PNNL-18570

U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
Under Contract DE-AC05-76RL01830

Safety Evaluation Report

Development of a Novel Efficient Solid-Oxide Hybrid for Co-generation of Hydrogen and Electricity Using Nearby Resources for Local Applications

Materials and Systems Research, Inc. (MSRI)
Salt Lake City, UT
February 17, 2009

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July 2009

Pacific Northwest
NATIONAL LABORATORY

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

Following a telephone interview with Materials and Systems Research, Inc. (MSRI)[1] by members of the Hydrogen Safety Panel on December 4, 2008, a safety review team was dispatched to Salt Lake City, UT to perform a site-visit review. The major topic of concern was the presence of a hydrogen storage and dispensing shed on the MSRI premises close to both its own laboratory/office building and to the adjoining property. The metal shed contains 36 cylinders (two 18-cylinder "pods") of hydrogen all connected to a common manifold and used to supply hydrogen to a U.S. Department of Energy (DOE) fuel cell project plus several other projects using an entire pod as a common supply. In busy times, MSRI uses and replaces one pod per week. As a result of the site visit, the safety review team has raised some concern with the shed's location, design, use, and safety features as well as other components of the facility, including the laboratory area.

Summary of Recommendations to MSRI

- The safety review team recommends that MSRI consider methods to mitigate a potentially dangerous sudden release of hydrogen from a cylinder or a pod of cylinders into the storage shed. One potential solution would be to retain the roof but replace the shed's solid walls with a chain-link fence enclosure. (*Recommendation 1, Section 3.1*)
- The safety review team recommends that MSRI consider performing routine periodic maintenance on the hydrogen system in the storage shed. This should include inspection for physical damage and/or leaks with attention to fittings and connections that are not brazed or soldered. MSRI should also consider using a more sensitive hand-held hydrogen detector rather than a liquid leak-detector for leak checks. (*Recommendation 2, Section 3.1*)
- The safety review team recommends that the piping system be designed either to contain the full cylinder pressure or relieve excess pressure in the event of a regulator failure. The relief device would be installed downstream of the regulator and should discharge to a safe location. (*Recommendation 3, Section 3.1*)
- The safety review team recommends that the project team inform the local fire department of the location of the shed and its contents. Additionally, an MSRI staff member should be designated as a liaison for interfacing with the fire department during emergencies. This individual should be knowledgeable in the operations and hazards of the hydrogen system as well as be familiar with the location of isolation valves and safety equipment. The response procedure, including the above responsibilities, should be included in the facility's emergency plan. (*Recommendation 4, Section 3.1*)
- The safety review team recommends that MSRI personnel and visitors not park within 15 ft of the shed. (*Recommendation 5, Section 3.2*)
- The safety review team recommends that bollards or some other means be provided to protect the shed and its contents from vehicular damage. (*Recommendation 6, Section 3.2*)

[1] DOE Hydrogen Program. Telephone Safety Interview Report. "Development of a Novel Efficient Solid-Oxide Hybrid for Co-generation of Hydrogen and Electricity using Nearby Resources for Local Applications." January 4, 2009.

- The safety review team recommends that MSRI consider the following steps to mitigate the risk of a hydrogen leak in the laboratory area:
    - Determine (perhaps through calculation) if the hood has adequate capture velocity for removal of flammable gases in the event of a large hydrogen leak. If it does not, then fire-retardant “curtains” enclosing the area under the canopy could be one solution.
    - Use excess flow valves at workspaces to reduce the risk of a localized fire.
    - Replace or modify the existing fail-open valve in the hydrogen line where it enters the building, with a fail-closed valve as a preferred choice.
    - Physically separate the fuel cell stacks from one another and from other equipment by using enclosures.
    - Relocate the fuel cell vents to a position high in the hood. (*Recommendation 7, Section 3.3*)
- The safety review team recommends that MSRI consider a means to limit or prevent people from walking under the canopy when there is a test in progress. (*Recommendation 8, Section 3.3*)
- The safety review team recommends that MSRI consider the implications/risks of the loss of ventilation in the laboratory. This would include installing an exhaust fan to avoid the potential for having hydrogen in the duct when the system restarts. (*Recommendation 9, Section 3.3*)
- The safety review team recommends that signage be placed at entrances stating that safety glasses must be worn in the laboratory, and this rule should be enforced. (*Recommendation 10, Section 3.3*)
- The safety review team recommends that MSRI consider adding National Fire Protection Association 45 (*Standard on Fire Protection for Laboratories Using Chemicals*), Chapter 8 (“Laboratory Ventilating Systems and Hood Requirements”) to its list of referenced standards. (*Recommendation 11, Section 3.4*)

Acronyms and Abbreviations

ASME	American Society of Mechanical Engineers
CGA	Compressed Gas Association
cu ft	cubic feet
DOE	U.S. Department of Energy
LFL	lower flammability limit
MSRI	Materials and Systems Research, Inc.
NFPA	National Fire Protection Association
OSHA	Occupational Safety and Health Administration

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1.0 Introduction

The U.S. Department of Energy's (DOE's) Hydrogen Program gives paramount importance to safety in all aspects of its research, development, and demonstration projects. The Hydrogen Safety Panel helps the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Office with integrating safety planning and practices into projects that address the production, storage, distribution, and use of hydrogen and related systems. Operated on behalf of DOE by the Pacific Northwest National Laboratory (PNNL),[2] the Panel conducts project safety reviews through site visits using an established protocol that emphasizes open discussion of safety practices and lessons learned. Working with the DOE project officer and the contractor's project team, a safety review team evaluates project safety practices and potential improvements and documents the results and recommendations in a report issued by PNNL to DOE.

Materials and Systems Research, Inc. (MSRI) is developing a solid oxide fuel cell/solid oxide fuel-assisted electrolysis cell hybrid system to cogenerate hydrogen and electricity. MSRI uses a solid oxide electrolysis system to produce hydrogen by steam methane reforming while the fuel cell component produces electricity. Areas of concentration include materials research and development, stack design and fabrication, and system design and verification.

2.0 Project Description

Members of the Hydrogen Safety Panel performed a telephone interview with MSRI on December 4, 2008. During the telecom, MSRI reported that the hydrogen it uses for this project was being stored in a shed (Figure 1) near its experimental facility and in quite close proximity to the fence-line on the adjoining property. The shed was reported to contain 36 cylinders of hydrogen in two 18-cylinder "pods." Both pods were connected to a common manifold within the shed, where a regulator reduced the hydrogen pressure to 30 psi into a stainless steel pipe to the building. The telephone interview report recommended that "**a site visit be made to MSRI to allow us to better understand the potential issues with the hydrogen shed.** A break in the common manifold could cause a release of 36 tanks of hydrogen at once. There is the potential that this could result in a hazardous situation – possibly a fire or even an explosion."

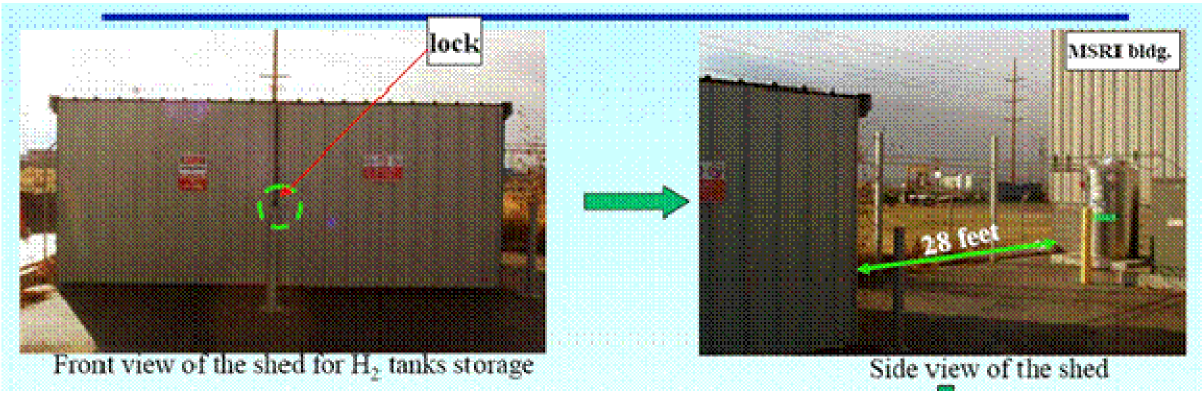

Figure 1. The MSRI shed

[2] Pacific Northwest National Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC05-76RL1830.

3.0 The Facilities

The safety review team held a site visit to MSRI focusing on the shed and hydrogen delivery system but also including the laboratory area. For this visit, the safety review team was not given detailed drawings of the shed. For a full list of attendees, please refer to Appendix A.

3.1 The Shed, Hydrogen Storage, and Usage

Sloping upward back to front, the shed has an internal volume of about 1700 cubic feet (cu ft) and is enclosed by metal walls, a roof, and doors. There are small openings between the wall and gaps around the doors. In addition, there are many flow channels in the shed ceiling (Figure 2) that, along with the sloping roof and the many gaps, allow adequate paths and locations for venting minor hydrogen leaks. These would be far from adequate, however, as a means to disperse a large, rapid release of hydrogen into an otherwise enclosed space.

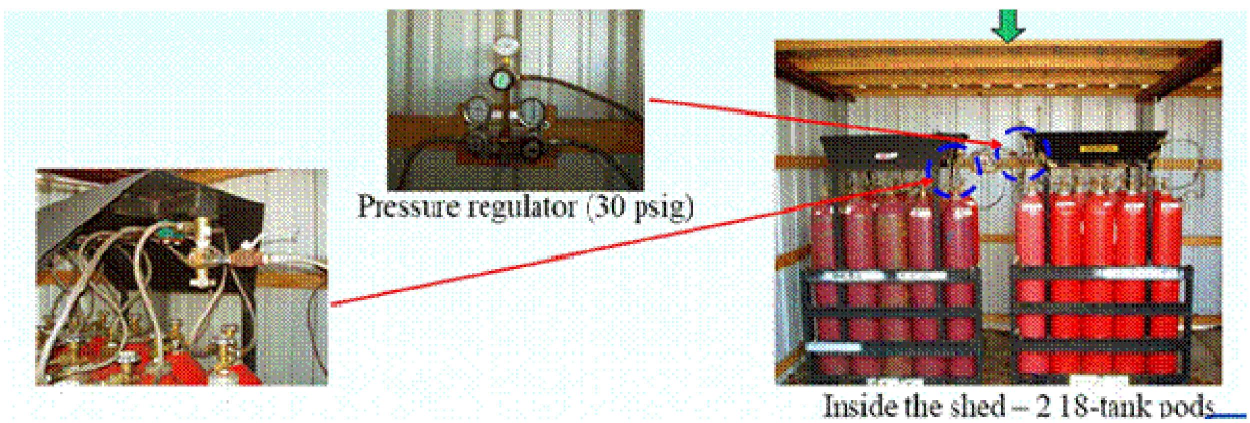

Figure 2. The inside of the shed, showing the pods, manifold, and hydrogen flow channels in the ceiling.

The shed contains 36 size T cylinders of hydrogen in two 18-cylinder pods connected to a common manifold/regulator. In addition, the shed provides storage for about 20 other cylinders. Visible labels indicate those cylinders that contain carbon monoxide, but the project team noted that most of these containers were empty. When full, each hydrogen cylinder contains 320 standard cu ft of hydrogen at 2400 psi. There are no automatic shutoff valves to isolate the pods. If the shutoff valves were installed, the potential hydrogen release would be reduced to the amount contained in one pod. However, 18 cylinders at 320 standard cu ft per cylinder are equal to 5760 standard cu ft of hydrogen, over three times the volume of the shed. Thus, a release of hydrogen from one pod could still present a significant problem.

Should a large hydrogen release occur, the shed's solid walls increase the risk in three ways. First, the walls will confine a hydrogen release and increase the size and duration of the flammable gas cloud. Second, should an ignition of the flammable cloud occur, confining walls could allow an explosion to develop with potentially dangerous pressures and an expanding fireball. Third, the walls and roof could become projectiles and increase the potential for personnel injury and damage to nearby equipment and facilities.

Although it did not perform detailed calculations, MSRI recognizes the fact that it has a potentially dangerous problem and needs to consider mitigation options.

- ***Recommendation 1.*** The safety review team recommends that MSRI consider methods to mitigate a potentially dangerous sudden release of hydrogen from a cylinder or a pod of cylinders into the storage shed. One potential solution would be to retain the roof but replace the shed's solid walls with a chain-link fence enclosure.

  MSRI: "MSRI plans to replace up to half of the shed's walls and door with chain-link fence material. The bottom half of the walls will be retained to reduce the accumulation of foreign matter."

  In a later phone conversation, MSRI mentioned two concerns that create difficulty with replacing the full height of the shed walls with chain link fencing: (1) frequent snowstorms with blowing snow; and (2) security. MSRI has had previous break-ins and has installed a security camera but remains concerned about possible theft or vandalism.

  Safety Review Team: The safety review team recognizes the limitations under which MSRI is operating. The removal of the top halves of the four walls of the shed will likely provide significant improvement to the virtually enclosed storage shed. If there is a hydrogen leak in the storage area, there is a reduced probability that the released hydrogen will remain confined by the half-walls for a sufficient amount of time for an explosion to occur. However, the level of confinement, over-pressurization, and potential damage would likely be higher if there were only chain-link fence walls.

  The safety review team also recommends that MSRI consult with the local building/fire code officials (or other authority having jurisdiction) to determine the codes and requirements applicable to the proposed modifications of the storage shed. These code officials could have specific interpretations or requirements that may impact these modifications (e.g., the code official may consider the hydrogen storage structure to be a building rather than just weather protection).

  National Fire Protection Association (NFPA) 55 does not appear to apply directly to this situation. Section 6.5.3 of that document states that "supports and walls shall not obstruct more than one side or more than 25 percent of the perimeter or storage area." It does not appear to address low or short walls.

Previously, MSRI actually stored hydrogen in its main building in an enclosed room. A few years ago, MSRI built the shed to mitigate risk.

Several on-site projects use hydrogen. During high-usage periods when hydrogen is flowing at about 30-40 standard liters per minute, MSRI consumes about a pod (18 cylinders) every week. It was noted that when a pod is changed, there exists the potential for high torque being placed on the manifold joint. MSRI estimated that hydrogen is used at that maximum rate for only two weeks each year; for approximately two months per year, MSRI consumes hydrogen at a lower rate (expressed as "up to 30 liters per minute"). "Almost always," MSRI operates on "button cell" fuel cell tests, consuming about 1 liter of hydrogen per minute. Despite the co-generation project ending in July, the shed will still be in use, and hydrogen usage patterns are expected to remain constant. Other hydrogen-based on-site projects generally use safety policies similar to what this project uses.

Hydrogen is delivered to the shed about once a week during the high-usage periods. MSRI Research Engineer Bruce Butler is almost always the individual who places the new pod in the shed and connects it to the manifold. On rare occasions, one of two trained technicians will perform this task, for which there is a written procedure. This procedure is attached as Appendix B.

The shed hydrogen supply to the testing laboratory is essentially never shut down. Lines are always left pressurized with hydrogen. The only time leak checks are performed is when hydrogen pods are replaced using Snoop®, a bubbling liquid leak detector. The leak checks are performed only in the shed, with no regular system-wide checks.

- ***Recommendation 2.*** The safety review team recommends that MSRI consider performing routine periodic maintenance on the hydrogen system in the storage shed. This should include inspection for physical damage and/or leaks with attention to fittings and connections that are not brazed or soldered. MSRI should also consider using a more sensitive hand-held hydrogen detector rather than a liquid leak-detector for leak checks.

  MSRI: "MSRI will continue to leak test with SNOOP for the present; a fugitive emission detector has been quoted and purchase is planned but is not an immediate priority. MSRI will continue to inspect removable fittings at the time of each hydrogen pod replacement. Other hydrogen distribution fittings (non-welded) will be visually inspected and tested with SNOOP monthly. When the fugitive emission detector is purchased, it will replace SNOOP as the method of validating hydrogen containment."

Another concern is that if the regulator failed, high-pressure hydrogen would surge through the system.

- ***Recommendation 3.*** The safety review team recommends that the piping system be designed either to contain the full cylinder pressure or relieve excess pressure in the event of a regulator failure. The relief device would be installed downstream of the regulator and should discharge to a safe location.

  MSRI: "MSRI has evaluated the location and cost of a potential pressure relief device and will incorporate such a device into the distribution system as soon as possible."

Compressed Gas Association (CGA) 5.5 (*Hydrogen Vent Systems*) and CGA 5.4 (*Hydrogen Piping Systems at Consumer Locations*) will be helpful standards to review.

There are no electrical connections or sources of heat or flame within the shed. Although static discharges are a possibility, the pods are equipped with grounding lines.

If there were a fire within or external to the shed, MSRI employees have been instructed to vacate the premises. The project team is unaware if local firefighters are informed about the large volume of hydrogen within the shed, which leads to the next recommendation.

- ***Recommendation 4.*** The safety review team recommends that the project team inform the local fire department of the location of the shed and its contents. Additionally, an MSRI staff member should be designated as a liaison for interfacing with the fire department during emergencies. This individual should be knowledgeable in the operations and hazards of the hydrogen system as well as be familiar with the location of isolation valves and safety equipment. The response procedure, including the above responsibilities, should be included in the facility's emergency plan.

  MSRI: "MSRI will take immediate steps to alert the local fire department of the contents of the hydrogen storage shed, and will include the fire department emergency on-site notification procedures in the MSRI response plan. A fire department liaison has been assigned."

3.2 Area Outside the Shed

Access to the shed is through a black-topped area that also serves as a parking lot for MSRI employees. On the day of the safety review team's site visit, there were four or five cars parked in this area, with one or two cars no more than 10 or 15 ft away from the shed. A hydrogen release could result in a jet fire, with vehicles parked in close proximity to the shed potentially causing a secondary fire location. Also, having vehicles parked in this area increases the risk of an accident between a vehicle and the shed. Finally, there is the possibility that the forklift used to replace hydrogen pods could accidentally be driven into the shed wall.

- ***Recommendation 5.*** The safety review team recommends that MSRI personnel and visitors not park within 15 ft of the shed.

  MSRI: "MSRI has implemented a parking policy which does not allow for parking within 20 ft of the hydrogen storage shed."

- ***Recommendation 6.*** The safety review team recommends that bollards or some other means be provided to protect the shed and its contents from vehicular damage.

  MSRI: "Additional barriers (bollards) to prevent vehicular impingement upon the hydrogen storage area have been investigated and cost evaluated. The barriers will be purchased and installed as soon as possible."

3.3 The Experimental Facility

Hydrogen from the shed is piped into the building through stainless steel tubing with standard welds.

An open area of approximately 30 sq ft in the main building contains an array of fuel cells, fuel cell components, and test equipment. A canopy vent-hood is located over the middle of the area covering about 15 by 10 ft. There are several hydrogen sensors in the area near the ceiling approximately 25 ft off of the floor.

If hydrogen is detected above 25 percent lower flammability limit (LFL), an alarm will sound. Above 50 percent LFL, it will trip an automatic shut-off valve, which turns off the hydrogen just inside the building. The valve, however, fails in the "open" position, which will prevent ruining some fairly costly experiments in the event electric power is lost. It is not as safe as a fail-closed valve.

The safety review team was concerned about the consequences in the laboratory if a joint broke and caused a hydrogen leak. The canopy hood does not provide a very strong updraft, and does not draw from the entire work area. Even if there were no injuries, a fire in the laboratory could result in a serious business interruption.

- ***Recommendation 7.*** The safety review team recommends that MSRI consider the following steps to mitigate the risk of a hydrogen leak in the laboratory area:
  - Determine (perhaps through calculation) if the hood has adequate capture velocity for removal of flammable gases in the event of a large hydrogen leak. If it does not, then fire-retardant "curtains" enclosing the area under the canopy could be one solution.
  - Use excess flow valves at workspaces to reduce the risk of a localized fire.
  - Replace or modify the existing fail-open valve in the hydrogen line where it enters the building, with a fail-closed valve as a preferred choice.
  - Physically separate the fuel cell stacks from one another and from other equipment by using enclosures.
  - Relocate the fuel cell vents to a position high in the hood.

MSRI: "MSRI has planned and will modify the testing area to include hood curtains to increase the effectiveness of the canopy ventilation system; MSRI will also install a flow verification device interlocked to the station gas supply to prevent flammable gas buildup in the ventilation system during a ventilation failure/power outage.

"MSRI also plans the replacement of the normally open solenoid valves with normally closed valves in the emergency gas shutoff system.

"MSRI does not plan on physically separating the fuel cell stacks from one another using enclosures in the immediate future.

"MSRI will vent all gases to appropriate locations in the collection hood."

In a later phone conversation, MSRI added that it investigated excess flow valves to reduce the risk for a potential fire at the workstations, but the pressure upstream of the regulators/valves that direct hydrogen to the various workstations is only 30 psi. MSRI is unable to find excess flow valves that activate at pressures as low as 30 psi.

Safety Review Team: Excess flow valves described by Advanced Specialty Gas Equipment at http://www.asge-online.com/PurValpg136.html appear to have the desired properties. Some show operating capabilities with inlet pressures as low as 10 psi.

- ***Recommendation 8.*** The safety review team recommends that MSRI consider a means to limit or prevent people from walking under the canopy when there is a test in progress.

  MSRI: "MSRI has and will continue to train all personnel to avoid entry into restricted testing areas unless they are authorized for such entry and have relevant tasks to perform in the area."

  Safety Review Team: It is a small group of workers, so it is reasonable to control access the way MSRI describes. Still, the safety review team suggests that alerts in the form of signs or "danger" tape in such areas are appropriate to remind personnel of restricted testing areas.

- ***Recommendation 9.*** The safety review team recommends that MSRI consider the implications/risks of the loss of ventilation in the laboratory. This would include installing an exhaust fan to avoid the potential for having hydrogen in the duct when the system restarts.

  MSRI: "See comment attached to Recommendation 7 (flow verification device)."

  Safety Review Team: MSRI seems to be saying that the H_2 flow to an experiment would be shut off if there were no air flow in the ventilation system. This approach would be a significant improvement but does not specifically address a leak upstream of the experiment's shutoff valve.

  The safety review team noted that there is no sign in the laboratory area cautioning personnel and visitors to wear safety glasses. During the tour of the area, neither the project team nor the safety review team members wore safety glasses.

- ***Recommendation 10.*** The safety review team recommends that signage be placed at entrances stating that safety glasses must be worn in the laboratory, and this rule should be enforced.

  MSRI: "MSRI will enforce safety policy regarding protective gear in the laboratory (especially protective eyewear)."

During the conference call, one of the safety review team's concerns was that Inconel nickel alloys were being used in areas where it would be exposed to hydrogen and perhaps become embrittled. The site visit discussion clarified that Inconel was being used only for support plates and rods for the fuel cell stacks, not for a stack component itself. The use of Inconel is no longer considered to be a potential safety issue for this project.

3.4 Codes and Standards

MSRI adheres to the following codes and standards for the shed and experimental facility:

- NFPA 55 (*Standard for the Storage, Use, and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders, and Tanks*)
- NFPA 70 (*National Electrical Code®*)

- NFPA 853 (*Standard for the Installation of Stationary Fuel Cell Power Systems*)
- American Society of Mechanical Engineers (ASME) B31.3 (*Standards of Pressure Piping*)
    - An independent contractor performed installation of process piping.
    - Gas pods and pod manifolds are the property and responsibility of Praxair.
- Occupational Safety and Health Administration (OSHA) 1910.103 (*Occupational Safety and Health Standards: Hydrogen*)

- ***Recommendation 11.*** The safety review team recommends that MSRI consider adding NFPA 45 (*Standard on Fire Protection for Laboratories Using Chemicals*), Chapter 8 ("Laboratory Ventilating Systems and Hood Requirements") to its list of referenced standards.

  MSRI: "MSRI will study and include pertinent information from NFPA 45 in its laboratory safety policies and procedures."

4.0 Project Team Questions and Comments

MSRI's major concern is that there are too many scattered codes and standards, making emergency referencing difficult. The safety review team mentioned that NFPA 2 will condense much of the well-distributed information. Even then, references will be made to other documents. The suggestion was also made to access http://h2bestpractices.org for more information. Nevertheless, the safety review team admitted there is no simple answer: one has to pick and choose the codes and standards that one purchases and uses.

Appendix A

MSRI Site Visit Safety Review

Appendix A

MSRI Site Visit Safety Review

MSRI:

Greg Tao, Research Scientist; Principal Investigator, MSRI
Bruce Butler, Research Engineer, MSRI

Safety Review Team:

Don Frikken, Becht Engineering, Hydrogen Safety Panel Member
Nick Barilo, Pacific Northwest National Laboratory, Panel Technical Support
Ed Skolnik, Energetics Incorporated, Panel Technical Support, Team Leader

Appendix B

MSRI Procedure for Placement and Attachment of New Hydrogen Pods in the Shed

Appendix B

MSRI Procedure for Placement and Attachment of New Hydrogen Pods in the Shed

H_2 POD CHANGING PROCEDURES:
(AUTHORIZED MSRI EMPLOYEES ONLY)

1. Point the regulator on the pressure manifold to the full side.
2. Close primary lever valve on empty pod.
3. Close primary rotary valve on empty pod.
4. Close valves on all 18 individual cylinders (empty pod).
5. Using wrench, disconnect reinforced hosing from empty pod.
6. Remove pod grounding clamp from grounding cable.
7. Replace empty pod with full pod.
8. Clamp new pod grounding clamp to grounding cable.
9. Attached reinforced hosing to new pod. Tighten snugly with wrench; DO NOT OVERTIGHTEN.
10. Open valves on individual cylinders.
11. Open primary rotary valve.
12. Use SNOOP® or other leak detecting fluid to inspect new threaded fitting for leaks.
    a. If leak is detected, close individual cylinders and primary valve, remove hose and check threads and sealing surfaces for damage or foreign materials.
    b. If damaged, DO NOT RE-ATTACH. Contact Praxair for service.
    c. If dirty, remove foreign material. Reattach, open cylinders and primary (non-lever) valve, and recheck for leaks.
13. Open primary lever valve.
14. Lock shed.

Authorized Personnel:

I have read and understand the above operations, and affirm that I will adhere to established MSRI procedures during hydrogen cylinder (H_2 pod) replacement.

Name:	Signature:	Date:
Bruce J. Butler	______________________	______________
F. Marshall Thompson	______________________	______________
Michael King	______________________	______________

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