



## CCEMC Project

Final Project Report

Project Duration: May 1<sup>st</sup> 2011 to October 31, 2012

**Project Title:** Novel ceramic membrane-based technology for CO<sub>2</sub> capture and sequestration and hydrogen production

**Agreement Number:** C103184

**Project Leader:** Mr. Garry Reid, GE Canada  
Dr. Hrishikesh Keshavan, GE Global Research

**Lead Institution:** GE Canada

**Project Partners:** GE Global Research, University of Alberta, Alberta Innovates Technology Futures

### Project Schedule

- (1)  Project on schedule
- (2)  Project delayed
- (3)  Project cancelled
- (4)  Project complete

### Cost Status

- (1)  Cost unchanged
- (2)  Cost overrun
- (3)  Cost underrun

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FINAL REPORT - MAY BE RELEASED FOR PUBLIC DISSEMINATION

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## 1. Introduction – Brief description of the project

A part of Alberta's CO<sub>2</sub> emissions result from the extraction of bitumen and upgrading to synthetic crude oil. Capture and sequestration of these emissions is a key component of Alberta's climate change strategy. Since the cost of CO<sub>2</sub> capture decreases with increasing CO<sub>2</sub> concentration in the gas stream, concentrated sources, such as syngas streams used to produce H<sub>2</sub> for the upgrading process, offer the most favorable capture economics.

CO<sub>2</sub> capture can occur either prior to combustion (pre-combustion) or after combustion (post-combustion) capture. Pre-combustion capture involves separating H<sub>2</sub> from CO<sub>2</sub> and in post-combustion involves separating CO<sub>2</sub> from N<sub>2</sub>. The economics are more favorable in pre-combustion CO<sub>2</sub> capture since the gas streams are more concentrated than post-combustion. In traditional CO<sub>2</sub> capture, the gas stream is first cooled to approximately 200 °C and then dissolved in a chemical solvent. The solvent is regenerated and reused upon heating. This method of CO<sub>2</sub> capture is expensive; the solvent used is toxic and corrosive and reduces the overall plant efficiency.

Membrane technologies offer the potential to reduce the cost of capture by decreasing both the required capital investment and the parasitic energy loads needed to produce sequestration-grade CO<sub>2</sub>. Applied to pre-combustion capture, membranes can be permeable to either H<sub>2</sub> or CO<sub>2</sub>, with the details of the system configuration dependent on which gas permeates the membrane. Currently, all known active efforts to demonstrate pre-combustion membrane-based capture use H<sub>2</sub>-selective membranes.

According to an analysis performed by General Electric (GE), an integrated H<sub>2</sub> production system with membrane-based capture and appropriate complementary technology has the potential to reduce the operating expense relative to a petroleum coke gasification system using conventional liquid solvent-based CO<sub>2</sub> capture. Since ceramic membranes operate at high temperatures, such separation processes are less energy-intensive than traditional amine-based solvent capture processes because the system does not need to be cooled and re-heated. To date, efforts to develop H<sub>2</sub>-selective membranes for pre-combustion capture have been limited by two key technology gaps - performance and scalability. The performance gap stems from the inability of existing materials to simultaneously achieve the required selectivity, permeance, and stability under realistic operating conditions. The scalability gap exists because current methods for fabricating defect-free membranes at large scale are too expensive to be commercially attractive.

The membrane materials investigated in this project are naturally occurring zeolites with well-defined cage structures (molecular sieve) that are small enough to allow H<sub>2</sub> (2.7 Å) to pass, but not CO<sub>2</sub> (3.3 Å). Zeolites are generally aluminosilicates, although other materials

could be zeolitic in nature. Many occur naturally as minerals, and are extensively mined in various parts of the world. Others are synthetic, and are made commercially. Natural zeolites are sedimentary rocks that are formed when volcanic rocks and ash reacts with alkaline ground water and are naturally compressed under extremely high geological pressures. All natural zeolites are hydrated aluminosilicates. Some examples of natural zeolites are Chabazite, Clinoptilolite and Stilbite, etc. The zeolite investigated in this project is Clinoptilolite. Man-made zeolites are synthesized either using a templated process or a hydrothermal process. In the former, a templating agent along with respective metal precursors is used to grow the zeolites crystals under moderate temperatures (80°C – 100°C) under controlled conditions. In the latter process, aluminium and silicon precursors are heated (150°C to 250°C) in the presence of a strong base at elevated pressures to form zeolites. Due to the nature of the synthesis process, these zeolites are free of second phases and contamination. They are also more expensive than natural zeolites since the chemicals used to synthesize zeolites and the synthesis process are energy intensive. Synthesized zeolites tend to be approximately 4 – 5 times expensive than natural zeolites on a mass basis. Therefore using naturally occurring zeolites in commercial applications are economically attractive.

## **2. Originally proposed scope and duration**

The project consists of two phases with two years per phase. Phase 1 is funded by CCEMC and the second phase is not yet funded. The goal of the first phase (first two years) is to develop and demonstrate the technical/commercial feasibility of a novel ceramic membrane that will have a major impact on CO<sub>2</sub> capture within Alberta. Phase 1 will have five technical tasks and one system level task. These tasks will focus on abating technical risks associated with membrane module manufacturability. The primary objectives of these five tasks will be to determine how to manufacture and scale up defect-free membranes using Clinoptilolites as the base membrane material. The system level task will understand the commercial feasibility of the technology in greater detail through system-level modeling and analysis. The outcome of the first phase will consist of a detailed prototype module design and manufacturing capability needed to fabricate it with a thorough understanding of the system dynamics of the technology. During this phase, a demonstration partner for the slipstream test will be identified.

The second phase, outside CCEMC's scope had three technical tasks. These tasks focus on demonstrating the technology in a field test. The three tasks will fabricate the prototype module and on-site testing at a demonstration partner facility. The anticipated scale of the slipstream module prototype will be 500 kg H<sub>2</sub>/day, sufficient to upgrade approximately 150 to 250 bpd of bitumen.

To enable monitoring of progress toward specific milestones and deliverables, clearly defined Go/No go decisions were put in place as tollgates. Go/No Go decision points occur after the first, second and final years of the program to manage the technical risks associated with technology development. The Go/No go decision criteria for Phase 1 are shown below.

Only if the team answered “Yes” to all below questions for both years would the project proceed to Phase 2.

### **Year 1 Go/No Go decision**

#### **Year 1: Proceed to detailed module design?**

Approach These are the questions that were addressed

- (1) Is the preliminary design ready?
- (2) Does the zeolite material exhibit at least 25% of material entitlement (e.g., H<sub>2</sub>/CO<sub>2</sub> selectivity >25, H<sub>2</sub> permeance > 250 GPU) and less than 50% degradation in H<sub>2</sub> permeance over 50 h at >200°C?
- (3) Is there a process to coat 5 cm long defect-free tubes?
- (4) Has a viable sealing method been identified?
- (5) Has a preliminary slipstream test site been identified?
- (6) Are all additional significant risks identified during a risk assessment accompanied by a reasonable mitigation plan (commercial risks)?

### **Year 2 Go/No Go decision**

#### **Year 2: Is the technology ready for field test?**

Approach These are the questions that were addressed

- (1) Is the detailed module design ready for slipstream testing?
- (2) Does the zeolite material exhibit at least 75% of material entitlement (e.g., 750 GPU H<sub>2</sub> permeance, 75 H<sub>2</sub> selectivity) and less than 50% degradation in H<sub>2</sub> permeance over 500 h at >200 °C?
- (3) Is there a process to coat 10 cm long defect-free tubes that exhibit at least 75% material entitlement (e.g., 750 GPU H<sub>2</sub> permeance, 75 H<sub>2</sub> selectivity) for at least 500 h under hydrothermal conditions at >200°C?
- (4) Has the slipstream test site been confirmed, is there a comprehensive test plan, and are all necessary agreements in place?
- (5) Are all additional significant risks identified during a risk assessment accompanied by a reasonable mitigation plan?

## **3. Modified scope and Go/No go criteria**

During the first year of the project (Apr 2011 – May 2012), the market dynamics changed significantly. The case that was originally presented to make coal gasification attractive was no longer true due the drastic reduction in natural gas prices; therefore CCEMC requested the team to re-establish the business case. The team responded by considering natural gas reforming in lieu of coal gasification. Additionally, during the end of

the first year of the project (May 2012), the technical team discovered a narrow process window to manufacture defect-free 10 cm long membranes. Many tubes had microcracks that resulted in defective tubes. To address this, three methods to repair defective membranes were investigated for 6 months to improve the manufacturability of membrane tubes. Based on these changes, the original Go/No Go criteria were modified and Go/No Go deferred until Oct 31<sup>st</sup> 2012.

### **Modified Year 1 Go/No Go decision**

#### **Year 1: Proceed to detailed module design?**

Approach      These are the questions that were addressed

- (1)      Is the preliminary design ready?
- (2)      Does the zeolite material exhibit at least 25% of material entitlement (e.g., H<sub>2</sub>/CO<sub>2</sub> selectivity >25, H<sub>2</sub> permeance > 250 GPU) and less than 50% degradation in H<sub>2</sub> permeance over 50 h at >200°C?
- (3)      Is there a process to coat 5 cm long defect-free tubes *reproducibly* that is?
  - (i) *is at least 5 cm long and*
  - (ii) *has H<sub>2</sub>/CO<sub>2</sub> selectivity of > 25 and*
  - (iii) *has H<sub>2</sub> permeance of > 1000 GPU and*
  - (iv) *at differential pressure of 5 psi across the membrane at 25 °C.*
- (4)      Has a viable sealing method been identified?
- (5)      Has a preliminary slipstream test site been identified?
- (6)      Are all additional significant risks identified during a risk assessment accompanied by a reasonable mitigation plan (commercial risks) *i.e., is natural gas reforming a viable path to commercialize this technology?*

## **4. Scientific Achievements**

There were a number of scientific achievements accomplished by the project team including the development of intellectual property, conference presentations and peer-reviewed publications that are shown in Table 1. Additionally, the funds also supported a number of graduate students at University of Alberta. The details of graduate students supported by the CCEMC project is shown in Table 2

Table 1. Detailed list of patent applications technical publications completed using CCEMC funds

Category	Title	Inventors/Authors	Organization
1 Patent application	Zeolite membrane and methods for making the same	Kevin Mc Evoy	GE - GRC
		Hrishikesh Keshavan	GE - GRC
		Anthony Ku	GE - GRC
		Steven Kuznicki	UA
		An Weizhu	UA
		Paul Swenson	UA
2 Patent application	Membrane structures suitable for gas separation and related processes	Hrishikesh Keshavan	GE - GRC
		Anthony Ku	GE - GRC
		Steven Kuznicki	UA
		An Weizhu	UA
3 Patent disclosure	Chemical Vapor Infiltration for ceramic membrane repair for CO <sub>2</sub> capture and sequestration and hydrogen production	Sheng Zhong	GE - GRC
		Hrishikesh Keshavan	GE - GRC
		Anthony Ku	GE - GRC
4 Conference Presentation	Hydrogen separation using membranes based on natural zeolites presented at 2011 International conference of membranes at Amsterdam, Netherlands	Hrishikesh Keshavan	GE - GRC
		Kristi Narang	GE - GRC
		Vidya Ramaswamy	GE - GRC
		Anthony Ku	GE - GRC
5 Peer-reviewed publication	"A sieve for CO <sub>2</sub> " TCE Membranes, Filtration & Separation, April 2011	Amy Dambrowitz	UA
6 Peer-reviewed publication	Selective separation of hydrogen from C <sub>1</sub> /C <sub>2</sub> hydrocarbons & CO <sub>2</sub> through dense natural zeolite membranes, 2011., J. Memb. Sci., 369, 414	An Weizhu	UA
		Paul Swenson	UA
		Wu Lan	UA
		Terri Waller	UA
		Anthony Ku	GE - GRC
		Steven Kuznicki	UA
7 Peer-reviewed publication	Characterization of natural zeolite membranes for H <sub>2</sub> /CO <sub>2</sub> single gas permeation, 2011., Ind. Eng. Chem Res., 50[22], 12717	S.A. Hosseinzadeh Hejazi	UA
		A.M. Avila	UA
		Tatiana Kuznicki	UA
		An Weizhu	UA
		Steven Kuznicki	UA
8 Peer-reviewed publication	Evolving applications of zeolite molecular sieves, 2012., Canadian Journal of Chemical Engineering, 90, 207	Christopher C. H	UA
		Amy Dambrowitz	UA
		Steven Kuznicki	UA
9 Peer-reviewed publication	Natural zeolite-based cement composite membranes for H <sub>2</sub> /CO <sub>2</sub> separation., 2012, Separation and Purification Technology, 88, 24	Amir Hossein Shafie	UA
		An Weizhu	UA
		S.A. Hosseinzadeh Hejazi	UA
		James Sawada	UA
		Steven Kuznicki	UA

	Category	Title	Inventors/Authors	Organization
10	Peer-reviewed publication	Improvement of H <sub>2</sub> /CO <sub>2</sub> selectivity of the natural clinoptilolite membranes by cation exchange modification., 2012, J. Memb. Sci, Submitted	An Weizhu Tatiana Kuznicki Wu Lan Paul Swenson A. Gupta Steven Kuznicki	UA UA UA UA UA UA
11	Peer-reviewed publication	Clinoptilolite-phosphate composite membranes for H <sub>2</sub> /CO <sub>2</sub> separation., In preparation	An Weizhu Tatiana Kuznicki E. B. Tapia Paul Swenson Amanda S. M Steven Kuznicki	UA UA UA UA UA UA

Table 2. Graduate students' thesis supported by the project

	Student Name	Degree pursued	Thesis Title	Year
1	S.A. Hosseinzadeh Hejazi	M.Sc	Characterization of natural zeolite for H <sub>2</sub> /CO <sub>2</sub> separations by single gas	2011
2	Paul Swenson	M.Sc	Natural zeolite membranes for gas and liquid separations	2011
3	Elia Margarita Bastida Tapia	M. Eng	Molecular sieves pore opening by acid treatment	2011
4	Amir Hossein Shafie	M.Sc	Gas separation membranes using cementitious-zeolite composite	2012
5	John Yu	M.Sc	Natural zeolite membrane reactor for dehydrogenation of ethane	In Progress

## 5. Task level technical accomplishments

Fig. 1 shows the project planned followed from May 2011 (Quarter 1) until the project stopped on October 2012 (Quarter 6). The red line in the project plan indicates the decision to defer the original Go/No criteria from April 2012 (Quarter 4) to October 2012 (Quarter 6) due to the manufacturing challenges. This led the technical team to modify the Go/ No go criteria as discussed previously. A summary of the task level accomplishments is presented in this section. Details of the technical achievements are discussed in Appendix A of this report.

	Who	Phase 1							
		Year 1				Year 2			
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
<b>Phase 1 - Validate technology approach</b>									
<b>Task 1</b>	<b>Develop preliminary module prototype design and validate technology readiness.</b>								
1.1	GRC	◆	◆	◆	◆	◆	◆	◆	◆
1.2	GRC				◆	◆	◆	◆	◆
	Phase 1, Year 1 Go/No Go decision: Proceed to detailed module design?								
<b>Task 2</b>	<b>Optimize membrane material performance and stability.</b>								
2.1	UA	◆	◆	◆	◆	◆	◆	◆	◆
2.2	UA				◆	◆	◆	◆	◆
<b>Task 3</b>	<b>Develop manufacturing processes for coated membranes.</b>								
3.1	GRC	◆	◆	◆	◆	◆	◆	◆	◆
3.2	AI-TF	◆	◆	◆	◆	◆	◆	◆	◆
3.3	GRC	◆	◆	◆	◆	◆	◆	◆	◆
3.4	GRC	◆	◆	◆	◆	◆	◆	◆	◆
<b>Task 4</b>	<b>Identify slipstream test site and define slipstream test parameters.</b>								
4.1	AI-TF	◆	◆	◆	◆	◆	◆	◆	◆
4.2	AI-TF				◆	◆	◆	◆	◆
<b>Task 5</b>	<b>Develop detailed module prototype design and evaluate readiness for slipstream test.</b>								
5.1	GRC								
5.2	GRC								
5.3	GRC								
	Phase 1, Year 2 Go/No Go decision: Proceed to slipstream test?								
<b>Task 9</b>	<b>Program management</b>								
	GEC	◆	◆	◆	◆	◆	◆	◆	◆
<b>Total</b>		◆	◆	◆	◆	◆	◆	◆	◆

Fig. 1. Project plan from Q1 to Q6. The red line indicates the decision to deferred Go/No Go decision from April 2012 to October 2012 arising due to manufacturing challenges.

### (a) Task 1.1 – Module Design

**Task Aim** – Develop preliminary module prototype design and validate technology readiness

#### Technical accomplishments/executive summary

- Down selected tube-in-shell design after completing a thorough mechanical risk analysis. The risks were identified at various levels including (a) component level (coating, seals, substrate), (b) module level and (c) system level.
- Determined the optimal process for assembling the module through finite elemental modeling (FEM) analysis. FEM analysis was completed to understand the stress state of the module under nominal operational conditions (300 °C temperatures and a maximum pressure of 30 bar) to assess the structural integrity of the module and identify the components at a high risk of failure.
- Constructed a membrane module that was ~1.5 m in length and weighed ~300 kg.

#### Status of the task w.r.t Go/No go criteria

The task deliverable was completed successfully and on time

### (b) Task 1.2 – Validate material performance and scalability entitlement

**Task Aim** – Verify the technology feasibility for H<sub>2</sub> separation using membrane in natural gas reforming

### **Technical accomplishments/executive summary**

- Successfully completed a detailed system modeling analysis to evaluate the feasibility and potential benefits of using a Water Gas Shift Membrane Reactor (WGS-MR) to replace the water gas shift reactors in typical steam methane reforming hydrogen production process.
- Concluded that there was no net performance advantage was observed in using WGS-MR for the configuration studied. Additionally, this configuration did not reduce the amount of natural gas required to produce hydrogen. A slightly higher natural gas requirement was attributed to the energy required to generate the sweep gas.
- No net benefits were observed by reducing the steam to carbon ratio entering the reactor. Lower steam to carbon (S/C) reduces steam methane reformer (SMR) performance so that the natural gas feed stream was increased in order to produce the same amount of hydrogen. The feed rate increase was offset by a reduction in supplemental gas such that the overall natural gas requirement was unchanged.
- Examined the two major pieces of equipment that would influence the cost of the hydrogen production system. Estimated that the smaller size of the Methyl-diethanolamine (MDEA) absorber column would reduce the equipment cost by \$.94 million. The addition of the H<sub>2</sub> compressor is expected to add \$9.5 million in cost. With the assumption that the WGS-MR reactor cost would be the same as the replaced WGS units, the new configuration would add \$8.6 million to the \$343 million plant equipment costs of a National Energy Technology Laboratory (NETL) reference design.
- Concluded that there was no observed benefit to using the WGS-MR for SMR hydrogen production.

### **Status of the task with respect to Go/No go criteria**

The task deliverable was completed, but results did not meet success criteria.

### **(c) Task 2 – Materials Development**

**Task Aim** – Optimize membrane material performance and stability

### **Technical accomplishments/executive summary**

- Successfully identified the two most reliable and optimal sources of clinoptilolite zeolite in the world. A thorough study involving eight down-selected zeolites was completed using various materials characterization techniques. These techniques were chosen to understand the geomorphic variability normally found in these minerals. It was found that only two sources, both from a mine in New Mexico,

USA were found to satisfy the metrics listed for a successful clinoptilolite zeolite membrane.

- Down selected two mineral deposits (a) St. Cloud deposit and (b) Ash Meadows for further investigation. In addition to the two clinoptilolite deposits, one mordenite deposit from New Zealand also satisfied the set metrics for an exemplary membrane material. However, since this project focused exclusively on clinoptilolite zeolites, this deposit was not further investigated.
- Completed preliminary gas testing and chemical conversions on sliced and polished 1” buttons that were between 2 – 5 mm thick. Chemical modifications/treatments named Type I and Type III treatments were also completed on 1” sliced and polished buttons. Chemical treatments were essential to improve the materials gas separation performance.
- Identified alternate methods to manufacture disc-shaped clinoptilolite membranes. A process to prepare zeolite – cement composites buttons was developed that required autoclaving a mixture of zeolite powder and non-silicate cement. This resulted in a dense composite with a percolating network of clinoptilolite.
- An inverse gas chromatography (IGC) technique was developed to help determine the gas selectivity entitlement of both natural and chemically treated clinoptilolites. This technique provided insight to the CO<sub>2</sub> diffusion into the pores. Ash Meadows material was found to exhibit superior entitlement. The IGC results of Ash Meadows show molecular exclusion of CO<sub>2</sub> i.e., a possibility of an infinite H<sub>2</sub>/CO<sub>2</sub> selectivity.
- Concluded that Ash Meadows exhibited superior hydrothermal stability than St. Cloud deposit. X-ray diffraction (XRD) data of the 500 hours steam exposed St. Cloud showed a formation of an amorphous hump indicating phase degradation of the zeolite, whereas Ash Meadows showed little to no phase change at the same duration.
- Discovered that the water absorbing capacity of St. Cloud clino zeolite reduced by 2% after steaming for 500 h, whereas there was no change in the water absorbing capacity observed in the Ash Meadows zeolite.
- Concluded that Ash Meadows is a better Clinoptilolite deposit than St. Cloud zeolite.

**Status of the task with respect to Go/No go criteria**

The task deliverable was completed successfully and on time

**(d) Task 3.1 and Task 3.4 – Membrane Manufacturability and testing**

**Task Aim** – Develop and characterize manufacturing processes for coated membranes

### **Technical accomplishments/executive summary**

- Successfully prepared a consolidated clinoptilolite button using reconstituted powder. 15 mm diameter buttons was produced using reconstituted powder that had identical gas separation ability to 15 mm diameter sliced rock at up to 200 °C and 10 psi membrane differential pressure ( $\Delta P$ ).
- Thoroughly characterized and identified the fundamental processing limitations of natural clinoptilolites. This fundamental understanding became critical for further processing challenges in the project.
- A simple yet scalable manufacturing method was developed to coat clinoptilolite materials on porous ( $Al_2O_3$ ) scaffolds without any macroscopic defects like cracks, voids, bubbles etc. However, with clinoptilolites thermal limitations, this process was unable to produce dense coatings. The coating porosity was large enough to allow both  $H_2$  and  $CO_2$  to permeate. Therefore an alternate manufacturing process was identified to produce dense coatings at relatively low temperatures.
- Successfully adopted the cement based composite clinoptilolite membranes process developed for producing 1” substrates at University of Alberta (UA). Discovered a narrow processing window to produce defect-free clinoptilolite-cement composite membranes.
- Investigated three novel technologies to repair defective membranes. They are (a) chemical and hydrothermal healing (b) chemical vapor infiltration (CVI) and (c) targeted electrophoretic deposition (EPD) using  $SiO_2$ .
- Chemical and hydrothermal healing – UA developed this novel process. An aluminosilicate reactive gel was injected into the micro-cracked composite membrane tube and hydrothermally treated at elevated pressures and temperature. The reactive gel was transformed *in-situ* to a zeolite and healed the cracks to produce defect-free membranes.
- Chemical vapor infiltration – General Electric Global Research Center (GE-GRC) use CVI for the first time to repair defective membranes. The precursors, in this case tetraethyl orthosilicate (TEOS) and water ( $H_2O$ ) to produce  $SiO_2$  flows in counter-current direction on either ends of the defective tube. At elevated temperatures these precursors react at the plane of the coating forming  $SiO_2$  and closing any defects. The driving force for the reaction is a combination of temperature, flow rates and partial pressure of steam. This method produced defect-free tubes, however, failed to produce defect-free membranes.
- Targeted electrophoretic deposition – Alberta Innovates – Technology Futures (AI-TF) developed this repair process technology. This process was investigated to selectively repair defective areas in the clinoptilolite-zeolite composite

membrane. This concept was successfully demonstrated on idealized membranes where SiO<sub>2</sub> particles closed the pores in the anodized Al<sub>2</sub>O<sub>3</sub> discs. However, targeted repair using EPD was not as effective on membrane tubes where zeolite is coated on porous Al<sub>2</sub>O<sub>3</sub> substrates. Since SiO<sub>2</sub> and clinoptilolites (aluminosilicates) possess similar zeta potential in EPD suspension there was significant counter electroosmotic resistance during EPD. Therefore methods were investigated to reduce this resistance and fill the defects with SiO<sub>2</sub>. A process to increase the zeolite tube separation ability from 50 – 200% was discovered.

**Status of the task with respect to Go/No go criteria**

The task deliverable was not completed successfully since the team was unable to produce 5 tubes with H<sub>2</sub>/CO<sub>2</sub> selectivity  $\geq 25$  at  $\Delta P = 5$  psi and 25 °C.

**(e) Task 3.2 – Targeted Electrophoretic deposition**

**Task Aim** – Optimize electrophoretic deposition for defect-repair

**Technical accomplishments/executive summary**

- Benchmarked EPD process to achieve targeted deposition of material at defects. The benchmarking process was completed using a model “edge” defect.
- Demonstrated feasibility of defect repair by plugging the void channels of model porous substrate (AAO) with silica nanoparticles.
- Selective deposition of material was demonstrated on edges that are (a) porous and (b) edges that had different surface charges. The former captured the effect of electro-osmosis, and other effects related to flow through the porous substrate. The latter captured the scenario that was slightly more representative of a defective surface. It also captured effects related to different electrohydrodynamic flows near the surface, as well as differences in flow through supports with different porosities.
- Demonstrated spatially selected deposition on the masked AAO substrates and solid oxide fuel cell (SOFC) tubes. Preferentially deposited SiO<sub>2</sub> nanoparticles on a scratch scribed on a dense yttria stabilized zirconia (YSZ) coating.
- Discovered co-directional motion of electroosmotic flow and electrophoretic motion of particles provides the best condition for deposition of SiO<sub>2</sub> particles on idealized substrates.
- Effectively adapted EPD process for zeolite deposition to repair defective membrane tubes. Discovered that zeolite coated tube has more complex electroosmosis flow with distinctly different surface properties of alumina support and the zeolite coating.

**Status of the task with respect to Go/No go criteria**

The task deliverable was completed successfully and on time

**(f) Task 3.3 – End sealing**

**Task Aim** – Develop and optimize sealing technology

**Technical accomplishments/executive summary**

- Systematically evaluated sealing options against the mechanical and functional requirements of the module and selected seal glasses for further development
- Various glass seal joint designs were evaluated to verify the optimal configuration to attach a porous ceramic to a dense ceramic tube.
- A *grooved* seal approach was selected in which a narrow groove is machined into the end of the dense alumina tube. The porous alumina tube is seated in this groove and filled with the glass frit. Upon heating the glass fills forms a hermetic seal between the two tubes.

**Status of the task w.r.t Go/No go criteria**

The task deliverable was completed successfully and on time.

**(g) Task 4 – Skid level testing site identification**

**Task Aim** – Identify slip stream test site and define slipstream parameters

**Technical accomplishments/executive summary**

- 11 potential sites were originally considered. From these, Advanced Energy Research Facility (AERF) pilot plant was identified as the most suitable option for the slipstream testing. The AERF facility has space and utilities set aside for pilot scale test units along with appropriate slipstream connections. Syngas compression will not be necessary as the pilot gasification facility will be able to supply syngas at 3 MPa (450 psi) and 60°C in the quantity required. It should be noted that AERF is a unique facility that is under construction when this report was written (December 2012).
- Test skid design parameters were completed. The target scale for the slipstream demonstration is 1 – 10 moles of syngas per second (60 to 600 l/min at STP) at the inlet with membrane operating conditions of temperature of 200 to 300°C and pressure of 2 MPa (300 psi).

**Status of the task w.r.t Go/No go criteria**

The task deliverable was completed successfully and on time.

**(h) Task 5 – Detailed module design and readiness**

**Task Aim** – Develop detailed module prototype design and evaluate readiness for slipstream test

Since the Go/No Go decision was deferred by six months to October 31<sup>st</sup> 2012, the technical team felt prudent to delay Task 5. However, since we were unable to continue the project beyond October 31<sup>st</sup> 2012, Task 5 never started.

**Status of the task w.r.t Go/No go criteria**

The task deliverable was delayed and not started.

## **6. Recommendation against the Go/No Go criteria**

The team was unable to deliver a scalable process to manufacture defect-free clinoptilolite membrane tubes. Despite some progress in repairing defective tubes, the team was not able to deliver tubes with H<sub>2</sub>/CO<sub>2</sub> selectivity of  $\geq 25$  at 5 psi  $\Delta P$ . Additionally, system modelling clearly indicated that using a membrane reactor for natural gas reforming has no net benefits. There was neither an operational benefit nor capital expenditure benefit of using a water gas shift – membrane reactor for natural gas reforming. After a thorough review by the program sponsor and team (CCEMC, GE, UA, AITF) it was mutually decided to stop the project.

However, this technology could still be viable for coal gasification. With the natural gas prices at ~\$3.50 per MM BTU (November 16, 2012), there is little commercial value in investigating coal gasification. There could be other potential technology needs that require size based separation. For example, the natural clinoptilolites have the ability to separate He and steam. Perhaps, other application space within the oil sands sector could utilize this intrinsic property of clinoptilolites zeolites.

Other recommendation include (a) continue identifying alternate methods of manufacturing the tubes in lieu of using cement composites, (b) continue to advance the repair technologies.

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