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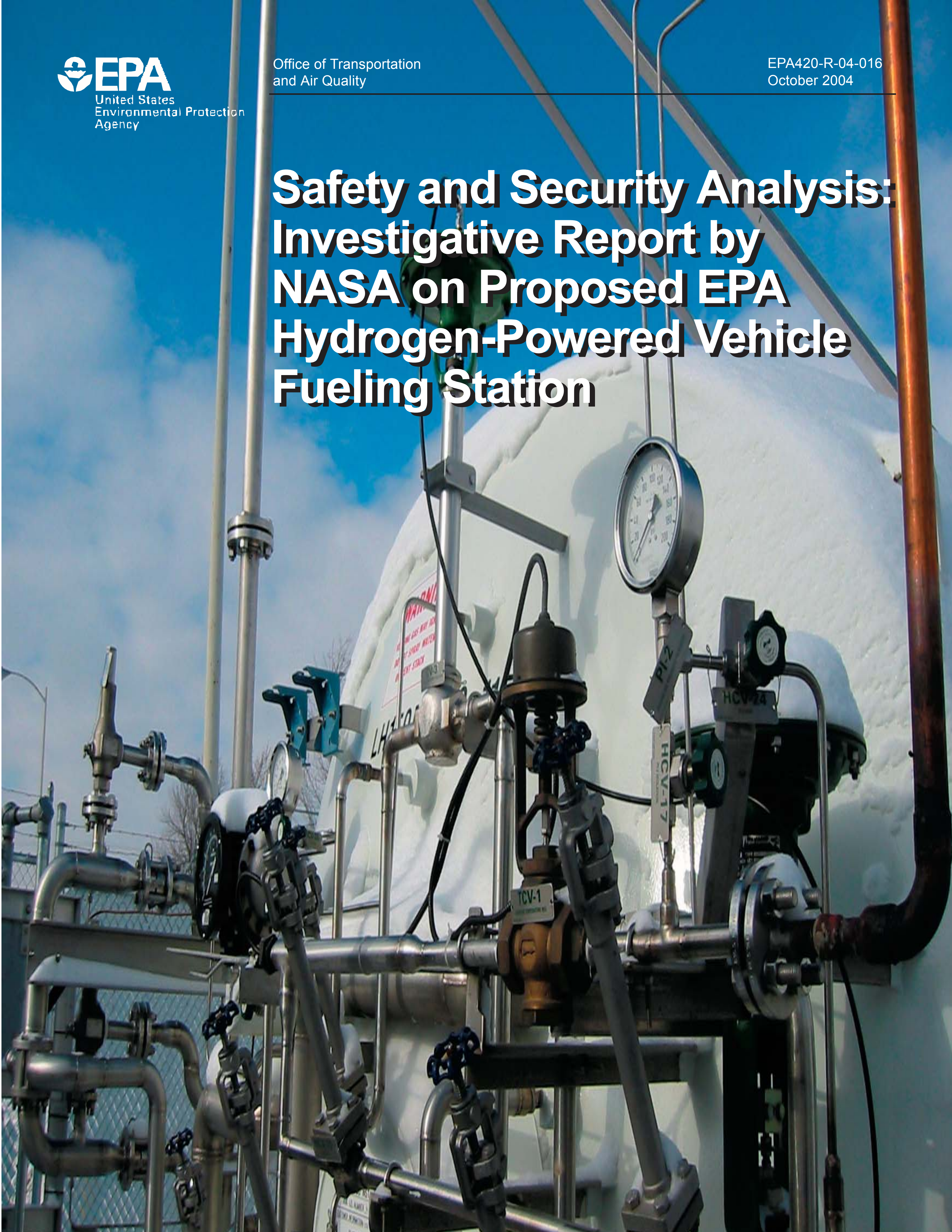
Safety and Security Analysis: Investigative Report by NASA on Proposed EPA Hydrogen-Powered Vehicle Fueling Station



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Safety and Security Analysis: Investigative Report by NASA on Proposed EPA Hydrogen-Powered Vehicle Fueling Station

Assessment and Standards Division
Office of Transportation and Air Quality
U.S. Environmental Protection Agency

With the exception of minor changes, this Report is identical to National Aeronautics and Space Administration Report No. WSTF-IR-0184-001-03, titled “Environmental Protection Agency Hazard Analysis Report” and prepared for EPA by Stephen Woods, Harold Beeson, and Harry Johnson of NASA Johnson Space Center White Sands Test Facility, Las Cruces, NM, (September 19, 2003). The Report was prepared under Interagency Agreement No. DW809 39 802-01-0

PREFACE

EPA’s Office of Transportation and Air Quality commissioned NASA (National Aeronautics and Space Administration) to prepare this technical report in support of the Agency’s hydrogen and fuel cell program. EPA’s program is a part of the federal government’s efforts to encourage the development and testing of new technologies that may define a path toward an international hydrogen economy. A key component of the EPA program is a unique partnership with DaimlerChrysler and UPS that is placing fuel cell powered package delivery vehicles into normal commercial service in the region surrounding EPA’s National Vehicle and Fuel Emissions Laboratory in Ann Arbor, Michigan. EPA is installing a state of the art hydrogen vehicle fueling station at its laboratory that will provide the hydrogen fuel for the fuel cell delivery vehicles and for other hydrogen vehicles that may be operated in Southeast Michigan.

Because of the newness of hydrogen as a fuel and because this is the first hydrogen fueling station to be installed at a federal facility, it was necessary to very carefully consider each aspect of this project for a number of factors, including safety and security. NASA has extensive experience with the handling and use of hydrogen, and EPA commissioned NASA to address a wide range of issues relating to system safety, security, and siting. This report identifies issues, discusses them, and makes recommendations. EPA has incorporated essentially all of NASA’s recommendations in the siting and design of our hydrogen fueling station.

While this report focuses on a specific type of hydrogen fueling station at a specific location, we recognized at the onset that issues applying to the NVFEL setting and facility are much the same as those applying to other federal and private facilities. Thus, this report is designed to be of sufficient scope to have broad applicability, and we believe that the information NASA has assembled and the analysis they have performed will be of interest to others considering working with hydrogen as a fuel. The report will be particularly useful to parties proposing to site such fueling stations in close proximity to commercial or residential property or as a part of federal facilities.

This report represents a significant initial component of a larger comprehensive body of materials that EPA expects to compile and distribute documenting our experience with hydrogen fueling infrastructure and the use of hydrogen. Readers will find additional information on EPA’s hydrogen and fuel cell program at www.epa.gov/fuelcell.

Executive Summary

This report addresses primary safety and siting issues associated with the installation of cryogenic liquid and high-pressure gaseous hydrogen systems in proximity to a laboratory facility, commercial facilities, a shopping mall, and public thoroughfares.

The U.S. Environmental Protection Agency (EPA) National Vehicle and Fuel Emissions Laboratory (NVFEL), located in Ann Arbor, Michigan, tests experimental and state-of-the-art vehicles for emissions and fuel economy. Preparations for a program to evaluate a hydrogen-powered medium-duty delivery truck and other hydrogen-powered vehicles necessitate the construction of a vehicle-fueling facility able to dispense up to 40 kg of hydrogen per day. The bulk of the hydrogen (1500 gal) is to be stored in a conventional pressurized cryogenic tank designed to American Society of Mechanical Engineers standards. The hydrogen vehicle fuel is to be dispensed as a gas at ambient temperatures into 5000-psi vehicle fuel tanks. This facility must coexist safely with existing hazardous materials and operations at NVFEL, and must not pose unacceptable hazards to nearby commercial concerns.

Facility siting locations and hazards for the proposed design were evaluated according to aerospace and commercial practice by specialists from the NASA White Sands Test Facility. An important design consideration for a potentially hazardous facility is the selection of the facility location. Although there is a low probability for a catastrophic occurrence, selecting a site that will minimize the effects of such an event is prudent. This document summarizes the potential for catastrophic hazards arising from the operation of the EPA proposed hydrogen dispensing station on the EPA site.

Categories of causes and severity were established for equipment failure, operational error, and the effects of attack or sabotage under weather conditions expected in Michigan. Three regions with separate safety implications were identified, as follows, to best mitigate the identified hazards:

1. The region in the immediate vicinity of the equipment should be secure and exclude all but maintenance personnel, to protect personnel from small leaks.
2. An exclusion zone in the immediate area of the facility, as by defined according to the National Fire Protection Association (NFPA) 50B, can be adopted to provide protection against unplanned minor releases of hydrogen and shrapnel. This exclusion zone requires 75 ft of separation. Personnel within the NFPA exclusion zone will typically be fuel suppliers, maintenance workers, or dispenser operators who are specifically trained to use the dispensing system equipment. General personnel and the public are not under this category.
3. An additional margin, as large as 175 ft for the 1500-gal quantities planned, is necessary to protect against a large, potentially catastrophic release of hydrogen, despite its unlikely ocurrence.

For the purposes of this study, a catastrophic event is one that has the potential to extensively threaten facilities, general personnel, or the public beyond the immediate area of the dispensing station. While there are many ways the dispensing system might fail or be assaulted, only failures or assaults that can release a large portion of the stored liquid hydrogen, or assaults that completely sever pieces of the high pressure system, stand to present a threat beyond the NFPA exclusion zone.

The planned hydrogen dispensing system will store approximately 1500 gal of liquid hydrogen and possess three high-pressure gas cylinder assemblies, each with approximately 18 ft^3 of 6000-psi hydrogen for "ready" dispensing to vehicles. The WSTF analysis has identified two general scenarios for catastrophic events:

1. Any component failure or attack/sabotage which leads to a spill of a significant portion of the liquid hydrogen storage
2. Violent attack/sabotage capable of completely severing pieces from the high-pressure assemblies

Summaries for assessment of the two scenarios are provided in the following paragraphs:

First Scenario

Assessment for the first scenario was for spills of 1500 gal[1], a worst-case event, under various weather conditions. In general, the spilled liquid hydrogen, a cryogenic liquid, rapidly vaporizes and mixes with air, forming a flammable mixture. Initially, the mixture stays on the ground with the cold hydrogen vapors that are denser than air; but as the hydrogen warms, the mixture becomes buoyant and soon rises. The potential for a catastrophic scenario can arise if the flammable mixture impinges upon public spaces and surrounding structures. Weather conditions that would contribute to hazards beyond the NFPA exclusion zone include wind conditions near 8 mph or greater. Under these circumstances, the flammable mixtures can be borne beyond the NFPA 75-ft exclusion zone. Analysis based on WSTF liquid hydrogen spill data and combined with TRACE TM[2], an industrial code for the evaluation of the movement of flammable mixtures, shows flammable mixtures will likely rise 30 ft or more over the nearest surrounding structures. The closest approach of flammable mixtures to structures was found for wind velocities near 8 mph. The primary hazard is for ignition of the plume and an ensuing flash fire out in the open. The amount of thermal radiation could burn exposed personnel caught between the NFPA exclusion zone and adjacent structures, but is unlikely to set structures on fire or threaten the general public beyond the structures. This threat is short term and will last only several minutes while the cloud passes overhead. Without ignition, the further rise of flammable cloud and its continued dispersion will lead to dissipation of the hazard.

A variety of conditions were evaluated and found not to lead to catastrophic scenarios. Low wind speeds (4 mph or less) and low outdoor temperatures result in rapid rise of the flammable mixtures. High wind speeds dissipate the hydrogen rapidly. While some portions of the flammable clouds will possess mixtures with hydrogen-air concentrations that are detonable, the large energies necessary to initiate detonation are not available after the mixtures form. The hydrogen dispenser is sited away from buildings and constructed without confining surfaces or walls. Should a combustible cloud form and be ignited, the resulting deflagration will not produce significant overpressures or accelerate into a detonation. Moreover, if the hydrogen dispensing system were breached, the likely outcome would be a fire located within the NFPA exclusion area. This in itself will prevent a catastrophic situation from developing.

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[1] Analysis was performed for 1500-gal quantities of liquid hydrogen. Recent communications with Air Products system designers indicate that the tank that is actually installed may have a slightly larger capacity, but the fill point may be set to less than 1500 gal of liquid hydrogen.

[2] TRACETM (Toxic Release Analysis of Chemical Emissions) SAFER Systems, L.L.C., Camarillo, California.

Second Scenario

Should an explosive charge strike the pressure assembly in such a way that a cylinder is simultaneously freed from the assembly and opened on an end, analysis indicates the component could move with sufficient velocity to clear the NFPA exclusion zone and pose lethal danger to everything in its path.

This is a theoretical result obtained using the PVHAZARD code.[3] It requires precise application of an explosive force. The high-pressure portions of the system are built to ASME specifications and are fairly tough and not likely to be severed easily; therefore, this is a highly unlikely outcome. Small pieces of shrapnel confined to the NFPA exclusion zone are the most likely result.

Conclusions and Recommendations

In summary, the primary catastrophic hazard is a large release of liquid hydrogen that forms a large flammable cloud. The cloud can extend over the surrounding facilities and, if ignited, could expose the surroundings to a flash-fire threat. Analysis shows that the cloud is likely to rise above the surrounding facilities and harmlessly dissipate. The WSTF report evaluates the potential outcomes that arise from the release of hydrogen. No attempt is made to numerically determine risk. It was determined that the best course is to promote the hydrogen to rise as quickly as possible. An infrastructure incorporating a spill pond with gravel and a vapor barrier is recommended.

Safety information and training must be coordinated as necessary with NVFEL personnel, non-NVFEL personnel that may work in proximity to the dispensing system, the Fire Marshall and first responders, and local authorities.

With these precautions observed, the analysis supports the contention that the hydrogen hazards accompanying the operation of a hydrogen dispensing station would not pose a risk greater than the materials and operations already present at NVFEL.

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[3] The PVHAZARD Pressure Vessel Hazard Assessment Software was sponsored by the Air Force (45th Space Wing, PAFB) and NASA, with contributions by General Physics Corporation, ACTA, Inc., and Aerospace Corporation.

Abstract

This report addresses primary safety and siting issues associated with the installation of cryogenic liquid and high-pressure gaseous hydrogen systems in proximity to a laboratory facility, commercial facilities, a shopping mall, and public thoroughfares. The US Environmental Protection Agency National Vehicle and Fuel Emissions Laboratory (NVFEL), located in Ann Arbor, Michigan, tests experimental and state-of-the-art vehicles for emissions and fuel economy. Preparations for a program to evaluate a hydrogen-powered medium-duty delivery truck and other hydrogen vehicles necessitate the construction of a vehicle-fueling facility able to dispense up to 40 kg of hydrogen per day. The bulk of the hydrogen (1500 gal) is to be stored in a conventional pressurized cryogenic tank designed to American Society of Mechanical Engineers standards. The hydrogen vehicle fuel is to be dispensed as a gas at ambient temperatures into 5000-psi vehicle fuel tanks. This facility must coexist safely with existing hazardous materials and operations at NVFEL, and must not pose unacceptable hazards to nearby commercial concerns.

Facility siting locations and hazards for the proposed design were evaluated according to aerospace and commercial practice by specialists from the NASA White Sands Test Facility. Categories of causes and severity were established for equipment failure, operational error, and the effects of attack or sabotage under weather conditions expected in Michigan. Three regions with separate safety implications were identified, as follows, to best mitigate the identified hazards:

1. The region in the immediate vicinity of the equipment should be secure and exclude all but maintenance personnel, to protect personnel from small leaks.
2. An exclusion zone, as specified by NFPA 50B, can be adopted to provide protection against unplanned minor releases of hydrogen and shrapnel.
3. An additional margin, as large as 175 feet for the 1500-gal quantities planned, is necessary to protect against a large release of hydrogen, despite its unlikely occurrence. The primary threat from such an event is a flash fire. The best course is to promote the hydrogen to rise as quickly as possible. An infrastructure incorporating a spill pond with gravel and a vapor barrier is recommended.

Safety information and training must be coordinated as necessary with NVFEL personnel, non-NVFEL personnel that may work in proximity to the dispensing system, the Fire Marshall and first responders, and local authorities.

With these precautions observed, the analysis supports the contention that the hydrogen hazards accompanying the operation of a hydrogen dispensing station would not pose a risk greater than the materials and operations already present at NVFEL.

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Abbreviations

ASME	American Society of Mechanical Engineers
APCI	Air Products and Chemicals, Inc.
BLEVE	Boiling Liquid Expanding Vapor Explosion
CGA	Compressed Gas Association
DoD	US Department of Defense
EPA	US Environmental Protection Agency
GH_2	Gaseous Hydrogen (pressurized)
LH_2	Liquid Hydrogen (cryogenic)
MIE	Minimum Ignition Energy
mJ	MilliJoule
NFPA	National Fire Protection Association
NVFEL	National Vehicle and Fuel Emissions Laboratory
OSHA	Occupational Safety and Health Administration
PPE	Personal Protective Equipment
TRACE™	Toxic Release Analysis of Chemical Emissions
WSTF	White Sands Test Facility

1.0 Introduction

The United States Environmental Protection Agency (EPA) National Vehicle and Fuel Emissions Laboratory (NVFEL) located in Ann Arbor, Michigan, is developing the means to demonstrate and test hydrogen-powered vehicles. A hydrogen-powered vehicle fueling station is planned for operation in 2004. However, on-site storage of cryogenic liquid and high-pressure gaseous hydrogen presents serious technical, safety, and security challenges that must be addressed before actual work on the project can begin. The station, located on the NVFEL facility, will have neighboring industry laboratories and commercial concerns and will be in proximity to public thoroughfares. Safety issues in the handling and storage of hydrogen, as well as the consequences of terrorist attack, must be examined. NVFEL requested engineering support services from NASA White Sands Test Facility (NASA WSTF) to evaluate safety issues for the planned hydrogen dispensing station.

1.1 Background

The EPA NVFEL in Ann Arbor tests experimental and state-of-the-art vehicles for emissions and fuel economy. Recent developments in fuel cell technology have required an expansion of test capabilities to include fueling and testing of new hydrogen-powered vehicles. Preparations for a new hydrogen-powered, medium-duty delivery truck test program necessitate the construction of a vehicle-fueling site capable of dispensing up to 40 kg of hydrogen per day. The bulk of the hydrogen will be stored as liquid in a pressurized cryogenic tank holding approximately 1500 gal, or 60 fills. Hydrogen vehicle fuel will then be dispensed as a gas at ambient temperatures into 5000-psi vehicle fuel tanks.

1.2 Scope

The work consisted of engineering services in support of the installation of a hydrogen-powered vehicle fueling station at the NVFEL. The primary task was to develop siting plans and concept design options based on 1500 gal of liquid storage and high-pressure cylinders for gas storage. Review services were also required to assist EPA with proposed vendor layout and equipment designs and with the resolution of any National Environmental Policy Act and permitting issues that could arise in the planning process. EPA provided site drawings for the NVFEL and technical specifications for the proposed equipment, as necessary.

Accomplishing the project objectives included multiple site visits for measurements, verification, communication, training, analysis, and planning review. Engineering services included site assessment, code review, detailed equipment and process hazard analyses, assault mode identification, catastrophic failure characterization, and development of alternative mitigation strategies.

NASA WSTF developed a draft siting and hazards analysis for the fueling station based on a typical Air Products and Chemicals, Inc. (APCI) 1500-gal liquid hydrogen (LH_2) storage and dispensing station, design developed for the California Fuel Cell Partnership. The draft analysis incorporated the results of:

- Preparatory work
- EPA facility site visit
- Review of code requirements
- Hazard analysis of component and operational failures
- Hazard analysis of catastrophic failures

NASA WSTF presented the draft report, along with the underlying safety and security analyses, in a meeting with EPA engineering, safety and security personnel, APCI engineers, and other EPA contracted technical consultants, at the NVFEL on June 10, 2003. The meeting served to confirm a mutual understanding of the design requirements; educate EPA personnel on technical, safety, and security risks; identify mitigation strategies for reducing risks; and facilitate discussion of attendee questions and suggestions. The meeting results and subsequent NASA WSTF collaboration in the development of the final site design was incorporated into this report.

2.0 Study of Failure Scenarios

The potential consequences of a hydrogen release are directly related to factors inherent in the environment, the rate of release, and the quantity released. The characteristics of the potential consequences dictate where and how systems are sited. It should be noted that the cause of the release, while important in understanding it occurred, may or may not have a bearing on the potential consequences of the release.

2.1 Analysis Approach

First, three hazard zones are identified, categorized by potential consequences 1) within the immediate enclosed area; 2) within a 75-ft exclusion zone; and 3) outside the NFPA 75-ft exclusion zone. Any failure scenario that produces consequences that extend beyond the NFPA exclusion zones can be considered catastrophic. The following analysis identifies three categories of likely causes of hydrogen releases for the proposed hydrogen dispenser system: 1) component failure; 2)operator error; and 3) deliberate sabotage or attack. The analysis then categorizes potential consequences according to the extent of effects. The categories chosen match operational requirements and applicable codes and regulations.

2.2 Categorization of Hazard Zones

The potential siting locations, types of hydrogen storage components, and layout of the hydrogen system on the EPA facility property suggest three hazard zones categorized by potential consequences. The first is defined by small leaks, hydrogen combustion, or controlled releases of hydrogen confined within the chain-link fence isolating the system from unauthorized personnel. This area is accessed only by authorized, specially trained personnel. The second hazard zone includes scenarios with the potential for threat beyond the fencing but within the general locale of the equipment. An exclusion zone of a 75-ft radius from storage equipment is required by NFPA 50A and 50B, and the functions of the storage components in the hydrogen system are applicable. The third category represents the greatest threats that come from events with effects that reach to the buildings and beyond. Any failure scenario that produces consequences that extend beyond the NFPA exclusion zones can be considered catastrophic.

This analysis does not quantitatively assess the ability of attacks or explosives to inflict damage or of the equipment to resist damage. The degree of component or equipment failure is simply assumed, the effects of high pressure are noted, the amount of hydrogen released is estimated, and the potential effects of hydrogen combustion are evaluated. These are the factors assessed to determine consequences.

2.3 Analysis of Hazards

Hazards may arise from component failure, from operational mistakes, and through sabotage or attack. Discussion of each of these potential causes for hydrogen release is given separately. Code analysis of hydrogen dispersion, mixing, and combustion is deferred until Section 2.4.

2.3.1 Hydrogen Release Hazards Caused by Component Failures

The hydrogen dispensing system design proposed by APCI is to provide up to 40 kg/day of high pressure gas derived from cryogenic LH_2 storage. No attempt is made in this report to describe the design or operation of the system, except that the system includes an approximate 1500-gal LH_2 storage tank, a pressurizing system with 6500-psi storage, and a dispensing system. The proposed system components have been examined for failures that would lead to significant releases of hydrogen. The evaluation includes the most probable occurrences of concern, low probability events with severe consequences, and venting rates.

2.3.1.1 Component Analysis Methodology

The hydrogen fueling station was analyzed for component failure and resultant hydrogen release. Major components identified in the main flow path of hydrogen are included in the analysis. Minor components and instrumentation discussed in the following paragraphs are categorized by subsystem.

2.3.1.2 Analysis of Release by Subsystem

Analysis is considered by subsystem.

Liquid Storage and Vaporizer

Three categories of potential release are noted in the data received from APCI:

- Small leaks at connections much less than 1 ft^3/min of hydrogen
- Medium leaks at connections and valve stems around 1 to 10 ft^3/min
- Large leaks from catastrophic failure of component.

Small leaks at connections are common and may occur at any of the piping connections. Initially, the leak test required by American Society of Mechanical Engineers (ASME) B31.3 should catch any connection leakage, and regular leak checks at maintenance intervals should detect leaks early. Small connection leaks are considered the most plausible under normal conditions, and they would release very small quantities of hydrogen.

Medium-sized leaks from the fill connection, manual valve stems, and liquid vaporizer tubing are possible but are mitigated. Leaks at cryogenic liquid-fill connections are common. The estimated leak rate of less than 5 ft^3/min would continue until the operator stopped the operation and fixed the leak. The extended stem on cryogenic liquid valves greatly reduces the chance of stem leakage, but it still may occur over time due to valve cycling. Initially, the leak test required by ASME B31.3 will catch any stem leakage. Regular leak checks at maintenance intervals should detect leaks early.

Large leaks from catastrophic failure of the storage vessel, the liquid isolation valve, and components such as the liquid strainer and pressure-building regulator are very unlikely without outside forces acting on the component. Piping components purchased and installed per ASME B31.3 are rated for the environment (pressure and temperature) they will experience. If any of the components in this category were to fail catastrophically, the maximum potential release would be the entire contents of the liquid storage vessel.

Compressor System

Based on the input from APCI, component failures in the compressor system, including the gas purifier assembly can be grouped into two categories: a very small leak rate (less than 1 ft^3/min); or a medium leak rate (less than 5 ft^3/min).

A system leak at a connection is much more likely than one caused by a major failure, and it would result in the release of very small quantities of hydrogen.

Leaks at the connections of the compressors and inter-coolers, or those caused by major failure of the separators and purifier might have a 5 ft^3/min leak develop. The leak would vent until a sensor closes a supply valve. This large of a leak is possible but unlikely with system leak checks.

Gas Storage and Filling Station

Component failures in the gas storage and filling station areas can also be grouped into two categories based on the APCI data: small leaks, and leaks that would vent one bank of the storage cylinders. Small gas leaks at valve stems or connectors are more likely and would result in the release of very small quantities of hydrogen.

The breakaway fitting seems to be a special case, but it is handled by various safety controls. If the system works as designed, it seems unlikely that a large release would follow a breakaway fitting failure.

If the cylinders or the valves attached to either end fail, then one bank of cylinders (13 kg of gas) would be released. Since the vessels are built to ASME standards and the valves are purchased and installed per ASME B31.3, this is very unlikely under normal operating conditions.

2.3.1.3 Implications for Release Caused by Component Failure

Not surprisingly, since the system is per ASME standards, the most likely event under normal operating conditions is that of small leaks at connections.[4] Regulators, check valves, the 37-degree flare, the current-to-pressure controller, and the nozzle are also identified as components that may be expected to leak during the planned period of system performance. The LH_2 vessel and the pressure vessels have a very low probability of failure. With the exception of the nozzle, all the components in question are only approached by the vendor's maintenance personnel. Large releases caused by the failure of system components are considered unlikely; but should they occur, the consequences are explored in Section 2.4.

2.3.2 Hydrogen Release Hazards Caused by Operation-Induced Failure

System operations involving personnel and the potential effects of operations unrelated to hydrogen dispensing were examined for actions that would lead to significant releases of

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[4] Small leaks at connections are common, although unwanted. Depending on the kind of leak check that is performed on a regular basis, these leaks may be found and corrected. A decay lead check may not be sensitive enough to detect this small of a leak. A portable hydrogen sensor or "bubble" test with a soap film fluid may be more likely to detect the leak.

hydrogen. These operations include maintenance activities, hydrogen loading operations, dispensing activities, trespassing, emergency procedures, and accidents involving other EPA operations. It is well known that human error overshadows equipment failure as the predominant cause of hydrogen incidents.

2.3.2.1 Discussion

A discussion of maintenance, filling operations, dispensing, trespassing, emergency procedures, and potential accidents involving other EPA operations is given in the following paragraphs.

Maintenance

Maintenance and repair operations on the hydrogen system are only conducted by vendor-trained technicians. Standard procedures for repairs involving hydrogen-wetted components require purging of the hydrogen before personnel start repairs and, if necessary, purging the air before hydrogen is again introduced to the system. Operations are performed with several personnel on hand using the “buddy system,” appropriate personal protective equipment (PPE), and hydrogen detectors. Emergency shut-off switches are conveniently located. Only small hydrogen releases are expected from maintenance operations.

Filling Operations

Supply of hydrogen to the dispensing system is performed by trained vendor crews. Operations will be coordinated in advance with EPA facility receiving staff, and the vendor crews will use the “buddy system” during the refueling operation. Barriers protect the LH_2 storage tank and system from collision by the hydrogen tanker truck or other vehicles. Both the hydrogen dispensing station and the refueling truck possess automatic shutoff equipment, in case connecting lines fail or disconnect. Hydrogen gas lost during chill-down of system components during refueling is vented in a controlled manner. Only small hydrogen releases are expected from refueling operations.

Dispensing

Training is required for vehicle operators who refuel the hydrogen-powered vehicles. The hydrogen dispensing system requires a security password, and fuel nozzle interconnects must be electronically verified before hydrogen fueling can commence. The dispensing system is designed for breakaway and automatic shutdown should a driver inadvertently drive away with the nozzle connected to the vehicle. Only small hydrogen releases can result.

Trespassing

Trespassing and vandalism are mitigated by EPA area security and system location. Housing of the liquid and high-pressure gas handling portions of the system is behind a locked security fence. The controls described under dispensing also serve to protect the system against unauthorized use and manually inflicted damage. Only small hydrogen releases are expected to result from intruders who are just curious or bent on minor vandalism.

Emergency procedures

Emergency procedures for system failure modes and for EPA personnel response are not yet available for review. General system shutdown switches will be provided in accessible locations, both remote from and at the hydrogen dispensing station. The vendor will control what specific responses are taken to mitigate failure modes. The vendor's actions to mitigate an emergency should be carefully reviewed in advance of fuel-dispensing operations by the EPA. The EPA should also establish facility-wide emergency procedures in response to potentially catastrophic occurrences. Errors in judgement handling emergency situations, combined with malfunctioning instrumentation, although very rare, have led to catastrophic failures of hydrogen vessels in the past (Edeskuty and Stewart 1996). Depending on the circumstances, a large hydrogen release could occur.

Accidents Involving Other EPA Operations

Operation of heavy vehicles, fuel tankers, and other activities that could threaten the hydrogen dispensing station should be carefully reviewed and controlled. Failure of the barricades that protect the hydrogen dispensing station from vehicles could result in a large release of hydrogen. The circumstances surrounding the release of hydrogen from a vehicle collision could be further compounded should the colliding vehicle contain fuel, oxidizing materials, or hydrogen. EPA will consider these factors in siting, design of barriers, and in planning other operations.

2.3.2.2 Implications for Release Caused by an Error in Operations

The operation of the hydrogen dispensing station as a demonstration system is planned to last several years. For a project of this duration, it is realistic to expect that, from all the operations considered above, a small leak is likely to occur. A small release of hydrogen poses a safety hazard in the immediate area of the leak. A catastrophic leak of hydrogen resulting from operations is very unlikely with this system; however, consequences and considerations for catastrophic leaks are presented in the sections that consider catastrophic releases Section 2.4.

2.3.3 Hydrogen Release Hazards Caused by Sabotage or Attack

Sabotage or attack differs from other scenarios in that there is a deliberate intent to make the system fail in a violent manner. There are too many ways attack or sabotage can occur to consider them individually. Therefore, the approach is to consider several likely means as examples and group them by their potential consequences.

2.3.3.1 Small Penetration

Any action that causes a small penetration into a hydrogen system and leads to the unplanned release of hydrogen is considered here. Examples would include rifle fire or the use of a large crowbar to spear or shear the equipment. Consequences might include:

- Loss of vacuum in the vacuum annulus of the LH_2 storage tank, which could lead to a large heat leak and excessive venting of product through the relief system
- A jet of LH_2 or cryogenic gaseous hydrogen (GH_2) from the LH_2 storage tank
- A jet of GH_2 from connecting hardware

- A jet of GH_2 from the pressure bottles
- A jet of GH_2 from the dispenser or fill line

Considerations can be separated for the cryogenic subsystem and the high-pressure components.

2.3.3.1.1 Cryogenic Vessel Subsystem

Two cases can be considered: penetration of the outer wall, or penetration of both the outer and inner walls of the LH_2 storage vessel.

Outer Wall

Breaching only the outer wall introduces air to the vacuum-jacketed region, but does not release hydrogen from the inner vessel. The loss of vacuum and introduction of air will increase the heat impinging on the inner vessel and cause an increase in the rate of GH_2 boil-off from the vessel. A larger heat leak caused by a bridge of frozen water or nitrogen is considered unlikely.[5] The vacuum annulus is filled, to a large extent, with thermal insulating material (pearlite or Mylar®[6]). This material, given a penetration of the outer wall, would slow entry of air into the annulus and significantly reduce the amount of air that can enter by displacing the available volume. Both of these effects will limit the effect of the heat incursion to the immediate area of the penetration. The relief system is specifically designed to safely vent hydrogen should vacuum be lost.

Penetration of Inner Wall

With both walls of the vessel breached, air and hydrogen can potentially meet at some point external to the inner vessel. However, as noted above, the vacuum-jacketed space is filled with pearlite or Mylar in sufficient quantities to displace most of the volume in which a hydrogen-air mixture could form, leaving little to combust.[7] The hydrogen within the inner vessel is under a maximum working pressure of 150 psig and will exit in a plume or jet through the hole in the outer vessel wall. Ignition of the hydrogen outside of the outer wall might lead to further heating of the system on the outside vessel walls. Given the low emissivity of hydrogen-air reactions, radiative heating is not a major concern. External regions with direct exposure to the hydrogen combustion will experience high temperatures, but the ASME vessel design can withstand the fire. Loss of pressure in the vacuum annulus or heating of the inner vessel if sufficiently extreme, will lead to an emergency shutdown of the system. Should a fire result in an internal pressure rise greater than the maximum allowable working pressure for the volume, the relief system will protect against over-pressure (APCI Proposal).

2.3.3.1.2 Pressure Components

A penetration in a pressurized line, connection, or vessel will result in a high-pressure jet of hydrogen that can impinge anywhere in the immediate vicinity of the system. Analysis by

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[5] Private communication. Walter Stewart's telephone conversation with S. Woods, May 2003.

[6] Mylar® is a registered trademark of E.I. Du Pont de Nemours and Company, Wilmington, Delaware.

[7] Eichelberger, D.P. APCI Proposal to US EPA RFQ #PR-CI-03-10315. *Design, Installation, Operation, and Hydrogen Supply of a Compressed Gaseous Hydrogen Refueling Station Using Delivered Liquid Hydrogen*. Air Products and Chemicals, Inc., Allentown, Pennsylvania, March 25, 2003.

PVHAZARD shows the 0.75-in. ASME construction of the cylinder walls is likely to prevent penetration by standard bullets. Smaller lines and fittings would be more difficult to specifically target. However, should a component failure occur, TRACETM[8] analysis shows that, for a 0.25-in. diameter penetration of a 6000-psi vessel, the flammable region of a plume will extend no more than 9 m horizontally from the hole. This represents a worst-case scenario for both the driving pressure of the plume and the direction of the plume.

2.3.3.1.3 Summary

Penetration in either the cryogenic or pressure subsystems will present a fire and/or pressure release hazard to personnel, ancillary equipment, or vehicles in the immediate area of the hydrogen dispensing system. The safety equipment incorporated into the hydrogen dispensing system will preclude the further escalation of hazards such that the exclusion zones specified by standards NFPA 50A and NFPA 50B are thought to be adequate. This reasoning applies to equipment/component failure noted in the component analysis and failures caused by attack or sabotage.

Additionally, it is noted that, in the opinion of those contributing to this report, the LH_2 storage tank, ASME pressure cylinders, and compressor sections are sufficiently tough to survive an assault by direct rifle-fire.

2.3.3.2 Explosive Charge

This analysis examines the consequences of the release of hydrogen. Large explosive charges with yields that far exceed the hazard posed by the hydrogen are not considered here since their effects would be greater than that of the hydrogen inventory in the dispensing system. Therefore, explosive-charges of interest might include a rocket-propelled grenade, plastic explosive, or stick(s) of dynamite. The results are distinguished from the penetrations considered above by the large size of the opening and attendant shrapnel.

2.3.3.2.1 Effect of Attack on the Liquid Hydrogen Vessel

High explosives can produce a large hole or rupture of the vessel, the worst case leading to a spill of the entire contents. Ambient surface temperatures, regardless of season, are so high relative to the temperature of liquid hydrogen that the spilled LH_2 will flash to a gas on contact. Heating the LH_2 to 300 K will result in an 845-times increase in the volume of the hydrogen. The process of heating the liquid to a gas is rapid, with the air supplying much of the heat during mixing. The resultant mixture behaves as a plume, subject to weather conditions. The results of this scenario are characterized in Section 2.4.

2.3.3.2.2 Effect of Attack on the Pressure Components

The hydrogen dispensing system uses three gas storage modules, each with 12 high-pressure steel cylinders in a 3- by 4-ft matrix. Each cylinder possesses 1.5 ft^3 and in operation will hold hydrogen at 6500-psig or, if released, approximately 22.2 m^3 at 70 °F, 1 atmosphere.
Violent failure of pressure components presents several hazards possibilities:

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[8] TRACETM (Toxic Release Analysis of Chemical Emissions), SAFER Systems, L.L.C., Camarillo, California.

- Shrapnel due to the explosive
- Shrapnel accelerated by the high-pressure gas
- Rocketing of components
- Shock waves
- Fireball

The design of the modules is such that certain cylinders, should they fail, will act as conduits for the release of gas from all 12 cylinders. However, shrapnel from the failure of a cylinder will not penetrate adjacent cylinders; hence, by itself, the violent failure of one cylinder is not likely to cause a “cascade” failure of the other cylinders in the module. Therefore, the worst case is likely to be the sudden release of gas from one cylinder, followed by a flow of hydrogen supplied from all of the other 11 cylinders. Given the placement of the cylinders, other system equipment, and the chain-link fence, small shrapnel will be dangerous only in the immediate vicinity of the system.

Should an explosive act cleanly cut through a cylinder and simultaneously sever the cylinder from its attachments to the module, the free piece will be propelled like a rocket by the compressed hydrogen. This scenario is distinguished from small shrapnel and is extremely unlikely. The cylinders are fabricated to ASME specifications and are unlikely to undergo brittle failure. However, should this event occur, the horizontal orientation of the cylinders increases the risk for injury and greater damage. In the vertical position, a downward trajectory is stopped by the ground and upward trajectories with a small pitch will fall back to the ground near the system. It is conceivable, given the horizontal orientation that a rocketing cylinder could impinge directly on a sister storage module, and rupture another cylinder. The worst-case outcome in this scenario would be a larger impulsive release (two cylinders), followed by gas flowing from the other 22 cylinders of both modules.

Any sudden release of a gas at 6500 psig will produce a shock wave that may be deadly to personnel in close proximity. With any release of hydrogen, ignition is a possibility, so a fireball of burning hydrogen may follow its release. The explosion may not be the ignition mechanism, since it will act well before the hydrogen can form a flammable mixture with air.

2.3.3.3 Bonfire

A bonfire may possess sufficient fuel to heat the system beyond the point where the internal hydrogen pressure trips the relief systems and vents. This could arise by an accident involving the delivery of other fuels at the facility or by deliberate action.

The system design and ASME construction provide fail-safe operation under considerable heating and provide redundant relief paths to allow hydrogen to be safely vented without rupture of the vessel. Boiling liquid expanding vapor explosion (BLEVE) is theoretically possible if the contents of the LH_2 tank are heated above the critical point causing a BLEVE, but this is not considered a reasonable threat.

2.3.3.4 Vehicle Collision

Deliberate efforts to use a vehicle collision might succeed in causing extensive damage to the system. The vehicle barriers planned for this system are designed to prevent inadvertent contact by a maneuvering vehicle. Acceleration of a large ground vehicle could overcome the barrier. Impact from a small aircraft could also damage the system and release hydrogen. Either scenario, or others like it, are likely to cause a release of all the hydrogen.

2.4 Analysis of Released Hydrogen

Hydrogen, with high levels of purity as found in storage systems, must mix with an oxidizer before any hazardous reaction can take place. In terrestrial hydrogen systems, air provides the greatest concern, whether hydrogen is released into the air, or air enters the hydrogen system. One line of reasoning traditionally used to establish the degree of possible hazard is to determine the greatest quantity of energetic material that can participate in an accident and determine the range of its effects. This so-called quantity-distance evaluation assumes the energetic material is premixed to provide a theoretically optimum release of energy, localized at a point, with a manner of energy release similar to solid explosives. These assumptions seldom fit hydrogen accident scenarios. Therefore, in the case of hydrogen, the key to a realistic evaluation of hazards is to determine the following:

- How much of the released hydrogen can participate to form a combustible mixture
- The extent of formation of the combustible mixture
- The type of reaction (fire, deflagration, or detonation)
- The importance of environmental factors such as temperature, wind, and the effects of confinement

A chemical dispersion code was used to evaluate dispersion of hydrogen from liquid spills and gas jets. The code also was used to evaluate combustion of hydrogen-air clouds. A pressure code helped to evaluate the release of hydrogen and shrapnel from pressurized components.

2.4.1 TRACE Computations for the Release of Hydrogen

Toxic Release Analysis of Chemical Emissions (TRACE) is a state-of-the-art chemical dispersion analysis code maintained by Safer Systems, L.L.C. of Camarillo, California. The code computes the effect of turbulent diffusion and meteorological conditions upon a chemical emission according to the Pasquil model of atmospheric dispersion (Pasquil 1961), a model with wide acceptance (Burgess et al. 1976). This model assumes Gaussian distribution vertically and horizontally of a wind-borne gas entering the air from a localized source.

2.4.1.1 Liquid Hydrogen Spill Characteristics

A spill could involve the entire cryogenic inventory of the LH_2 vessel (approximately 1500 gal). A typical fill of the vessel would result in a saturation pressure of 60 psig. Given a large rupture, the sudden exposure of the inventory to ambient pressure or 0 psig will instantly boil or “flash” a significant portion of the liquid to cryogenic vapor. At 60 psig, 19 percent would flash, leaving approximately 1200 gal to spill onto the ground.[9]

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[9] Farese, David (APCI). Private communication with Don Danyko (EPA), June 13, 2003.

Several factors influence the characteristics of cryogenic spills. Liquid hydrogen boils at 20.3 K under 1 atmosphere of pressure, so any surface at ambient temperatures will have sufficient heat to vaporize the LH_2. The amount of surface to which the spilled cryogen is exposed affects the rate at which the liquid flashes to vapor and warms. The cross-sectional area of the liquid spill determines the plume diameter or cross section. At hydrogen's boiling point, the cold hydrogen vapor is heavier than air until it warms to 23 K, where it becomes neutrally buoyant. As the cold vapors mix with air, the air is chilled below the dew point, causing condensation and forming a visible cloud. After dwelling near the ground and warming sufficiently, the visible vapor cloud forms a plume as it rises.

Time-lapse photographs of LH_2 spills conducted at NASA WSTF in 1980 show the general behavior of cryogenic hydrogen-air plumes (Witcofski, August 1981). For wind speeds ranging from 1.6 to 6.3 m/s, the water vapor clouds traveled 50 to 100 m near the ground, then rose at a rate of 0.5 to 1.0 m/s (Witcofski 1981).

2.4.1.2 Hydrogen-Air Cloud Flammability

Several points are of interest concerning the flammability of hydrogen-air mixtures within the plumes formed by LH_2 spills. From the information that follows, it was decided that 4, 8, and 18 percent-by-volume hydrogen in air would be useful levels of hydrogen to depict in TRACE computations.

The flammability limits for hydrogen-air mixtures range between 4 and 75 percent-by-volume hydrogen in air. These data are for combustion in the upward direction. It is the convention to provide this information as representative of hydrogen's flammability limits. However, flame fronts observed in hydrogen-air mixtures burn less readily when constrained to burn in a horizontal direction, and even less so in a downward direction. The lower flammability limit for downward propagation increases to 9 percent-by-volume hydrogen in air, as a direct effect of the buoyancy of hydrogen (Benz 1988). In uniform mixtures with low hydrogen concentrations (4 to 9 percent-by-volume concentration), combustion of the entire volume of a mixture in an upward direction is not complete. The combusted region tends to form a volume in the shape of a cone that expands in the upward direction, but the mixture outside of the cone is left unburned (Sherman et al. 1981). In general, the release of a large quantity of hydrogen forms a plume that possesses an increasing concentration of hydrogen towards the centerline of the plume. Initially, the central region of the plume may be above the upper flammability limit. In addition, the lower-concentration, hydrogen-air mixtures require greater initiation energy to ignite. Flow and water vapor will also result in greater initiation energy when compared to the same composition mixture, but dry and without movement. This fact has importance in the context of a hydrogen system located where it is desirable for any release of hydrogen to rise above and clear the tops of nearby structures.

Therefore, as a plume of hydrogen rises, the exterior regions of the plume (the regions likely to encounter an ignition source) are less likely to ignite when compared to near-stoichiometric mixtures. Should ignition occur in an exterior region of the plume, only the gas in the immediate vicinity of the ignition source will tend to burn and the potential for flame propagation or deflagration throughout the cloud is reduced. Therefore, unless some process rapidly mixes the hydrogen plume to form a near-stoichiometric mixture with air throughout the cloud, the normal factors that typically influence mixing (diffusion, buoyancy, wind, and turbulence) in a release will not result in complete combustion of the plume.

The movement of flammable mixtures can be partially deduced by observing the movement of the vapor cloud associated with a LH_2 spill. From the work performed at WSTF, it was determined that the concentration of hydrogen within the water vapor clouds had to be greater than 6.8 percent to cool the air below the dew point (Witcofski, March 1981). It must be stated, however, that there is an invisible region outside of the vapor cloud, with concentrations between 4 and 6 percent hydrogen in air, that is flammable in the upward direction. However, for mixture compositions in this range, the ignition sources must have energies greater than 1 mJ, or approximately 100 times greater than the minimum ignition energy (MIE). The presence of wind or water vapor will further increase the amount of energy needed to ignite the mixture. The direct initiation of the detonation in hydrogen-air mixtures in free air (or unconfined by solid surfaces) requires high-energy shock waves, typically produced from high explosives. With confining surfaces present, smaller ignition sources initiate a flame that accelerates until a deflagration-to-detonation transition can initiate detonation. Ignition sources commonly found within buildings could initiate a detonation, should some portions of a hydrogen-air plume become entrained within the associated confined spaces or ducts. Under such circumstances, the lower detonability limit[10] is 18 percent hydrogen in air.

2.4.1.3 Limitations of TRACE

The code is designed to compute the dispersion of a gas in air as either a ground release or a low momentum stack release. The code logic assumes that any release initiated from the ground stays on the ground and there is no buoyancy. A low-momentum stack release assumes the gas enters the atmosphere through an orifice with a defined size, a bulk flow, and then buoyancy is computed. The code further checks the elevation of stack emissions for sufficient height, or it reverts to a ground computation. These two algorithms do not account for the complete observed behavior of spilled LH_2. It is possible that should the hydrogen mix and diffuse sufficiently fast within the air, the bulk mixture could be dominated by the behavior of the air. However, photographs taken of the 1500-gal LH_2 spill tests at NASA WSTF (Witcofski 1981) show a more complex behavior. When cryogenic hydrogen vapor mixes with air, the air temperature drops below the dew point and water vapor clouds form. Time-elapsed photographs of the vapor cloud show a short period of wind-dependent ground travel, always followed by their achieving positive buoyancy. Therefore, both TRACE algorithms must be used and connected at some point to simulate the hydrogen vapor cloud behavior.

2.4.1.4 Interpretation of TRACE Computations with NASA WSTF Spill Data

Based on the behavior of hydrogen observed in cryogenic spills, the dispersion of hydrogen, using TRACE, was evaluated in two steps. The first step, a TRACE ground computation for a given wind speed, is considered for distances that match ground travel for NASA WSTF data. The second step is a low momentum stack calculation for an orifice size approximately the diameter reached by the ground spill and located at the upper elevation reached by the ground spill. An assumption was used in the selection of the temperature of the hydrogen leaving the "stack" orifice. While the hydrogen-vapor and hydrogen-air mixture is traveling near the ground, the hydrogen is warming. This warming is not computed by TRACE. Trial computations indicated that when the initial temperature of the hydrogen is at least 100 K, the plume would rise

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[10] Initiation of detonation is a function of a variety of factors in addition to concentration. The experimentally measured detonation cell size has been shown to be the critical parameter, most useful in predicting detonation.

at a rate simulating the cloud behavior observed during NASA WSTF tests. This is the basis for the rationale of selecting a temperature of 100 K for the initial temperature of the hydrogen as it exits the stack. From the two computations, the distance of horizontal travel was computed and compared to the elevation of cloud rise. This result was then compared to site plan distances and facility building elevations.

We note that at odds with this rationale is at temperatures below 100 K, TRACE predicted the cloud would sink back to the ground. This predicted sinking behavior runs counter to our expectations for the behavior of bulk hydrogen[11] above 23 K. This apparent contradiction does not necessarily mean that TRACE is wrong.[12] Clarification of this issue will require further investigation beyond the scope of this effort. However, the experimental evidence shows only the vapor cloud moving along the ground then rising.

2.4.2 Extent of Flammable Clouds

There are several general risks presented by a hydrogen plume impinging on a structure. It is assumed the bulk-air flow would carry the plume around and/or over the structure. The greatest risk is for flash fire, which is evaluated in Section 2.4.3. Flammable mixtures aspirated into open windows or ventilation ducts will have the confinement and exposure to ignition sources necessary to allow accelerating deflagrations or detonation. The fact that most ventilation systems mix a stream of outside with internal air (make-up) will lead to a dilution of the mixture. This works to reduce hazards. Spaces created by hard surfaces create confinement that can lead to deflagration or detonation and the creation of overpressures. Confining walls that cause the wind to swirl will improve mixing of the hydrogen with the air. However, only the confined portion of the cloud will contribute to the overpressure, except in cases where the shock strength reaches the level of explosives and can impinge back on the remainder of the unconfined cloud.

The TRACE code was run for conditions that pertain to hydrogen-release scenarios in order to evaluate hydrogen concentrations downwind of the spill point.

2.4.2.1 Ambient Temperature Gas Release

The hydrogen, ready for dispensing, is stored at high pressure under ambient conditions. Releases coming from this portion of the system will expand into the surrounding air, forming a buoyant plume. With a density 1/15 that of air, a plume of pure hydrogen can rise as fast as 9 m/s. Combustible regions of hydrogen and air will form at the surface of the plume where mixing occurs. Small leaks, if not ignited, will diffuse harmlessly into the atmosphere within the chain-link security fence that is planned to surround the system. Larger penetrations will result in a high-pressure jet of hydrogen. TRACE analysis of such a jet, released through a 0.25-in. penetration and oriented to produce a horizontal plume, shows a flammable plume may extend 2 to 3 m from the source. If ignited, this would create a loud jet of nearly invisible flame that would be extremely dangerous to anything in its path. The jet would only persist as long as high-

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[11] It is well known that pure hydrogen vapor is neutrally buoyant in air at 23 K and less dense than air at greater temperatures.

[12] For example, one possible explanation can arise from hydrogen's thermal conductivity being much greater than that of air. Consider a bubble of hydrogen vapor surrounded by air with mixing between the two gases occurring along the surface of contact. The thermal conductivity of hydrogen may be sufficient to cool the air and density or even condense it in the immediate vicinity of the surface. This dense air surrounding the hydrogen would for a time, until the hydrogen warms further, cause the combined mass of cooled air and hydrogen to sink to the ground.

pressure hydrogen is supplied, with the worst case being the entire inventory of a 12-pack pressure bottle assembly (approximately 45 to 50 lb of hydrogen at 70 °F). Without ignition, the release will safely disperse well within the 75-ft exclusion zone specified by NFPA 50B.

2.4.2.2 Large Spills with Little Wind

The tests devised at WSTF in the 1980s constrained the LH_2 within a 30-ft diameter pond. The 1500 gal were spilled into the pond over a period of 35 s. In one test, conducted under low wind speed conditions (4 mph), the vapor cloud initially covered a 20 m (60 ft) diameter area generally centered over the pond. From the photographs, the outer edge of the vapor cloud appears to rise at a rate of approximately 1.5 m/s. After 37 s (see the third frame) the outer edge of the vapor cloud appears approximately 50 to 60 m in elevation over the ground, 60-m distant from the spill point. Smaller wind speeds or still air will result in the hydrogen plume taking a more vertical ascent, harmlessly dissipating in the air. In general, given a small wind velocity, the NFPA exclusion zone will not provide adequate safety for this kind of hydrogen release.

2.4.2.3 Worst-Case Spill Scenarios

Weather effects were evaluated to see what conditions might create greater hazards for the surrounding area. Greater wind speed will move the plume further across the ground while increasing turbulence and mixing with air. The WSTF spill tests were conducted under several different wind conditions. The data show that with an increase in wind speed the vapor cloud is “dragged” further along the ground in comparison to its elevation. However, there is indication that the vapor cloud dissipates more rapidly with higher wind speed.

Stack and ground runs were performed using TRACE for wind conditions at 4, 8, 14, and 20 mph with other parameters held constant and simulating the WSTF spill conditions.[13] The 8-mph case provided the closest encroachment of the hydrogen plume on the surrounding structures. Note the cloud spreads along the ground at approximately 45 mph.

The cloud cross section on the ground is approximately 20 m in diameter and, based on the WSTF data, the vapor cloud begins to rise approximately 20 m from the spill. Therefore, the horizontal axis shown in the plots must be corrected by translating the plume 20 m. A graphical analysis finds the lower 4-percent edge of the plume approximately 30 m above the ground. Such a plume originating from the recommended site would clear all neighboring buildings. The duration for passage of the plumes in all the cases is several minutes. This assessment is closely based on the results of the WSTF tests. The 1500 gal of LH_2 was spilled over a 30- to 40-s period during those tests. An accident or attack might produce different spill results.

2.4.2.4 Release with Mitigation

Two worthwhile strategies are to increase the rate at which the LH_2 is vaporized and to reduce the diameter of the plume. Given the positions of facilities surrounding the hydrogen dispensing station, it is desirable to make a potential release of hydrogen rise as rapidly as possible. Several features have been discussed for incorporation into the facility design. These include a spill pond that contains crushed rock to enhance heat transfer to the spilled liquid, and slats inserted within the chain-link security fence.

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[13] This includes a 30-ft diameter spill cross-section and 80 °F.

TRACE computations were conducted to assess the effects of crushed rock and slatted fence on potential spills. Little information was found in the literature on how to use crushed rock to increase the rate of LH_2 boil-off. Preliminary work (Zabetakis and Burgess 1961) suggests that the boil-off rate of LH_2 using crushed rock is double the rate for moist sand. Installing slats within the security fence that encloses the spill pond should help direct the hydrogen plume upward as it warms rather than letting it spread out over the ground. This kind of control, known as a vapor fence or barrier, has been used to reduce vapor travel of flammable cryogenic vapors such as liquid natural gas (LNG) (Moorhouse and Roberts 1988).

This information was used to set up a TRACE stack run for an 8-mph wind, but with input to simulate double the vaporization rate. It is assumed that ground travel of the plume is stopped by the combination of the pond and a 6-ft-high[14] slatted fence. A chimney effect lifts the plume off the ground at the pad, and the plume clears 25m approximately 25 m from the center of the pond. This is computed to occur within 18 s.
Results suggest that the hazard might be contained within the NFPA 50B-exclusion zone should the pond and slats work as predicted by TRACE.

2.4.3 Flash Fire Hazards

Hydrogen fire has several characteristics of note. Hydrogen flames, unless seeded with impurities, are very hard to see in daylight. This property, combined with its low emissivity (puts out very little infrared radiation), makes hydrogen combustion hard to sense until physical contact is made with the flame. Hydrogen combustion in air also produces ultraviolet (UV) radiation capable of producing effects similar to overexposure to the sun. Direct exposure to hydrogen flames produces immediate burns.

Hydrogen is so easily ignited that where it is released, one should expect or be prepared for ignition and fire. The dispensing equipment is designed to ASME standards that provide redundant protection in the case of fire. Small leaks may occur and ignite, but go unnoticed until maintenance personnel enter the secure area. Leaks from a pressurized line will present a greater hazard that may extend beyond the security fence (see Section 2.3.3.1.2). A pressurized leak, whether ignited or not, will be audible, even though hard to see. A plume of hydrogen that is ignited will rapidly flash back to the source of hydrogen. From the perspective of controlling hazards, hydrogen fire localized to a source or leak is often preferable to a growing hydrogen plume.

The worst-case scenario is a large plume that, if ignited, can burn personnel or initiate other fires in readily combustible materials. TRACE computations indicate the thermal flux from an ignited hydrogen-air mixture will range between 10 to 100 kW/m_2 for exposures at distances from tens of feet to near contact with the mixture. Combustion of a hydrogen cloud will occur completely within 1 to 2 seconds. There is not enough deposition of thermal energy to ignite typical materials of construction. Personnel caught in close proximity may be severely burned; and flammable liquids, if directly exposed, may be ignited.

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[14] Woods, Stephen. Telephone conversation with Donald Danyko (EPA) September 10, 2003. Computations were performed for a 2-m fence; however, for security reasons the height was increased to 10 ft, or approximately 3 m. This will further improve the “chimney” effect.

2.4.4 Deflagration and Detonation Hazards

Deflagration and detonation are two modes of hydrogen combustion capable of producing high temperatures, shock waves, and high overpressures. Table 1 lists some of the characteristics of deflagrations and detonations.

Both processes require confinement such as pipes, ducts, narrowly spaced walls, or large initiation energies to occur. Keeping the hydrogen dispensing system away from structures will give plumes from a large release a chance to rise. Both detonations and energetic deflagrations require the formation of mixtures of hydrogen and air that are close to stoichiometric. In the open air, powerful explosives or very large sparks[15] are required to initiate detonation. In the case of attack on the system, the explosives used in the attack are not considered initiation sources since they act before the hydrogen mixes with the air. Shorts that occur within the transformer of the EPA power substation may be sufficient to initiate detonation. Although TRACE and the NASA data predict hydrogen-air plumes will clear nearby structures, if a plume were to brush up against intake ducts, a potentially detonable mixture could form in a confined space. A process that might mitigate the formation of a detonable mixture is the dilution of the mixture (as make-up air) with air already in the building. Potential spaces outside include small courtyards. Hydrogen-air mixtures swirling in spaces with walls approximately 15 ft apart or less have produced significant overpressures when ignited.[16] TRACE computation of overpressure for combustion of a stoichiometric hydrogen-air mixture in free air indicated that pressures less than 0.1 psia would be produced.

Table 1
Deflagration and Detonation Characteristics

Characteristic	Deflagration	Detonation
Energy Transport Type	Diffusion of radical species	Shock wave
Flame Temperature	2045 °C (3713 °F)[a]	2674 °C (4845 °F)[a]
Flame Velocity	2.7-1294 m/s	> 1800 m/s
Rate of Pressure Onset	1 – 100 ms	2 – 20 ∝s
Range of Final Pressure to Initial Unburned Gas Pressure	1-8	15-20

[a] Values were computed for a stoichiometric mixture at 1 atmosphere and 300 K.

In summary, detonation or energetic deflagration is an unlikely outcome for a large hydrogen release if the system is located away from structures.

2.4.5 Fragment Hazards

Analysis of potential fragment hazards was conducted using the gas code PVHAZARD. The results are theoretical in nature and should not be taken literally except to see that, at the storage pressure used in the system, gas-propelled shrapnel can reach high velocities. The results are theoretical because the released energy is evenly partitioned between the pieces, as if the vessel or component simply shattered and all the potential energy was optimally converted into the kinetic energy of the shrapnel. The code analyzes only the pressurized component and does not include

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[15] Initiation source with energy of the order of 5000 Joules.

[16] Beeson, H. Communication concerning GASL accident investigation, August 2003.

the mechanical effects of the entire module structure. This is not realistic for components that meet ASME design criteria. For example, a lot of energy would be absorbed in bending and severing the metal and colliding with other system components. In addition, a lot of energy would simply be released in a shock wave and not accelerate shrapnel. Nonetheless, some shrapnel released in a component failure could attain the energies indicated.

The hazards noted here are not different in nature from the hazards in other areas where gas cylinders may be stored.

2.4.6 Summary of Release Hazards

The consequences of equipment failure, operational error, accidents, attack, or sabotage can be categorized as producing one of three types of releases: a leak; a penetration (or very large leak/jet); or a rupture (a rapid emptying of the containment). If the high-pressure portion of the system is involved, the hydrogen release may be accompanied by shrapnel. The division seeks to separate the consequences of the release into three increasing levels of potential hazard to the surroundings:

- Leaks may pose a hazard to adjacent system components or attending personnel directly exposed to combustible mixtures in the immediate vicinity of the leak. Here, the concern is for direct exposure to hot hydrogen reaction products.
- A penetration produces a larger release that can pose a hazard to the entire fueling system and personnel or equipment near the filling station. The concern includes not only direct exposure to hydrogen combustion over a larger area, but exposure to thermal and UV radiation capable of producing burns, minor shrapnel, and the potential for secondary ignition of station components or nearby materials.
- A rupture in the liquid storage system may pose a hazard to equipment and personnel in the greater vicinity of the fueling station, and threaten adjacent structures and public spaces located outside of the exclusion zone as specified by NFPA code. The most likely outcome from the threat is flash fire.

3.0 Conceptual Siting Design

The general requirements, code requirements, and site hazard analysis are examined to evaluate the several options for siting of the hydrogen dispenser system.

3.1 General Requirements Review

General requirements arise from considerations of functionality, safety, security, and cost. The primary functional requirement for the hydrogen dispenser system is that ready access be provided for the vehicles to be fueled and for the tanker truck to refill the station. Additionally, it is desired that the area given to the dispenser system be as small as possible and that dispensing operations have minimal impact on parking and surrounding EPA activities. The hydrogen dispensing system and associated operations should be safe, posing no risks greater than current EPA operations to the personnel, operations, existing facilities, and surrounding public. The dispensing station and associated operations should not compromise the level of security at the EPA facility. The EPA is responsible for providing the pad and power infrastructure for the hydrogen system equipment leased from APCI. The cost for the infrastructure and cost for its removal after the project is complete must not be excessive.

3.2 Code Requirements Review

At this time there are no codes or standards published that are specific to hydrogen dispensing stations to clarify siting requirements. However, a review of relevant existing codes and standards are provided here to help resolve siting issues.

3.2.1 General Considerations for Siting

A brief discussion of general safety issues as it pertains to siting is provided here as background.

3.2.1.1 Safety and Siting

Hydrogen safety issues can be summarized according to priority as follows:

- *Combustion*: Unplanned mixing of hydrogen and oxidizing substance results in fire, deflagration, or detonation.
- *Pressure*: System confinement fails, releasing high-pressure hydrogen or propelling fragments.
- *Low Temperature*: Inadequate design or improper maintenance leads to the use of inappropriate materials, leading to component failure.
- *Embrittlement*: Selection of materials susceptible to hydrogen attack leads to component or vessel wall failure.
- *Health*: Exposure of personnel to high concentrations of hydrogen, cryogenic temperatures, fires, overpressures, and shrapnel leads to injury or health hazards. Siting, or the determination of a safe exclusion zone for operations with hydrogen, is predominantly influenced by potential combustion and pressure hazards for a given hydrogen system. Proper siting reduces health hazards, while low-temperature and embrittlement concerns may figure among the causes of a system failure.

3.2.1.2 Approaches to Siting

Site planners have several options in choosing a basis for the determination of an exclusion zone. The simplest and most conservative approach is to consider the worst-case event conceivable and place all personnel, vulnerable equipment, and activities out of range of harm. From a military perspective, the worst-case events are overpressure and shrapnel. To facilitate siting determinations, the Department of Defense (DOD) has tabulated safe standoff distances for hydrogen used as a propellant[17] for military or aerospace applications. Another option is to determine siting according to the requirements of a relevant application-based standard. While there are currently few such standards for hydrogen systems, the standards for commercial storage of hydrogen are well known.[18] The primary assumption is that the intended use and design of the hydrogen system being sited reasonably match the assumptions inherent in the selected standard. The final option is to develop a rationale based on a study of potential releases of hydrogen and their related hazard scenarios. This rationale, usually documented through hazard analysis, must satisfy the authorities that would grant permission to operate the sited system.[19]

Often the determination of an exclusion zone to protect personnel and equipment is based on the traditional quantity-distance approaches to siting, where the quantity of an energetic material determines the size of an exclusion zone for safe operation. Separation distances are tabulated as a function of quantity. However, the nature of the hydrogen release, rather than the quantity or precipitating cause, has the greatest effect on siting.

3.2.2 Review of Mandatory Codes

The primary mandatory regulations that apply to the installation and operation of the proposed hydrogen dispensing station come from the Occupational Safety and Health Administration (OSHA), Code of Federal Regulations Title 29. Section 1910.103, *Hydrogen*, specifies the use of the following standards:

- NFPA 50A *Gaseous Hydrogen Systems at Consumer Sites*
- NFPA 50B *Liquefied Hydrogen Systems at Consumer Sites*
- NFPA 70 *National Electric Code*
- ASME BPV *Boiler and Pressure Vessel Code*
- ASME B31 *Code for Pressure Piping*

The requirements of OSHA 1910.119 (*Process Safety Management of Highly Hazardous Chemicals)* and Title III of the Superfund Amendments and Reauthorization Act (SARA) under Environmental Protection Agency apply only for systems that have 10,000 lb (16,900 gal) or more of hydrogen. The DoD-6055.9 document provides directives on the siting and storage of explosives and liquid propellants for aerospace purposes. Application of DoD directives to the hydrogen dispensing system is not appropriate, since the hydrogen dispensing system possesses criteria that more closely match a commercial storage system rather than a propellant system.

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[17] DoD 6055.9. *Ammunition and Explosives Safety Standards.*

[18] NFPA 50A, *Standard for Gaseous Hydrogen Systems at Consumer Sites*; and NFPA 50B. *Standard for Liquefied Hydrogen Systems at Consumer Sites.*

[19] This authority, or the authority having jurisdiction (AHJ), is usually an entity recognized by state and local authorities, such as the Fire Marshall.

3.2.3 Other Requirements, Standards and Guidelines

The USEPA NVFEL as a government facility retains authority over its facilities where other than federal codes are required. However, it is prudent practice to follow local and state codes where applicable, keep local government planners and officials aware of potential hazards, and coordinate with the Fire Marshall.

Compressed Gas Association (CGA) maintains a variety of standards that serve as a good reference for recommended practice in hydrogen operations. Examples include:

- CGA G-5 *Hydrogen*
- CGA G-5.4 *Standard for Hydrogen Piping Systems at Consumer Locations*
- CGA G-5.5 *Hydrogen Vent Systems*

3.3 Siting Review

The requirements for the siting options identified in Section 2.0 have been reviewed against code requirements and the findings of the hazard analysis and communicated to EPA.
Selected general NFPA 50A and 50B code requirements are given in Table 2.

Table 2
Selected NFPA Storage Guidelines

Type of Exclusion	Gas Storage (ft) NFPA 50A	Liquid Storage (ft) NFPA 50B
Places of Public Assembly	50	75
Ventilation Equipment	50	75
Inlet to Underground Sewers	-	5
Flammable Liquids	20 (above ground) 25 (below ground)	50
Oxidizers	-	75

4.0 Conclusions and Recommendations

System failures, whether caused by component failure, operational error, or attack, have been assessed for the quantity of hydrogen released and the severity of consequences. Several conclusions and recommendations are advanced to help ensure the overall successful use of hydrogen dispensing system on the NVFEL facility.

This analysis concludes that there are different safety implications for the three regions surrounding the hydrogen dispenser system. The security fence planned around the storage equipment defines the first region. The isolation it provides can protect outside personnel from small hydrogen leaks (likely through connections sometime during the life of the facility), and from normal, controlled hydrogen releases through the system vent. The inherent safety features of the vendor-supplied equipment meet accepted industry standards and should provide excellent service. A second region, as specified by NFPA 50B, is needed for further protection of personnel against larger releases, potential fire, and minor shrapnel due to component failure. While such events are deemed unlikely to occur during the period of use planned for the dispensing system, their occurrence could pose a hazard beyond the security fence. This review concludes that training of operations personnel and observation of the exclusion zone and other precautions specified by standard NFPA 50B will provide protection against moderate threats due to component failure.

Major component failure or significant damage caused by attack, while very unlikely, would feature the release of significant quantities of hydrogen or large pieces of shrapnel that could threaten areas beyond the NFPA 50B exclusion zone, which is defined as the third region. Among these hazards, the greatest concern is for flash fire. Against this possibility, the review of the NVFEL grounds conducted in April led to the recommendation of a specific site, which was communicated, to EPA. Further conclusions are that design features such as a spill pond with gravel, and a slatted security fence to act as a vapor barrier, will improve evaporation of liquid hydrogen and promote the upward movement of hydrogen vapor above nearby structures during a large spill. In summary, the storage and dispensing of hydrogen in the planned system does present hazards, but in the context of the NVFEL facility, the hazards involving hydrogen do not appear substantially different or new.

To best mitigate the identified hazards, the following recommendations are given:

- The security fence surrounding the system must be locked to exclude all but vendor maintenance personnel.
- The exclusion zone specified by NFPA 50B should be observed for protection against unplanned minor releases of hydrogen and shrapnel.
- To provide an additional margin of safety against an unlikely large release of hydrogen, it is recommended that the infrastructure provided for the equipment incorporate a spill pond with gravel and a vapor barrier.
- Safety information must be coordinated as necessary with NVFEL personnel, non-NVFEL personnel that may work in proximity to the dispensing system, the Fire Marshall and first responders, and local authorities.

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