1. Capture Studies

Task - 1.0 Develop Post-Combustion Separation and Capture Scenarios
Task - 2.0 Develop Pre -Combustion Decarbonization Techniques
Task - 3.0 Develop Oxyfuel Technologies

The program began in mid-2001 with the assessment summarized here, an intense period of program development and technology provider selection, and in early 2002 with the technology development phase of the program. This report includes the results of the early part of the program and from the past six months of technology development activity. Some projects have been completed while many are in progress.

The capture technologies are divided into the three categories that were identified in the CCP State of the Art (SOA) review; namely:

- **Post Combustion (PC) C**apture technology. Where CO_2 is captured from the exhaust of a combustion process
- **Precombustion De-Carbonization (PCDC)**. Where a hydrogen-rich fuel is produced and CO_2 is captured from the produced syngas
- **Oxyfuel** Here a pure oxygen stream is produced which results in a combustion product containing only CO_2 and water.

The DOE currently funds one PC and nine PCDC studies in the overall CCP Capture program.. More studies are planned in Phase 2 of the program. Table 3 shows the status of each project in January 2003.

Table 3: Capture Studies Status, July 2003

Capture Category	**Project Title**	**Principal Investigator**	**Co Funder ***	**Technology Provider**	**Status**
Post Combustion	Self-Assembled Nanoporous Materials for CO_2 Capture	Malhotra Ripudaman	DOE	Stanford Research Institute	Ongoing
PCDC	Sorption Enhanced Shift Reaction	Allam, Rodney	DOE	Air Products Inc.	Ongoing
PCDC	Coke Gasification and Gas Separation Case Study	Reddy, Satish	DOE	Fluor	Ongoing
PCDC	Copper Palladium Membrane Research	Alptekin, Gokhan	DOE	TDA Research	Ongoing
PCDC	Electro-Ceramic Membrane Research	Mundschau, Michael	DOE	Eltron	Ongoing
PCDC	Membrane WGS Reactor Development Study	Reddy, Satish	DOE	Fluor	Ongoing
PCDC	Develop Silica Membranes	Van Delft, Yvonne	DOE	ECN	Ongoing

Table 3: Capture Studies Status, July 2003 (Cont'd)

Capture Category	Project Title	Principal Investigator	Co Funder *	Technology Provider	Status
PCDC	Develop Supported Copper Palladium Alloy	Way, Doug	DOE	Colorado School of Mines	Ongoing
PCDC	Develop Supported Silicalite Membranes	Lin, Jerry	DOE	Univ. of Cincinnati	Ongoing
PCDC	Membrane WGS reactor design	TBA	DOE	SOFCo	Ongoing

In addition, four Oxyfuel studies are underway within the CCP program. None are funded by the CCP / DOE award and are listed here for information only.

1. **Chemical Looping** (Vienna University, Alstom Power, CSIC and Chalmers University). This new combustion technology is based on oxygen transfer from combustion air to the fuel by means of a metal oxide acting as an oxygen carrier. Cost reduction will likely be derived from the combustion of pure oxygen, avoiding the requirement for air separation. This is a new technology, which carries significant risk but reasonable potential for cost reductions.

2. **Advanced Zero Emission Power** (AZEP) (Alstom Power and Norsk Hydro). This technology would integrate a gas turbine system with an innovative membrane air separation technique. It is part of a separate European Union study, but CCP will economically evaluate it on a basis consistent with other CCP projects.

3. **Advanced Boilers** (Praxair and Alstom). This is similar to AZEP , this time funded by the DOE outside the CCP except that it integrates the same membrane air separation technique with a boiler (rather than a gas turbine). CCP will evaluate the technology as above. The Praxair study was considered for CCP funding but was set aside when they obtained direct DOE funding.

4. **Boilers and Heaters Conversion Study (Air Products)** Conversion of gas turbines for oxyfuel combustion requires major redesign of turbines and is being studied extensively outside the CCP. It is also research requiring funding beyond the means of the CCP. The conversion of boilers and heaters for oxyfuel combustion is regarded as practicable in the near term. This study aims to understand the costs and issues around such conversion using heaters and boilers similar to those in our refinery scenario. This technology would combust oxygen derived either from conventional cryogenic separation or from innovative ionic membranes, using flue gas or steam as the diluent. Work started at the end of 2002.

1.1 Post Combustion Studies

Task - 1.0 - Develop Post Combustion Separation and Capture Scenarios

General

In post-combustion capture, CO_2 is recovered from the exhaust gases of large sources such as boilers, heaters, and turbines. These sources are present everywhere throughout refineries, power plants, gas processing plants and chemical plants of the world. Post-combustion sources of CO_2 are also significant for the U.S. as a whole, with power plants contributing roughly one-third (~1.7 billion tonnes/year) of all the CO_2 emitted. Improving the economics of post-combustion capture is therefore a critical goal for the entire CO_2 Capture Project (CCP).

The current post-combustion capture practice is to install an amine separation unit at the flue-gas source. This is a very difficult separation, since the gases are hot, dilute in CO_2 content, near atmospheric pressure, high in volume, and often contaminated with other impurities (SO_x, NO_x, ash). The presence of oxygen in the flue gas is problematic for conventional amine plants because of oxidative degradation of the amine. Collectively, these factors result in enormous amine circulation rates, large equipment, and large energy requirements. In the case of CO_2 capture from power plants, the heat duty of the amine stripper places a substantial burden on the low-pressure steam supply. Despite the maturity of amine technology, there appears to be ample opportunities for finding improvements with new technology.

Post-combustion capture of CO_2 from flue gas has been researched for over 30 years, resulting in fewer opportunities to significantly reduce the cost of capture relative to conventional amine technology. However a small but steady stream of potential ideas continues to emerge. Many are at the concept stage and may not reach the full proof of concept stage in the lifetime of this program. The team felt it was important to continue to review and evaluate these as they appear. Thus, the CCP Post-Combustion team takes a balanced approach with regards to maturity and technical risk in technology selection. We seek to reduce the cost of CO_2 capture through:

- Step-change cost reduction through improving existing amine technology (e.g., better solvents, better solvent contactors, cost-effective plant design).

- High-risk, entirely novel approaches to post-combustion capture (e.g., DOE-funded work in Self-Assembled Nanoporous Adsorbents).

The CCP has funded several engineering studies and technology development programs in the post-combustion area. The individual programs all vary in degrees of maturity, technical risk, and cost-reduction potential.

Co-funded by NORCAP
- Amine Scrubbing with a Membrane Contactor (Mitsubishi Heavy Industries (MHI) and Kvaerner Process Systems (KPS))
- Cost Effective Design and Integration Study (Nexant)
- Radical Chemistry Concepts (Norsk Hydro and numerous academic partners)

Funded directly by CCP
- Baseline Design and Cost Estimation (Fluor)
- Electric Swing Adsorption (Oak Ridge National Laboratories and Kvaerner Process Systems)
- Novel Channel adsorption technology (Norsk Hydro)

Co-funded by DOE

- Self-Assembled Nanoporous Materials for CO_2 Capture (SRI)

From the work completed thus far, the CCP has learned that entirely new radical approaches would be required to reduce the cost of post-combustion CO_2 capture by the levels specified at the outset: by 50% for retrofit and 75% below conventional amine technology for new-build scenarios. The only CCP project sponsored by DOE, "Self-Assembled Nanoporous Materials for CO_2 Capture," is a high-risk program that may be applicable for both retrofit and new-build, as well as pre-combustion CO_2 capture. Work is ongoing and final results will not be available until 3Q 2003.

The planned study on electric swing adsorption technology was abandoned when CCP funded studies demonstrated that the benefits anticipated from this approach would not materialize for our scenarios.

The post-combustion capture technologies for which comments, observations and recommendations are provided are:

- Membrane/KS-1 Amine solvent system - MHI/Kvaerner (Klimatek funded)
- Electrical Swing Adsorption – Oak Ridge National Laboratory (CCP funded)
- Cost Efficient Design – Nexant (Klimatek funded)
- Self-Assembled Nanoporous Materials for CO_2 Capture– SRI (DOE funded)
- Novel Chemistry – Norsk Hydro (Klimatek funded)

MHI/Kvaerner Membrane/Amine Solvent System

This process combines two established technologies for the capture of CO_2 from industrial flue gas streams.

- Mitsubishi Heavy Industries – KS-1 Hindered Amine Solvent process.
- Kvaerner Process Technology's – Membrane contactor.

The technology was evaluated in the context of the NORCAP (Norwegian 400 MW Natural Gas-Fired Power Plant) scenario.

Technical Issues

Performance tests for the MHI solvent/Kvaerner membrane combination at the Nanko Power Plant in Japan revealed some solvent loss across the membrane system into the CO_2 lean flue gas stream. For commercial designs, a water wash stage will be required to minimize the impact of solvent loss on the environment. For the initial design and cost estimate (Case 1) a conventional wash column was assumed downstream of the membrane unit. Additional study work (Case 2) looked at replacing the wash column with a water wash membrane unit.

Capital Cost

Two design cases were generated for the MHI solvent/Kvaerner membrane combination:

- Case 1 - Conventional water wash column.
- Case 2 - Membrane water wash unit.

In both cases the cost of the membrane components account for about 15% of the total unit cost.
Case 1 capital cost is, 'within the estimate accuracy', the same as conventional equipment performing the same duty (1.6% capex reduction), despite overall weight and space reductions for the membrane unit. Capital cost reductions are not significant because the water wash tower is still required due to amine loss through the membrane. Case 2 capital cost shows a further small reduction, but this is not fully leveraged

in the NORCAP case since there is no weight or space premium for the scenario. An overall capital cost reduction of only 8.2% is realized for this case when compared with a conventional unit.

Operating Cost

There is a significant reduction in operating cost arising from the use of KS-1 solvent (about 20% versus MEA solvent). This operational cost saving will also be realized with conventional absorber tower equipment; hence there is no benefit accruing to its use in combination with the Kvaerner membrane contactor.

Performance in Other Scenarios and Team Conclusion

Other CCP scenarios are unlikely to show cost reduction benefits by using this technology combination. Grangemouth, NORCAP and the Canadian scenario's will all employ 'stick built' facilities and none should place a high value on space/weight reductions.

The Alaska scenario, which utilizes pre-fabricated modules, could be an exception, however, the team does not recommend this technology combination for further development in the Alaska scenario for the following reasons;

- Major costs for the Alaska scenario are associated with supporting utility systems, CO_2 compression and the Heat Recovery/Steam Generator facilities. All of these are essential regardless of the capture elements employed.
  The capture facility represents less than 30% the total capital cost.

- Translating the NORCAP derived capture facility cost reduction (8.2%) to the Alaska scenario will realize an overall cost saving of less than 3% across the entire facility within the Alaska scenario.

For the above reasons the Post Combustion team sees no point in progressing this technology any further at this time. This technology should show increased cost benefits where it is used in a scenario where its low weight and space requirements are valuable – e.g. on offshore platforms.

Electrical Swing Adsorption – Oak Ridge National Laboratory

The Post Combustion team worked with Oak Ridge National Laboratory (ORNL) to evaluate their 'Electrical Swing Adsorption' (ESA) process. A limited range of tests were undertaken to assess the loading potential of the Carbon Fiber Composite Molecular Sieve (CFCMS) material, to develop adsorption/desorption curves and to assess the benefit of the electrical swing effect. A process scheme was developed from the laboratory scale test results and some preliminary economics were generated for the system.

Technical Issues

The loading of CO_2 (dry) onto the CFCMS material was limited to 0.7 wt% (expected to extend to 1.0 wt% at best) due to the low partial pressure of CO_2 in the feed gas. The presence of water appears to reduce loading capacity by 10%. Observed cycle times were between 12 and 18 minutes (adsorption) and 25 to 30 minutes (desorption).

The test equipment used was not capable of analyzing CO_2 stream concentrations greater than 20,000-ppm v/v, which obscured the initial phase of regeneration so that the 'Electrical Swing' effect could not be seen clearly. The laboratory regeneration technique utilized purge gas to create low CO_2 partial pressures during the desorption step. This approach cannot be used in a real processing situation since it reverses the separation achieved by the process. A vacuum desorption system was assumed for the process scheme and associated cost assessment.

The power applied to initiate the ‘Electrical Swing’ was not optimized and it wasn’t clear from the laboratory results whether the dominant effect for the regeneration step was electrical or thermal (electrical resistance heating) driven desorption. High power consumption figures were apparent and peak internal bed temperatures of 50 deg C were achieved leading to the suspicion that the thermal resistance effect was dominant. ORNL made no attempt to optimize the power applied for regeneration.

Capital Cost

An in-house BP assessment was made for the likely capital cost for a unit sized to capture 200,000 tonnes/annum of CO_2 from two LM2500 gas turbine exhausts. This basis was taken from an earlier BP study based on an Alaska scenario (not the CCP baseline).

Comparison of the key elements of the BP amine based route with the ESA route concluded that, like the CCP Alaska baseline, total cost is heavily influenced by the exhaust gas conditioning/cooling system and other auxiliary plant. The cost for the ‘core’ capture facility was similar, with the ESA unit cost trending higher per tonne of CO_2 captured. The large number and size of adsorber vessels required by the process design (which assumed a 10 minute adsorb and a 10 minute desorb cycle) and the large inventory of CFCMS adsorbent required combined to add significantly to the overall unit cost. The capital cost for an ESA capture unit is expected to be higher than for a conventional amine system.

Operating Cost

A brief review of operating costs for the two approaches suggests that ESA will display higher costs due to its high import power requirement (for electrical regeneration). However, it should be noted that the laboratory experiments conducted by ORNL did not attempt to optimize, or even minimize the power required for regeneration. This conclusion may not be reasonable without further work to confirm minimum (optimized) power needs for ESA.

Performance in Other Scenarios and Team Conclusion

The performance of the ESA process within the three other CCP baseline scenarios is not expected to favor its use over post capture (amine based) technologies given its likely higher capital and operating costs.

Some rather fundamental technical issues need addressing before it is likely to compete with and/or better the performance of conventional amine systems;

- The low CFCMS CO_2 loading
- The ‘Electrical Swing Effect’ – is it real?
- The impact of other gas components (water, NOx, SOx etc.).
- Cycle pressure drop and its influence on cycle time (particularly desorption).
- Power requirements for desorption.

The Post Combustion team cannot recommend this technology for further development at this time.

Cost Efficient Design – Nexant – Klimatek funded

This work focuses on reducing the cost of amine capture systems by employing novel process configurations and reduced cost design standards reflecting the ‘non-hydrocarbon’ nature of the process when used in a flue gas/exhaust gas environment.

The work is being undertaken by Nexant and is being executed in three phases;

Phase 1	Cost reduction ideas generation and review of current codes, standards, and amine plant practice.

Phase 2a	Design and cost estimate for a conventional amine capture plant.
Phase 2b	Design and cost estimate for a ‘lower cost’ capture unit employing the ideas, codes and standards selected from phase 1.
Phase 3	Integration of the ‘lower cost’ design into a 350 MW power generation plant, within the NORCAP scenario. Complete process design and cost estimate.

Technical Issues

Nexant has developed a low-cost capture plant based on a number of non-refinery, yet technically viable process design ideas. The plant performance and cost were estimated by commercial process simulators or by vendors with specialized know-how. However, it is recommended that the more radical cost-saving ideas by verified by either pilot or demonstration plant testing. Out of 46 potential cost-saving ideas, Nexant has recommended the following design changes for the standalone, low-cost capture plant:

- Use compact, plate and frame heat exchangers for liquid-liquid service
- Elimination of the flue-gas cooler (relying on evaporative cooling inside the absorber as the flue-gas enters hot)
- Use of structured packing in the absorber to reduce diameter
- Use ANSI-standard pumps instead of API-standard pumps when possible
- Use of a single-train CO_2 compressor instead of two smaller trains
- Reduce overall reboiler steam demand by using lean solution flash and steam ejector
- Relax flue gas blower metallurgy from stainless steel to carbon steel

Capital Cost

The low-cost plant, with all of the above modifications, is expected to have a total capital savings of 42% over the Base Case Amine Plant using traditional refinery standards.

Operating Cost

For operating cost comparisons, the low-cost plant uses 15% less steam, 11% less power, and 12% less cooling water than the Base Case Amine Plant.

Performance in Other Scenarios and Team Conclusion

Although this study was based on the NORCAP scenario, Nexant plans to do an assessment on the effect of other hydrocarbon fuels, such as butane, diesel, and IGCC syngas.

The cost-saving ideas generated by this work appears promising thus far, and the team recommends the completion of the study to 3Q 2003. Additional cost-savings may result from integrating the low-cost plant with the power plant.

Self-Assembled Nanoporous Materials for CO_2 Capture – SRI – DOE funded

This work is investigating the 'design' of adsorbent materials for improved adsorption of CO_2 from low-pressure flue gas streams. SRI International is under taking the work, which is being executed in three phases:

Phase 1	Thermodynamic assessment of co-operative bonding in adsorption processes.
Phase 2	Modeling co-operative bonding effects with Copper Dicarboxylate materials.
Phase 3	Testing of Copper Dicarboxylate materials including the development of a preliminary process design to adsorb CO_2 from low-pressure, dilute, flue gas streams.

Technical Issues

Several samples of Copper Dicarboxylate adsorbents were synthesized and characterized (by XRD, TGA, SEM, BET). The material synthesis procedure is not yet optimized, and it remains a challenge to make high-surface area adsorbents in a reproducible manner. SRI has thus far made about 10-g of material with material in excess of 900 m^2/g. SRI has also received 300-g of similar material from Dr. Seki of Osaka Gas, which only has 600 m^2/g. Both adsorbents will be sent to Adsorption Research, Inc. (ARI) for performance testing and PSA process design.

Initial laboratory results show that the adsorbents exhibit a linear adsorption isotherm for CO_2 and N_2, which is ideal for PSA. The adsorbent reaches its equilibrium CO_2 loading in a matter of minutes, which is similar to commercial zeolites such as 13X and 5A. One key critical issue is whether the CO_2 loading is sufficiently high for a PSA process to by economically viable for flue-gas capture.

Capital Cost

A capital cost estimate of a PSA processing utilizing the SRI material will be generated at the end of 3Q 2003.

Operating Cost

An operating cost estimate of a PSA processing utilizing the SRI material will be generated at the end of 3Q 2003.

Performance in Other Scenarios and Team Conclusion

If successful, the nanoporous adsorbents can be applicable to both post-combustion (low CO_2 partial pressure) and pre-combustion (high CO_2 partial pressure) of CO_2. Although the initial laboratory materials made at SRI are not yet optimized, nominal results appear promising. The structure of the Copper Dicarboxylates appears highly microporous, and the material appears capable of adsorbing large amounts of CO_2 in a reversible manner based on the isotherm measurements.

1.1.1 Adsorption Technology

1.1.1.1 Radical Post-Combustion Technology Investigations

Task - 1.4 - New and Novel Concepts

Given the time available and the need for funds in higher potential areas, this work was stopped.

The CCP Post Combustion Team was to screen many new technology ideas for novel ways to capture CO_2 after combustion. The objective was to evaluate and select up to three promising candidates for further exploratory development during 2003. In each case, up to $50,000 was to be made available to technology developers for preliminary studies.

1.1.1.2 Self-Assembled Nanoporous Materials for CO_2 Capture

Task - 1.4 - "New and Novel" Concepts
Principal Investigator: Ripudaman Malhotra
Technology provider: Stanford Research Institute (SRI)

Highlights

- The synthesis of the copper terephthalate 3-D complex has been achieved, based on literature data by Seki (Osaka Gas). Surface area of the prepared materials ranged from 20 m^2/g to 1200 m^2/g.
- The pore size distribution performed on one sample (surface area, 450 m^2/g) resulted in over 90% of the area with pores less than 20 A°.
- Surface morphology analysis by SEM showed, for a high surface area SRI sample, a multi-lamellar structure whereas the reference Seki material showed a cubic morphology.
- The adsorption of CO_2 and N_2 was measured on the SRI product. The CO_2 isotherm did not level off at the highest pressures tested (1 atm. CO_2), which is consistent with a high capacity of the material to adsorb CO_2. The selectivity of the material for CO_2 over N_2 was estimated to be about 8.

Summary

SRI International, Chemical Science and Technology Laboratory, proposed and is executing the title study to produce sorbent materials for CO_2 capture in pressure swing adsorption (PSA) processes. The overall objective of this fundamental research is to develop new nanoporous materials that will effectively capture CO_2 from power plant flue gases. The study materials were based on work of Seki (Osaka Gas) who has shown that a range of nanoporous structures can be made from copper salts of dicarboxylic acids. The materials have a square cavity whose dimensions can be controlled by the choice of the dicarboxylic acid. Solids with cavities large enough to accommodate four to five methane molecules were shown to have the highest capacity for methane. SRI proposed to synthesize and test these materials that would physi-sorb CO_2 by relatively weak van der Waals forces and that would have a high adsorption capacity for CO_2.

Structures that could accommodate multiple CO_2 molecules at each site may exhibit cooperative binding of CO_2. Binding is considered cooperative when subsequent molecules of CO_2 adsorb onto the material with slightly greater heats of adsorption. In such a case, the PSA system would require less work to capture an equivalent amount of CO_2 than a non-cooperative system. The key objectives of the project have been identified as follows:

- Phase 1 - Demonstrate the thermodynamic validity of the proposed concept and also to demonstrate the computational tools necessary for designing these materials,
- Phase 2 - Synthesize and characterize the new materials, to test them as CO_2 sorbents under PSA conditions, and to perform a cost analysis of a process based on the new materials.

The thermodynamic validation of the proposed concepts and the ability of molecular modeling to describe the adsorption behavior were reported in the February Semiannual Report. It was determined that the optimal heat of adsorption should be only 27kJ/mole to allow a PSA system to operate near ambient temperature. Calculations showed that a modest level of cooperativity would markedly reduce the pressure swing needed to desorb CO_2 from the material. Molecular structure calculations showed that a copper oxalate structure would hold one molecule of CO_2 while the larger copper terephthalate lattice would accommodate four molecules of CO_2 in a single cell.

During the present reporting period synthesis, characterization and evaluation of copper terephthalate, prepared by the procedures of Seki, was undertaken. The two-step synthesis procedure first produced the 2-D complex by reaction of terephthalic acid with copper sulfate followed by pillarization with triethylenediamine to produce the 3-D complex. Over fifty different preparations were conducted to optimize the process. The best materials with high surface areas were obtained with preparations on a 3-6 gram size scale. Larger scale preparations gave poorer results. The complexes obtained had BET surface area measurements between 20 m^2/g and 1200 m^2/g. The pore size distribution of a 450 m^2/g surface area sample was found to have over 90% of its pores less than 20 A° in size. Earlier molecular structure calculations indicated that cavities should be about 10A° in size. The materials have been characterized using scanning electron microscopy(SEM), X-ray diffraction(XRD) and thermogravimetric analysis. SEM studies included a comparison of a high surface area SRI material with Seki's material. Seki's sample showed a cubic morphology while the SRI sample exhibited a multi-lamellar structure. XRD analysis showed that the $2\theta = 9°$ peak intensity that is an indicator of nanoporosity was intermediate between Seki's published data and that measured in our laboratory for Seki's sample. These results give us confidence that our laboratory procedures are capable of producing nanoporous copper phthalate materials.

10 grams of SRI material with surface area exceeding 900 m^2/g and a 30 g sample received from Seki (surface area, 600 m^2/g) were sent to ARI (Adsorption Research Inc.), a subcontractor, to perform further testing. Preliminary measurements of CO_2 and N_2 adsorption on the SRI sample showed that the CO_2 isotherm did not level off even at the highest pressures tested (1 atm. CO_2, corresponding to 20 atm. flue gas containing 5% CO_2). The result is consistent with a high capacity of the material to adsorb CO_2. The selectivity of the SRI material for CO_2 over N_2 was estimated to be about 8.

Plans for the next reporting period include flowing adsorption tests in which simulated flue gas will be passed through a packed bed of pellets pressed from the copper terephthalate 3-D complex. CO_2 breakthrough will be monitored as a function of flow conditions. Pelletization of the powdered material is necessary to maintain a low pressure drop across the bed. Breakthrough tests will yield parameters that will help SRI/ARI design a laboratory PSA system whose performance will then be used in a process model to design and estimate the cost of a full scale PSA system. These are Tasks 5 through 7 in the contracted work:

- Task - 5: **Breakthrough Tests.** Column-flow adsorption experiments (breakthrough tests) will be conducted where both the inflow and effluent gas composition are monitored continuously by mass spectrometry. Some of the parameters that will be varied include: feed velocity, dry versus wet feeds and type(s) of adsorbent. Breakthrough tests provide information on capacity, selectivity, and kinetics under dynamic conditions that simulate those in a PSA cycle.

- Task - 6: **Laboratory-Scale PSA Testing.** A laboratory system for PSA will be assembled to assess the performance of the nanostructured materials. Performance will be measured in terms of CO_2 product recovery, purity, and productivity. A mathematical model will be used to facilitate the selection of the optimum PSA cycle under a given set of operating conditions.

- Task - 7: **Process and Economic Modeling.** The laboratory test data will be used to model and design a PSA system to process a commercial CO_2-capture process (e.g., effluent from a 350-MW combined-cycle gas turbine). After sizing all of the relevant equipment, SRI will use in-house programs to generate a capital and operating cost for the nanostructured adsorbents.

Reports and Publications

- No formal reports or presentations were made during the reporting period.
- The semiannual progress report for this project is in Appendix A under the same heading as this summary.

1.2 Pre-Combustion Technology

Task - 2.0 Develop Pre-Combustion Decarbonization Techniques

The CCP Pre-Combustion Decarbonization Program is based on 13 projects carried out by about 20 different technology suppliers. The studies are divided into 6 main categories as listed below:

- 1.2.1 Membrane studies
- 1.2.1.2 Sorption Enhanced Technology
- 1.2.2 Coke Gasification
- 1.2.3 Integration and Scale-up Studies
- 1.2.3.1 Generation of Hydrogen Fuels for Gas Turbines
- 1.2.4 Integrated Report and Communication

Table 4 provides a complete list of all sub-projects and their status in July 2003.

Table 4: Pre Combustion Technology Studies, Status July 2003

Internal Ref Number	Project Title	Co Funder*	Technology Provider	Status
1.2.1.1.1	Sulfur Tolerant Membrane Study	DOE	Fluor, SOFCo, Eltron, TDA Research, CSM, ECN, University of Cincinnati	Did not pass complete stage gate review Entered into phase II with reduced and revised scope. Eltron, Fluor and SOFCo are remaining technology providers
1.2.1.1.6	Hydrogen Membrane Reactor	EU	BP, Norsk Hydro, KTH, SINTEF, University of Twente, Institute for membrane technology, University of Zaragoza	Passed stage gate review Entered into phase II
1.2.1.1.12	Precombustion Membrane Reactor Study	CCP	Haldor Topsoe	Completed in Feb 2001
1.2.1.2	Production of Hydrogen Fuel by Sorbent Enhanced Water Gas Shift Reaction	DOE	Air Products and Chemicals	Passed phase II stage gate review Entered into phase III which is soon to be completed
1.2.1.3	Compact Reformer with Advanced Pressure Swing Adsorption System for Hydrogen Fuel Production	DOE	Fluor/Davy	Contract Negotiation
1.2.1.4	Hydrogen Membrane Reformer	Klimatek	Norsk Hydro	Passed stage gate Entered into phase II
1.2.2.1	Advanced Technology for Separation and Capture of CO_2 from Gasifier Process Producing Electrical Power, Steam and Hydrogen	DOE	Fluor Federal	Ongoing – close to completion
1.2.3.1	Study of Gas Turbine Retrofit Requirements to Burn Decarbonized Fuel (Hydrogen)	DOE	General Electric	Contract Negotiation

Table 4: Pre Combustion Technology Studies, Status July 2003 (Cont'd)

Internal Ref Number	Project Title	Co Funder*	Technology Provider	Status
1.2.3.2	Standardized PCDC	Klimatek	Jacobs	Contract Negotiation
1.2.3.3	Very Large Scale Autothermal Reforming	CCP	Jacobs	Completed in May 2003
1.2.3.4	Advanced Syngas Study	CCP	Foster-Wheeler	Completed in Feb 2001
1.2.4.1	Capture Study Integrated Reports	DOE	ARI	Contract Negotiation
1.2.5.1	Generation of H_2 Fuels	Klimatek	IFE	Completed Feb 2002

Project Progress and Stage Gate Review

The technology providers were required to define a program scope that would bring the technology to a "proof-of-concept" stage. A stage-gate process was adopted to monitor progress and differences in timing and to be able to redirect the program. Each project identified critical milestones for each stage in the development work. These stage gate criteria were established in collaboration between the CCP and technology supplier with agreed-upon metrics and goals. The stage gate process has been used to make program decisions by a clear process.

The four major projects (bullet list below) in the Pre Combustion technology program were subjected to stage-gate reviews. Three projects passed their stage-gate reviews while one, the Sulfur Tolerant Membrane Study passed part of the criteria and was re-directed in March 2003. The study is underway based on the new focus and direction.

- 1.2.1.1 Sulfur Tolerant Membrane Study
- 1.2.1.1.6 Hydrogen Membrane Reactor
- 1.2.1.3 Hydrogen Membrane Reformer
- 1.2.1.2 Production of Hydrogen Fuel by Sorbent Enhanced Water Gas Shift Reaction,

The results indicate that the membrane technologies have advanced much more than anticipated at the beginning of the project in view of the short development work periods (12-16 months.) The projects were high risk with a substantial likelihood of failure. The membrane developers have overcome significant barriers and are well positioned to continue their work.

The Sorbent Enhanced Water Gas Shift Reaction Study passed its second stage gate in April 2003 and is now in the middle of phase III.

Several integration and scale-up studies will hopefully start up during AUG 2003 with completion in NOV 2003. These studies will bring a broader view of the potential of pre combustion technologies in the different scenarios.

The coke gasification study is close to completion and provides important new information on CO_2 capture from coke-based power plants (like IGCC.) This study includes co-production of high grade hydrogen thus the results gives insight of hydrogen fuel supply cost for hydrogen fuel cell vehicles.

Successes and Highlights

Some of the major successes and highlights in the reporting period FEB 2003 through JUL 2003 were:

- Development of a novel compact design for a membrane water gas shift reactor by SOFCo and improved membrane for a water gas shift reactor by Eltron that will lead to reduced reactor and membrane cost in the US DoE refinery scenario.
- Development of an IGCC unit producing steam and power with CO_2 capture and co-production of hydrogen by Fluor using conventional CO_2 removal technology and new advanced technology called CO_2LDSep. Preliminary results indicates that very low CO_2 avoided cost can be obtained in the US DOE Canadian scenario by adopting pre combustion technology
- Improved design of the membrane reformer process in the NorCap Norwegian scenario which leads to very high energy efficiency, approx. 90-91% (LHV)
- A mathematical reactor model and 2nd generation membranes have been developed for reactor testing in the hydrogen membrane reactor project for the EU supported refinery scenario.
- The leading adsorbent material ADS1-2 has a CO_2 removal capacity of up to 1.1% in PDU cyclic testing. However, a new material has been identified which has the potential for significantly higher CO_2 capacities than the other adsorbents tested. This could lead to significant improvement of the sorption enhanced water gas shift reactor scheme for gas turbine application like the US DOE scenario for Alaska.

Commercial Value - Present and Future

Pre-Combustion technology for CO_2 capture has broader potential than any other capture technology. The technology is widely applicable within syngas production for methanol, synfuel, ammonia and hydrogen etc. Thus technology improvements made by the CCP can be adopted as well in these areas. For example, a large GTL (gas-to-liquids) plant costs about $ 1billion with 60% of the cost being related to the syngas technology.

Significant improvement in some of the technologies could be the basis for low-cost hydrogen for hydrogen fuel cell vehicles in the future. Hydrogen production with capture and storage of CO_2 may be able to “bridge-the-gap” towards the renewable hydrogen economy and make a transition more economically viable.

1.2.1 Membrane Studies

Task - 2.2 Fuel-Grade Hydrogen Generation

Technology Providers:	**Fluor Federal**
	McDermott Technology (SOFCo)
	Colorado School of Mines (CSM)
	TDA Inc,
	Eltron Inc
	Energy Research Center of the Netherlands (ECN),
	University of Cincinnati

The objective of this study is to integrate a hydrogen transfer membrane into a water gas shift reactor to simultaneously produce a high purity hydrogen stream for use in boilers and furnaces and a concentrated high pressure CO_2 stream for geologic sequestration. The MWGS reactor combines water gas shift and CO_2 removal. The hydrogen stream pressure is low therefore this system is not suitable for use in gas turbines.

The project comprises two phases. Phase I focuses on identifying the most promising membrane developed by the four consortia that were selected for testing by the CCP program. The first phase included the development and laboratory-scale testing of the four membrane types for their hydrogen transfer potential and their sensitivity to hydrogen sulfide, water and other gases. Sensitivity to contaminant gases is a key technology issue for the membranes. The membrane classes include palladium alloy, silicate, dense ceramic and microporous silica. All four classes of membrane have been developed and testing began in late 2002. Concurrently, ECN (Netherlands) developed a membrane simulation model for the four membrane types. Fluor Daniel is responsible for incorporating this model into a process simulation model of an actual refinery.

The CCP Pre Combustion Technology Membrane Study program includes 3 individual projects and screening studies by about 15 different technology suppliers. The study is divided into 4 sub-projects as listed below:

1.2.1.1	Sulfur Tolerant Membrane Study
1.2.1.1.6	Hydrogen Membrane Reactor
1.2.1.3	Hydrogen Membrane Reformer
1.2.1.2	Production of Hydrogen Fuel by Sorbent Enhanced Water Gas Shift Reaction

Membrane Studies dominate the CCP Pre Combustion Technology program with major funding by DOE, EU and Klimatek because the analysis and selection processes in 2000 and 2001 showed that the hydrogen membrane was one of the best candidates for achieving the CCP cost reduction target. This is analysis was later supported by economic modeling. All the membrane development work is focused on technologies that combine chemical reaction and hydrogen separation in one step. Two systems has been the key target:

- A one-step process for producing hydrogen-rich fuel and separating CO_2. This is system is normally called the hydrogen membrane reformer.
- A two-step using a conventional syngas-producing technology like autothermal reforming, partial oxidation or steam methane reforming, in which the downstream shift section and physical and/or chemical CO_2 removal system is replaced by a technology that converts the remaining CO in the syngas and simultaneously separates out hydrogen and CO_2. The system is normally called membrane water gas shift reactor.

The key results, highlights and future plans for the projects is discussed below.

1.2.1.1 Sulfur Tolerant Membrane Study

Conclusions from Phase I of the project was:

- The 12-month time frame for Phase I was extremely challenging for developing and testing hydrogen transfer membranes for sour MWGS service.
- Obtaining an adequate selectivity between hydrogen and carbon dioxide is as important as obtaining adequate hydrogen permeation performance. H_2:CO_2 permselectivities of over 50 are required to obtain adequate carbon recovery.
- H_2S can severely reduce the performance of palladium alloy and cermet membranes.
- Based on our process simulation work and preliminary cost analysis, the concept of the membrane water gas shift reactor still shows promise for reducing the CO_2 avoided capture costs.

Based on the Phase I results, the Phase II tasks were modified to:

- The process flow scheme will be modified so that H_2S is removed upstream of the water gas shift section of the plant. This change will provide H_2S-free syngas to the MWGS reactor. The process design will be based on the cermet membrane. Process flow diagrams, heat and material balances and equipment specifications are the deliverables. This work will be transmitted to a CCP cost estimator, who will determine the cost of the capture plant and determine the cost of CO_2 capture with MWGS technology.
- The effort to develop a laboratory-scale, proof-of-concept MWGS reactor will be based on the cermet membrane because it was the only membrane that demonstrated adequate selectivity.
- The preliminary design of a commercial scale MWGS reactor will be based on the Phase I results from the cermet membrane.

1.2.1.1.6 Hydrogen Membrane Reactor

Conclusions from Phase I are:

Significant efforts have been made to improve existing and develop new membrane preparation techniques. The following results have been obtained:

- Very high hydrogen permeances of planar Pd membranes on stainless steel supports have been achieved while permeation of other gases was below the detection limit.
- By deposition of Pd nanoparticles from Pd micro-emulsions on zeolite membranes improved selectivity was achieved.
- The stability of the silica membranes was increased by doping of the γ–alumina support with lanthanum and coating the support with mono-aluminum phosphate.

The work in phase II is focusing on further improving the membranes, reactor testing and development of a process concept.

1.2.1.3 Hydrogen Membrane Reformer

Key results and highlights from Phase I were:

- More than 26 candidate materials were synthesized and permeability measurements were made on 20 of these during Phase I.
- Several process concepts integrating the membrane reformer in combined cycle gas turbine (NorCap scenario) have been developed.
- A reactor model was established to estimate the required membrane surface area. Based on this the hydrogen flux target was defined as a 5 Nml/min/cm^2 H_2 flux at 1000 °C with a total pressure of 20 bar, an initial steam/carbon ratio of 2 with 20% of the hydrogen extracted, and a permeate hydrogen partial pressure of 0.1 bar. This target may give a CO_2 cost reduction close to 50% compared with the NorCap baseline technology.
- Several of materials synthesized reached the flux target at stable conditions

In addition to continuously improve the best candidate membrane the work in Phase II is to produce tubular membrane modules and perform testing at real conditions, i.e. high temperature and pressure.

1.2.1.1 Sulfur Tolerant Membrane Water Gas Shift Reactor System

Background

Phase I of the Membrane Water Gas Shift project was kicked off on March 1, 2002 after a six month delay to finalize the contracts. Four teams were selected to work on developing hydrogen membranes for a membrane water gas shift reactor fed with sour synthesis gas. The Phase I work plan involved screening potential membrane materials, conducting preliminary permeance performance tests with pure or binary gases, and, finally, conducting permeance tests on a prescribed sour syngas composition. The four membrane developer teams are:

- Eltron - Proton-conducting ceramic-metal composites
- Colorado School of Mines/TDA – palladium alloy
- University of Cincinnati – zeolite
- Energy Centre of the Netherlands (ECN) - microporous silica

Phase I also involved developing a membrane simulation program (ECN), which was used to compare the performance of the various membranes. The membrane simulator was integrated into an overall program (Fluor) that simulated an entire pre-combustion de-carbonization facility. The facility was based on the Grangemouth refinery scenario with the feed streams consisting of fuel oil and fuel gas.
In Phase II, the plan called for one or two teams to develop a lab-scale membrane water gas shift reactor. Additional work involved providing a sized equipment list for the PCDC plant and designing a commercial membrane water gas shift reactor.

The original schedule called for these teams to complete their testing with the protocol sour syngas on December 31, 2002. Since none of the teams were able to meet this date, the deadline was moved back to February 28, 2003.

Phase I Summary

The following are brief descriptions of the progress reported by each of the membrane development teams.

Eltron

The Eltron membrane is clearly the most novel and has evolved into a metal alloy membrane 130 microns thick. A thin layer (<0.5micron) of palladium catalyst is coated onto the dense metal substrate. This palladium layer catalyzes hydrogen dissociation and reassociation and may protect the membrane from hydrogen embrittlement. There are two advantages of this membrane:

- The permselectivity between H_2 and CO_2 is infinite because the metal alloy is a “dense” membrane and CO_2 cannot pass through. Leaks through the membrane are eliminated and the catalyst coating does not have to be leak-free.
- The requirements for expensive palladium have been significantly reduced.

Table 5 compares the performance of the Eltron membrane to the “state of the art” membrane that was assumed in the March 2001 Haldor Topsoe (HT) hydrogen membrane feasibility study. It is important to note that the Eltron performance is based on tests conducted with a hydrogen/nitrogen/helium mixture and thus represents a "best case" performance. Values such as driving force, hydrogen flux, and palladium unit costs were kept the same as in the Haldor Topsoe study.

It is clear that the Eltron membrane potentially represents a significant improvement over the "state of the art" assumptions made in the Haldor Topsoe report. Although the permeance is not as high as what HT assumed, the low palladium requirements results in very low palladium costs. These low costs are very close to the costs calculated by the screening task force for the "future" MWGS reactor. Unfortunately, more recent tests conducted with sour syngas showed a drastic reduction in permeance. It was surmised that the H_2S affected the hydrogen disassociation at the catalyst surface. These results are also shown in Table 5.

Table 5: Comparison of Eltron Membrane to Haldor Topsoe's State of the Art Membrane

	Haldor Topsoe study	Eltron Best Case No H_2S	Eltron With H_2S
Thickness, microns	25	0.5	0.5
Temperature, C	?	400	400
Permeance, mol/sm^{2}Pa$^{0.5}$		3.35E-04	2.61E-06
Permeance, Nm^3/hm^{2}bar$^{0.5}$	20	8.6	0.07
Driving force, bar$^{0.5}$	0.7	0.7	0.7
Hydrogen flow, Nm^3/h	230,000	230,000	230,000
Area, m^2	16,429	38,420	4,941,180
Cost, $/oz	1,100	1,100	1,100
Palladium density, g/cc	11.97	11.97	11.97
Palladium volume req., m^3	0.41	0.02	2.47
Palladium weight req., g	4,916,250	229,946	29,572,962
Palladium weight req., oz	173,396	8,110	1,043,038
Palladium cost, MM$	191	9	1147
Membrane cost, $/m^2	11610	232	232

CSM/TDA

Prior to the start of Phase I, this program was rated as having the highest chance of success. Several papers indicated that obtaining an infinite selectivity between hydrogen and other components was achievable. The key questions centered on reducing the thicknesses (and costs) of the palladium layer and determining the robustness of the membrane under sour syngas conditions.

Work has been conducted on palladium/copper alloys on both alumina and stainless steel porous supports. Initial alloy film layers were around 4 microns thick. Unfortunately, defects in the film and/or the seals resulted in very poor H_2:CO_2 selectivities of around 10. (Previous evaluation work by Fluor showed that a minimum H_2:CO_2 selectivity of around 50 is required to meet retentate and permeate purity specifications. This selectivity target was clearly presented to each of the membrane developers at the Mid-Phase I meeting in October of 2002). CSM/TDA suspects that diffusion through the defects is following a mechanism other than Knudsen diffusion. CSM/TDA have been having problems in producing thicker films (~15 microns) to reduce or eliminate defects. Sour syngas tests were conducted with membranes that have previously demonstrated poor selectivity.

University of Cincinnati

The focus of the University of Cincinnati program was to improve the H_2:CO_2 selectivity of zeolite membranes by eliminating intercrystalline micropores. Performance tests on the initial set of zeolite membranes showed very poor H_2:CO_2 selectivities in the range of 3-4. Later membranes showed a slight improvement in H_2:CO_2 selectivity to the 6-8 range.

Table 6: Comparison of Membrane Performance

Membrane Vendor/Type	**ECN - Silica**	**Eltron (Sweet Syngas)**	**Eltron (Sour Syngas)**	**CSM/TDA - Pd-Alloy**	**UCinn - Zeolite**
Overall Gasification Plant Performance					
Gasifier feed (41% fuel oil/59% refinery fuel gas), MMBtu/hr (LHV)	3605.2	3605.2	3605.2	3605.2	3605.2
Natural gas required (for power generation in gas turbine), MMBtu/hr	716.5	716.5	716.5	716.5	716.5
Total feed plus fuel, MMBtu/hr LHV)	4321.7	4321.7	4321.7	4321.7	4321.7
Hydrogen fuel (return to existing boilers), MMBtu/hr (LHV)	2753.8	2654.6	2652.4	2743.5	2776.4
Overall thermal efficiency	64%	61%	61%	63%	64%
CO_2 to sequestration, MMtonnes/yr*	0.70	2.02	2.01	0.92	0.25
Expansion factor	186%	-1%	0%	117%	700%
Non-sequestered CO_2, MMtonnes/yr**	n/a	n/a	n/a	n/a	n/a
Power required, MW	n/a	n/a	n/a	n/a	n/a
HP steam produced, Klbs/hr	n/a	n/a	n/a	n/a	n/a
IP steam produced, Klbs/hr	n/a	n/a	n/a	n/a	n/a
LP steam produced, Klbs/hr	n/a	n/a	n/a	n/a	n/a
Water Gas Shift Membrane Performance					
Syngas feed temperature, C	315	315	450	350	315
Syngas feed pressure, barg	34	34	34	34	34
Sweep gas pressure, barg	2	2	2	2	2
Carbon recovery,%	35.1	100.0	100.0	45.6	12.4
CO_2 purity, dry %	90.0	90.2	90.0	90.0	86.6
Hydrogen recovery, %	95.9	95.3	95.2	97.8	98.9
Hydrogen LHV, Btu/SCF (Note 1)	149.8	149.7	149.8	150.7	150.1
Hydrogen purity, % (Note 2)	53.0	54.7	54.7	54.6	54.4
Permeate H_2, kmol/hr	11653.7	11582.9	11582.4	11883.7	12023.3
H_2 flux, mol/m^2-sec	0.22	0.19	0.08	0.15	0.17
H_2 permeance, mol/m^2-sec-Pascal	1.77E-07	n/a	n/a	2.38E-07	3.27E-07
H_2 permeance, mol/m^2-sec-Pascal$^{0.5}$	n/a	1.966E-4	2.650E-05	n/a	n/a
H_2 pre-exponential factor, mol/m^2-sec-Pascal	4.93E-07	n/a	n/a	2.38E-07	1.46E-07 Note3
H_2 pre-exponential factor, mol/m^2-sec-Pascal$^{0.5}$	n/a	2.87E-02	7.14E+08	n/a	n/a
H_2 Activation Energy, J/mol	5007	24896	186000	0	-3941
H_2:CO_2 permselectivity at feed conditions	4.7	infinite	infinite	5.5	2.6 Note3
Membrane area required, m^2	15,000	17,325	39,000	21,500	19,400
Nitrogen sweep gas required, kgmol/hr	7,000	9,100	9,100	5,000	4,500
Steam sweep gas required, kgmol/hr	230,000	8,800	20,000	20,000	8,000

* Based on 90% on-stream factor

** Includes CO_2 in hydrogen stream and gas turbine exhaust

Notes:

(1) Cooling of fuel to 95F was required to meet LHV requirement

(2) H_2 Purity after water condensation

(3) Permeance at 10 bar

(4) n/a = not available

ECN

The focus of the ECN program was to improve the hydrothermal stability of silica membranes by modifying the silica structure. They also proposed to examine alternative materials such as zirconia or titania. Unfortunately, ECN was not able to investigate these avenues so only standard silica membranes were tested. H_2:CO_2 selectivities of around 18 were reported with dry syngas. Adding water reduced the H_2:CO_2 selectivity to around 9. Tests with sour syngas resulted in H_2:CO_2 selectivities in the 3-5 range.

Membrane Comparison

Each of the membrane developers was requested to provide permeance equations for each of the major components of the entering syngas (H_2, CO_2, CO, H_2O). This information was fed into the membrane model and the results are summarized in the Table 6.

The CCP established performance targets for all membranes were:
The concentration of the CO_2 in the retentate stream must be over 90%.
The lower heating value of the permeate stream must be greater than 150 btu/scf.
The previously mentioned H_2:CO_2 selectivity target of 50 was determined by using the membrane model and adjusting the H_2:CO_2 selectivity until the above two targets was met.

It is clear that only the Eltron membrane has demonstrated sufficient H_2:CO_2 selectivity to meet the purity targets. Unfortunately, the Eltron membrane demonstrated a significant reduction in performance when subjected to a sour syngas feed gas.

Phase I General Conclusions

- The four membrane developers were not successful in developing sulfur tolerant hydrogen membranes.
- Membrane development and testing in a twelve month time span was extremely ambitious and that the firm performance targets were unreasonable.
- More reasonable stage-gate goals such as those adopted for the Membrane Reformer and EU Grace projects should have been adopted.
- In perfect hindsight, other palladium-based membrane developers may have been a better choice than the CSM/TDA team
- The ECN membrane simulation program was inflexible and required high convergence times at elevated membrane areas. Reducing the syngas feed rate did not improve the convergence time.
- The failure of the membrane developers should not be a reason for completely dismissing the MWGS concept
- The Eltron membrane should be considered for development of a MWGS reactor fed with H_2S-free Syngas

Phase II Recommendations

It is clear that the DOE MWGS project has not been able to develop a membrane demonstrating adequate flux and selectivity in a sour syngas environment. Therefore, it has not passed the required stage-gate evaluation. However, the project has provided a novel membrane, having promising design and performance characteristics. The PCDC team recommended that this membrane be the basis for further development and evaluation. Since the membrane cannot tolerate H_2S, a sulfur removal system must be added to the flowsheet upstream of the water gas shift system.

Task 1 –Eltron will develop a MWGS reactor for sweet syngas

Eltron is the only developer who has demonstrated membrane performance that can meet CCP purity targets. By minimizing the use of palladium they have approached the palladium costs estimated in the "future MWGS" case developed by the screening task force. At these cost levels, the screening task force estimated that this represented a reduction of about 25% in avoided CO_2 capture cost. Unfortunately, the catalyst that is used for the hydrogen disassociation step showed a significant sensitivity to H_2S. Although this precludes the Eltron membrane from a sour syngas situation, it is still a viable membrane for desulfurized syngas. It was recommended that Eltron be asked to develop a proof-of-concept membrane water gas shift reactor operating with sweet syngas. Desulfurizing the syngas upstream of the MWGS reactor would produce the sweet syngas.

Task 2 – Fluor will develop the equipment list for the PCDC plant

The Phase I plant simulation model is based on a sulfur tolerant MWGS reactor and removal of H_2S from the CO_2-rich retentate stream.

It was recommended that Fluor be requested to:
- Modify the process simulation model to provide sulfur removal from the syngas so that H2S-free syngas is fed to the water gas shift section of the plant.
- Use this model for providing a process design and major equipment specifications

Task 3 – SOFCo will design and cost estimate the commercial WGS reactor

It was recommended that SOFCo be asked to design a commercial scale MWGS reactor and estimate the cost of this reactor.

Phase II Status

- Phase II of the MWGS project is on schedule.
- Eltron has made considerable improvement in their metal foil membrane, increasing the permeability four-fold.
- SOFCo has developed an innovative design to provide support to Eltron's membrane. Overall, costs should be significantly lower than the costs assumed in the Haldor Topsoe study.
- Fluor is currently finalizing the flowsheet for the revised process scheme.

1.2.1.1.1 Development of Sulfur Poisoning Resistant Palladium/Copper Alloy Membranes for Hydrogen Fuel Production by Membrane Reaction

Task - 2.2 Fuel-Grade Hydrogen Generation
Technology Provider: Colorado School of Mines (CSM)
TDA Research

Highlights

CSM and TDA noted the following achievements:

- Prepared thin films on ceramic supports that can separate hydrogen with a flux of 0.36 $mol/m^2.s$ while maintaining an ideal selectivity of 70,000.
- Pd-Cu alloy membranes were tested under WGS reaction conditions with high sulfur concentrations. We believe that these tests are the first ever completed.
- Binary gas experiments with H_2/CO, H_2/CO_2 and H_2/H_2O showed that hydrogen can be separated from these mixtures without significant degradation in the membrane performance.
- Binary gas experiments also showed that the Pd-Cu alloy films do not catalyze any undesirable side reactions to any significant extent.
- Membranes exposed to the H_2S-free WGS stream performed reasonably well, achieving H_2/CO, H_2/CO_2 and H_2/H_2O selectivity of 20, 12 and 18, respectively. We observed that the separation factor decreased with the addition of the mixture gases.
- H_2/H_2S binary gas experiments showed that in the presence of H_2S, the hydrogen flux decreases due to sulfur inhibition. Under dry gas streams with no water vapor present, a lower (up to 30 to 40% of the original flux) but stable hydrogen flux can be maintained at 20 ppm, 115 ppm and 600 ppm H_2S inlet concentrations. The membrane also maintained its integrity when exposed to H_2S.
- In two attempts, the membranes failed when exposed to WGS gases with 630 ppm H_2S (protocol conditions). In these experiments, overall gas flux increased and the separation effectiveness decreased to Knudsen diffusion level.

Summary

Prior to the start of the project, this initiative by CSM/TDA represented the most promising membrane in terms of both permeance and selectivity. Being a dense membrane, it was expected that the H_2:CO_2 selectivity would be infinite. The key question was whether the palladium alloy layer could be fabricated thin enough so that the permeance was satisfactory and the raw material costs were acceptable. Unfortunately, defects in the film and/or in the seals reduced the performance considerably. The expected H_2:CO_2 permselectivity at the MWGS reactor feed conditions was only 5.5, which resulted in a carbon recovery of only 46% (the target was 90%). The target permselectivity was 50. The presence of H_2S reduced the permeance by 50-60 percent.

The failure of CSM/TDA to produce a leak-free membrane was very disappointing. The short time period of Phase I (12 months) was probably insufficient time to allow this team to rectify this key problem in leakage.

Reports and Publications

- No formal reports or presentations were made during the reporting period.
- The semiannual progress report for this project is in Appendix A under the same heading as this summary.

1.2.1.1.2 Development of Silica Membranes for Hydrogen Fuel Production and Development of A Mathematical Model of the Membrane Reactor

Technology Provider: Energy Resource Centre of the Netherlands (ECN)

Project objectives were to develop microporous silica membranes for use in a water gas shift membrane reactor and to develop a software model of the membrane water gas shift reactor. The project work period was from March, 2002 to February, 2003 and represented Phase I of the Membrane Water Gas Shift study.

Highlights

ECN noted the following achievements:

- The maximum H_2/CO_2 permselectivity measured at 350°C for standard silica membranes calcined at 400ºC was 39 against a target of 50. At a H_2/CO_2 permselectivity of 50, the hydrogen permeance is expected to be between 1 and $0.5*10^{-7}$ mol/m^{2}sPa (= 0.01-0.02 cc (stp)/sec/cm^2 at dP= 1 bar).
- Exposure of standard silica membrane to steam at 350ºC shows as expected a decline in permeance and selectivity. In 15 days the H_2/CO_2 selectivity decreased from 29.7 to 20.9 and the hydrogen permeance with a factor of 3. A modified silica membrane has been on stream in wet gas stability testing for 1000 hours and shows stable and reproducible performance.
- H_2/H_2S selectivity is 400. Three days testing with H_2S has no detrimental effect on a standard silica membrane.
- Gas separation with a dry gas mixture showed that from a feed stream containing 35% hydrogen a permeate stream containing 75% hydrogen could be derived. The presence of water in the feed mixtures reduces the hydrogen permeance and hydrogen purity in the permeate compared to the tests without water.
- The final version of the water gas shift membrane reactor model program was delivered in November 2002. The model is running successfully at Fluor. It includes models for Pd alloy and proton-conducting membrane.

Summary

Prior to the start of the project, there were two concerns over the use of silica-based membranes in a water gas shift reactor. The first concern was over the stability of the membrane in a high moisture environment. The second concern was over the ability of porous membranes, in general, to achieve the target $H_2:CO_2$ permselectivity.

The hydrogen permeance, derived from the hydrogen partial pressure driving force during gas separation testing with a dry gas mixture is well above 0.1 mol/s.m^{2}bar, which is the target permeance for the application. The maximum H_2/CO_2 permselectivity measured at 350°C for standard silica membranes calcined at 400ºC was is 39. At a H_2/CO_2 permselectivity of 50 the hydrogen permeance is expected to be between 1 and $0.5*10^{-7}$ mol/m^{2}sPa (= 0.01-0.02 cc (stp)/sec/cm^2 at dP= 1 bar). H_2/H_2S selectivity is 400. Three days testing with H_2S had no detrimental effect on a standard silica membrane.

Selectivity improvement research is focused on higher sintering temperatures. Increase of the H_2/CO_2 selectivity by increasing the sintering temperature of the silica membranes has not yet been experimentally proven at ECN. Heat-treating the modified silica membranes (with built in inert groups) at 600°C instead of 400°C did not increase selectivity. The majority of these membranes cracked and further testing was not possible.

Exposure of standard silica membranes to steam at 350ºC showed, as expected, a decline in permeance and selectivity. In 15 days the H_2/CO_2 selectivity decreased from 29.7 to 20.9 and the hydrogen permeance with a factor of 3. Thermodynamic calculations at ECN with FactSage™ show that the hydrothermal stability of zirconia and titania is not expected to be significantly better than standard silica. ECN has focused on modified silica membranes for improved hydrothermal stability. A modified silica membrane has been on stream in wet gas stability testing for 1000 hours and shows stable and reproducible performance.

Gas separation with a dry gas mixture showed that from a feed stream containing 35% hydrogen a permeate stream containing 75% hydrogen could be derived. The presence of water in the feed mixtures reduces the hydrogen permeance and hydrogen purity in the permeate compared to the tests without water. Values for Q_o (permeance) and E_{act} (activation energy) to be used as input in the software model have been obtained for the different components in the feed mixture (H_2O, H_2, CO_2, CO and H_2S) through silica membranes.

The preliminary water gas shift membrane reactor model program was provided to Fluor in August 2002 and was run successfully at Fluor. Critical improvements were made and final version with both the Pd alloy and the proton-conducting membrane was transmitted to Fluor in November 2002. The temperature-dependent hydrogen permeance and the flux equations of the dense membrane model have been extensively tested.

Membrane Stability concerns

In their proposal, ECN indicated that they would address the stability concerns by 1) replacing OH-groups with alkyl- groups to reduce viscous sintering and 2) examining alternative materials, such as zirconia or titania. Method 1) was largely successful in that modified membranes showed stable performance for periods over 1000 hours in steam atmosphere testing. The presence of H_2S did not effect performance. Literature research indicated that using alternative materials, such as zirconia or titania, would not increase stability and this approach was abandoned.

Selectivity concerns

The key failure of this technology was the inability of the membrane to achieve the target H_2:CO_2 permselectivity of 50. Permeance equations supplied by ECN showed that the expected H_2:CO_2 permselectivity was only 4.7 at feed conditions. This poor selectivity resulted in an unacceptable carbon recovery of 23% against a target carbon recovery of 90%. The failure of ECN's microporous silica membrane to achieve the target H_2:CO_2 permselectivity was not unexpected.

Membrane water gas shift reactor model

The model supplied by ECN fulfilled the minimum requirements stated by the CCP. However, the model suffered from a lack of flexibility.

- Alternative reactor configurations, such as cross or co-current flow, could not be analyzed.
- Pressure drop on either side of the membrane could not be considered.
- User inputs were limited to seven categories.
- Convergence times were excessive. Work-arounds, such as reducing the gas flows and membrane areas, did not alleviate the problem.

Reports and Publications

- No formal reports or presentations were made during the reporting period.
- The semiannual progress report for this project is in Appendix A under the same heading as this summary.

1.2.1.1.4 Development of Dense Ceramic Hydrogen Transport Membranes for Hydrogen Fuel Production by Membrane Reaction

Technology Provider: Eltron Research, Inc.

Highlights

Phase I extended from March, 2002 to February, 2003. Phase II work period began in April, 2003 and extends to the end of 2003. Eltron noted the following achievements in Phase I:

- Composite membranes were developed with 100% selectivity towards hydrogen permeation.
- New ceramics with the perovskite crystal structure were designed and synthesized to both lattice match and possess similar coefficients of thermal expansion to palladium. Palladium-perovskite cermets were successfully fabricated and tested and found to have hydrogen permeabilities comparable to pure palladium.
- Composite membranes of low-cost metals were fabricated, tested, and found to have hydrogen flux of 12 $mL\text{-}min^{-1}\text{-}cm^{-2}$ (STP) corresponding to permeabilities for hydrogen of up to 6.4×10^{-8} $mol\text{-}m\text{-}m^{-2}\text{-}s^{-1}\text{-}Pa^{-0.5}$ at 320°C, which is superior to that of palladium under similar conditions.
- Membranes of select elements were successfully operated in high-pressure reactors and remained leak-free to helium up to 15 bar differential pressure and 450°C in hydrogen-helium test mixtures.
- A membrane of a select element was run continuously for over three months at 400°C in a hydrogen-helium test mixture, demonstrating long-term stability of the membrane materials towards hydrogen diffusion.
- Various hydrogen dissociation catalysts were screened under the full water-gas shift mixture with steam. Supported platinum-based catalysts showed the best promise.

Eltron noted the following achievements in Phase II:

- Hydrogen transport membranes are being developed and tested. These membranes have ten times the hydrogen permeability of palladium membranes under the same conditions at a fraction of the cost.
- High-pressure reactors have been designed, built, and tested to operate at an absolute pressure of 3.2 million Pascal (32 bar), with a differential pressure of 3.1 million Pascal (31 bar) across the membranes in the water-gas shift temperature range between 593-713 K. Reactors were designed to operate with a partial pressure of steam on the feed side of the membrane of 1.2 million Pascal (12 bar), a partial pressure of hydrogen of 1.3 million Pascal (13.2 bar), and partial pressures of 570,000 Pascal of CO_2 and 106,000 Pascal of CO, to simulate conditions in industrial water-gas shift reactors.
- Membranes, 127 microns thick, have already been tested in preliminary tests for over 300 hours under a hydrogen partial pressure of 0.6 million Pa at 673 K (400°C), and an absolute pressure on the hydrogen feed side of the membrane of 3.2 million Pascal (32 bar), with a differential pressure of 3.1 million Pascal (31 bar) across the membrane. Membranes have successfully resisted the differential pressure without leak and have shown a steady hydrogen permeability of over 2×10^{-8} $mol\cdot m\cdot m^{-2}\cdot s^{-1}\cdot Pa^{-05}$, which is comparable to membranes of pure palladium. In a separate 100hour test at 3 bar partial pressure hydrogen, absolute pressure of 3.2 million Pascal, and differential pressure of 3.1 million Pascal, membrane disks, 1.5 cm in diameter, were found to distort 0.5 mm at the center due to the pressure. Membranes purged of hydrogen and cooled show only the original metallic phase by X-ray diffraction without evidence of hydrides.

- More recent batches of membrane, with improved deposition procedures for membrane catalysts, have consistently shown initial values of hydrogen permeability as high as 2×10^{-7} mol m m^{-2} s^{-1} Pa$^{-0.5}$, which is approximately ten times better than pure palladium under comparable conditions. If these values of hydrogen permeability are maintained under water-gas shift conditions, cost of membrane materials and catalysts is estimated at U.S $1.45 million for a power plant emitting two million metric tons of carbon dioxide annually. For perspective, pure palladium membranes, of similar thickness, would cost U.S. $137 million, at current prices. At carbon dioxide emissions tax rates of U.S. $60 per ton, as in Norway, the annual tax on a power plant with annual carbon dioxide emissions of two million metric tons would be $120,000,000 per year or $329,000 per day. At this tax rate, costs for Eltron membrane materials could be recouped in less than one week, whereas that of pure palladium would require over one year for the materials alone. Eltron's membrane materials thus appear to be economically viable.
- In the first ten weeks of the Phase II project, hydrogen transport membranes have already be integrated with beds of commercial high-temperature water-gas shirt catalysts. New ambient pressure reactors were designed, built and tested. A shift in the chemical equilibrium of the reaction has already been observed as predicted by calculations.

Summary

Phase I, 3/02 – 2/03

This initiative, focused on ceramic membranes, was considered a long range, high-risk alternative to the palladium alloy membranes.

Initially, Eltron focused on two membrane configurations. The first type consisted of a cermet that is a mixture of ceramic oxide and metal (palladium) sintered together. The ceramic oxide was a perovskite that was specifically designed and synthesized to match the coefficient of thermal expansion of palladium and to match the lattice constants of palladium at the atomic level. The ceramic provided mechanical integrity at the temperature levels of the MWGS reactor (300- 400°C) but did not aid in the transfer of hydrogen. This configuration was dropped because of low hydrogen flux rates and high palladium requirements. The second configuration that was initially considered was a ceramic-metal composite. In this case, the ceramic served as a porous support for a dense layer of palladium. The ceramic was again chosen to provide good lattice matching to the palladium. This configuration was dropped because of unacceptable flux rates and high palladium requirements.

Eltron moved on to alternative metals that have hydrogen permeance qualities much higher than palladium at much lower costs. The key concern was a tendency of these metals to swell and be embrittled by hydrogen. A very thin coating of palladium is required on both sides of the metal alloy membrane to provide hydrogen disassociation and reassociation. Preliminary tests conducted at 15 bar differential pressure indicated that the metal alloy membrane may be able to withstand the required pressure differential (~30 bar) without the need of a porous support. This configuration was used for testing with the protocol MWGS reactor syngas feed composition.

Initial flux testing with pure hydrogen/inert gas mixtures and sweet syngas mixtures showed very favorable permeance results. Permeability values were higher than what would be expected with pure palladium. It appears that the hydrogen disassociation step is rate limiting. H_2:CO_2 selectivity was essentially infinite. No stability problems were observed. Unfortunately, when subjected to H_2S containing syngas, performance deteriorated significantly. For this reason, it was decided to modify the flowsheet to provide H_2S-free syngas feed to the MWGS reactor.

Phase II, 4/03 – present

Eltron continues to report significant improvements in the permeabilities of their metal alloy film membrane. Demonstrated permeabilities are as much as an order of magnitude higher than pure palladium and about 4.5 times higher than the performance demonstrated in Phase I. Tests are also being conducted to verify the ability of this membrane to withstand full differential pressure (~30bar).

A water gas shift catalyst has been added to the test system. Apparently, H_2S evolves from this catalyst and poisons the palladium on the membrane. The sulfur on the WGS catalyst is a residue from the catalyst production process. A guard bed was added to adsorb the H_2S.

Eltron was chosen to continue membrane development in Phase II because they were the only membrane developer that could demonstrate adequate H_2:CO_2 permselectivity. Since this membrane is significantly impaired by H_2S, the flowsheet was modified to eliminate H_2S.

Eltron has demonstrated significantly higher permeabilities than achievable with pure palladium. In addition, the metal alloy they are proposing is significantly less expensive than palladium.

Reports and Publications

- No formal reports or presentations were made during the reporting period.
- The semiannual progress report for this project is in Appendix A under the same heading as this summary.

1.2.1.1.5 Development of Sulfur Poisoning Resistant Zeolite Membranes for Hydrogen Fuel Production by Membrane Reaction

Technology Provider: University of Cincinnati

The objective of this project was to develop microporous silicalite (zeolite) membranes for use in a water gas shift membrane reactor. Improvements in H_2:CO_2 permselectivity were to be achieved by reducing or eliminating intercrystalline pores. The project work period was from March 2002 to February 2003 and represented Phase I of the Membrane Water Gas Shift study.

Highlights

The University of Cincinnati noted the following achievements:

- Good quality silicalite membranes were prepared by the template-free secondary growth method. The membranes exhibit a good p-xylene/o-xylene separation factor (as high as 40), indicating that intercrystalline pores of the silicalite membranes have been minimized.
- H_2:CO_2 selectivities as high as 12 were achieved at low pressures. However, at elevated pressures, the H_2:CO_2 selectivity decreased significantly. Based on results from the MWGS reactor model, the expected H_2:CO_2 permselectivity at feed conditions would be only 2.6. This is far below the target permselectivity of 50.

Summary

Prior to the start of the project, the main concern was the H_2:CO_2 selectivity of microporous zeolite membranes. The goal of the development work was to determine if the reduction in intercrystalline pores would improve selectivity significantly.

Silicalite membranes were prepared by the template-free secondary growth method. XRD analysis indicates that silicalite can grow well without an organic template on the surface of silicalite-seeded α-Al_2O_3 supports. SEM showed that the silicalite membranes were about 5 μm thick. The membranes were further characterized by pervaporation experiments with 1,3,5-triisopropylbenzene and xylene and the results indicated good quality with few intercrystalline pores.

Under dry conditions, the ideal separation factors of H_2/CO and H_2/CO_2 were as high as 6 at 500ºC with hydrogen permeance of 1.2×10^{-6} mol/m^2.s.Pa. At lower temperatures the separation factors of H_2/CO and H_2/CO_2 are not so high. The ideal separation factors of H_2/CO and H_2/CO_2 for the silicalite membranes under wet conditions were as high as 9.4 and 8.8, respectively, and the permeance of hydrogen is around 10^{-7}mol/m^2.s.Pa. With the proposed syngas as the feed in the separation experiments, separation factors for H_2/CO and H_2/CO_2 as high as 11.6 and 12, respectively, were obtained for the silicalite membrane. The separation factor decreases at the higher feed side pressure, especially for H_2/CO_2.

The silicalite membranes are chemically very stable. Temperature dependency for the permeability for the linear flux equation was obtained for H_2, CO and CO_2 for the silicalite membrane prepared in this project.

Reports and Publications

- No formal reports or presentations were made during the reporting period.
- The semiannual progress report for this project is in Appendix A under the same heading as this summary.

1.2.1.1.7 Development of Gasification Process Incorporating Membrane Water Gas Shift Reactor for Producing Hydrogen Fuel With CO_2 Capture”

Technology Provider: Fluor Federal

Highlights

Phase I – March 2002 through February 2003:

Fluor developed an AspenPlus process simulation model of the entire capture plant, including the following units.

- Air Separation Unit
- Gasification Island
- Preheating and Bulk Shift Catalyst Unit
- Membrane WGS Reactor
- Permeate Cooling Unit
- Retentate Cooling Unit
- Condensate (Ammonia) Stripper Unit
- Sulfur Recovery (Sulferox) Unit
- CO_2 Compression/Dehydration Unit
- Natural Gas Fired Combined Cycle
- Utilities and Support Systems

A key piece of the work scope was the integration of the WGS membrane simulation model into the flowsheet. The plant model was used to determine the overall plant efficiency, to determine the feed composition to the MWGS reactor, and to provide the basis for equipment sizing that is part of Phase II. Using the WGS membrane simulation model developed by ECN, Fluor provided feedback to the membrane technical providers on the performance of their membranes.

Phase II

Fluor modified the Phase I flowsheet to provide a H_2S-free feed to the MWGS reactor. Fluor is currently developing a equipment specifications list that will be used for cost estimation purposes.

Summary

Phase I 3/02 – 2/03

The original plan called for Fluor to create a simulation model for each of the four types of membranes that were being evaluated in Phase I. Because of the inability of three of the membrane developers to reach the target H_2:CO_2 selectivity, it was decided that only one flowsheet (for the Eltron membrane) was required. The savings were used for various sensitivity studies.

The thermal efficiency based on the production of hydrogen fuel was 61.4%. This was based on sequestrating 2 million tonnes per year of CO_2. The efficiency does not include 37 MW of exported power.

Phase II, 4/03 – present

Flowsheet development and equipment sizing are on schedule.

Reports and Publications

- No formal reports or presentations were made during the reporting period.
- The semiannual progress report for this project is in Appendix A under the same heading as this summary.

1.2.1.2 Sorption Enhanced Water Gas Shift (SEWGS)

Task - 2.1 Gas Turbine Fuels

Technology Provider: Air Products and Chemicals Inc (APCI)

Highlights

- The Phase 2 adsorption development program has been essentially completed and the leading adsorbent material identified for use in the Phase 3 sizing and performance calculations. The Phase 3 work has been initiated, Phase 1 work indicated suitability of the sorption enhanced water gas shift (SEWGS) process for two of the CCP scenarios, both of which involve CO_2 capture from gas turbines, the Phase 3 work has therefore been extended to cover both these cases.
- A novel adsorbent has been identified which has potential for significant future improvement in system performance and cost, but will require additional development and characterization to determine how it should best be deployed and under what conditions, a small additional piece of work (Phase 4) has been initiated to investigate this material. This work is expected to feed into any future development of the SEWGS concept.

Summary

The project is investigating a process to produce hydrogen for use as a decarbonized gas turbine fuel with integral CO_2 capture for geologic sequestration. A combined shift reaction and CO_2 removal process is being developed that could be applied to fired heaters and boilers as well. The initial development program focuses on sweet gas fed systems that could be extended for use in sour gas environments downstream of a coal, coke or residual oil fed gasification system.

The work comprises experimental studies for the development and measurement of the performance of improved adsorbents tailored to the above application. For the experimental studies a single adsorber experimental rig that can be operated in cyclic mode was designed and built to simulate the operation of a multi-bed system. Modeling studies of the combined reaction/adsorption process are underway.

Characterization tests have been conducted on several prospective adsorbent materials, including thermo-gravimetric analysis, breakthrough and cyclic tests in the process development unit (PDU). The adsorption properties of a number of different adsorbent materials have been tested in cyclic service, these cover several different classes of adsorbent and different formulations of each material type.

The leading adsorbent material ADS1-2 has a CO_2 removal capacity of up to 1.1% in PDU cyclic testing. The cyclic adsorption capacity of ADS1-2 has been found to be relatively independent of operating temperature in the region of interest (400-500 ^oC), this is believed to be due to desorption rate increase with temperature compensating for the reduction in equilibrium CO_2 capacity as exhibited in the adsorption isotherm, this implies that the sorbent enhanced reactor is not tightly constrained in operating temperature and can be designed for the optimum temperature for the overall capture process.

A material has been identified which has the potential for significantly higher CO_2 capacities than the adsorbents tested above. This material would require some significant changes to conditions of operation of the SEWGS reactor system. An extension to the adsorption development and characterization study has been initiated to evaluate the options for deployment of this material. Although the state of development is at an early stage, early tests suggests that the material could offer significant improvements in performance and reduction in cost of the SEWGS concept.

Following calibration checks against experimental data, it was concluded that whilst the dual site Langmuir adsorption model can accurately predict the adsorption cycle of the system, the desorption step cannot be accurately represented by this model and extensive additional model development work would be required to correctly predict the unusual desorption characteristics observed. In order to determine the size of the adsorbent/reactor beds, the system has been experimentally operated under PDU conditions, which most closely approach those of the operating plant and this data used as the basis for the sizing calculations. In addition, parametric studies of key parameters such as purge gas flow and steam content has been undertaken to provide a better understanding of the effects of translating this data to the real plant.

An additional experimental investigation was to establish whether the ADS1-2 material exhibited any water gas shift reaction catalytic activity under the high operating temperatures of the sorption enhanced water gas shift (SEWGS) process. This work was delayed by the need to undergo an additional safety review of the suitability of the metallurgy of the experimental rig for syngas service due to concerns about possible metal dusting corrosion, but have now been completed and established that ADS1-2 has no significant water gas shift catalytic activity under proposed process conditions. An assessment will therefore be made of the required quantity of catalyst to be mixed with the adsorbent. It is however considered feasible to support an active catalytic material (e.g. iron/copper) onto the ADS1-2 material, which would reduce the vessel size, hence the sizing is likely to be conservative.

Discussions with valve manufacturers have been initiated to establish the requirements for valve operation under the severe service of SEWGS with process specifications submitted to several vendors to make technical and pricing proposals.

The Phase 3 design study has been initiated, with scope extended to include designs for CO_2 capture from two of the CCP scenarios.

i. Alaska Prudhoe Bay oil production facility gas turbines
ii. 400 MW combined cycle gas turbine

APCI are preparing process designs incorporating the SEWGS system into each of the these cases, starting with the Alaska scenario, the design information for which will be fed into the CCP cost estimating process to give direct cost comparison with the baseline (post-combustion) costs. APCI are liaising with a gas turbine manufacturer to ensure compatibility between the fuel processing plant and the machines and to accurately determine the performance of these machines when fired on de-carbonized (hydrogen) fuel. This will influence the process design, specifically the selection of oxygen or air blown autothermal reformer as the syngas generation step, the steam content and temperature of the fuel all of which influence performance in terms of efficiency, peak power output and NO_X emissions.

It is planned to link this work to a study of the requirements to retrofit the gas turbines to operate on the selected fuel, this will complete the picture of costs of CO_2 capture and address other influencing factors including reliability and maintenance (RAM).

Reports and Publications

Air Products and Chemicals Inc. have prepared the following report for submission with this summary.

- *Production of Hydrogen Fuel by Sorbent Enhanced Water Gas Shift Reaction -Semi-Annual Report February-July 2003*, Jeffrey Hufton, Robert Chiang, Rodney Allam, Ed Weist, and Vince White. (Non-confidential with confidential appendix)
- No formal reports or presentations were made during the reporting period.
- The semiannual progress report for this project is in Appendix A under the same heading as this summary.

1.2.1.3 Compact Reformer with Advanced Pressure Swing Adsorption System for Hydrogen

Technology Provider: Davy Process Technology
Air Products, Ltd.

Highlights

- Proposals have been received from both Davy Process Technology (for the Compact Reformer) and from Air Products Ltd (for the Gemini PSA system).
- Contract details have been submitted to enable the production of a draft contract. This draft is still to be issued to the two above named companies for their approval and signature. Contract start date is likely to be early August 2003 with report delivery at the beginning of November 2003.

Summary

The CCP will develop new and novel technologies to reduce the cost of capturing CO_2 from large industrial combustion sources. Targets have been established for a 50% reduction in the cost to capture CO_2 from existing (retrofit) facilities and a 75% reduction from new-build facilities. To measure progress towards these goals, cost estimates for the application of the technologies must be developed which are prepared on a common, consistent, and comparable basis.

The CCP has defined a number of ‘scenarios’ (combinations of fuel burning equipment and fuel types) that are commonly found in its operations. The scenarios include:

- Large gas-fired turbine combined-cycle power plant;
- Distributed small/medium simple cycle gas turbines;
- Refinery heaters and boilers;
- Petroleum coke gasification.

The main objective of the technology developers will be to prepare process engineering designs and associated cost estimates that allow the technology under development to be compared with other technologies under consideration, on a transparent and comparable basis. The designs and associated costs developed will also be bench marked against a series of baseline studies, developed by the CCP using conventional CO_2 capture technology. The focus of this study will be the Pre-Combustion capture of CO_2 via the Hydrogen production route. The study will incorporate two distinctive technologies:

- Compact Reforming – Davy Process Technology
- Gemini Pressure Swing Adsorption (PSA) – Air Products Limited

The aim of the study is to develop a process design and associated cost estimate that integrates the Reforming and Adsorption units into a single process for the production of hydrogen with the co-incident capture of CO_2 within scenario 3 (Refinery heaters and boilers).

The study aim is to capture 2.0 million tonnes per annum of CO_2 by utilizing refinery fuel gas streams as feed to the combined Reformer/PSA unit and subsequently utilizing the produced Hydrogen as a substitute fuel in the refinery heaters and boilers. The CO_2, captured as a pressurized product from the Gemini PSA unit, will be further compressed for export for use in an offshore enhanced oil recovery scheme.

Reports and Publications

- No formal reports or presentations were made during the reporting period.
- The semiannual progress report for this project is in Appendix A under the same heading as this summary.

1.2.2 Coke Gasification

1.2.2.1 Advanced CO_2 Separation Technologies for Integrated Gasification Combined Cycle (IGCC) Processes

Task - 2.3 Systems Integration and Optimization
Technology Provider: Fluor Daniel

Highlights

- Baseline cost estimates for the Canadian Petroleum Coke Scenario were completed and the final non-confidential report was delivered to the CCP

- A reliable CO_2 avoidance cost can be calculated for a world-scale Integrated Gasification Combined Cycle (IGCC) facility designed to capture CO_2 using today's commercially available technologies. This cost that is being calculated by the CCP Common Economic Modeling Team will be transparent and robust and able to withstand stakeholder scrutiny as a result of this rigorous process design and cost estimating work done by a credible third party (Fluor).

- Total Installed Costs for a Fort McMurray, Alberta plant are:
  - No CO_2 capture, uncontrolled release, case: $870million USD
  - 90% CO_2 capture case: $1,360million USD

- Qualitative screening on ten advanced technologies with potential application to the Canadian Petroleum Coke Scenario was conducted using these criteria:
  - Ability to capture between 85% and 90% of carbon
  - Ability to produce CO2 with less than 30 ppmv of H2S
  - Ability to produce CO2 at greater than 97 mol %
  - H2 produced at pressure to minimize compression costs
  - Sulfur tolerant process

- Qualitative screening exercise identified CO_2LDSep as the most promising advanced technology for reducing CO_2 capture costs as compared to the controlled baseline

Summary

This work evaluates advanced (i.e. not yet commercially available or commercially demonstrated) CO_2 separation technologies for integration into a pre-combustion IGCC process scheme. The objective is to identify those technologies that can deliver a 50% to 75% cost reduction in the capture costs of CO_2 over today's IGCC technologies.

The conceptual IGCC plant used in this study would gasify petroleum coke to produce steam, electricity, and refinery grade hydrogen. It is based on the Canadian petroleum coke scenario being used by the CCP to focus their CO_2 capture work.

Baseline costs were defined for an IGCC process using commercially available technologies. Two baseline cost estimates were prepared; an uncontrolled case without no CO_2 capture and a controlled case in which where 90% of the CO_2 is captured by commercially available technology. Both baselines consist of an IGCC plant that gasifies petroleum coke using high purity oxygen in a high pressure total quench gasifier based on ChevronTexaco technology.

The base cases produce the same amount of steam (1,300,000 lbs/hr) and hydrogen (60,000,000 SCF/day); however, the controlled base case electrical power output is about 100 MWe higher than the uncontrolled case because of the addition of another combustion turbine.

Since the Uncontrolled Baseline Case represents state-of-the-art with no CO_2 capture and the Controlled Baseline Case represents currently available commercial technologies to capture CO_2, these base cases represents the reasonable estimates of the costs industry would incur if they were required to capture CO_2 for storage purposes today.

Advanced Technologies:

The Advanced Cases are similar to the Controlled Baseline Case except that new, technologies are inserted in place of commercially available technologies. The Advanced Cases were used to:

(i) learn how best to integrate these new technologies into a practical IGCC design,

(ii) determine the reduction in CO_2 capture costs that can be obtained by using advanced technologies, and

(iii) elucidate process performance and cost goals the advanced technologies must meet in order to deliver on the CCP cost reduction targets (75% for new facilities and 50% for retrofits)

The list of considered technologies included the following, in addition to those technologies under development in the CCP program:

- sorbent enhanced reforming
- water gas shift membranes
- Gemini pressure swing adsorption

In addition to the above technologies, Fluor Daniel has identified their proprietary autorefrigeration COLDSEP technology as having cost reduction potential in an IGCC application tailored to the Canadian petroleum coke scenario. CCP asked that this technology be included as an advanced technology Fluor Daniel.

Reports and Publications

- "CCP Baseline Costs for Four Real-Life Scenarios", presentation given by Iain Wright of the CCP at the 2nd Annual DOE NETL Conference on Carbon Sequestration, May 5-8, 2003.
- The semiannual progress report for this project is in Appendix A under the same heading as this summary.

1.2.3 Integration and Scale-up Studies

The CCP Pre-Combustion Technology Integration and Scale-up Study program includes five studies.: The objective in the integration and scale-up studies is to apply commercially -, or close to commercially-, available pre-combustion technology to the four CCP scenarios. By system integration, optimisation and value engineering it is expected that significant cost reductions can be obtained at very low risk.

The results, highlights and future plans for different activities is given below:

- 1.2.3.1 Study of Gas Turbine Retrofit Requirements to Burn Decarbonized Fuel (Hydrogen). The study has not started and is still in contract negotiation.

- 1.2.3.2 Standardised PCDC: The study has not started and is still in contract negotiation. The work will be done in collaboration with IEA. Norsk Hydro prepared a report summarizing earlier pre-combustion studies and included recommendations on technology choices.

- 1.2.3.3 Very Large Scale Autothermal Reforming: A plant concept using a gas-heated reformer was suggested by the technology provider. An internal assessment identified very small benefits so no further work was initiated.

- 1.2.3.4 Advanced Syngas Technology: The advanced syngas technology was screening study of different technology options for an integrated reforming combined cycle focusing on commercially available technologies. The results showed no significant improvement over the base case thus no further work was recommended in this area.

- 1.2.3.5 Compact Reformer with Advanced Pressure Swing Adsorption System for Hydrogen Fuel Production: The study has not started and is still in contract negotiation.

1.2.3.1 Gas Turbine Retrofit Requirements to Burn Decarbonized Fuel (H_2)

Highlights

- GE manufactured seven of the eleven gas turbines in the Alaska scenario and is the only gas turbine manufacturer to have published data on the firing of carbon free hydrogen rich fuels for CO_2 capture applications. A Statement of Requirements for the Study has been prepared and agreed by the CCP Precombustion Team and submitted to GE to tender and discussions held to clarify the aims and deliverables of the study.

- Contract Negotiations are underway.

Summary

One scenario that CCP uses evaluate CO_2 capture processes is a gas compression facility in Alaska's North Slope oilfields. It includes four GE Frame-6 and three GE Frame-5 gas turbines in gas compression service. Application of pre-combustion capture technology to this scenario requires that the gas turbines can be modified to burn hydrogen as a fuel without adversely affecting the key performance characteristics such as power output, turndown, emissions and reliability. This retrofit study will evaluate a range of hydrogen fuel mixtures on generic GE Frame-5 and GE Frame-6 Gas Turbines. Fuel compositions will be selected to cover the composition range anticipated from PCDC capture technologies.

The study will cover issues of hydrogen firing feasibility and its effects on the performance and emissions from the machine. Key considerations in the design of the overall capture scheme such as the fuel temperature and steam content will be studied. It is anticipated that some of the hydrogen fuel compositions available will enable significant reductions in the NO_X emissions from the existing machines, and all PCDC schemes will totally eliminate sulphur oxide emissions.

GE will also evaluate the engineering modifications required to accommodate the change to hydrogen fuel and provide scoping engineering work requirements and estimate the cost of implementation.

The objectives of the Gas Turbine Retrofit Study as follows

1. Establish the feasibility of firing a carbon-free hydrogen rich fuel on generic GE Frame 5 and GE Frame 6 type Gas Turbines.
2. Evaluate alternate hydrogen fuel mixtures for gas turbine firing
3. Predict the performance of the gas turbines on the same range of fuels.
4. Determine costs of retrofitting an existing machine to permit hydrogen firing

The major tasks that will be completed in this study are:
1. Requirements definition.
2. Condition assessment
3. Combustion assessment
4. Performance predictions
5. Conversion Requirements
6. Summary Report

Reports and Publications

None – project has not yet been started.

1.2.4 Capture Studies Integration and Reporting

1.2.4.1 Capture Study Integrated Reports

Technology Provider: Advanced Resources International.

Early stage work for final reporting of the Capture Studies effort is underway. A rough outline for the book has been prepared.

1.3 Oxyfuel Technology

Overview

The principle of CO_2 capture by oxyfuel combustion is to burn fuel with oxygen rather than air so that the flue gas consists mainly of CO_2 and water with little nitrogen. CO_2 can then easily be separated. However, oxygen combustion would result in very high combustion temperatures without the nitrogen diluent from air. It is usually proposed that a fraction of the flue gas be recycled as a substitute diluent. Other novel solutions may be feasible such as injecting recycled water as a diluent or using high temperature materials in place of recycle.

Studies, including pilot scale testing on coal, indicate that oxyfuel combustion with flue gas recycle can be retrofitted to boiler and other heating plants with no major technical obstacles. Gas turbine applications would require costly development of new combustors, compressors, and turbines to accommodate the change in working fluid. These studies have shown that the major additional capital and operating costs in oxyfuel combustion for CO_2 capture are those associated with oxygen production when development and new gas turbine design costs are excluded.

No oxyfuel technologies have been demonstrated on a commercial scale for CO_2 capture and therefore there is no existing oxyfuel technology against which to assess cost reductions for new approaches. However, most studies suggest that overall capture costs for the oxyfuel flue gas recycle techniques would be comparable with those for existing post-combustion capture methods. Therefore for the purpose of this assessment the basic oxyfuel flue gas recycle techniques have been taken as baselines.

While oxyfuel combustion is not currently used for CO_2 capture, it should be noted that combustion in pure oxygen or in oxygen enriched air in special high temperature furnaces is widespread in the metallurgical, glass and other industries, and therefore the operational and safety issues of oxygen combustion are well understood.

New and lower cost oxygen production methods are under active development which means that the overall cost of oxyfuel concepts, i.e. those using flue gas recycle, should fall significantly. The potential for oxyfuel combustion to be retrofitted to existing boilers and heaters makes this route attractive to the CCP. Other concepts under consideration are integration of oxygen generation directly with the combustion system that may have further cost reduction potential. Other proposals seek to take advantage of the distinctive characteristics of oxyfuel combustion to conceive power plants with higher efficiency and/or lower capital cost, in order to offset the cost of generating oxygen. One proposal, called chemical looping, looks at a novel, potentially energy saving, process that combines air separation with fuel oxidation.

The future economic driver for the adoption of oxyfuel technologies lies mainly in novel technologies for air separation that are able to reduce drastically the cost of oxygen production. The CCP may benefit from DOE co-funded R&D projects aimed to develop novel ceramic membranes for air separation that are able to permeate oxygen with 100% selectivity. The CCP funded several studies to assess the technical and economic potential of these technologies applied to CO_2 capture. A baseline using conventional air separation for oxygen supply was also established.

Other approaches, considered in the technology selection phase of CCP (high pressure boilers, zero recycle boilers, advanced cycles), were discarded after preliminary studies showed no promising economics.

Novel Ceramic Membranes
This period saw the completion of the baseline study funded by the CCP and commissioned to Air Products concerning the retrofitting boilers and heaters in the Grangemouth refinery (BP – UK) using conventional cryogenic air separation to capture 2 million tonnes per year of CO_2 from refinery combustion effluents. Phase II of the study evaluating retrofitting the same boilers and heaters in Grangemouth using the novel ITM (Ionic Transport Membranes) technology being developed by a consortium led by Air Products and co-funded by the DOE with the target of commercialization by 2008. The results of this study will allow assessment of the economic potential of ITM in CO_2 capture.

A novel technology, AZEP (Advanced Zero Emission Power), based on the integration of ceramic air separation membranes being developed by Norsk Hydro with a gas turbine system designed by Alstom Power. The AZEP development is co-funded by the European Community in a three-year project started in January 2002. CCP funded an evaluation of this concept for a selected turbine in the Alaskan scenario of the CCP. Activity started in May 2003 and the final reports will be issued in October 2003.

Chemical Looping
The only large Oxyfuel R&D project funded by the CCP is the chemical looping project briefly described above. This project has seen a remarkable development since the start in January 2003. Due to the wide range of disciplines involved, the activity has been split into five different packages, covering different aspects of the work:

- T-051 Project Management (BP).
- T-079 Particle Screening and Development (CSIC).
- T-089 Pilot Unit Design, Construction and Operation (Chalmers).
- T-095 Hydrodynamic experiments (Vienna Univ.).
- T-058 Engineering scale-up and Economics (Alstom).

The chemical looping combustion concept is based on the transfer of oxygen from the combustion air to the fuel by means of an oxygen carrier such as a metal oxide. Central to the system are an air reactor and a fuel reactor. The gaseous fuel is introduced to the fuel reactor, where it is oxidized by the oxygen carrier (the metal oxide, MeO). A description of the combustion process for methane fuel follows:

$$\mathrm{MeO} + \mathrm{CH_4} \rightarrow \mathrm{ME} + 2\mathrm{H_2O} + \mathrm{CO_2} \qquad (1)$$

The exit gas stream from the fuel reactor contains CO_2 and H_2O, and almost pure CO_2 is obtained when H_2O is condensed. The particles of the oxygen carrier are transferred to the air reactor where they are regenerated by taking up oxygen from the air:

$$\mathrm{Me} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{MeO} \qquad (2)$$

The air reactor gives a flue gas containing only N_2 and some unused O_2. The total amount of heat evolved from reactions (1) and (2) is the same as for normal combustion, where the oxygen is in direct contact with the fuel. The significant advantage compared to normal combustion is that the CO_2 is not diluted with N_2.

While this approach may not be suited for air separation, since it does not convey pure nitrogen, it may extract from air the required amount of oxygen for oxyfuel combustion. The CCP is directly funding R&D activities on chemical looping through the GRACE Project (co-funded by the European Community), managed by BP, with Alstom Power, Chalmers University, Vienna University and CSIC as Partners. The Project started in January 2002 and activities will be completed by end of December 2003. Target of the Project is the achievement of Proof-of-Feasibility through operation of a large fluidized bed pilot unit (riser reactor 2 meters high per 2 inches internal diameter) complete with reactor/regenerator system and continuous circulation of solid, at Chalmers University.

Main achievements of the last semester are:

- Completion of the pilot unit and operation in hot hydrodynamic mode with sand for troubleshooting and training of operators.
- Preparation of 15 kg of Ni/Al catalyst as the first batch to be tested in the pilot unit. Preparation was made by freeze granulation that should simulate spray drying on a small scale.
- Detailed kinetics on Fe/Al and Cu/Ti particles that will constitute next batches for the pilot unit.
- Construction of a large “mock-up” at Vienna University to define rules for hydrodynamic scale-up of the reactor/regenerator and solid circulation system.

The next period will see operation of the pilot unit with different catalysts to reach the main target of the Project and operation of the “mock-up” to define hydrodynamic rules. Alstom will perform a technical/economical evaluation to assess the potential of the technology at the commercial level.

Post-CCP activities and conclusions

As stated above, no oxyfuel technology will be ready for commercialization by the end of 2003. The novel technologies required to perform oxyfuel CO_2 capture will be ready for the market by 2008, at best.

Oxyfuel technologies may fit into different scenarios from atmospheric pressure boilers to high pressure gas turbine applications. Even chemical looping, currently investigated for atmospheric pressure boilers may be extended to high pressure combustion for gas turbines as already proven in a DOE-funded project. The main additional issue in this case is the feed of dusty gases to the turbine. This might require turbine mechanical development or high temperature filtering systems still in the development phase. This extension may be feasible using work on high temperature filters being carried out independently by major companies in the field.

1.3.1 Advanced Boiler Study

Technology Provider: Praxair

Highlights

- Contract negotiations are in the final phases. The work should be completed by end of October 2003.

Summary

This study is in coordination with a DOE funded study by Praxair. The objective of the Praxair study is development of technology to fit novel ceramic membranes for air separation (OTM – Oxygen Transport Membranes) into a newly designed boiler that combines air separation and combustion in a single unit. The CCP add-on study will consider the replacing an existing boiler in the Grangemouth refinery with a novel boiler including OTM membranes.

Publications

None at this time.