Robust and Energy Efficient Dual Stage Membrane Based Process for Enhanced CO$_2$ Recovery

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Dr. Richard J. Ciora, Jr, Media and Process Technology Inc.

- Dr. Paul KT Liu, Media and Process Technology Inc., Pittsburgh, PA
- Professor Theo T. Tsotsis, University of Southern California, Los Angeles, CA
- Dr. Eric C. Wagner, Technip Stone & Webster Process Technology, Inc., Morovia, CA

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Overall Theme:

• Use inorganic membrane technology advantages to achieve CCS goals.
• Move inorganic membrane technology from lab scale novelty to commercial reality.

Overall Project Objectives:

1. Demonstrate the carbon molecular sieve membrane as a bulk H₂ separator and to improve the efficiency of the WGS reactor

2. Demonstrate the Pd-alloy membrane for residual H₂ recovery from “captured” high pressure CO₂

3. Perform bench scale testing (equivalent to a syngas throughput for 0.01MWe power generator) of the innovative pre-combustion process scheme for power generation with CO₂ capture and sequestration (CCS).

4. Key process components will be tested under simulated and real gasifier syngas conditions for their potential to effectively separate H₂ and CO₂.

5. Collected data will be utilized to assess the potential of the concept for achieving the DOE Carbon Capture Program goal.
M&P Dual Stage Membrane Process

Project Overview

**Funding:** Overall project budget: $2.5MM including $500,000 (20%) cost share

**Overall Project Performance Dates:** October 1, 2013 - September 30, 2016

**Project Participants:**
- Media and Process Technology…Membrane manufacturer/supplier and technology developer
- University of Southern California…Membrane reactor testing, membrane model development
- Technip Stone and Webster Process Technology Inc…Engineering and system design, analysis and economics
**CMS Membrane (coupled with WGS reactor)**

1. Deliver enhanced CO conversion with reduced water consumption versus conventional WGS.
2. “Roughing” step to recover the bulk H₂ and reduce load on the CGCU.
3. Ideal location for CMS membrane due to its material and temperature stability.

**Pd-Alloy Membrane**

1. High selectivity yields excellent residual H₂ recovery.
2. Ideal to achieve the CO₂ capture and purity targets.
TECHNOLOGY BACKGROUND

Multiple Tube Membrane Bundles – versatile, low cost

Our Core Expertise/Technology

#1: Packaging individual membrane tubes into commercially viable modules for field use.
TECHNOLOGY BACKGROUND

Specific thin film deposition for advanced separations

Importantly Features of MPT Inorganic Membranes

• Low cost commercial ceramic support
• High packing density, tube bundle
• Module/housing for high temperature and pressure use

Our Core Expertise/Technology

#2: Thin film deposition on less-than desirable but low cost porous tubular substrates
TECHNOLOGY BACKGROUND

Membrane Bundles for Separations at High Temperature and Pressure

Multiple Tube Bundle Styles

**Dense Ceramic Tube Sheet (DCT-style)**
- Performance: >500°C; >1,000 psig
- Packing: 57-tube current and 71-prototypes, spaced pack

**Potted Ceramic Glass (PCG-style)**
- Performance: ~300°C; <450 psig
- Packing: 86-tube, close pack

Common Features

- CMS Membrane
- Pd-alloy Membrane

Glass Transition Zone

Dense alumina “tips” for Candlefilter
Our Innovation

- **CMS membrane to enhance CO conversion efficiency with concomitant bulk H₂ recovery** to improve power generation efficiency.

- **Pd-alloy membrane for residual H₂ recovery** during the post compression of CO₂ for CCUS to achieve the CO₂ capture goals and fuel efficiency requirements.

Unique Advantages

- **No syngas pretreatment required.** CMS membrane is stable in all of the gas contaminants associated with coal derived syngas.

- **Improved CO conversion efficiency and bulk H₂ separation.** Separation of hydrogen as well as enhanced CO conversion from the raw syngas occurs at elevated temperatures at reduced steam requirement for the WGS reaction.

- **Reduced Gas Load to CGCU:** The proposed use of the CMS membrane with the WGS reactor results in substantial hydrogen and steam recovery, resulting in reduced stream size for the CGCU.

- **CCS Post Compression Power Reduction:** CO₂-enriched gas is delivered to the CGCU at relatively high pressure reducing total compression load.

- **Enhanced residual H₂ recovery from the CCS stream to achieve the CO₂ recovery goals.** The Pd-alloy membrane is ideally suited to remove residual H₂ from the CCS stream to deliver the CO₂ purity and capture targets.
Our Solutions to the Well-known Deficiencies of A Membrane Process

• **Bulk Separation Limitation**… Membranes are generally intended for bulk separation, usually not very efficient for fine separations. Our use of very high selectivity Pd-alloy membranes to supplement CMSM overcomes this deficiency to achieve the program goals.

• **High Cost of Pd Membranes**… Pd-based membranes are expensive and the worldwide supply is constrained considering commercially available technology. Our ceramic substrate and bundle designs permit thin films to overcome both of these problems.

• **Pd Membrane Stability**… The Pd-based membranes in this application is exposed to a H₂/CO₂ stream after CGCU. Thus, chemical stability of the membrane is not an issue.
BP1 Tasks Completed to Overcome Key Technical Challenges
• CMS/Pd membrane operation meeting targets for CO₂ sequestration and cost.
• Long term and other membrane performance stability
• Full-scale WGS-MR and membrane separator designs for mega-scale applications
• Updated membrane and membrane reactor modeling

BP2 Tasks Underway/Completed to Overcome Key Technical Challenges
• Performance stability in actual gas testing (NCCC) with multiple tube bundles.
• Model verification in actual gas testing with multiple tube bundles.
• Long term membrane performance stability.
• Process design and techno-economic evaluation.
• Environmental, health and safety assessment.
## Project Technical Approach

### Overview of Project Technical Approach - Workplan

<table>
<thead>
<tr>
<th>Budget Period 1</th>
<th>Budget Period 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Task 1. Project Management and Planning</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Task 2. Establish Performance Database:</strong> Focus here is to complete the membrane performance database under more severe operating conditions in the presence of simulated WGS contaminants at long times. Also reactivate the bench top WGS-MR system for Task 3 activities.</td>
<td><strong>Task 6. NCCC Field Testing:</strong> Focus here is testing at the NCCC of the two stage process for demonstration and operational stability.</td>
</tr>
<tr>
<td>Task 3. CMS WGS-MR experimental verification and modeling under extreme conditions: Focus here is lab scale testing of the CMS WGS-MR at gasifier conditions and includes model development/verification.</td>
<td><strong>Task 7. Process Design and Engineering:</strong> Focus here is comprehensive process development and economic evaluation.</td>
</tr>
<tr>
<td>Task 4. Preparation of CMS for bench testing at NCCC: Focus here is design and fabrication of the pilot scale (86-tube bundles) for process evaluation at the NCCC.</td>
<td><strong>Task 8. Conduct Environmental Health and Safety Analysis:</strong> Focus here is assessment of the environmental impact.</td>
</tr>
<tr>
<td>Task 5. Preparation of Pd Module for 2nd Stage H₂ Recovery for bench scale test at NCCC: Focus here is design and fabrication of the pilot scale Pd module.</td>
<td></td>
</tr>
</tbody>
</table>
Progress and Current Status of Project
### Typical Performance and Performance Targets

#### CMS Single Tube Characterization

<table>
<thead>
<tr>
<th>CMS Membrane Characteristic</th>
<th>Preliminary Target to Achieve DOE Goals¹</th>
<th>Laboratory Single Tubes Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeance, H₂ [GPU] @ 250°C, 20 psig</td>
<td>550</td>
<td>420 to 1,100</td>
</tr>
<tr>
<td>Selectivity, H₂/X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂/N₂</td>
<td>70</td>
<td>80 to &gt;180</td>
</tr>
<tr>
<td>H₂/CO</td>
<td>70</td>
<td>70 to &gt;130</td>
</tr>
<tr>
<td>H₂/CO₂</td>
<td>35</td>
<td>35 to &gt;65</td>
</tr>
<tr>
<td>H₂/H₂S</td>
<td>N/A²</td>
<td>100 to 150²</td>
</tr>
<tr>
<td>H₂/H₂O</td>
<td>1.5</td>
<td>1.5 to 3</td>
</tr>
</tbody>
</table>

#### CMS 86-Tube Bundle Characterization

<table>
<thead>
<tr>
<th>CMS Bundle ID</th>
<th>He Permeance [GPU]</th>
<th>He/N₂ Selectivity [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>86-6</td>
<td>731</td>
<td>100</td>
</tr>
<tr>
<td>86-7</td>
<td>1,020</td>
<td>187</td>
</tr>
<tr>
<td>86-8</td>
<td>658</td>
<td>91</td>
</tr>
<tr>
<td>86-9</td>
<td>950</td>
<td>102</td>
</tr>
<tr>
<td>86-10</td>
<td>365</td>
<td>200</td>
</tr>
<tr>
<td>86-11</td>
<td>584</td>
<td>142</td>
</tr>
<tr>
<td>86-12</td>
<td>548</td>
<td>77</td>
</tr>
<tr>
<td>86-13</td>
<td>840</td>
<td>126</td>
</tr>
<tr>
<td>86-14</td>
<td>1,020</td>
<td>117</td>
</tr>
<tr>
<td>86-J1</td>
<td>973</td>
<td>120</td>
</tr>
<tr>
<td>86-MB1</td>
<td>421</td>
<td>122</td>
</tr>
<tr>
<td>86-MB2</td>
<td>665</td>
<td>87</td>
</tr>
<tr>
<td>86-MB3</td>
<td>438</td>
<td>85</td>
</tr>
</tbody>
</table>

Notes:
1. Target performance is that required to achieve 90% CO₂ capture at 95% purity with 95% fuel utilization (H₂ + CO to the turbine).
2. At this selectivity, approximately 200 ppm H₂S in the fuel to turbine.
**Typical Performance and Performance Targets from Economic Analysis**

### Pd-Alloy Single Tube Characterization Overview

<table>
<thead>
<tr>
<th>Pd-Alloy Membrane Characteristic</th>
<th>Preliminary Target to Achieve DOE Goals¹</th>
<th>Laboratory Single Tubes Performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeance, H₂ [GPU] @ 350°C, 20 psig</td>
<td>3,470</td>
<td>1,750 to &gt;5,500</td>
</tr>
<tr>
<td>Selectivity, H₂/X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂/N₂</td>
<td>300</td>
<td>300 to &gt;3,000</td>
</tr>
<tr>
<td>H₂/CO</td>
<td>300</td>
<td>300 to &gt;3,000</td>
</tr>
<tr>
<td>H₂/CO₂</td>
<td>300</td>
<td>300 to &gt;3,000</td>
</tr>
<tr>
<td>H₂/H₂S</td>
<td>N/A²</td>
<td>NA²</td>
</tr>
<tr>
<td>H₂/H₂O</td>
<td>300</td>
<td>300 to &gt;3,000</td>
</tr>
</tbody>
</table>

**Notes:**

1. Target performance is that required to achieve 90% CO₂ capture at 95% purity with 95% fuel utilization (H₂ + CO to the turbine).
2. Feed gas to the Pd-alloy membrane has been pretreated to remove residual sulfur species in the CGCU.

### Pd-Alloy Comments

1. **Pd-Cu** offers thermal cycling stability and low temperature operational capability (>200°C).
2. **Pd-Ag** offers higher flux and selectivity but higher minimum operating temperature (>300°C).
PROGRESS: CMS Membrane Stability

Key Technical Hurdles Focused on Long Term Stability (CMS Membrane)

CMS 86 - Tube Bundle Long Term Stability (>16,000 hrs)

- He Permeance [GPU]
- He/N₂ Selectivity [-]
- Run Time [hours]

Part ID: Bundle CMS J-1
Temperature: 250°C
Pressure: 20 psig

Repack Bundle. Orings Failed
PROGRESS: CMS Membrane Stability

Key Technical Hurdles Focused on Long Term Stability (CMS Membrane)

**300°C**

- Part ID: Single Tube CMS 3x40-#11
- Temperature: 300°C
- Pressure: 20 psig

**500°C**

- Cool and repack part (graphite), retest at 250°C.

- Part ID: Single Tube CMS STD-#1
- Temperature: 500°C
- Pressure: 20 psig

**High Temperature Excursions above the 250°C Design Temperature**
PROGRESS: Pd Membrane Stability

Key Technical Hurdles Focused on Long Term Stability (Pd-alloy)

**Pd-Alloy Pd-Ag (80/20) Long Term Stability (~24,000 hours)**

- Temperature: 350°C
- Pressure: 20 psig

<table>
<thead>
<tr>
<th>Permeance [GPU]</th>
<th>Run Time [hours]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10000</td>
<td>0</td>
</tr>
<tr>
<td>1000</td>
<td>5000</td>
</tr>
<tr>
<td>100</td>
<td>10000</td>
</tr>
<tr>
<td>10</td>
<td>15000</td>
</tr>
<tr>
<td>1</td>
<td>20000</td>
</tr>
<tr>
<td>0.1</td>
<td>25000</td>
</tr>
<tr>
<td>0.01</td>
<td>30000</td>
</tr>
<tr>
<td>0.001</td>
<td>35000</td>
</tr>
</tbody>
</table>

- H₂: PdAg-63
- H₂: PdAg-66
- N₂: PdAg-66
- N₂: PdAg-63
PROGRESS: CMS Membrane Bundle Stability

NCCC Testing: CMS Membranes Highly Stable in Coal Gasifier Syngas

Testing Parameters

Membrane
86-tube CMS

Operating Conditions
T~ 250 to 300°C
P~ 150 to 300 psig

Pretreatment
Particulate trap only, no other gas cleanup.

Composition
H₂ ~ 10 to 30%
CO ~ 10%
CO₂ ~10%
N₂,H₂O ~Balance

Trace Contaminants
NH₃ ~ 1,000ppm
Sulfur Species ~ 1,000ppm
HCl, HCN, Naphthalenes/Tars, etc.

NCCC Slip Stream Testing: No gasifier off-gas pretreatment

He or N₂ Test Conditions
Pressure: 20 to 50 psig
Temperature: 230 to 265°C

Performance stability of multiple tube CMS membrane bundles during H₂ recovery from NCCC slip stream testing. He and N₂ Permeances measured periodically during >400 hr test.
### Results

1. **Good agreement with NCCC “once per day” water content determinations using our new reject and permeate water capture units.**

2. **Substantial water content variability outside this “once per day” window.**

3. **We now can determine accurate real time water composition in the membrane feed.**

### NCCC Testing: Improve Prediction of Membrane Performance

**In-situ real time water composition analysis required**

**Added water capture units prior to recent NCCC testing round.**

**Table: Water Content Analysis**

<table>
<thead>
<tr>
<th>Time</th>
<th>WGS In</th>
<th>WGS Out</th>
<th>Perm</th>
<th>Reject</th>
<th>WGS Out [%]</th>
<th>MPT Water Collection Units</th>
<th>NCCC/MPT Water Closure</th>
<th>NCCC GC Dry Gas Mass Closure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
<td></td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>Day 1</td>
<td>16.2%</td>
<td>8.5%</td>
<td>39.5</td>
<td>5.7%</td>
<td>8.8%</td>
<td>103.9%</td>
<td>105.1%</td>
<td>105.1%</td>
</tr>
<tr>
<td>Day 2</td>
<td>10.6%</td>
<td>6.7%</td>
<td>23.2</td>
<td>5.3%</td>
<td>6.5%</td>
<td>96.4%</td>
<td>101.7%</td>
<td>101.7%</td>
</tr>
<tr>
<td>Day 3</td>
<td>7.5%</td>
<td>2.5%</td>
<td>19.9</td>
<td>5.5%</td>
<td>6.6%</td>
<td>267.2%</td>
<td>99.5%</td>
<td>108.2%</td>
</tr>
<tr>
<td>Day 4</td>
<td>5.0%</td>
<td>1.7%</td>
<td>23.5</td>
<td>0.2%</td>
<td>1.6%</td>
<td>98.4%</td>
<td>102.3%</td>
<td>102.3%</td>
</tr>
<tr>
<td>Day 5</td>
<td>7.4%</td>
<td>2.7%</td>
<td>31.1</td>
<td>0.6%</td>
<td>2.6%</td>
<td>98.5%</td>
<td>103.0%</td>
<td>103.0%</td>
</tr>
</tbody>
</table>
**PROGRESS: Membrane Performance Modeling**

**NCCC Testing: DCT-Style 57-tube CMS Membrane Bundle**

**Operating Conditions and Flow Rates**

![Graph showing operating conditions and flow rates over time](graph.png)
Feed, Permeate and Reject H₂ Composition

Supplemental H₂ Added to Feed Gas
PROGRESS: Membrane Performance Modeling

NCCC Testing: DCT-Style 57-tube CMS Membrane Bundle

Verification of the Mathematical Model in Actual Gas Testing at the NCCC
Permeate Flow Rate: Predicted versus Actual

Run Time [hours]

Permeate Rate [cm³/min]

Ratio, Permeate Rate, Actual/Simulation [%]

Reset Membrane “Baffles”
PROGRESS: Membrane Performance Modeling

NCCC Testing: DCT-Style 57-tube CMS Membrane Bundle

Verification of the Mathematical Model in Actual Gas Testing at the NCCC
Permeate $H_2$ Content: Predicted versus Actual

Reset Membrane “Baffles”

H$_2$ Permeate Composition [%]

Run Time [hours]
Effect of Total Gas Feed Rate on Membrane Performance with Baffles

Ratio of Actual to Predicted Permeate Rates

- 80/20 He/N2 Mixture; Test 1 Minimal Baffles
- 80/20 He/N2 Mixture; Test 2
- 50/50 He/N2 Mixture; Test 4
PROGRESS: Techno-economic Analysis

Enhanced CO Conversion
98.1% (v. B5B at 97.4%)
With less steam consumption

CO₂ Capture: 90.7%
CO₂ Purity: 93.4%

Pd-alloy Membrane for Residual H₂ Recovery
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Case B5B*</th>
<th>Case MPT</th>
<th>Target</th>
<th>MPT vs B5B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Capture</td>
<td>90.0%</td>
<td>90.72%</td>
<td>90%</td>
<td></td>
</tr>
<tr>
<td>CO₂ Purity</td>
<td>99.48%</td>
<td>93.4%</td>
<td>95%</td>
<td></td>
</tr>
<tr>
<td>H₂ in Fuel</td>
<td>99.98%</td>
<td>98.72%</td>
<td>NA</td>
<td>+1.8%</td>
</tr>
<tr>
<td>Net Power Production, MW</td>
<td>543</td>
<td>553</td>
<td>N/A</td>
<td>+1.8%</td>
</tr>
<tr>
<td>Cost of CO₂ Captured [$/tonne]</td>
<td>63.1</td>
<td>62.0</td>
<td>N/A</td>
<td>-1.7%</td>
</tr>
<tr>
<td>Cost of CO₂ Avoided [$/tonne]</td>
<td>91.6</td>
<td>87.8</td>
<td>N/A</td>
<td>-4.1%</td>
</tr>
<tr>
<td>COE no T&amp;S [$/MWh]</td>
<td>135.4</td>
<td>134.0</td>
<td>N/A</td>
<td>-1.1%</td>
</tr>
<tr>
<td>Total as-spent Cost [$/kW]</td>
<td>4,782</td>
<td>4,639</td>
<td>N/A</td>
<td>-3.0%</td>
</tr>
</tbody>
</table>

Final Remaining Technical Issues

- Complete Bench Scale Field Testing at the NCCC with DCT-style bundle with updated flow distribution/baffles and model verification
- Conduct Bench Scale Field Testing at the NCCC with Pd-alloy bundle
- Conduct high pressure mixed gas H₂/CO₂ performance testing with Pd-alloy membrane
- Conduct Sensitivity Analyses on the Process Design and Economics (Impact of CO₂, H₂S, and other slow gas selectivity; Impact of WGS Operating Temperature; Introduction of RTI warm gas cleanup for H₂S removal)
- Complete the Environmental, Health, and Safety Evaluation
Summary and Conclusions

Key Findings to Date

• Database updates show that the capabilities of our CMS and Pd-alloy membranes meet or exceed the performance targets required to deliver the DOE CCS goals.
• The CMS (250°C) and Pd-alloy (350°C) membrane tubes and bundles (full ceramic) have been demonstrated to be stable in thousands of hours of thermal stability testing.
• The CMS membrane has been shown to be stable in various tests for hundreds of hours of exposure to synthetic and actual coal gasifier syngas with only particulate pretreatment.
• Extreme pressures to >1,000psig can be achieved with our DCT-style bundles making them suitable for the proposed IGCC with CO₂ capture environment.
• Modeling has been successfully used to predict membrane performance at the NCCC.
• The proposed membrane based IGCC with carbon capture process achieves the 90% CO₂ capture target at 93.7% purity, just under the 95% purity target. Sensitivity analysis is underway on the H₂/CO₂ selectivity to establish the minimum target.
• Net power production for the proposed process is 553MW, 1.8% above the NETL base case.
• Total capital cost for the proposed process is $32MM (3%) below the NETL base case.
END