Eltron Research & Development

Report on all ARRA Funded Technical Work
Topical Report

Reporting Period: 10/1/2010 - 6/19/2013

Report Issued: October 4, 2013

DOE Award Number: DE-FC26-05NT42469

Eltron Research & Development, Inc.
4600 Nautilus Court South
Boulder, CO 80301-3241
303-530-0263

TABLE OF CONTENTS

Page

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

I. Abstract

The main focus of this American Recovery and Reinvestment Act of 2009 (ARRA) funded project was to design an energy efficient carbon capture and storage (CCS) process using the Recipient's membrane system for H_2 separation and CO_2 capture. In the ARRA-funded project, the Recipient accelerated development and scale-up of ongoing hydrogen membrane technology research and development (R&D). Specifically, this project focused on accelerating the current R&D work scope of the base program-funded project, involving lab scale tests, detail design of a 250 lb/day H2 process development unit (PDU), and scale-up of membrane tube and coating manufacturing. This project scope included the site selection and a Front End Engineering Design (FEED) study of a nominally 4 to 10 ton-per-day (TPD) Pre-Commercial Module (PCM) hydrogen separation membrane system. Process models and techno-economic analysis were updated to include studies on integration of this technology into an Integrated Gasification Combined Cycle (IGCC) power generation system with CCS.

Project objectives included:

- Accelerate design, construction, and operation of Eltron's 250 lbs/day PDU.
- Develop and implement fabrication techniques and establish economics for scale-up of membrane manufacturing.
- Design, construct, and operate a Pre-Commercial Module to confirm hydrogen transport membrane benefits for efficient and cost-effective CCS from carbon based fuels.

Project accomplishments included:

- Membrane fabrication was scaled up to ten foot long membrane tubes
  - Eltron worked with two vendors to produce substrate tubes.
  - Eltron demonstrated deposition of catalyst on the inside and outside surfaces of ten foot long tubes. The process developed by Eltron was then transferred to two commercial vendors for large scale production of membrane tubing.
  - Welded membrane substrate tube seals were developed and tested under expected operating conditions.
- Three potential sites for operation of the PDU and PCM were evaluated.
- A Pre-FEED engineering analysis was completed on the down-selected site. The entire Pre-FEED package was provided to the federal program manager for review in the first quarter of 2012.
- Designs for the 250 lbs/day PDU reactor and membrane module were completed and issued for construction bids.
- A FEED package was initiated, but not completed for the PCM.

Quarterly Milestones Achieved:

Quarter	Milestone(s)
FY11 Quarter 1	Identify potential sites for PCM operation.
FY11 Quarter 2	Down-select sites for Pre-FEED engineering analysis.
FY11 Quarter 3	Complete preliminary process flow diagram based on site requirements.
FY11 Quarter 4	Complete Pre-FEED engineering package. Initiate plan for accelerated design of 250 lbs/day PDU.
FY12 Quarter 1	Finalize plot plan and utility requirements.
FY12 Quarter 2	Complete control strategy & site interface definition.
FY12 Quarter 3	Down-select membrane substrate tube manufacturer.

All work under ARRA funding was put on hold by NETL starting July 1, 2012. On June 19, 2013 NETL determined not to authorize future use of Recovery Act funds for any technical work on the project, and to initiate close out of the ARRA project.

II. Introduction & Background

The overall objective of this ARRA project was to scale-up the hydrogen transport membrane (HTM) technology system for energy efficient carbon capture and hydrogen separation from industrial sources thereby enabling early technology commercialization by reducing time, technology risk, and cost.

ARRA funds were used to accelerate and complete the design of a nominally 250 lbs/day process development unit (PDU) for testing at a commercial gasification site using coal-derived synthesis gas shift mixtures. The PDU work scope was covered in the base project SOPO.

In parallel, the Recipient selected a site and designed a 4-10 TPD pre-commercial module (PCM). The PCM was designed to produce several tons per day of CO_2 at high purity and high pressure suitable for capture, transport, and storage. In addition, the PCM would produce 4-10 TPD hydrogen at purity suitable for a variety of downstream industrial applications, such as energy, fuels, and chemicals. The PCM was designed to provide scale-up data for a commercial scale HTM module suitable for industrial CCS applications.

III. Summary of Results

Task 1 - Project Management, Planning and Reporting

In addition to the required quarterly technical and financial reports, several additional topical reports were submitted to DOE-NETL. These included:

- Topical report: Technical Support for Scale-Up of Hydrogen Transport Membranes. Submitted March 7, 2012
- UND-EERC membrane field test report submitted to DOE on March 19, 2012
- NETL lab scale test report submitted to DOE January 13, 2012
- NCCC membrane field test report submitted to DOE January 11, 2013

Other project management activities included:

- Eltron presented at the annual AES merit review meeting on April 25, 2012 in Morgantown, WV.
- On May 11, 2012 Eltron staff traveled to Pittsburgh for a project update with NETL staff.
- On May 30, 2012, and at the request of NETL, Eltron put a hold on PCM related engineering activities by URS.
- On June 5-7, 2012 DOE-NETL staff visited Eltron for an in-depth technical review of Eltron’s techno-economics and membrane module design.

- All work under ARRA funding was put on hold by DOE-NETL starting July 1, 2012.

Subtask 1.1 – Project Management Practices

A project risk assessment was conducted in April, 2011. Several event trees and risk probabilities for schedule, budget, and PDU test risk were prepared by Eltron, DOE-NETL, and Deloitte & Touche personnel. Project risk was re-evaluated by DOE in 2013 using information provided by Eltron; however, Eltron was not included in the working meetings of this analysis.

Subtask 1.2 – Project Management Plan

A project management plan specific to the ARRA portion of DE-FC26-05NT42469 was prepared and submitted to DOE-NETL.

Subtask 1.3 – Project Communication

Biweekly conference calls were held between the Recipient and DOE-NETL personnel.

Subtask 1.4 – Development and Management of Third Party Relationships

To complete the Pre-FEED and FEED engineering work described in Tasks 3 and 4 Eltron solicited bids from three Engineering, Procurement, and Construction (EPC) firms. After evaluated bids from three firms, Eltron down-selected URS as the EPC firm for this project.

Relationships with three potential sites for operating the pilot plants were developed as described in Task 3.

Task 2 - Membrane Technology Development Acceleration and Scale-up

Work in Task 2 included all membrane development work specific to scale-up of the Recipient's membrane system as required for the PCM and accelerating the base project's SOPO. This effort included lab simulation and membrane testing under expected PCM operating conditions, and scale-up of membrane manufacturing required for PCM.

Subtask - 2.1 Membrane Development and Testing

Membrane development and testing was conducted under both the Base and ARRA portions of the project. Some testing was performed on ARRA as described below; however, most membrane testing was conducted on the Base project after DOE-NETL put a hold on ARRA spending. This data will be included in the final technical report for the Base project.

Membrane testing and development under ARRA included:

Bench Scale Reactors: Three new bench-scale reactors were designed and constructed for operation at Eltron's facility in Boulder, CO. These reactors were designed to allow testing under expected operating conditions at any of the potential sites for the 4-10 T/day reactor. All three reactors were built with the ability to test simulated water gas shift feed gas compositions under a range of temperatures and pressures. One of the reactors also had the capability of adding hydrogen sulfide to the feed stream. This new reactor capacity allowed Eltron to accelerate testing including cycling stability and membrane lifetime.

Mechanical Testing and Membrane Seals: Mechanical characterization of substrate materials was performed and described under Task 2.3.1. Cycling tests were conducted in conjunction with seal development and are described under Task 2.3.3.

Lifetime Testing: Lifetime testing was conducted under the conditions expected for operation of the PDU and PCM. Lifetime data was collected after the ARRA project was put on hold. A detailed discussion of lifetime was included in the Decision Point 1 topical report and will be summarized in the final technical report on the Base project.

Catalyst Development: Catalyst deposition testing was conducted as described in Task 2.3.2 to determine the effect of deposition method on both absolute performance and lifetime. Prepared membranes were tested up to 450 psig feed pressure. Permeation results show that a 20-30% difference in hydrogen flux performance can be expected depending on the method used to deposited catalyst on the surface of the membrane; however, lifetime was similar for both deposition methods tested. The topical report submitted on March 7, 2012 and the Decision Point 1 report submitted to DOE-NETL contained detailed descriptions of catalyst development and membrane testing.

Additional testing included in-situ measurements of membrane chemical expansion. Expansion tests were carried out in both a reactor modified with a gauge to measure membrane expansion during permeation testing and in a separate pressure chamber with controlled atmosphere. The goal of these measurements was to provide better understanding of the expansion properties of the membranes when permeating/absorbing H_2. Figure 1 shows the expansion of a tubular membrane as hydrogen feed concentration was increased in the pressure chamber. Linear expansion of the tube increases as the hydrogen partial pressure in the chamber was increased.

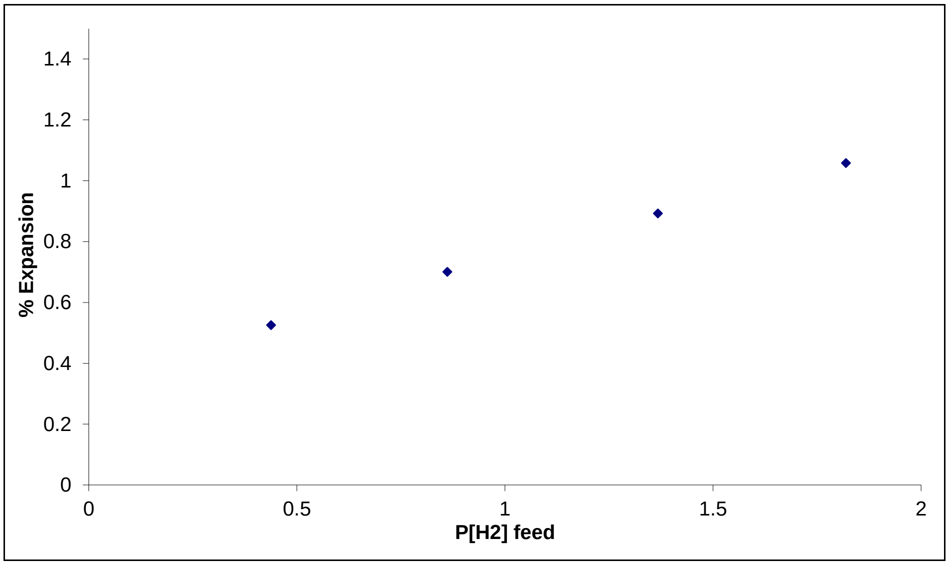

Figure 1. Membrane expansion vs. partial pressure of hydrogen.

Subtask - 2.1.1 Membrane Testing at NETL

In November 2011 Eltron's membrane was tested at NETL's bench scale facility for comparison to data collected at Eltron. Two sections of tubular membrane from the SEP test were retested: one at NETL's facility and one at Eltron's facility. Significant effort was made to ensure the testing conditions were as similar as possible in both locations. Results showed that when taking into account the expected differences between two (2) one-off tests, that the hydrogen flux rates measured at NETL and Eltron were essentially equivalent. The results of this test were submitted to DOE-NETL in a separate topical report on January 13, 2012.

Subtask 2.1.2 Membrane Testing at the University of North Dakota's Energy and Environmental Research Center (EERC)

A week long, 80 hour, continuous test was successfully completed at UND-EERC using both 6" and 60" long tubular membranes. Improved catalyst deposition methods discussed in the Topical Report submitted on March 7, 2012 were employed in preparation of membranes used in the test at UND-EERC. New startup procedures were developed to correlate with gasifier conditions at UND-EERC. Experimentally measured flux closely matched calculated performance based on CFD modeling. A detailed report on the membrane data collected at UND-EERC was submitted separately to DOE-NETL on March 19, 2012.

Subtask 2.3 - Membrane Manufacturing and Scale-Up

The goal of subtask 2.3 was development and scale-up of membrane production techniques appropriate for the 4-10 T/day HTM module. Work focused on three key areas:

- Tubular membrane substrate manufacturing
- Catalyst deposition
- Membrane seals

Subtask 2.3.1 - Tubular Membrane Manufacturing

Eltron evaluated membrane substrate tubing from several different suppliers. Initially, small orders were obtained for mechanical evaluation and membrane testing. Figure 2 shows a picture of twenty (20) each 10’ long substrate tubes that were received from one supplier.

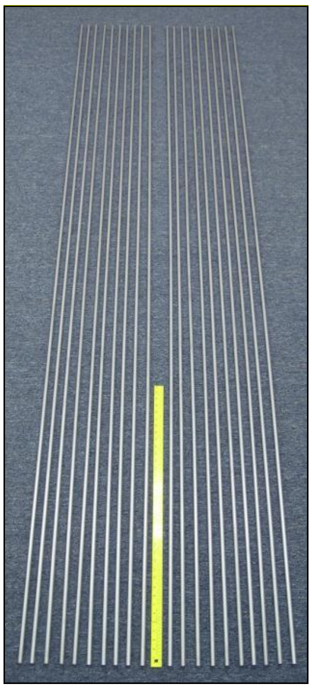

Figure 2. Image of as-received 10' long tubular hydrogen membranes. A yellow yard stick is included for reference.

Mechanical properties of tubing from two suppliers were evaluated including hardness, tensile strength, ductility, and elongation. Results were reported under the Base project and will be included in the final report. In addition, a detailed summary of mechanical testing results was included in the Decision Point 1 topical report submitted under the base program.

After the preliminary evaluation of small orders, Eltron placed large scale orders of substrate tubing from two different manufacturers. Tubing from each manufacturer was evaluated for mechanical properties, metallurgical properties, and permeation performance. Figure 3 shows a large tubing order received from one manufacturer.

Figure 3. Photograph of a partial shipment of tubing received from one of Eltron's tubing vendors.

Subtask 2.3.2 - Study and Scale-up Catalyst Deposition Techniques

Subscale Engineering Prototype (SEP) reactor testing showed lower flux results than expected. In an effort to improve flux up to the rates observed previously in the program, Eltron initiated a matrix of experiments to understand the effect of different catalyst deposition methods on membrane performance. Multiple techniques were evaluated including sputtering and electrodeposition of alloy catalysts. Eltron executed a matrix of experiments to understand the effect of different catalyst deposition methods on membrane performance. Experiment details were summarized in the Topical Report submitted to DOE-NETL on March 7, 2012. The key result of that study is shown in Figure 4.

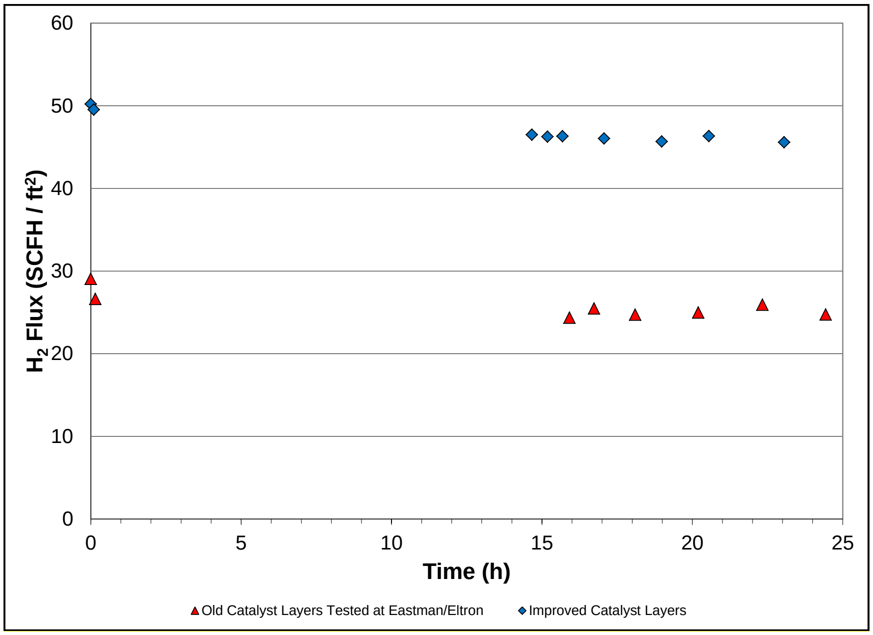

Figure 4. Hydrogen flux vs. time for the tubular membrane tested in the SEP reactor (red triangles) and a tubular membrane with improved catalyst layers (blue diamonds).

The tubular membranes that were tested in the SEP reactor and returned to Eltron for further testing had a flux rate of 26 SCFH/ft^2 when tested at Eltron under our standard testing conditions. Figure 4 shows that a membrane with improved catalyst layers had a flux rate of 46 SCFH/ft^2 when tested under the same conditions. By improving the catalyst layer(s), membrane flux was doubled compared to the membranes tested in the SEP.

Eltron designed and constructed a scale-up catalyst deposition set-up for electrodeposition of catalyst alloys on the inside and outside surface of ten foot long membrane substrates. Figure 5 shows a picture of the completed deposition set-up.

Figure 5. Photograph of apparatus for plating catalyst coatings on ID and OD surfaces of 10' long membrane tubes.

Ten (10) foot long tubular membranes prepared using the set-up in Figure 5 were sectioned for characterization and testing. Catalyst layers were characterized for catalyst thickness, alloy composition, and uniformity along the length of the membrane. Membrane were tested under expected operating conditions and compared to membranes prepared in the bench-scale setup. Results showed that membranes prepared at both scales had equivalent performance.

Catalyst development work continued under Base funding after ARRA funds were put on hold.

Subtask 2.3.3 - Study of Membrane Seals

Eltron worked with two different welding vendors (the Edison Welding Institute and Liburdi) to develop the appropriate techniques for sealing Eltron's membrane tube. This work was initiated under the ARRA project and continued under Base program funding. The work performed with EWI is discussed here. The final report on the Base program will contain a summary of the work performed with Liburdi.

Eltron worked with the Edison Welding Institute (EWI) to evaluate several different welding techniques to provide an adequate seal for scaling up this technology. As an example of the work performed, Figure 6 shows a picture of a tubular membrane with a stainless steel stub welded to each end of the tube.

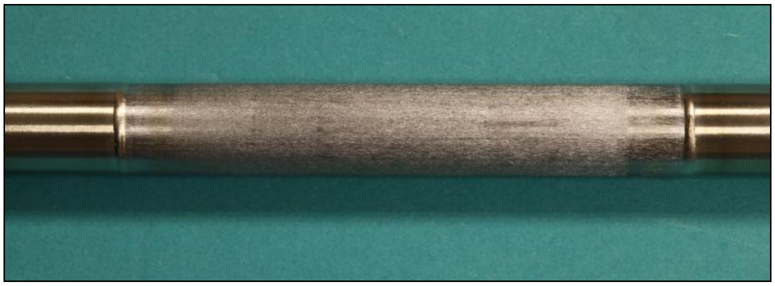

Figure 6. Tubular hydrogen membrane with a stainless steel stub welded to each end.

In addition to mechanical testing, seals were tested in bench-scale reactors under expected operating conditions. This permeation testing also included temperature, pressure and gas composition cycling experiments. Figure 7 shows cycling test results for a 6" membrane tested with welded seals.

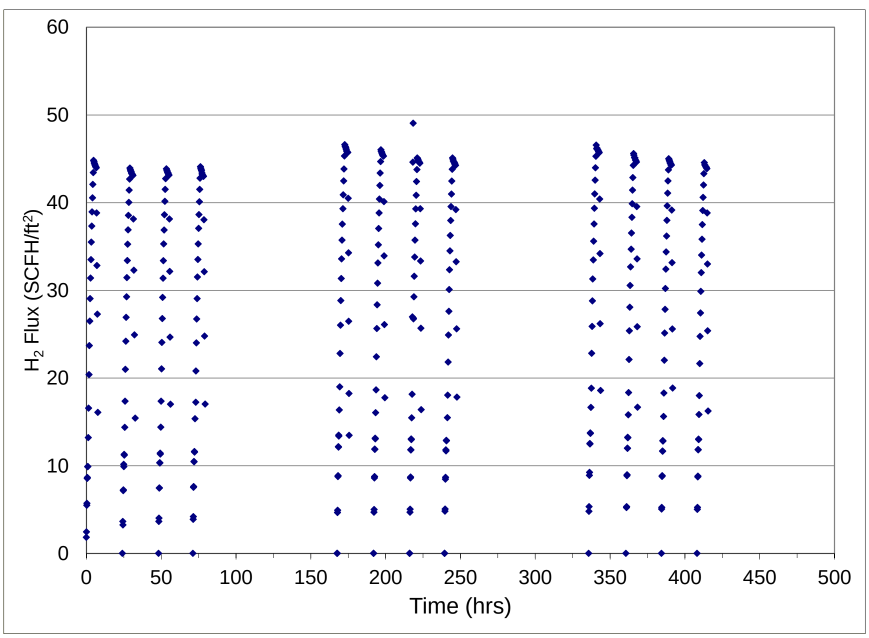

Figure 7. Hydrogen flux vs. time for a 6" long tubular membrane with welded seals exposed to pressure, temperature, and composition cycling.

Figure 7 shows measured hydrogen flux for a membrane with welded seals that was subjected to 12 pressure and composition cycles and two pressure, composition, and temperature cycles. The experiment was terminated by design after 400 hours to characterize the welds. During the entire 400 hour experiment no He leak was detected by GC.

Figure 8 shows a second tube subjected to 35 temperature cycles between ambient and operation temperature. No crack initiation or mechanical failure was observed in membrane or weld material after 35 temperature cycles.

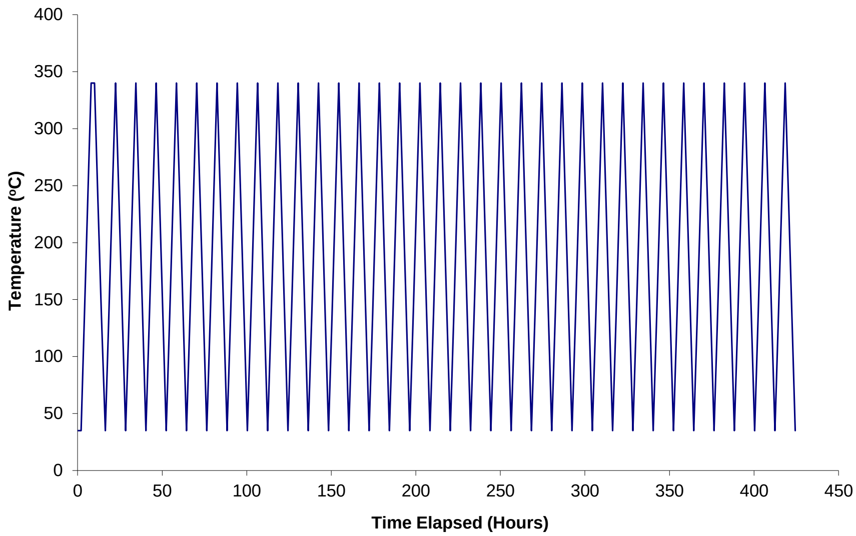

Figure 8. Demonstration of 35 thermal cycles of a welded, uncoated membrane tube in bench scale reactor between room temperature and 340°C.

Subtask 2.4 - Accelerated Design of the PDU

PDU design work was started under the Base project and accelerated under the ARRA portion of the project. Design work included both pilot skid and membrane module design work. Figure 9 shows the block flow diagram for the PDU. The design package was sent out for bid and URS reviewed the PDU skid construction bids. DOE did not authorize construction of the PDU. PDU design work will be summarized in the final Base program report.

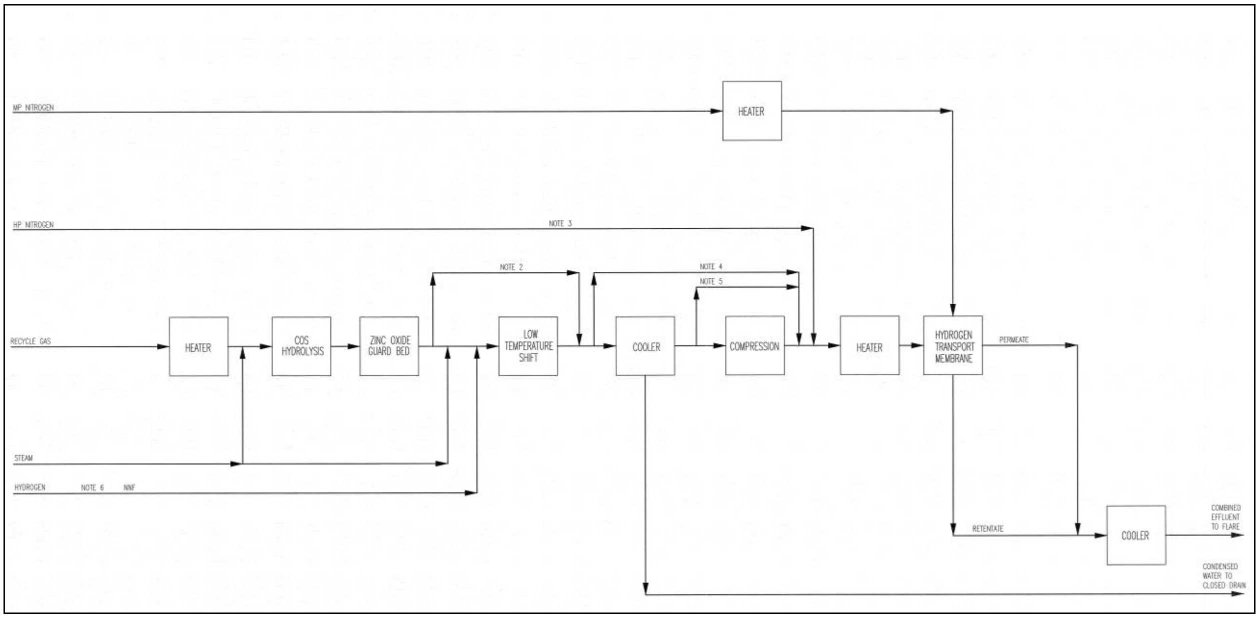

Figure 9. Block flow diagram for the PDU.

Task 3 - PCM Pre-FEED

Subtask - 3.1 Site Selection

Eltron identified and evaluated six different potential sites for installation of the planned 4-10 T/day pilot. Sites were evaluated based on a matrix of factors including syngas production volume, plot space availability, gas clean-up availability (gas composition), site regulatory environment, track record in technology development, commercial interest in Eltron's technology, and existence of a potential CO_2 sequestration site nearby.

Three potential sites were down-selected for further evaluation. All three sites expressed an interest in Eltron's technology and scale-up plan, and committed to participating in the Pre-FEED engineering process. As a first step in Pre-FEED, process flow diagrams were prepared after visiting each site potential tie-in points and site specific requirements were discussed. As discussed below, a Pre-FEED package was prepared on the down-selected site.

Subtask 3.2 - Pre-FEED Feasibility Study

A detailed Pre-FEED engineering package was completed for the site that Eltron down-selected. Eltron engineers worked closely with URS on Pre-FEED activities. The down-selected site was disclosed to DOE; however, Eltron did not publically disclose the site since negotiations had not been completed. The Pre-FEED engineering package included:

- Site descriptions
- Site selection matrix, summary, and conclusions
- Pre-FEED deliverables for the down-selected site:

- Process flow diagrams
- Equipment list
- Utility summary
- Chemical & catalyst summary
- Site plot plan
- Electrical description & load list
- Tie-Ins
- Battery limit summary
- Effluent summary
- Cost-Estimate
- Preliminary hazards review
- FEED scope, plan, and basis

The block flow diagram was very similar to PDU block flow diagram shown in Figure 9. A CD containing an electronic copy of the final Pre-FEED engineering package was provided to the DOE federal program manager for review.

Task 4 - PCM Front End Engineering Design (FEED)

Eltron and URS started the PCM FEED study for the pilot plant planned in Pre-FEED. Task 4 work included:

- Block Flow Diagrams (BFDs) and Process Flow Diagrams (PFDs) were completed and approved.
- Virtual Materials Group (VMG) process simulations were used to complete material and energy balances.
- Utility requirements were finalized.
- Equipment layout and plot plan was completed.
- Preliminary P&IDs were drafted.
- A site visit was made by Eltron and URS representatives to review technical details of the PCM design and provide an overview of the PCM FEED schedule.

Eltron and URS completed the control strategy and site interface definition for the PCM. All control modules (e.g. parameter inputs, controllers, control valves, automated valves, alarms, etc.) and operational configurations were defined. The control strategy describes startup, operating, and shutdown steps for the PLC (Programmable Logic Controller) and HMI (Human-Machine Interface). Fault monitoring and automated responses were determined. For the site interface definition the plot space was finalized and tie-in points identified. In addition, utilities including nitrogen, water, and electrical requirements and sources were defined.

Eltron and URS also completed updated P&IDs, equipment data specification sheets, and piping specifications for the PCM. Design Basis and Material Selection documents were issued.

Mechanical equipment arrangement diagrams, piping layouts, electrical specifications, and electrical one-line diagrams were developed. A Catalyst and Chemical Summary and a Utility Summary were also issued. Bids were solicited and received on major pieces of equipment, as well as catalysts. A Process Hazards Analysis review was conducted that included Eltron, URS, and the host site.

A mechanical design of the membrane module was completed. The module was designed as a bayonet type tube and shell arrangement, and was sized based on the flowrates expected in the PCM. Computational models were prepared and analyzed to determine tube bundle geometry and baffle spacing. Details on both the PCM and commercial scale design were included in the Decision Point 1 topical report submitted to DOE-NETL in May 2013.

The final FEED engineering package was not completed. PCM FEED engineering work by URS was put on hold by DOE-NETL on May 30, 2012.

Task 7 - Process Modeling and Techno-Economics

Process modeling and techno-economic evaluation were performed under both Base and ARRA statements of work. Detailed process and techno-economic were performed after shut-down of the ARRA portion of the project and therefore results will be included in the final technical report on the Base project.

Computational Fluid Dynamic (CFD) modeling was performed under the ARRA project. Detailed results were included in the March 7, 2012 topical report.

Operation of Eltron's SEP reactor showed low hydrogen flux rates that may have been limited by gas phase mass transfer resistance of hydrogen from the bulk feed stream to the membrane surface. CFD models were developed and showed that gas flow was very laminar across the entire surface of the membrane at the low feed stream velocities used during SEP testing. Combining permeation models with the CFD models showed that removal of hydrogen from that laminar flow stream created a hydrogen depleted layer at the surface of the membrane that severely limited hydrogen flux through the membrane.

CFD and Finite Element Analysis (FEA) modeling were conducted on bench-scale membrane reactors and the membrane reactor tested at UND-EERC. Computational models were used to predict the H_2 flux of 6 inch and 60 inch long membranes tested at EERC. Actual data collected under a range of conditions matched well with the predicted flux values, as reported in the UND test topical report.

CFD modeling was also performed on larger HTM modules. A computation fluid dynamics analysis of a hydrogen transport module (HTM) was completed with flow-only. AltaSim, a certified COMSOL consultant, performed a finite element analysis study of a reduced section of the Process Development Unit (PDU) to analyze flow characteristics for the proposed design.

Permeation was not modeled in this analysis. AltaSim developed and analyzed a reduced length model of the PDU by limiting the length to only three (3) baffles, while keeping all other dimensions the same as the actual PDU design. Additionally, they also develop and analyzed a five (5) baffle model to compare to the three (3) baffle model. Comparing both models they concluded, and Eltron concurred, that there was no significant difference between the flow characteristics of the three (3) and five (5) baffle models and that the three (3) baffle model could be used for future analyses. This saves a large amount of computation time while capturing the important flow information. (For example, the five (5) baffle model required almost four (4) CPU days to solve versus 1.5 CPU days for the three (3) baffle model).

A turbulent, flow-only analysis was used to evaluate the flow patterns and velocity of the PDU module which was designed initially by URS using Heat Transfer Research Inc. (HTRI) design software to determine preliminary specifications for baffle geometry and spacing. A full PDU design was prepared using the HTRI software and verified with CFD modeling. In the CFD analysis, the flow was shown to be cross-flow, with a flow velocity of approximately ten times that of the SEP and reduced mass transfer limitations in the PDU as compared to the SEP. Cross-section views, presented in Figure 10, visually showed uniform flow among tubes.

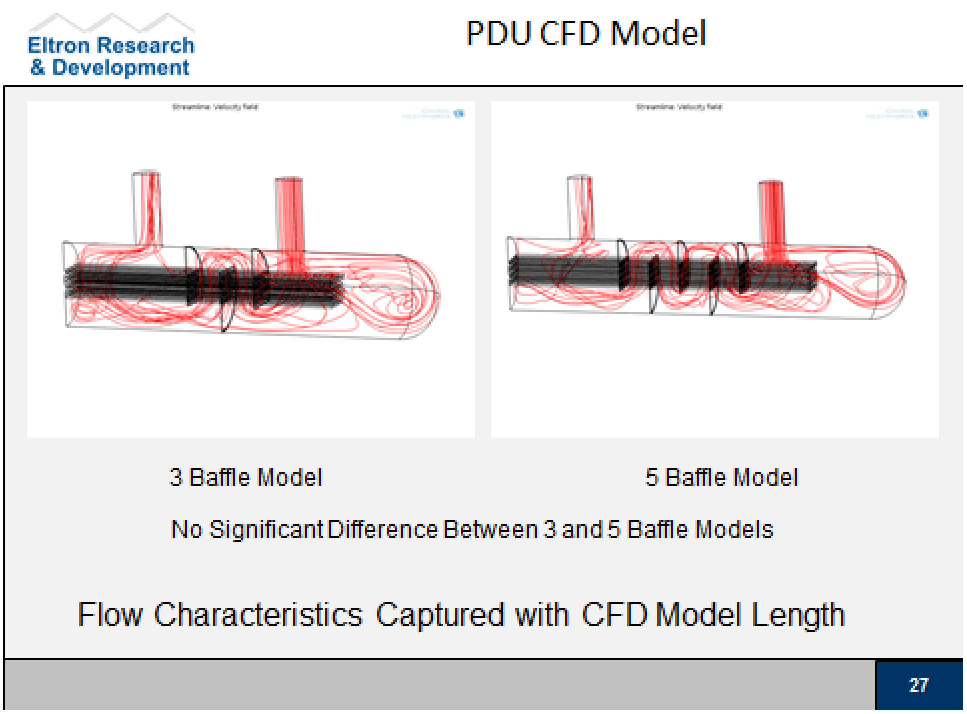

Figure 10. Cross-section views of 3 and 5 baffle models of PDU module showing flow characteristics.

IV. Conclusions

ARRA funds were used to accelerate development of Eltron's HTM technology towards pilot testing and commercializing. Specifically, ARRA funds were used to:

- Scale up membrane manufacturing to a commercially relevant size. Eltron worked internally and with required vendors to scale up manufacturing of Eltron's substrate metal tubing to a ten foot long membrane tube and the required deposition techniques for depositing catalyst on both the inside and outside surface of the substrate tubing.
- The required sealing techniques for a commercial scale membrane module were developed.
- Eltron worked with URS as our EPC firm to down-select a site for pilot testing and completed a Pre-FEED engineering package.
- A membrane module design for a pilot system was completed. This shell and tube design was scale-able to a commercial sized system.
- A FEED engineering package for the pre-commercial module was initiated, but not completed after funding was put on hold by DOE-NETL.