future proposed hydrogen storage pressures. For these tests, hardware modifications were completed to include a stagnation chamber located immediately prior to the jet exit that allowed direct measurement of the stagnation pressure and temperature. This approach will allow more accurate determination of the jet exit conditions for data reduction. Measurements included visible flame length and radiometer measurements of the radiative heat flux. The radiometers were positioned to verify whether the functional dependence of the radiative heat flux on distance along the flame holds at 41 MPa (6,000 psi) as it did for the 17 MPa (2,500 psi) tests. The radiometer data will also be used to compute radiant fractions for comparison with previous experiments. If the 6,000-psi results are in good agreement with our model, then we will feel comfortable with extending the model to 69 MPa (10,000 psi) storage pressure without additional experimentation.

Scenario Analysis, Risk Assessment: Flammability Limits for Hydrogen

A literature search was completed on flammability limits for mixtures of hydrogen and air. Nearly eighty investigations of hydrogen flammability limits between 1920 and 1960 were identified. The flammability limits measured in these studies were found to be very consistent once differences in test apparatus were accounted for. Based on this review, it was concluded that the flammability limits of hydrogen are well established and do not need further research. A unique aspect of hydrogen is that the lean flammability limit is significantly different for upward, downward and sideward propagating flames. Although the generally accepted value for the upward-propagating lower flammability limit of hydrogen in air is 4% mole fraction, experimental data in the literature indicate that the limit may be as high as 7.2% for horizontal-propagating flames and 8.8% for downward propagating flames. It is noteworthy that the value of about 8% agrees well with the 8% value for hydrogen in air observed in experiments by M. Swain at the University of Miami [1] as a requirement to achieve ignition of turbulent hydrogen jet flows.

Scenario Analysis, Risk Assessment: Modeling of Large-Scale Releases

Based on new data from the large-scale hydrogen jet flame tests, improved versions of the experimentally measured correlations for radiant fraction, X_{rad}, nondimensional radiant heat flux, C*, and nondimensional flame length, L*, were incorporated in the hydrogen jet flame radiation model. In addition, a model for the concentration decay of a momentum-driven unignited hydrogen jet was also completed to estimate distances beyond which the hydrogen-air mixture is no longer ignitable [2].

A formal Taguchi uncertainty analysis of the jet flame radiation model was completed to assess the relative importance of L*, C*, and X_{rad} in determining uncertainty in calculated radiation hazard distances. Based on an examination of the data from the large-scale hydrogen jet flame tests, an uncertainty of ±10% was assigned to each of the correlations for L*, C*, and X_{rad}. Results of the uncertainty analysis indicate that radiation hazard lengths can be computed to approximately 10% to 20% for an uncertainty of ±10% in the measured correlations (L*, C*, X_{rad}). The nondimensional flame length, L*, is the most important parameter in determining the uncertainty in the computed radiation distances, followed by the radiant fraction X_{rad}, and then the correlation for C*. This indicates that reducing the experimental uncertainty in the measurement of the flame length would have the greatest impact on reducing the uncertainty in calculated values of the radiation distances.

As part of the uncertainty analysis, the jet flame radiation model was used to simulate the most recent large-scale 17-MPa (2,500-psi) release tests. Bounding calculations of the radiative heat flux at the radiometer locations used in the tests were performed with the nominal values of the L*, C*, and X_{rad} correlations, an increase of +10% to each of the three correlations (upper bound on radiative heat flux), and a decrease of -10% to each of the correlations (lower bound on radiative heat flux). Figure 2 shows a comparison of the bounding radiation heat flux predictions with data from the radiometers at a time 5 seconds into the blow-down of the high-pressure cylinders. The range of calculations with either an increase of +10% or a decrease of -10% in the correlations for L*, C*, and X_{rad} are able to bound the range of the radiative heat flux experimental data.

An uncertainty analysis of the high-momentum unignited jet concentration decay model was also performed. Based on a review of the available literature, a ±10% uncertainty was assumed in the experimentally measured turbulent jet entrainment constant, K. For ±10% uncertainty in the value of K, the uncertainty analysis indicates that concentration decay distances can be computed to ±10%. Figure 3 shows a prediction of the unignited jet concentration decay distances for a tank pressure of 21 MPa (3,000 psig) for various diameter leaks.

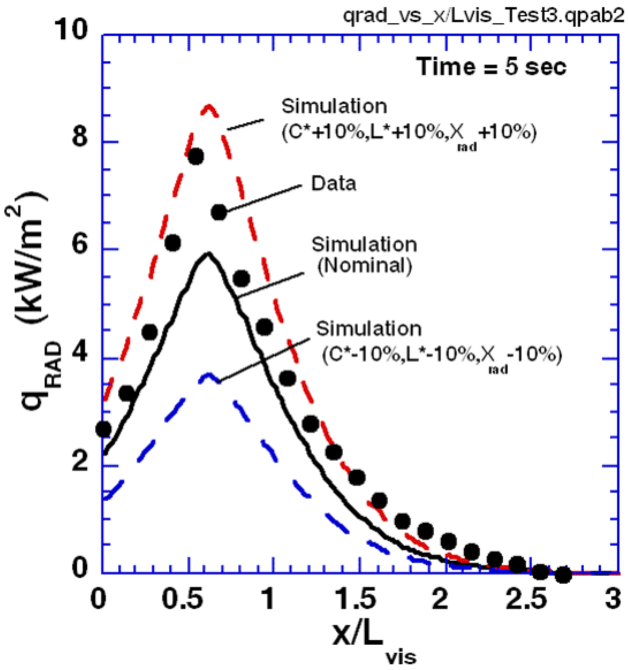

Figure 2. Comparison of Simulation of Radiative Heat Flux from a Hydrogen Jet Flame (Radial position of r=1.83 m with data from the large-scale tests at 5 seconds into the blow-down. Dashed lines show upper and lower bounds for distances with ±10% uncertainty in model parameters.)

Scenario Analysis, Risk Assessment: Parameter Study of Natural Gas and Hydrogen Unintended Releases

Jet flame radiation hazard distance and unignited jet flammability envelope calculations were performed for small diameter leaks of 3.175 mm (1/8 in) and 1.5875 mm (1/16 in) for both hydrogen and methane at pressures of 1.8 MPa (250 psig) and 21 MPa (3,000 psig). Gas exit velocities for the methane leaks exceed the blow-off velocity for

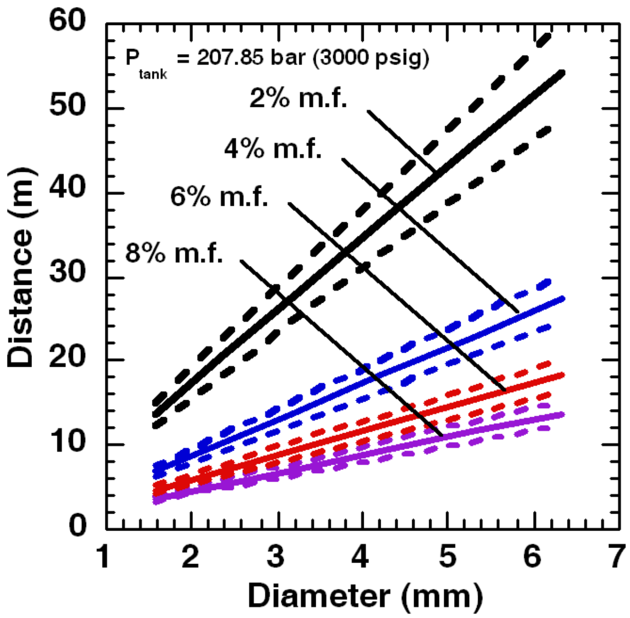

Figure 3. Simulations of Concentration Decay for Turbulent High-Momentum Unignited Hydrogen Jet from a Tank at Pressure 21 MPa (3000 psig) for Various Diameter Leaks (Results show axial distance from jet origin to the point where jet concentration reaches 2.0%, 4.0%, 6.0%, and 8.0% mole fraction on jet centerline. Solid lines show distances using the nominal value of the turbulent jet entrainment constant, K=5.40. Dashed lines show upper and lower bounds for distances with ±10% uncertainty in the value of K.)

methane; hence, no stable jet flame exists for methane leaks of this diameter and tank pressure. The unignited jet envelopes for methane and hydrogen leaks were compared assuming a lower flammability limit (LFL) of 4% mole fraction for hydrogen and 5% mole fraction for methane. For momentum-dominated leaks of the same diameter and tank pressure, the distance along centerline from the jet exit to the lower flammability limit was found to be approximately 3.5 times greater for hydrogen than for methane.

Scenario Analysis, Risk Assessment: Small Leak Scenarios

We collaborated with DOT staff in preparing a written report for the Canadian Standards Association (CSA) in support of standards for leak-testing pressure vessels. Math models were developed for the calculations of leak flow rates in various leak regimes. Leaks due to pressure-driven convection as well as permeation through metals were considered.

As part of our work for next year, one of the areas we will be focusing on is small and/or slow leaks. These leaks could come from damaged or improperly seated o-rings, poorly seated check valves, pinholes or cracks in vessels and/or manifolds, or even from volumetric sources such as permeation through vessel walls. The behavior of hydrogen slowly emanating from these point or volumetric sources needs to be understood through validated models in order to evaluate risk scenarios for future consumer products.

We envision that small-scale leaks may also occur in confined spaces, and we will address control area issues. Ventilation requirements for situating hydrogen installations inside buildings are defined in model building codes. We will utilize experimental data and computational fluid dynamics modeling to construct engineering models that describe dispersion of hydrogen in an arbitrary volume. These engineering models will be used to parameterize leak scenarios and define ventilation requirements for situating hydrogen equipment inside buildings.

Scenario Analysis, Risk Assessment: Combustion of Hydrogen in Air Under Simulated Accident Conditions (Josette Bellan, Jet Propulsion Laboratory)

The liquid hydrogen pool analysis of characteristic times for pool boiling and lateral flow conducted previously is now complemented by an evaluation of the pool evaporation due to radiative heating from a potential flame above the pool. Based on information from the literature, it is found that only for large pools (a statement quantified in terms of the inverse of the absorptivity) is the flame height consequential enough to induce a radiative flux that is of the same magnitude as that due to film boiling. Heat conduction induced evaporation is found to be negligible with respect to evaporation due to film boiling.

Buoyant convection in cloud fireballs has also been analyzed. A characteristic reference time has been derived which is shown to be proportional to the (1/6) power of the (cloud mass divided by the ambient pressure), with a dimensional proportionality constant based on H_2 properties. Wind effects were found negligible unless the wind velocity was larger than the convection velocity inside the cloud; this convection velocity is also proportional to the (1/6) power of the (cloud mass divided by the ambient pressure), with a dimensional proportionality constant based on H_2 properties.

A literature search showed that despite the fact that deflagration-to-detonation transition (DDT) is not well understood, there is experimental information to show that 'free' detonation requires vapor clouds of a size that is an order of magnitude greater than the cell size; the cells are the transverse structures observed in detonation waves, and for stoichiometric H_2 are approximately $1.5\text{x}10^{-2}$ to $1.6\text{x}10^{-2}$ m in size. The cell size increases rapidly for leaner or richer mixtures, or when other species, such as CO_2, are present. This global analysis indicates that 'free' DDT will not occur unless the structures are relatively large. The literature shows that obstacles and confinement increase the possibility of DDT.

A low-dimensional analysis for unintended leaks from gaseous hydrogen high-pressure vessels has also been initiated. Preliminary results indicate that combustion is not possible in the supersonic part of the jet and that the subsonic part of the jet is at a Mach number less than or equal to 0.4, independent of the conditions in the upstream supersonic region.

Hydrogen-Compatible Materials

The Technical Reference website was opened to public access in January 2005 at http://www.ca.sandia.gov/matlsTechRef/. Six chapters are currently available for download: (1) high-strength steel 9Ni-4Co, (2) type 304 and (3) type 316 stainless steels, nitrogen-strengthened stainless steels (4) 21-6-9 and (5) 22-13-5, and (6) A-286 precipitation-strengthened stainless steel. The chapters provide a comprehensive summary of the materials compatibility of each specific alloy in high-pressure hydrogen gas (or with internal hydrogen precharged from high-pressure hydrogen gas), including hydrogen transport, mechanical properties with emphasis on fracture properties, and the effects of materials processing on hydrogen embrittlement, such as how forging and welding affect the microstructure and materials behavior in high-pressure hydrogen gas. The website has received significant visibility and has resulted in individuals contacting Sandia for additional information on materials compatibility with hydrogen. One such contact culminated in a relationship with an individual from the Defense Nuclear Facilities Safety Board (www.dnfsb.gov), who will spend a year-long internship working in the high-pressure hydrogen laboratory at Sandia researching issues related to hydrogen-assisted fracture of materials.

Phase one of testing of 316 stainless steels is drawing to a close, and this initial round of fracture testing should be completed by October 1, 2005. This portion of work is part of a "no-cost" collaboration protected by nondisclosure agreement (NDA) that may continue into the future to support the understanding of hydrogen-assisted fracture in high-value components such as valves, pressure release devices, compressor components, etc. This study has demonstrated that while type 316 stainless steel in the cold-worked and annealed conditions retains significant fracture resistance when precharged to high internal hydrogen concentrations (~3 times room temperature saturation), high nickel concentrations provide improved resistance to hydrogen embrittlement compared to low-nickel heats of 316 stainless steel. A high-strength alternative to conventional stainless steel, duplex steel SAF 2507, was also tested and found to suffer a 70% reduction in ductility when precharged to high internal hydrogen concentrations. The smooth tensile properties of three heats of 316 stainless steel and one heat of SAF 2507 duplex steel are summarized in Figure 4. Fracture toughness tests on these materials are ongoing and will provide additional information on the hydrogen embrittlement of these steels.

Measurements of the hydrogen-assisted crack growth threshold, K_{TH}, in pressure vessel steels require crack extension from the fatigue precrack in the fracture mechanics specimens. The initiation time for crack extension in some steels, however, is unpredictable and can be very long: for air-melted AISI 4340, hydrogen gas exposures >5,000 hours

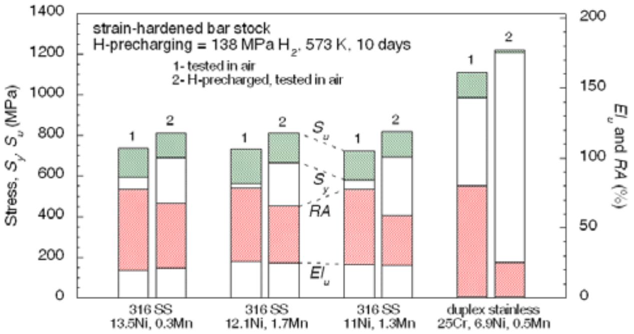

Figure 4. Smooth Tensile Properties of Three Heats of Cold-Worked Type 316 Stainless Steel and One Heat of SAF 2507 Duplex Steel, Measured in Air with Internal Hydrogen (thermal precharging in high-pressure hydrogen gas) (S_u = ultimate strength, S_y = yield strength, RA = reduction in area, El_u = uniform elongation.)

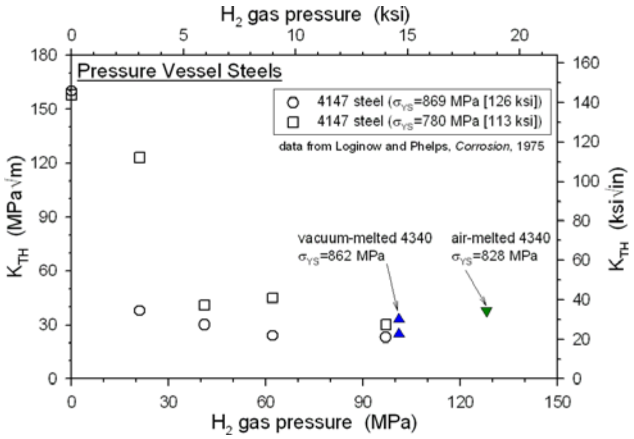

Figure 5. Threshold Stress Intensity Factor as a Function of Hydrogen Gas Pressure [Triangles are data determined in this study, the first high-pressure data on low-alloy steels to be reported in 30 years. "Modern" (low-sulfur, low-phosphorous) steels follow same trends established in previous studies despite having significantly lower trace impurities.]

(>200 days) did not produce crack extension, while for vacuum-melted AISI 4340, in the same 100 MPa hydrogen gas environment, crack extension initiated after only 65 hours. The pressure vessel steel SA 372-J in 100 MPa hydrogen gas has not exhibited crack extension after >3,500 hours. For specimens that did exhibit crack extension, K_{TH} was measured and results are plotted in Figure 5 along with the only available data of this type for pressure vessel steels in high-pressure hydrogen gas. These three data points represent the first high-pressure hydrogen thresholds for pressure vessel steels to be reported in 30 years. The expectation among the metallurgical community was that "modern" (low-sulfur, low-phosphorous) steels would exhibit improved resistance to hydrogen-assisted fracture. The data in Figure 5 demonstrate that modern steel-making practices do not significantly improve the resistance of AISI 4340 steel to hydrogen-assisted fracture. We are working toward augmenting the limited set of existing data to high pressures and quantifying hydrogen-assisted fracture in real code-certified pressure vessel steels.

Priorities for crack-growth testing of additional pressure vessel steels have been altered based on the anticipation of prolonged crack extension initiation times and materials data needs expressed by parties such as ASME. It is believed that the long initiation times are due to crack-tip oxides that form under ambient conditions since specimens are loaded in air, or due to gas impurities (such as oxygen) in the hydrogen at concentration levels as low as 1 ppm. Minor laboratory improvements are being considered as a means of reducing initiation times from many thousands of hours to less than 1,000 hours. Future crack-growth testing will focus on two steels obtained from a pressure vessel manufacturer through an NDA: DOT 3T and DOT 3AAX. These steels will be tested at two gas pressures of interest to ASME, that is, 20 MPa and 100 MPa. Crack-growth specimen preparation for the DOT 3T and DOT 3AAX steels was completed.

Code Change Process

We continued to work with the ICC Ad Hoc Committee on Hydrogen Gas to define separation distances for a hydrogen fueling station. We characterized the principle hazards for a series of pressure ranges and leak sizes set by refueling component operating conditions and piping. Scenario down-selects were performed, and final analysis was provided before the August 20, 2004, deadline for submitting new code changes.

We are becoming more active in support of NFPA code development activities. We hosted Carl Rivkin and Kathleen Almand for a site visit in early January, followed by participation in their Research

Foundation workshop at the end of the month. We also participated in the Industrial and Medical Gases meeting in June to discuss setbacks for hydrogen. A chapter on Combustion Fundamentals was completed for the NFPA Guide to Gas Safety.

Relationships with ASME, DOT and ASTM have continued to develop. Sandia is working with ASME to form a technical oversight group that will focus specifically on materials issues related to code-writing activities. Brian Somerday and Chris San Marchi have also officially become corresponding members of the Boiler and Pressure Vessel Project Team on Hydrogen Tanks and are working with this group to provide perspective on requirements and procedures for materials testing in hydrogen. DOT has made a nominal financial commitment to support Sandia in research on hydrogen-assisted fracture of materials relevant to DOT oversight obligations, i.e., pressure vessel and pipeline steels. Brian Somerday and Chris San Marchi delivered an invited presentation on materials testing in high-pressure hydrogen gas at the Workshop on High-Pressure Hydrogen in Reno, Nevada. This workshop was sponsored by ASTM committee G01 as a means of identifying expertise and technical issues related to hydrogen effects on materials. ASTM is planning additional workshops to establish the testing protocols and procedures to support comprehensive qualification of materials for service in high-pressure hydrogen gas. Somerday and San Marchi have been invited to a similar workshop in August 2005, which is jointly sponsored by ASME and Savannah River National Laboratory.

Summary

- We co-hosted a Risk Assessment Workshop and initiated a probability risk assessment of a hydrogen refueling station.
- We have developed a hydrogen jet flame technical database for hydrogen codes and standards development.
- We have developed the capability to perform consequence analysis of high-pressure momentum-dominated unintended releases of hydrogen and have used this capability to perform hazard analysis for codes and standards organizations. We have used formal uncertainty analysis to quantify the uncertainty in the predicted hazard distances.
- Six chapters of the Technical Reference for Hydrogen Compatibility of Materials have been completed, and a public website for distribution of the chapters has been established and online since January 2005.

Special Recognitions & Awards/Patents Issued

1. Invited to write a book chapter for the NFPA on the basic combustion behavior of hydrogen flames.
2. Invited to write a chapter on hydrogen compatibility of pipeline steels for the book "Materials for the Hydrogen Economy" edited by Russell Jones and George Thomas.

FY 2005 Publications/Presentations

1. Schefer, Houf, Bourne, and Colton, “Turbulent Hydrogen-Jet Flame Characterization,” International Journal of Hydrogen Energy, accepted for publication, January 2005.
2. Schefer, “Combustion Basics,” in NFPA Guide to Gas Safety, 2004.
3. Somerday, Balch, Novak, and Sofronis, “Mechanisms of Hydrogen-Assisted Fracture in Austenitic Stainless Steel Welds,” 11th International Conference on Fracture, March 2005.
4. Robinson, Somerday, and Moody, “Hydrogen Embrittlement of Stainless Steels,” 11th International Conference on Fracture, March 2005.
5. Houf and Schefer, “Predicting Radiative Heat Fluxes and Flammability Envelopes from Unintended Releases of Hydrogen,” NHA Annual Hydrogen Conference 2005, Washington, DC, March 2005.
6. Chernicoff, Englom, Houf, San Marchi, and Schefer, “Characterization of Leaks from Compressed Hydrogen Dispensing Systems and Related Components,” NHA Annual Hydrogen Conference 2005, Washington, DC, March 2005.
7. Keller, “Hydrogen Combustion Behavior,” Fuel Cell Summit, Coral Gables, FL, June 2004.
8. Moen, R&D Progress and Consequence Analysis, ICC Ad Hoc Meeting, Coral Gables, FL, June 2004.
9. 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, June 2004.
10. Keller, Hydrogen Codes and Standards Project Overview, National Academy of Sciences Review, February 2005.

11. Ohi, Cox, Moen, and Keller, Risk Assessment Workshop, Golden, CO, March 2005.
12. Moen, Keller, and Ohi, "Risk Assessment Workshop Report-Out," NHA Annual Hydrogen Conference 2005, Washington, DC, March 2005.
13. Someday 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.
14. Houf and Schefer, "Radiative Heat Fluxes and Flammability Envelopes from Unintended Releases of Hydrogen," NFPA World Safety Conference and Exposition, Las Vegas, NV, June 2005.
15. Moen, "Progress Report on the Use of Risk Assessment in Codes and Standards Development," NFPA H2 Coordinating Group, NFPA World Safety Conference and Exposition, Las Vegas, NV, June 2005.
16. Houf, Schefer, and Moen, "Predicting Radiative Heat Fluxes and Flammability Envelopes from Unintended Releases of Hydrogen," NFPA Industrial and Medical Gases Meeting, Oakland, CA, June 2005.
17. Someday and San Marchi, "A 1,000 MW Windplant Delivering Hydrogen Fuel from the Great Plains to a Distant Urban Market," ISES 2005 Solar World Congress, Orlando, FL, August, 2005.
18. Brian Someday co-organized and delivered two presentations at the Hydrogen Embrittlement symposium as part of the 11th International Conference on Fracture (Turin, Italy) in March (funded through a Sandia research foundation project).
19. San Marchi, Balch and Someday, "Effect of High-Pressure Hydrogen Gas on Fracture of Austenitic Steels," ASME Pressure Vessels and Piping Division Conference, Denver, CO, July 2005.

References

1. Michael Swain, "Hydrogen Properties Testing and Verification", Fuel Cell Summit Meeting, Coral Gables, FL, June 17, 2004.
2. William Houf and Robert Schefer, "Predicting Radiative Heat Fluxes and Flammability Envelopes from Unintended Releases of Hydrogen", NHA Annual Hydrogen Conference 2005, Washington, DC, March 2005.