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

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Start Date: FY 2002
Projected End Date: Project continuation and direction determined annually by DOE

Objectives

1. Scenario Analysis, Risk Assessments for Safety
   - 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 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.
2. Hydrogen-Compatible Materials
   - Collect and assess data from journals and reports, and execute materials testing for the Technical Reference for Hydrogen Compatibility of Materials.
3. Codes and Standards Advocacy
   - Provide technical management and support for the Safety, Codes and Standards Program element within the Hydrogen, Fuel Cells and Infrastructure Technologies program.
   - Participate in the hydrogen codes and standards development/change process.

Technical Barriers

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

- Development of 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).

Accomplishments

- Completed data reduction of 41 MPa (6,000 psi) jet flame experiments. Results show that flame length and radiative fraction characteristics for high-pressure jet flames obey the same scaling laws developed for low-pressure, smaller-scale flames. A paper on the 41 MPa jet flame experiments has been submitted to the International Journal of Hydrogen Energy.
- The range of calculations for high-momentum leaks was extended and results are now reported for pressures as high as 103.52 MPa (15,000 psig) and leak diameters as small as 0.25 mm. These new hazard distance results, including the uncertainty analysis, are reported in a 28-page paper that has been accepted for publication in the International Journal of Hydrogen Energy.

- Completed hardware to enable measurements of leak rates from various slow leak geometries as a function of pressure drop. Preliminary measurements were carried out for a 0.18 mm diameter semi-circular leak to verify the technique. Data from the apparatus will be used to validate engineering models for leak rates under conditions appropriate for the hydrogen infrastructure.
- Initial measurements were made of the concentration field in an unignited jet from a slow hydrogen leak using planar laser-Rayleigh scattering. Data from the experiment will be used to validate the engineering model for the buoyant jet from slow hydrogen leaks.
- An engineering model for the buoyant jet from a slow unignited hydrogen leak has been developed. The model computes the trajectory of the buoyant jet and the hydrogen concentration along the jet trajectory. The model has been initially validated against vertical slow leak jet data from the literature for helium. The model will be used to compute safety distances for hydrogen slow leaks.
- We are utilizing risk metrics as part of the process to develop hydrogen codes and standards. We have identified strategies for defining the relevant risk metrics and acceptable levels of risk for use in the risk analysis of hydrogen facilities. Risk comparability standards were established for gasoline, compressed and liquefied flammable gas fueling stations as a basis for comparing the risk associated with hydrogen fueling stations. Developed a prototype setback diagram that allows the comparison of setback requirements for various fuels.
- A risk assessment workshop was conducted with the participation of international experts as part of the IEA Task 19 meeting on hydrogen safety to discuss the proposed risk principle, gauge our approach against risk methods used by other countries, and to define the requirements for a risk assessment strategy to guide hydrogen codes and standards.
- Developed a literature database to support the risk assessment of the hydrogen refueling deployment infrastructure.
- We have initiated the development of a Failure Modes and Effects Analysis (FMEA) for a hydrogen refueling station.
- Identified a statistical approach to overcome data and design information limitations in the quantitative risk assessment of hydrogen facilities. The approach is currently being used to evaluate setback distances for refueling stations.
- A public website for distribution of chapters from the Technical Reference for Hydrogen Compatibility of Materials has been in operation since January 2005. A total of ten chapters have been completed and placed on the website.
- We continue to collaborate with original equipment manufacturers (OEMs) as part of the testing program to provide data for the Technical Reference from relevant materials of construction.
- Four new chapters of the Technical Reference for Hydrogen Compatibility of Materials were completed: low-alloy ferritic steels Fe-Cr-Mo and Fe-Ni-Cr-Mo, austenitic steel Fe-Ni-Co, and copper.
- Funding has been received from the National Nuclear Security Administration (NNSA) and design has begun on a high-pressure hydrogen dynamic fatigue testing facility. The facility is being designed for hydrogen pressures up to 100 MPa, and to our knowledge, there are no other facilities available in the U.S. for fatigue testing of materials at this high a pressure.
- Participated in codes and standards activities related to hydrogen compatibility of materials: developing a research program in collaboration with DOT; corresponding members of the ASME Boiler and Pressure Vessel (BPV) Project Team on Hydrogen Tanks; invited to participate in ASTM and ASME/SRNL workshops on testing materials in hydrogen; corresponding with the Canadian Standards Association (CSA) America common issues working group for Hydrogen Gas Powered Vehicle–4 (HGV4).

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. 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 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 Table 3.6.5 of the Multi-Year Research, Development and Demonstration Plan (2005, Revision 1). 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 Safety, Codes and Standards 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, 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) and the National Fire Prevention Association (NFPA). This participation ensures that the standards and codes development organizations have 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 adopted a risk principle to introduce risk metrics into the development of hydrogen codes and standards. The initial application of this principle has included performance of both qualitative and quantitative risk assessments of a hydrogen fueling station that utilizes below-ground storage of liquid hydrogen. Qualitative methods are being used to identify possible accident initiators and potential prevention and mitigation features. Quantitative risk assessment techniques are being used to evaluate the risk from identified accidents. A statistical approach for establishing setback distances based on risk considerations has been formulated and is being used in the analysis.

Use of risk considerations in the development of codes and standards requires the establishment of acceptable risk parameters. Risk parameters that can be utilized in this effort include accident initiation frequencies, consequence measures (fatalities, injuries, and property damage are all being considered), and risk measures (e.g., individual and population risk). To guide the establishment of acceptable risk levels, we developed a "no greater risk" principle for a hydrogen-based transportation infrastructure that states "the production, distribution, commercialization and use of hydrogen should not impose more risk to workers and the general public than fuel alternatives used today."

A review of accident statistics and risk levels for gasoline and compressed and liquefied flammable gas was performed to determine which fuel provides the best risk benchmark for a hydrogen system. Based upon NFPA and Major Hazard Incident Data Service fire and explosion statistics, the gasoline standards are surprisingly tight and compressed and liquefied flammable gases standards and operating practices seem to expose the public to higher risk than gasoline. We tentatively proposed to benchmark the "no greater risk" principle at two deployment levels, early and full deployment, and that compressed natural gas (CNG) and gasoline could provide the respective benchmark for each level. Gasoline's risk standard is implicitly accepted by the general public and provides an adequate risk goal during full deployment of the technology. We believe CNG may present an appropriate risk benchmark for early deployment due to the similarities between the way CNG is currently deployed and what hydrogen early deployment may look like. This review also provides lessons learned to identify potential risk areas and failure modes to be considered in the design and evaluation of hydrogen facilities.

We have initiated the development of a Failure Modes and Effects Analysis (FMEA) for a refueling station configuration with bulk liquid hydrogen storage below ground. The functions, failure modes, and causes of failure for critical components of this system have been identified. Our next step is to engage industry stakeholders and submit the outlined partial FMEA for review to ensure that the conceptual representation of the system is accurate. We intend to quantify the magnitude of consequences based on their impact on three different metrics: loss of life, injury, and property loss based on structural engineering tables and adverse effects on human body research.

A prototype setback (i.e., safety distance) diagram was developed to allow the comparison of setback requirements for various fuels at different fuel cycle stages: venting, storage, dispensing, etc. The analysis of current setback requirements suggests a lack of scientific basis between risk and current setback distances for different fuels (gasoline, liquefied petroleum gas, CNG). We believe that setback or safety distances should have a strong technical basis that includes input from quantitative risk assessments. Based on the input received at the Risk Assessment workshop (teaming with NREL and collocated with the IEA Task 19 meeting on hydrogen safety to ensure the participation of international experts), a modified version of the risk approach documented in European Industrial Gases Association/Industrial Gases Council (EIGA IGC) Doc. 75 for establishing setback distances is being explored. The proposed method utilizes a maximum exposure threshold for evaluating setback distances. Events with an exposure rate higher than the exposure threshold defined by normal fatality risk in the U.S. will be used in the calculation of safety distances with the goal of mitigating risk by minimizing this exposure. Events below the exposure threshold will be considered negligible and will not be taken into consideration in the development of safety distance recommendations.

Modifications to the EIGA IGC Doc. 75 approach include incorporation of uncertainty into the evaluation. Currently, there is a lack of detailed design information and available data on component failure rates. In addition, there is uncertainty in the size of releases and the resulting consequences. Uncertainty in these parameters will result in uncertainty in the calculated risk and the setback distances necessary to meet a risk acceptance criterion. The initial setback calculations will be based on the consequences of failure modes that have been modeled by our experimental efforts: ignited and unignited jet releases, where the size of the jet will be initially characterized by line pressure and leak diameter. Failures resulting in leak diameters of certain size will be a function of the facility design (including the amount and size of piping, couplings, seals, tanks, component material, and other features). No mitigation features will be credited in the demonstration effort. After the approach is demonstrated, actual setback distances will be calculated for specific refueling station designs utilizing the best available data. The impact of failsafe designs and other mitigation strategies on the setback distances will be evaluated as part of this effort.

Scenario Analysis, Risk Assessment: Completion of Studies of Large-Scale Releases

We completed the reduction of data obtained in the most recent 41 MPa releases (April, 2005). These high-pressures are typical of expected pressure ranges in future hydrogen storage vessels. At these pressures the flows exiting the jet nozzle are categorized as underexpanded jets and the gas behavior departs from that of an ideal gas. Non-dimensional flame length data for the 41 MPa releases showed good agreement with engineering correlations developed for lower-pressure jet flames.

The radiative fraction measurements for these hydrogen flames are about a factor of two lower than those from non-sooting hydrocarbon flames for the same residence time. This observation differs from the analysis of Turns and Myhr (1991), which shows that radiative fraction is correlated with global flame residence time, τ_g, and suggests that all data from non-sooting flames collapse onto a single curve. A more detailed analysis (Molina, Schefer and Houf, 2006) shows that the radiative fraction is proportional to the residence time, τ_g, multiplied by the factor ($a_p T_f^4$), where a_p is the Plank-mean absorption coefficient and T_f is the flame temperature. In this formulation, a_p accounts for the different radiative properties of product gas species (primarily H_2O and CO_2). Plotting the radiant fraction against the factor $\tau_g a_p T_f^4$ collapses data for CH_4, CO/H_2 and H_2 flames onto the same curve.

The pressure range and leak diameter range of the jet flame radiation heat flux and unignited jet concentration decay calculations were extended. Hazard distance calculations were performed for pressures as high as 100 MPa and leak diameters as small as 0.25 mm. These new hazard distance results, including the uncertainty analysis, are reported in a document that has been accepted for publication in the International Journal of Hydrogen Energy.

Scenario Analysis, Risk Assessment: Small Leak Scenarios

An experimental and modeling activity was initiated to characterize small-scale leaks. In contrast to the previous emphasis on large, momentum-dominated leaks, these studies are focusing on small leaks in the Froude (Fr) number range where both buoyancy and momentum are important or, in the limit, where buoyancy dominates leak behavior. In the slow leak regime buoyant forces affect the trajectory and rate of air entrainment of the hydrogen jet leak. Slow leaks may occur from hydrogen-based systems such as low-pressure electrolyzers, leaky fittings or O-rings seals where large amounts of pressure drop occur, or from vents from buildings or storage facilities containing hydrogen.

We characterized visible flame lengths for a 1.91-mm diameter jet flame in the range of operating conditions where buoyancy is important ($0.1<Fr<5$). Nondimensional flame length data for these hydrogen-jet flames showed good agreement with correlations based on hydrocarbon flame length data for the same Fr number range.

Experimental hardware was completed to measure leak rate, plume shape, and plume concentration for different slow leak geometries and pressures. Leaks of variable geometry are easily fabricated by machining the appropriate cross sections into two metal slabs that are force fit together. By varying the leak pressure, the flow rate can be determined over flow regimes varying from laminar to turbulent to choked at the highest pressures. Initial measurements were carried out for a 0.18-mm diameter semi-circular leak geometry to verify the technique. Figure 1 shows a plot of leak flow rate as a function of measured pressure drop, ΔP, across the leak. At the lowest pressure drops the data is proportional to ΔP [1]. This dependence is consistent with a laminar flow regime. At higher-pressure drops the data follows a $\Delta P^{1/2}$ dependence, which is consistent with a turbulent flow. At the highest pressure drops the data deviates from the $\Delta P^{1/2}$ dependence, which indicates the onset of the choked flow regime. This data will be used to validate engineering models for leak rate as a function of leak parameters under conditions appropriate for the hydrogen infrastructure.

It is also important to characterize the flow path of gases exiting the leak. In particular, predicting flammability envelopes for unignited leaks of various sizes is necessary for a better understanding of potential safety hazards related to unintended releases through small leaks. The apparatus shown in Figure 2a was developed to characterize the flow path of small hydrogen leaks over the conditions of interest. As shown in the figure, molecular (Rayleigh) scattered light from a laser sheet is imaged onto a charge-coupled device (CCD) camera. For an isothermal, two-component (air and hydrogen) mixture the scattered-light signal is linearly related to the hydrogen mole fraction. Thus, the concentration contours of hydrogen can be determined. Shown in Figure 2b are typical images of the hydrogen mole fraction distribution in the exit region of a 1.9-mm diameter hydrogen jet. The concentration is color coded with dark blue corresponding to pure air and red indicating the highest

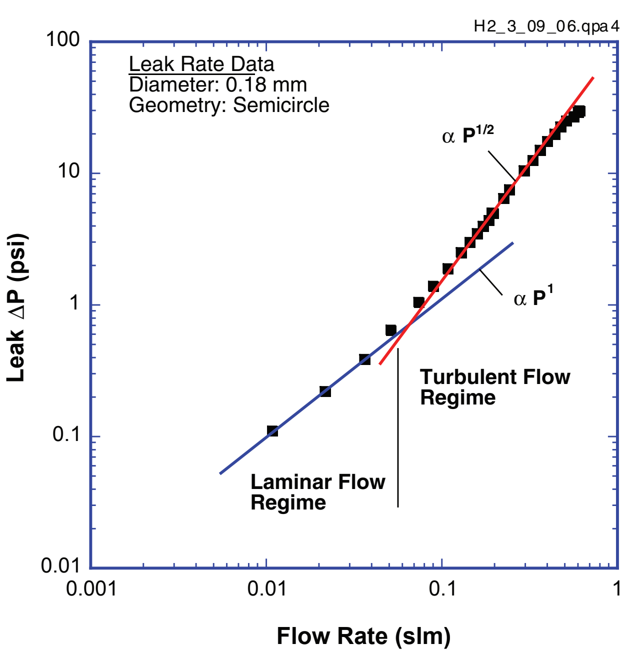

FIGURE 1. Hydrogen Flow Rates Through a 0.18-mm Diameter Semi-Circular Leak

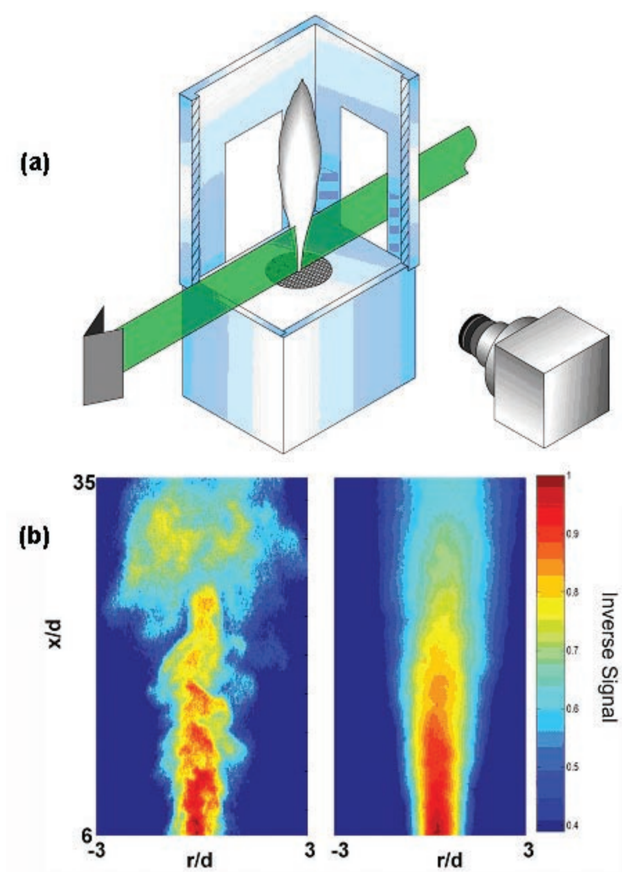

FIGURE 2. (a) Schematic of experimental apparatus for hydrogen leak concentration contours. (b) Rayleigh scattering images of unignited hydrogen leak originating from a 1.9-mm diameter tube at a volumetric flow rate of 10 slm. Re=1044, Fr=117.

hydrogen concentration. The image on the left is from a single laser shot and, due to the short (9 nanosecond) duration of the laser pulse, reveals the instantaneous distribution of hydrogen. The image on the right is an average of 50 singe-shot images and shows the time-averaged hydrogen distribution. Further analysis of the images will provide information on the flammable gas envelopes for various leak geometries and flow rates. These data will be used to validate the engineering model being developed to predict the trajectory of buoyant jets issuing from various leaks.

We have developed a fast-running engineering model for the buoyant jet from a slow hydrogen leak. The model is based on an integral buoyant jet model in streamline coordinates. Integral jet model equations for conservation of mass, horizontal and vertical momentum, hydrogen concentration, and jet trajectory are solved using Gaussian profiles for jet velocity and jet scalars. Simulation times for the engineering slow leak model are a few seconds on a Sun computer workstation as compared to many hours for a Navier-Stokes equation simulation of the same leak.

Figure 3 shows calculations of horizontal slow leak trajectories and the concentration decay (percent mole fraction hydrogen) from the engineering model for two different leak densimetric Froude numbers (Fr_{den}). Results are shown for densimetric Froude numbers of 100 and 1,000 which correspond respectively to leak volumetric flow rates of 88.35 slm, and 883.5 slm. The densimetric Froude number relates the ratio of momentum to buoyant forces at the leak exit and is given by an expression of the form

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

where U_{exit} is the exit velocity, g is the acceleration due to gravity, D is the leak diameter, ρ_{amb} is the ambient density, and ρ_{exit} is the exit density of hydrogen. The 5 mm diameter hydrogen leak (Figure 3) with a densimetric Froude number of 1,000 (883.5 slm) shows little effect of buoyancy since the jet trajectory remains nearly horizontal. This is an indication that high-momentum jet models are appropriate for hydrogen leaks where the densimetric Froude number is greater than 1,000. The jet trajectory for the Fr_{den} = 100 (88.35 slm) leak shows significant upward bending due to the effects of buoyancy. Concentration decay distance also appears to be larger for higher densimetric Froude number leaks with the Fr_{den} = 1000 leak taking the longest distance to decay to 4% mole fraction of hydrogen.

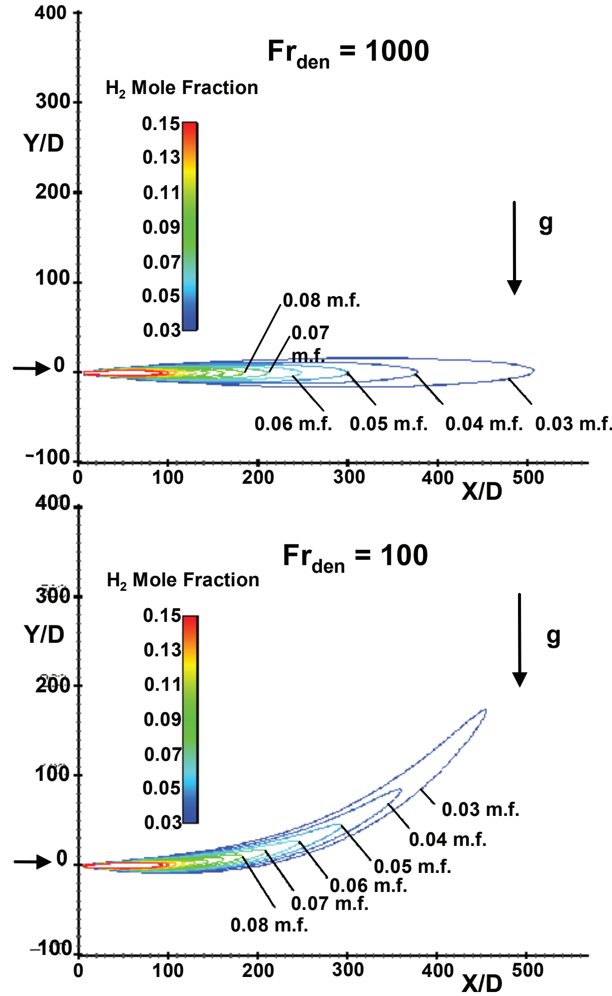

FIGURE 3. Jet trajectory and centerline concentration decay (percent mole fraction) for slow hydrogen leaks (5 mm leak diameter).

Hydrogen-Compatible Materials: Technical Reference

The Technical Reference for Hydrogen Compatibility of Materials, an internet-based resource that was opened to public access in January 2005, now consists of 10 chapters. Four chapters have been completed since the last annual report: low-alloy ferritic steels Fe-Cr-Mo and Fe-Ni-Cr-Mo, austenitic steel Fe-Ni-Co, and copper. Anticipated applications for low-alloy ferritic steels are seamless pressure vessels for hydrogen gas storage and transport, while the austenitic steel Fe-Ni-Co and copper are expected to find applications in seals. Much of the data for low-alloy ferritic steels was generated from high-strength steels in low-pressure hydrogen gas. Consequently, the data do not provide suitable design parameters for pressure vessels in high-pressure gas containment. However, the data show important trends, such as effects of gas pressure, temperature, material strength, and alloy composition on hydrogen-assisted crack-growth thresholds. Compiling data on pressure vessel steels clearly indicates that more materials testing is needed to generate data that reflect service conditions in hydrogen economy applications. The Technical Reference site has received significant visibility and has resulted in individuals contacting Sandia for additional information on materials compatibility with hydrogen.

Hydrogen-Compatible Materials: Materials Testing

Materials testing to measure the hydrogen-assisted crack growth threshold, K_{TH}, for the low-alloy pressure vessel steel SA 372-J in 100 MPa hydrogen gas, initiated in FY 2005 Q1, is still in progress. Cracking has not initiated in the SA 372-J steels. Previous crack-growth tests on vacuum-melted 4340 showed relatively short crack incubation times, so additional tests were initiated on the alloy in FY 2005 Q4 to explore the effects of lower gas pressure and lower material strength. Similar to the SA 372-J, cracking has not initiated in the 4340 steels. Table 1 summarizes conditions for the crack-growth tests in progress for SA 372-J and vacuum-melted 4340.

TABLE 1. Conditions for Crack-Growth Tests on SA 372-J and Vacuum-Melted 4340 Steels

Material	Yield Strength (MPa)	H2 Pressure (MPa)
SA 372-J	700	100
VM 4340	862	40
VM 4340	600	100
VM 4340	600	40

Crack-growth tests planned for the low-alloy pressure vessel steels DOT 3T and DOT 3AAX were postponed until the crack incubation time issue could be resolved.

Two potential sources for extended crack incubation times in pressure vessel steels were identified: hydrogen gas purity and surface oxides. Efforts were initiated to address these environmental impediments to hydrogen-assisted crack growth.

Literature results indicate that gas impurities such as O_2, CO, and CO_2 can inhibit hydrogen uptake into metals and could lead to prolonged incubation times in crack-growth tests. A series of analyses were conducted on the hydrogen gas used in the crack-growth test system. The 99.9999% hydrogen supply gas was sampled after three different sequences: after flowing gas through the high-pressure manifolding; after flowing gas through the manifolding and a molecular sieve; and after flowing gas through the manifolding and into the pressure vessel that contains the crack-growth specimens. Gas analyses after these three sequences revealed that O_2, CO, and CO_2 were well below 1 ppm and H_2O was less than 2 ppm. These levels of impurities compare favorably with gas analysis results reported from Rocketdyne in the 1970s and are not expected to impede hydrogen uptake and crack growth.

Other literature results suggest that oxides can inhibit dissociation of hydrogen gas on metal surfaces and thereby preclude hydrogen uptake. The presence of oxides on the surfaces of precracked low-alloy steels is a likely source for the prolonged incubation times. The surface oxides can be circumvented by loading the precracked specimens in a low-oxygen environment and then sealing the specimens in the materials testing pressure vessel in the same low-oxygen environment. To achieve a low-oxygen environment during crack-growth specimen preparation, a project was initiated to refurbish a surplus glove box and gas purifier, which were obtained gratis from Lawrence Livermore National Laboratory and Los Alamos National Laboratory, respectively. Custom-designed fixtures have been installed in the glove box to allow handling of crack-growth specimens and materials testing pressure vessels. This project has encountered some challenges from the Environmental Safety and Hazard group of Sandia and with staffing, but operation of the glove box is expected in FY 2006 Q4. When completed, the glove box will be a unique asset among the limited institutions that can conduct crack-growth tests in high-pressure hydrogen gas. An image of the customized glove box is shown in Figure 4.

Procedures for thermal precharging ferritic steels with hydrogen are being developed to facilitate tensile and impact testing of low-alloy steels with internal hydrogen. Maintaining internal hydrogen in ferritic steels is more challenging compared to procedures for stainless steels since the diffusion of hydrogen is orders of magnitude more rapid in low-alloy steels than in stainless steels, thus hydrogen quickly off-gases from ferritic steels during handling and test preparation. To achieve controlled tests, ferritic steels are being coated with copper prior to thermal precharging: the copper coating is relatively permeable to hydrogen at elevated

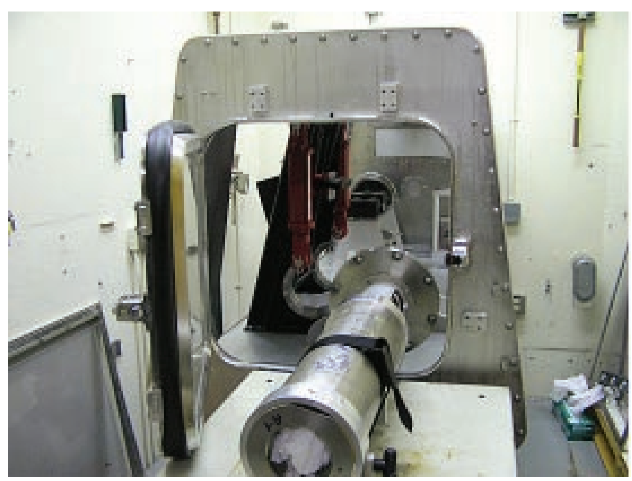

FIGURE 4. Glove Box for Preparing Crack-Growth Specimens in Low-Oxygen Environment

temperature but acts to control off-gassing of hydrogen at room temperature. The influence of the copper coating on hydrogen uptake and distribution in the steel-copper composite is being explored. Preliminary results (in collaboration with Tufts University) show that the hydrogen contents in the steels are much higher than expected; however, the hydrogen appears to have little effect on ductility in tensile tests.

Measurements of hydrogen-assisted fracture resistance in stainless steels for high-value components such as tubing, valves, pressure release devices, compressor components, etc. has continued as part of a "no-cost" collaboration protected by nondisclosure agreement. Phase two of testing austenitic 316 and duplex super austenite/ferrite (SAF) 2507 stainless steels has been completed. In phase one, tests on 316 and SAF 2507 stainless steels with very high concentrations of internal hydrogen focused on strength of materials properties such as ductility. Phase two testing emphasized fracture mechanics tests on cold-worked 316 and SAF 2507, which were subjected to the same hydrogen exposure conditions as the tensile specimens from phase one. Fracture mechanics data are instrumental for the design of components in high-pressure hydrogen gas. Results from the fracture mechanics tests showed similar trends compared to the tensile tests; i.e., after hydrogen exposure, SAF 2507 suffered severe reductions in fracture toughness while 316 maintained high fracture toughness (Figure 5). These trends are attributed to the microstructures of the alloys, where the SAF 2507 consists of approximately 50% austenite and 50% ferrite phases and 316 is nearly 100% austenite. Examination of hydrogen-assisted fracture modes in the two alloys clearly demonstrated that the ferrite phase is more susceptible to hydrogen-assisted fracture and leads to the dramatic toughness reduction in hydrogen-charged SAF 2507.

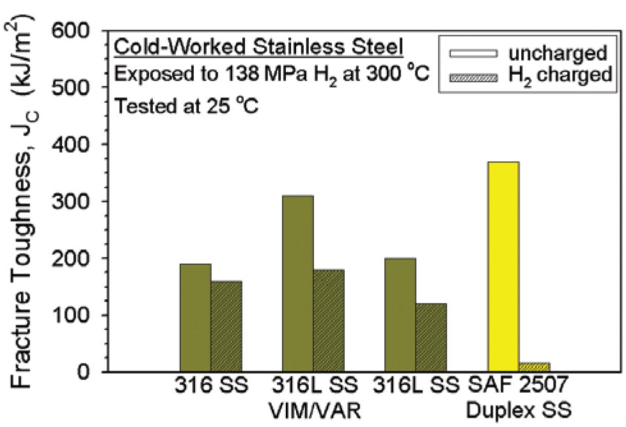

FIGURE 5. Fracture toughness (value of J-integral for crack propagation, J_c) for cold-worked 316 and SAF 2507 stainless steels in the hydrogen-charged and uncharged conditions.

A capital equipment request for constructing a system to conduct dynamic-loading materials tests in high-pressure hydrogen gas has been granted through the NNSA. This system will allow measurements of fatigue crack propagation rates of materials in 100 MPa hydrogen gas. No currently operational systems that can perform fatigue crack propagation measurements at this hydrogen gas pressure are known in the U.S., thus this facility will be unique to Sandia/CA. Design of the pressure vessel is in progress at Autoclave Engineers.

Hydrogen-Compatible Materials: Technical Interactions

Sandia is continuing its collaboration with a vendor that manufactures stainless steel piping and valve components. Sandia is conducting tests on stainless steels that have been exposed to high-pressure hydrogen gas. The data will be included in the Technical Reference. A broad testing matrix has been established, where further testing will include notched tensile specimens, sub-ambient temperatures, and welded stainless steels of several compositions. The collaboration has been extremely productive for both Sandia and the vendor, and the extensive test matrix suggests that the relationship could continue for several years. Test specimens are being prepared by the vendor. Data from phases one and two of this collaboration were presented at the National Hydrogen Association (NHA) conference and represented by the vendor.

BMW discovered the Technical Reference website and contacted Sandia for guidance on Fe-Ni-Co austenitic steels, which are used in metal-to-ceramic joints. Sandia directed BMW to the appropriate literature on hydrogen compatibility of Fe-Ni-Co alloys and composed a chapter on these alloys for the Technical Reference.

Sandia was contacted by Nexant, an energy consulting company, to provide guidance on hydrogen compatibility of pipeline steels. Sandia had extensive communications with Nexant and provided input on fracture mechanics-based design of structures in hydrogen gas, including forwarding a book chapter recently authored by Sandia entitled "Effects of Hydrogen Gas on Steel Vessels and Pipelines".

Code Change Process

We are becoming more active in support of NFPA code development activities. Presentations on unintended releases work were given at the NFPA World Safety Conference and Exposition in Las Vegas, Nevada (June 6-8, 2005) and the NFPA Industrial and Medical Gas Meeting in Oakland, California (June 14, 2005). We also hosted and participated in the NFPA Vehicular Alternative Fuel Technical Committee Meeting (May 9-10, 2006, Sandia National Laboratories, Livermore, CA).

Two Sandia staff members are Corresponding Members of the ASME Boiler and Pressure Vessel Project Team on Hydrogen Tanks and have been participating in quarterly meetings via teleconference. The Project Team on Hydrogen Tanks sought significant input from Sandia in creating a draft document entitled "Article KD-10: Special Requirements for Vessels in High Pressure Gaseous Hydrogen Service", which is a supplement to Section VIII, Division 3 that provides guidance on applying fracture mechanics to hydrogen pressure vessel design and measuring fracture mechanics properties of materials in hydrogen. Sandia provided ideas and wording in the document regarding measurement of fracture mechanics properties in hydrogen gas.

Conclusions and Summary

- We co-hosted a Risk Assessment Workshop as part of the IEA Task 19 Hydrogen Safety meeting and are working on qualitative and quantitative risk assessments of a hydrogen refueling station.
- We are using our large jet release models to perform hazard analyses for the fueling station risk analysis.
- We have developed a slow leak model that can track the trajectory and concentration of a buoyant jet releases without resorting to time consuming Navier-Stokes calculations.
- We have developed an experiment to measure the concentration decay in slow leak buoyant jets. Data from the experiment will be used to verify the slow leak buoyant jet engineering model.
- Four new chapters of the Technical Reference for Hydrogen Compatibility of Materials have been completed and added to a public website (online since January 2005) for distribution of all 10 chapters thus far completed.

Future Directions

- Submit our proposed risk-informed approach for developing codes and standards for public comment in a quest to reduce uncertainties, build industry confidence, and develop a data knowledge base for performing risk assessments. Identify risk mitigation strategies and failsafe technologies for the refueling infrastructure and evaluate the associated risk impact.
- Expand safety distance analysis to include the risk associated with additional risk drivers such as fast deflagration and taking into account possible failsafe and event mitigation design features at the refueling station.
- Perform risk assessments on remaining elements of hydrogen infrastructure to identify important safety drivers. Integrate risk assessment as a formal and commonly expected element in hydrogen codes and standards development. Apply insights from completed risk assessments to better select and manage R&D developments in hydrogen energy.
- Develop a risk communication strategy to guide officials in effective ways to communicate hydrogen risk information to the public in order to build and maintain public trust.
- Continue to identify critical safety scenarios and develop defensible models for small-scale hydrogen release scenarios. Continue experiments to develop benchmark data sets to cover slow leak non-choked flows and buoyantly-driven flows.
- Barrier walls at refueling stations are being considered as a means of reducing separation distances. Experimentally investigate and characterize flame behavior and heat transfer in release scenarios involving flame impingement on walls. Define wall configurations required to safely deflect unignited jets using computational parameter studies of fluid flow behavior. Obtain benchmark data to support model development and validation. Identify critical safety scenarios for enclosed and partially-enclosed spaces where possible hydrogen explosion could occur. Develop defensible models and benchmark experiments to cover these scenarios in partnership with researchers in Germany (FZK) and in the United Kingdom (Shell and HSE).
- The Technical Reference for Hydrogen Compatibility of Materials is a living document that is evolving as data is collected from the literature and generated from materials testing. Sections on pressure vessel steels, pipeline steels and aluminum alloys will be added in the coming year. We will work with stakeholders (such as ASME) to evolve and prioritize content addition.
- Execute testing to fill gaps in the existing database for hydrogen compatibility of materials. Testing to measure thresholds for hydrogen-assisted fracture under static loading on pressure vessel steels and stainless steels will continue. Dynamic fatigue testing of pressure vessel steels at hydrogen pressures up to 100 MPa is planned.
- 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 nondestructive inspection techniques to extend the lifetime or reduce safety factors as required in current codes for stationary composite pressure vessels.

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FY 2006 Publications/Presentations

1. San Marchi, Somerday, and Robinson, "Permeability, Solubility and Diffusivity of Hydrogen Isotopes in Stainless Steels at High Gas Pressures", International Journal of Hydrogen Energy, to be published, 2006.

2. Somerday and San Marchi, "Effects of Hydrogen Gas on Steel Vessels and Pipelines", *Materials for the Hydrogen Economy*, R.H. Jones and G.J. Thomas, Eds., to be published, 2006.

3. Somerday, San Marchi, and Balch, "Hydrogen-Assisted Fracture: Materials Testing and Variables Governing Fracture", presented at both SRNL/ASME Materials and Components for the Hydrogen Economy Codes and Standards Workshop and DOE Hydrogen Pipeline Working Group Workshop, Augusta, GA, August 2005.

4. Balch, Somerday, and San Marchi, "Hydrogen-Assisted Fracture of Ferritic Steels for High-Pressure Hydrogen Gas Storage and Delivery Applications", 2005 Materials Science & Technology Conference, Pittsburgh, PA, September 2005.

5. Somerday and San Marchi, "Permeability, Solubility and Diffusivity of Hydrogen in Stainless Steels at High Gas Pressures", ASTM TF G.01.06.08 Hydrogen Gas Embrittlement Workshop, Dallas, TX, November 2005.

6. San Marchi, Somerday, and Balch, "Hydrogen Effects in Engineering Materials", Materials Research Society Fall Meeting, Boston, MA, November 2005.

7. San Marchi, Somerday, Tang, and Schiroky, "Hydrogen Effects in Austenitic 316 and Super Duplex 2507 Stainless Steels", National Hydrogen Association Annual Hydrogen Conference, Long Beach, CA, March 2006.

8. Houf and Schefer, "Predicting Radiative Heat Fluxes and Flammability Envelopes from Unintended Releases of Hydrogen," accepted for publication International Journal of Hydrogen Energy.

9. Schefer, Houf, San Marchi, Chernicoff, and Englom, "Characterization of Leaks from Compressed Hydrogen Dispensing Systems and Related Components," accepted for publication International Journal of Hydrogen Energy.

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

11. Houf and Schefer, "Radiative Heat Flux and Flammability Envelope Predictions from Unintended Releases of Hydrogen," Proceedings of the 13th International Heat Transfer Conference, accepted for publication, April 2006.

12. Schefer, Houf, Williams, Bourne, and Colton, "Characterization of High-Pressure, Under-Expanded Hydrogen-Jet Flames," submitted to International Journal of Hydrogen Energy.

13. 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.

14. 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.

15. 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.

16. Mendez, Moen, Ohi, Keller, and Allen, "A framework and risk principle for Hydrogen Safety Codes and Standards", NHA Annual Hydrogen Conference, March 2006.

17. Mendez, "Maximum tolerable risk level for hydrogen systems/infrastructure", Joint Workshop on Hydrogen Safety and Risk Assessment, March 2006.

18. Moen, "Hydrogen modeling and experimental studies", IEA Annex 19, Hydrogen Safety Experts Meeting, March 2006.

19. Keller, "U.S. testing facilities and plans", IEA Annex 19, Hydrogen Safety Experts Meeting, March 2006.

Special Recognitions & Awards/Patents Issued

1. 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.