III.15 Hydrogen Regional Infrastructure Program in Pennsylvania*

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Subcontractors:
- Air Products and Chemicals Inc. (APCI), Allentown, PA
- Resource Dynamics Corporation (RDC), Vienna, VA
- HyPerComp Engineering Inc. (HEI), Brigham City, UT
- Savannah River National Laboratory (SRNL), Aiken, SC
- ASME International (ASME), New York, NY

Start Date: September 1, 2004
Projected End Date: January 31, 2009

*Congressionally directed project

Objectives

- Pennsylvania Hydrogen Delivery Studies and I-95 Corridor
  - Determine Pennsylvania's (PA) economic delivery scenarios using regional cost of indigenous energy resources using the Department of Energy (DOE) H2A model.
  - Assess the feasibility of a hydrogen infrastructure along the I-95 Corridor.
- Steel Pipeline/Composite Overwrapped Pressure Vessels
  - Facilitate DOE's pipeline working group (PWG) round robin testing (RRT) of pipeline steels in hydrogen through material procurement, specimen machining, procedure coordination, test observation and documentation and characterize low carbon steel pipeline material properties by conducting mechanical testing in high pressure hydrogen.
  - Improve composite overwrapped pressure vessels (COPV) design and fabrication methods to concurrently target DOE cost and volumetric efficiency goals for off-board gaseous hydrogen storage and monitor progress of United States COPV standards development and support data collection through mechanical testing of relevant composite materials.
- Separations/Sensors
  - Design a low-cost Rapid Pressure Swing Adsorption (RPSA) system capable of achieving hydrogen purity greater than 99.99% and quantify the state of technology for novel adsorbents using experimental and numerical methods.
  - Advance current hydrogen-specific sensors and sensor technologies to ensure reliable operation and performance in hydrogen applications.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Delivery Section (3.2.4) [1] of the DOE's Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (MYRD&DP):

(A) Lack of Hydrogen/Carrier and Infrastructure Options Analysis
(D) High Capital Cost and Hydrogen Embrittlement of Pipelines
(F) Gaseous Hydrogen Storage and Tube Trailer Delivery Costs
(G) Storage Tank Materials and Costs
(I) Hydrogen Leakage and Sensors
(J) Other Refueling Site/Terminal Operations
(K) Safety, Codes and Standards, Permitting

Technical Targets

The Hydrogen Regional Infrastructure Program in Pennsylvania project is conducting research in multiple areas. Insights gained from these studies are being used to address the following technical targets detailed in the Hydrogen Delivery section of the MYRD&DP:

- Pennsylvania Hydrogen Delivery and the I-95 Corridor
  - DOE's 2015 target of $2.00-$3.00/gasoline gallon equivalent (gge) at the pump (delivered, untaxed) for hydrogen.

- Steel Pipeline/Composite Overwrapped Pressure Vessels
  - Storage tank purchased capital cost ($/kg of hydrogen stored): $500 (2010), $300 (2015).
  - Volumetric capacity (kg hydrogen/liter of storage volume): 0.030 (2010), >0.035 (2015).
- Separations/Sensors
  - Hydrogen purity > 99.99%.
  - Hydrogen leakage (% of hydrogen leakage from pipeline): <0.5% (2017).

Accomplishments

The following items are accomplishments to date for the Hydrogen Regional Infrastructure Program in Pennsylvania project:

- Pennsylvania Hydrogen Delivery and the I-95 Corridor
  - Completed the study on indigenous feedstocks for PA hydrogen production case study, including coal, biomass, biogas (landfill methane manure sewage treatment plants), electricity (renewable and nuclear) and evaluated the cost of hydrogen from each of these feedstocks. Biogas emerged as a potential low-cost option for hydrogen production. Coal remains the lowest cost option in PA at higher demand levels.
  - Completed the initial study of the Northeastern I-95 Hydrogen Corridor focusing on the 1%, 10%, and 30% current population of light-duty vehicles (LDVs) fueled by hydrogen.
- Steel Pipeline/Composite Overwrapped Pressure Vessels
  - Procured X52 and X100 pipeline for PWG RRT; machined, inspected and distributed tensile specimens to multiple national labs; completed RRT procedural guidelines and test matrix.
  - Accumulated tensile, fracture toughness and threshold stress intensity data for low-carbon steel pipeline tested in high pressure hydrogen.
  - Confirmed heat affected zone (HAZ) tensile performance is affected most by presence of hydrogen, followed by weld metal, and base metal respectively.
  - Fabricated, burst tested, and fatigue tested twelve Type III COPVs and twelve Type II COPVs and demonstrated weight efficiency for Type III COPV and cost efficiency for Type II COPV.
- Separations/Sensors
  - Determined, via experimental analysis in the RPSA unit, that the mass transfer rate for a small beaded adsorbent can be increased by a factor of 3-4 by reducing particle size. Simulations suggest that a rapid cycle pressure swing adsorption with this adsorbent, would meet the technical goals of this work.
  - Conducted breakthrough experiments using formed adsorbents which indicate that certain structures have the potential to be competitive with packed beds.
  - Achieved successful contaminant mitigation (i.e., sulfur, carbon monoxide, and internal sensor leakage) of a palladium field effect transistor with the manufacturer and initiated intrinsically safe certification efforts with manufacturer of the palladium field effect transistor.

Section 1: Pennsylvania Hydrogen Delivery and the I-95 Corridor

Introduction

CTC focused on PA indigenous resources and the I-95 Corridor, with analytical support from RDC. The research being conducted builds upon the Phase I trade-off study on the most economically feasible hydrogen delivery scenarios based on population density, existing natural gas pipelines, broad resource categories, production technologies, and transport capabilities using the DOE H2A model. The objectives of this project are to determine the lowest cost solution for delivered hydrogen throughout PA and along the I-95 Corridor by capitalizing on indigenous energy sources and strategic locations.

Approach

To identify the lowest cost solution for delivered hydrogen throughout PA, the project team is assessing the most economically feasible production location/method and delivery methods, and the tradeoffs between these methods using the H2A model. This project is examining developed and underdeveloped indigenous energy resources, coal, biomass, biogas (landfill methane, manure sewage treatment plants), electricity (renewable and nuclear).

The I-95 Corridor work examines the major metropolitan statistical areas (MSAs) along the northeastern I-95 Corridor for hydrogen infrastructure needs under three progressively increasing demand scenarios, including 1%, 10%, and 30% of the current population of LDVs fueled by hydrogen. In these demand scenarios, prominent demand centers were identified and are used to define volume and distance

relationships. These values are subsequently used as input to a robust life cycle cost analysis using the DOE H2A model comparing a multitude of hydrogen production and transportation options. Future work will use the same method, but focus on transition phases using multiple use sites.

Results

Phase I of the project focused on identifying the viable resources and analyzing various scenarios with coal. Bituminous coal was found to be very prevalent in western PA and could easily provide 100% LDV demand. Coal also could provide 19 times more hydrogen compared to the next resource. However, during the initial phases of hydrogen production, biogas may be the lowest cost option, especially if this "green" natural gas used the existing natural gas pipeline infrastructure. CTC explored this option with natural gas distribution companies and determine that this option is feasible (Figure 1).

In regards to the I-95 Corridor work, the research has focused on characterizing the corridor and running looking at delivered costs. Through research, the I-95 Corridor was found to be the worst concentrated carbon dioxide source on the east coast and includes many ozone non-attainment areas. The corridor also contains several densely populated areas, 13% of U.S population in less than 1% of land and 22 million LDVs (15% of the total market). The 1st, 7th, 11th, and 19th largest MSAs within the United States are also located along the I-95 Corridor (Figure 2). Combining various MSAs (such as Philadelphia and Trenton) will lower the delivery cost of hydrogen during the initial phase, but not in higher demand phases. The research also found that total delivery cost for MSAs along the I-95 Corridor are between $3.00/kg - $4.00/kg at the 30% level and lower delivery costs are realized with increased demand scenarios and combined MSAs (Figure 3).

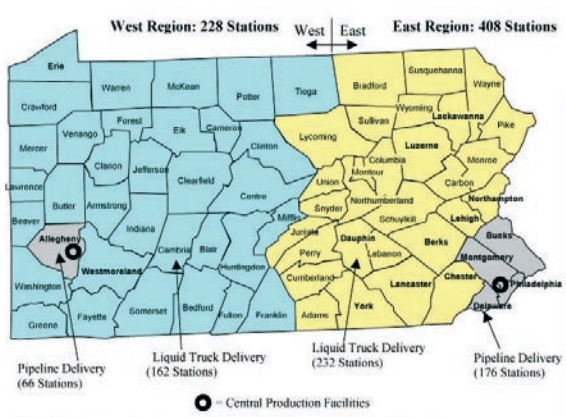
Conclusions and Future Directions

Biogas emerges as a lowest option for lower demand levels, suggesting that a renewable source, not a fossil fuel, may be the lowest option for hydrogen production in specific regions. This demonstrates that evaluating all options is important and may require state incentives to stimulate investment in renewable hydrogen (i.e. incent biogas cleanup for use for transportation fuels rather than power generation). Coal still remains an important option in PA. No future work is planned related to the PA Indigenous Energy Project.

Pennsylvania Indigenous Energy Study - Phase II Results

Two large central plant option

- Biogas emerges as an important feedstock in early demand scenarios
- Coal is the most economic feedstock for the Pennsylvania hydrogen economy at higher demand levels
- Lowest delivered cost for 1% LDV penetration is $4.28/kilogram (kg) using biogas and pipeline distribution for the East Plant and natural gas for the West Plant.
- Lowest delivered cost for 30% LDV penetration is $4.13/kg using central production, coal gasification, and a combination of pipeline and liquid truck delivery
- Generally, if carbon is sequestered, an increased cost is realized



30% Demand Scenario with Two Central Plants

		1% LDV		10% LDV		30% LDV	
		East Plant	West Plant	East Plant	West Plant	East Plant	West Plant
	Plant Size (kg/day)	74000	19000	428000	239000	1283000	718000
NO CARBON REGULATION	Lowest Delivered Cost ($/kg)	4.28	4.61	3.64	4.13	3.40	3.57
	Production and Delivery Method	Central Station Biogas (LFG and ADG); Pipeline Distribution	Distributed Natural Gas	Central Station Biogas (LFG and ADG); Pipeline Distribution	Central Station Coal Gasification; Pipeline/Liquid Distribution		
LOW CARBON	Lowest Delivered Cost ($/kg)	4.28	4.61	3.64	4.48	3.77	3.88
	Production and Delivery Method	Central Station Biogas (LFG and ADG); Pipeline Distribution	Distributed Natural Gas	Central Station Biogas (LFG and ADG); Pipeline Distribution	Central Station Coal Gasification w Seq; Pipeline/Liquid Distribution		

FIGURE 1. Final Results, PA Indigenous Energy

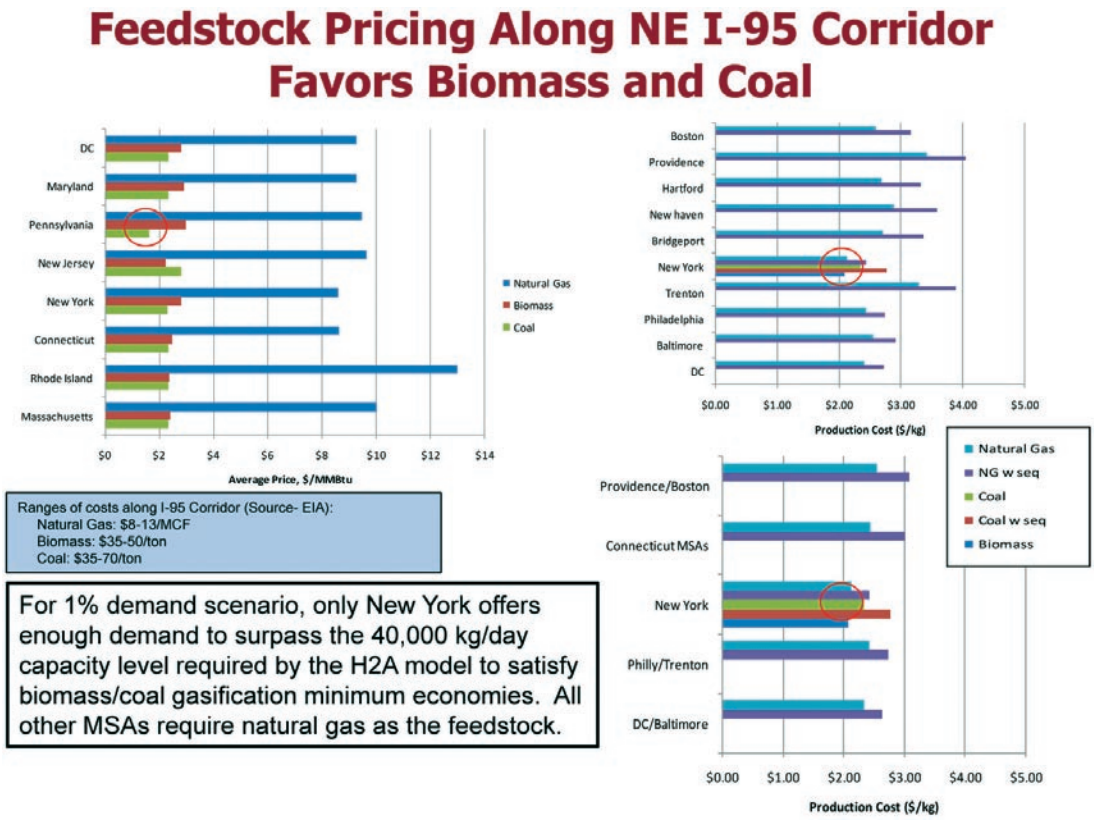


FIGURE 2. Final Delivered Hydrogen Costs, Northeastern I-95 Corridor

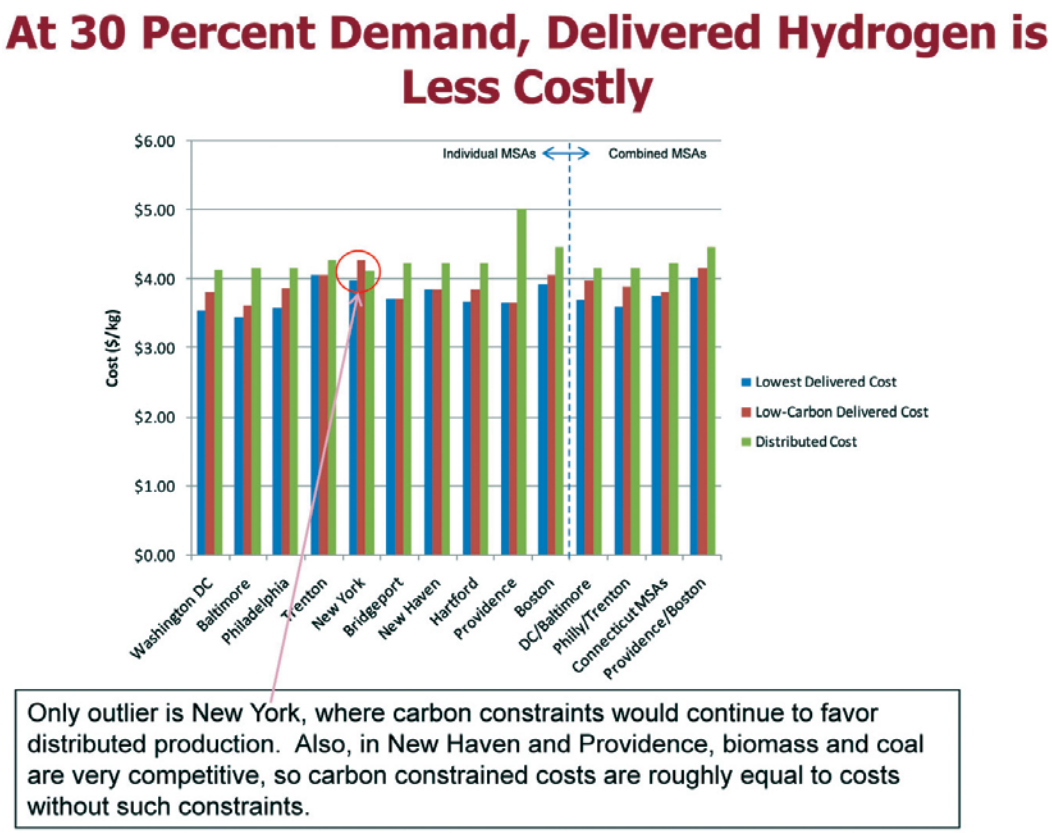


FIGURE 3. Effect of Combined MSAs on Delivered Hydrogen Cost

When demand builds to more modest levels, delivered costs approach the $3/kg DOE goal and compare with current gasoline prices. With hydrogen costs approaching the DOE cost target in the long term but still high in the near-term, the focus of the study recommendations was on the near-term cost reductions. Opportunities to improve upon the near-term hydrogen costs using conventional technology center on two potential improvements:

1. **Increase Hydrogen Production Volume.** Significant opportunities may be an option when siting refueling stations where there are additional hydrogen demands. These opportunities may increase hydrogen demand by sitting at or near, forklifts in warehouse, replacing battery usage, transmission load pockets where hydrogen can provide local power generation, reducing the demand on constrained local utility transmission and distribution facilities, fleets as a first adopter of hydrogen vehicles, airports, looking at hydrogen tugs and other hydrogen vehicles, and military installations and their possible need for hydrogen.

   In doing so, lower initial hydrogen costs may be attained as the on-site production volumes would be appreciably higher and economies of scale more favorable. The next phase of this work will focus on this potential.

2. **Decrease Feedstock Costs.** Some portions of the I-95 Corridor are rich in indigenous energy resources which could be used to supplement or replace natural gas in certain areas and possibly lower the delivered cost of hydrogen.

Section 2: Steel Pipeline/COPV

Introduction

The use of hydrogen as an energy carrier requires both delivery and storage. One potential delivery path is to transmit hydrogen through pre-existing steel pipelines, but the effects of hydrogen on the mechanical properties of the pipeline materials over time and at high pressure are not completely known. Accordingly, CTC facilitated the mechanical testing (tensile, fracture toughness and threshold stress intensity specimens) of a representative steel pipeline in 1,500 pounds per square inch (psi) hydrogen with SRNL. CTC requested and was granted the role of facilitator for RRT among the DOE's PWG member national laboratories. In that capacity, CTC has coordinated material procurement, machining and distribution of nominally identical test specimens, establishment of uniform test procedures, and documentation of the test results.

To address off-board hydrogen storage, CTC worked with HEI to engineer COPVs that are cost-effective and volumetrically efficient. COPVs are intended for use in applications such as fueling station storage.

Approach

Three main activities are being conducted under the Steel Pipeline subtask. CTC is participating in the DOE's PWG and interfacing with the ASME to assess and prioritize pipeline material mechanical test data requirements. CTC is also addressing a portion of those needs by facilitating and coordinating mechanical testing of pipeline steels in hydrogen with SRNL. Finally, the data being generated under those activities will be distributed to the hydrogen test community via publication.

To advance the state-of-the-art in off-board hydrogen storage, CTC teamed with HEI to model, design, construct and test COPVs. The second phase of COPV development, which concluded in Fiscal Year 2008, developed prototype Type II COPVs that realized significantly reduced costs relative to the first phase (Type III COPV) effort. Cost and volumetric efficiency are the DOE's primary goals for off-board hydrogen storage.

Results

Steel pipeline specimens extracted from base metal, HAZ, and weld metal locations were subjected to tensile, fracture toughness and threshold stress intensity testing in 1,500 psi hydrogen at SRNL. The tensile tests revealed the effects of high pressure hydrogen are most pronounced on the HAZ material, with a lesser effect on weld metal and only a modest impact on base metal specimens. Fracture toughness testing indicated a marked reduction of base metal and HAZ specimens in 1,500 psig hydrogen, relative to air, but the weld metal used for this testing displayed no adverse effects of the hydrogen. No crack growth was observed in any of the threshold stress intensity specimens loaded to approximately 12 ksi for more than 3,300 hours in 1,500 psig hydrogen (Figure 4).

Results of the Type III (i.e., aluminum-lined) COPV prototype development were reported last year. In this year's (FY 2008's) efforts, Type II (i.e., steel-lined) COPV prototypes were designed, produced and tested. Four each of the 15 liter capacity Type II COPVs were subjected to burst, fatigue, and post-drop fatigue. The mean results were 15,640 psi; 9,054 cycles at 8,375 psi; and 7,730 cycles at 8,375 psi; respectively. The cost and volumetric efficiencies were determined to be $642/kg stored hydrogen and 0.0292 kg hydrogen/liter COPV volume, both approaching the DOE's 2010 targets for off-board storage.

FIGURE 4. Fracture Toughness Specimen Tested in Air

Conclusions and Future Directions

The PWG RRT has already aided in streamlining test procedures among the participant national laboratories. Tensile testing of nominally identical specimens at two of the labs continues, to be followed by a third when those facilities are completed in late 2008/early 2009. A summary of the testing to date will be provided at a workshop in September 2008. Following the conclusion of tensile testing, CTC will continue to support the PWG according to the DOE's direction.

CTC worked closely with SRNL to characterize the tensile, fracture toughness and threshold stress intensity performance of steel pipeline material systems in 1,500 psi hydrogen. The results of the tensile testing were documented and shared with the PWG to address hydrogen embrittlement issues. Results of the fracture toughness and threshold stress intensity tests will be documented in a future deliverable report.

In FY 2008, CTC and HEI designed and tested Type II COPVs for off-board gaseous hydrogen storage. Those non-optimized tanks, which incorporated commercial-off-the-shelf steel liners, reduced the pressure vessel cost, relative to previous (FY 2007), Type III COPV efforts. The results of both COPV development phases were documented in deliverable reports and via an invited poster at the 2008 DOE Annual Merit Review.

Section 3: Separations/Sensors

Introduction

As part of this project, two areas are being researched to facilitate reducing the cost and increasing the safety and reliability of distributed hydrogen production. These areas are advanced separation technologies and improved hydrogen-specific sensors for field application. The improved hydrogen-specific sensors work was completed in November 2007 and will not be pursued as part of the Phase III work.

Approach

CTC has teamed with APCI to extend research in adsorbent technologies for hydrogen purification/separation to determine the limits of conventional adsorbent technology versus next-generation adsorbents and identify under what conditions (size, flow rates, and pressures) a hydrogen purifier has favorable cost and technical performance.

Work was also completed to control or eliminate the effects contaminants have on a palladium field transistor. Contamination exposure times and levels of exposure must be large enough to satisfy routine maintenance schedules and not be a burden on users' time. As part of this contaminant mitigation work, the work focused on sulfur mitigation, sensor leakage, and carbon monoxide mitigation concerns. Design modification recommendations were made to the sensor manufacturer to improve the performance of the sensors in regards to contaminant mitigation. The manufacturer made the recommended changes, and prototypes of the modified sensors were tested at the APCI facility to determine if the changes had the desired effect.

Results

Adsorbent evaluation in a RPSA test unit was the main focus of the separations work over the past year, including evaluation of both beaded and structured adsorbents. To conduct the beaded adsorbent evaluations, process simulations were first conducted using a computer simulation program to estimate the limits of small beaded adsorbents in a packed bed. The results showed that varying the bed and adsorbent geometry (e.g., bed length, diameter, adsorbent diameter) and the process cycle conditions (e.g., cycle time, purge amount) can greatly impact the efficiency of the RPSA unit and bed pressure drop. Next, various beaded adsorbents were evaluated in the RPSA test unit to help validate the process simulations. Equilibrium capacity and mass transfer rate were used to prioritize the adsorbents for testing in the RPSA unit. Eleven different

backed bed columns were evaluated on the RPSA test unit. Three of them exhibited a high performance in the test unit and are good candidates for use in the Phase II work. Various structured adsorbents were also evaluated as part of this work. Currently their performance is inferior to the performance of the beaded adsorbents. Initial theoretical analysis suggest that structured monoliths with >1,000 cells per square inch (cpsi) have the potential to be competitive with the packed bed. This is the direction further structured monolith work should drive towards.

As part of the sensors work, performance testing was conducted on the modified palladium field capacitor to determine if the modifications produced the desired effect in regards to contaminant mitigation. To reduce the effect of sulfur degradation it was recommended that the sensor manufacturer increase the thickness of the palladium coating. Follow-on testing of the sensor at APCI showed that the changes made by the manufacturer did eliminate the sulfur degradation. During the sulfur degradation testing, it was observed that the sensor and sensor housing showed considerable leakage of the test gases. Modifications were made by the manufacturer to improve the internal sealing mechanism between the sensor and the sensor housing. Follow-on testing showed that these modifications eliminated the leakage observed. The response time of the palladium field transistor in the presence of high levels of carbon monoxide was also explored during Phase II. The test results indicate that the sensor does show some equilibration response effects from carbon monoxide at high concentrations. The results also show that the coated sensors do not seem to have a significant carbon monoxide effect on initial response compared to uncoated sensors.

Conclusions and Future Directions

During the Phase III work, the selected beaded adsorbents will be fully developed and characterized. A series of single bed cyclic RPSA tests will be conducted to provide process data for adsorption parameter regressions. The multi-bed process performance will also be optimized through modeling and experimental work. Verification will be done using a modified hydrogen pressure swing adsorption Process Development Unit (PDU) which will provide process performance data under realistic operating conditions. Additional structured adsorbent modules will be constructed and tested in the lab and compared to the performance of small bead adsorbents in the single bed RPSA unit. If warranted, these modules will also be tested in the hydrogen pressure swing adsorption PDU. Finally, a preliminary design for a 5 normal meter^3/hour (Nm^3/hr) device will be developed from which costs, performance, and market attractiveness will be estimated. Guidelines for scaling up the device to higher flow rates will be provided as well as technology risks and future research needs to scale-up the device to projected commercial 500 Nm^3/hr and greater hydrogen production rates.

The sensors work was completed at the end of Phase II for this project. The possibility of developing a complete hydrogen analyzer using the input of a sensor manufacturer including remote monitoring was discussed as a possibility for the Phase III work. However, insufficient funding existed to complete this work.

FY 2008 Publications/Presentations

1. Eileen M. Schmura and Paul L. Lemar Jr., I-95 Hydrogen Corridor Hydrogen Delivery Tradeoff Study, Hydrogen Community of Interest, Washington, DC (March 2008).

2. Eileen M. Schmura, Paul L. Lemar, Jr and Sarah Largent, *Pennsylvania Indigenous Energy Hydrogen Delivery Tradeoff Study*, NHA Annual Hydrogen Conference 2008, (April 2008).

3. Paul L. Lemar Jr. and Eileen Schmura, *Development of the I-95 Hydrogen Roadway*, NHA Annual Hydrogen Conference 2008, Sacramento, CA (April 2008).

4. Eileen M. Schmura and Paul L. Lemar Jr., I-95 Hydrogen Corridor Hydrogen Delivery Tradeoff Study, SESC Worldwide Energy Conference, Washington, D.C. (April 2008).

5. Vladimir M. Shkolnikov, Serviceability Characterization of Composite Storage Tanks, 2007 ASME Pressure Vessels and Piping Division Conference, San Antonio, TX (July 2007).

6. Kevin L. Klug, Pipeline and Pressure Vessel R&D under the Hydrogen Regional Infrastructure Program In Pennsylvania, DOE Hydrogen Pipeline Working Group Meeting, Aiken, SC (September 2007).

7. Kevin L. Klug, Round Robin Testing Update, DOE Hydrogen Pipeline Working Group Meeting, Livermore, CA (February 2008).

8. Kevin L. Klug and Michael Olson, Cost Efficient Off-Board Tank Storage for Compressed Hydrogen Gas, NHA Annual Hydrogen Conference 2008, Sacramento, CA (April 2008).

9. Vladimir M. Shkolnikov, Analytical Technique for Composite Storage Tank Design Factor Specification, NHA Annual Hydrogen Conference 2008, Sacramento, CA (April 2008).

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1. DOE, "Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan," April 27th, 2007.