

Report Title

**CO<sub>2</sub> Capture Project - An Integrated, Collaborative  
Technology Development Project for Next Generation CO<sub>2</sub>  
Separation, Capture and Geologic Sequestration**

**Technical Progress Report**

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## Abstract

The CO<sub>2</sub> Capture Project (CCP) is a joint industry project, funded by eight energy companies (BP, ChevronTexaco, EnCana, Eni, Norsk Hydro, Shell, Statoil, and Suncor) and three government agencies (European Union {DG Res & DG Tren}, Norway {Klimatek} and the U.S.A. {Department of Energy}. The project **objective** is to develop new technologies, which could reduce the cost of CO<sub>2</sub> capture and geologic storage by 50% for retrofit to existing plants and 75% for new-build plants. Technologies are to be developed to “proof of concept” stage by the end of 2003. The project budget is approximately \$24 million over 3 years and the work program is divided into eight major activity areas:

- **Baseline Design and Cost Estimation** - defined the uncontrolled emissions from each facility and estimate the cost of abatement in \$/tonne CO<sub>2</sub>.
- **Capture Technology, Post Combustion:** technologies, which can remove CO<sub>2</sub> from exhaust gases after combustion.
- **Capture Technology, Oxyfuel:** where oxygen is separated from the air and then burned with hydrocarbons to produce an exhaust with wet high concentrations of CO<sub>2</sub> for storage.
- **Capture Technology, Pre -Combustion:** in which, natural gas and petroleum coke are converted to hydrogen and CO<sub>2</sub> in a reformer/gasifier.
- **Common Economic Model/Technology Screening**: analysis and evaluation of each technology applied to the scenarios to provide meaningful and consistent comparison.
- **New Technology Cost Estimation:** on a consistent basis with the baseline above, to demonstrate cost reductions.
- **Geologic Storage, Monitoring and Verification (SMV):** providing assurance that CO<sub>2</sub> can be safely stored in geologic formations over the long term.
- **Non-Technical:** project management, communication of results and a review of current policies and incentives governing CO<sub>2</sub> capture and storage.

Technology development work dominated the past six months of the project. Numerous studies have completed their 2003 stagegate review and are reported here. Some will proceed to the next stagegate review in 2004. Some technologies are emerging as preferred over others.

Pre-combustion De-carbonization (hydrogen fuel) technologies are showing excellent results and may be able to meet the CCP's aggressive cost reduction targets for new-build plants. The workscopes planned for the next key stagegates are under review before work begins based on the current economic assessment of their performance. Chemical looping to produce oxygen for oxyfuel combustion shows real promise. As expected, post-combustion technologies are emerging as higher cost options but even so some significant potential reductions in cost have been identified and will continue to be explored.

Storage, measurement, and verification studies are moving rapidly forward and suggest that geologic sequestration can be a safe form of long-term CO<sub>2</sub> storage. Hyper-spectral geo-botanical measurements may be an inexpensive and non-intrusive method for long-term monitoring. Modeling studies suggest that primary leakage routes from CO<sub>2</sub> storage sites may be along old wellbores in areas disturbed by earlier oil and gas operations. This is good news because old wells are usually mapped and can be repaired during the site preparation process. Wells are also easy to monitor and intervention is possible if needed. The project will continue to evaluate and bring in novel studies and ideas within the project scope as requested by the DOE. The results to date are summarized in the attached report and presented in detail in the attached appendices.

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# Executive Summary

The CO<sub>2</sub> Capture Project (CCP) is a joint industry project, funded by eight energy companies (BP, ChevronTexaco, EnCana, Eni, Norsk Hydro, Shell, Statoil, and Suncor) and three government agencies (European Union {DG Res & DG Tren}, Norway {Klimatek} and the U.S.A. {Department of Energy}). The merger of Chevron and Texaco (both were participants) at the end of 2001 caused the number of industry participants to drop from nine to eight for 2002.

The project **objective** is to develop new technologies, which could reduce the cost of CO<sub>2</sub> capture and geologic storage by:

- 50% for retrofit to existing plants and
- 75% for new-build plants.

Technologies are to be developed to “proof of concept” stage by the end of 2003.

Cost reductions will be benchmarked against four practical case studies (termed **scenarios within the CCP context**), which were chosen to represent real-life energy industry applications:

- An existing large European refinery (Grangemouth, UK).
- A large new-build electrical power generation facility in Norway.
- A group of existing distributed gas turbines Alaska, USA.
- A new-build integrated gasification combined-cycle coke de-gasification facility in Canada.

The project budget is approximately \$24 million over 3 years and the work program is divided into eight major activity areas:

- **Baseline Design and Cost Estimation.** For each of the four applications baseline designs have been developed. These define the uncontrolled emissions from each facility, developed a design for CO<sub>2</sub> abatement using the current best available technology (BAT), and estimated the current cost of abatement in \$/tonne CO<sub>2</sub>. Technology advances made by CCP will be benchmarked against the best available technology on a consistent basis.
- **Capture Technology, Post Combustion:** technologies, which can remove CO<sub>2</sub> from exhaust gases after combustion.
- **Capture Technology, Oxyfuel:** where oxygen is separated from the air and then burned with hydrocarbons to produce an exhaust with high CO<sub>2</sub> for storage.
- **Capture Technology, Pre -Combustion:** in which, natural gas and petroleum coke are converted to hydrogen and CO<sub>2</sub> in a reformer/gasifier. The CO<sub>2</sub> is compressed for storage and the hydrogen is mixed with air for combustion, emitting only nitrogen and water.
- **Common Economic Model/Technology Screening:** analysis and evaluation of each technology applied to the scenarios to provide meaningful and consistent comparison.
- **New Technology Cost Estimation:** on a consistent basis with the baseline above, to demonstrate cost reductions.
- **Geologic Storage, Monitoring and Verification (SMV):** providing assurance that CO<sub>2</sub> can be safely stored in geologic formations over the long term.
- **Non-Technical:** project management, communication of results and a review of current policies and incentives governing CO<sub>2</sub> capture and storage.

The two charts (Figures 1 and 2) below illustrate the total project budget, respectively split broken down by activity areas and by funder spend.

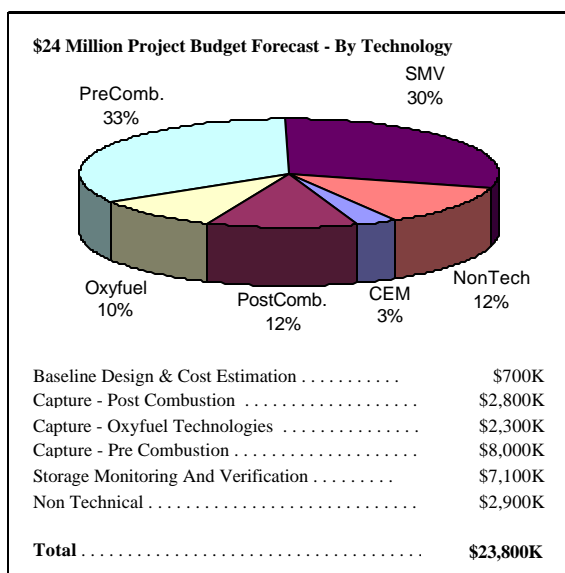


Fig 1. CCP Spend By Activity Areas

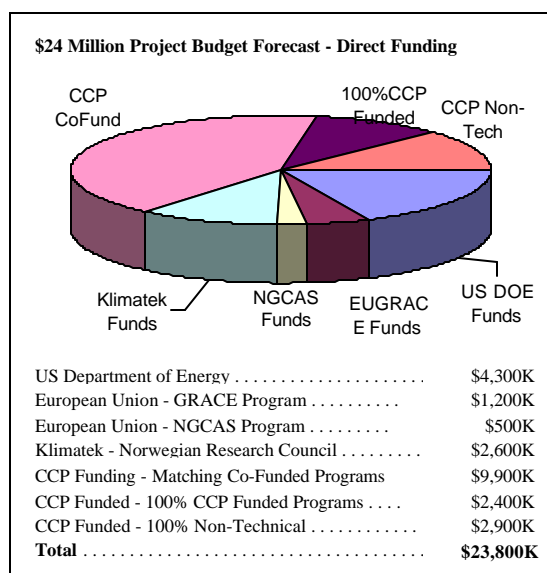


Fig. 2 Program Spending By Funder

During 2001, the project completed a comprehensive review and analysis of existing commercial technologies, technologies under development and identified high-potential technologies for further analysis. Fifty technologies were chosen for development within the CCP and over eighty contracts were signed with technology providers in multiple countries, to deliver that program. A **Common Economic Model (CEM)** was completed and peer reviewed by industry experts Ed Rubin (Carnegie Mellon University, Pittsburgh Pennsylvania) and Howard Hertzog (Massachusetts Institute of Technology Boston, Massachusetts.) The model was used to evaluate each scenario baseline (with and without CO<sub>2</sub> capture) as well as key capture technologies that show most promise.

During 2002, it became apparent that the cost of performing rigorous cost estimation for every technology in every scenario would be prohibitive, so the Executive Board established a **Technology Screening Task - Force (TSTF)** to provide early indications of abatement costs and help to choose the technologies most likely to meet CCP objectives. At the end of the year, the work of the CEM & TSTF yielded CO<sub>2</sub> avoidance costs (+/-30%) for several technologies of up to 60% below BAT. At major decision points, CCP processes and decisions were peer reviewed by a **Technology Advisory Board (TAB)** comprising independent experts from industry, government and academia. A **Policies and Incentives** team was formed during 2002 with the objective of producing a comprehensive review of existing policies governing CO<sub>2</sub> Capture & Storage. **Outreach** to stakeholders built on the two successful workshops held in Europe and the USA in 2000 and 2001. The project website <http://www.co2captureproject.org/> is updated regularly as the project develops and reports are delivered. The website has over 5000 non-project visitors monthly. Technical papers were delivered at several industry conferences - notably the International Energy Association's (IEA) Sixth GreenHouse Gas Technology conference (GHGT-6) in Kyoto, Japan.

# September 2003- February 2004 Progress

## Post-Combustion Studies

In post-combustion capture, CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> emitted. Improving the economics of post-combustion capture is therefore a critical goal for the entire CO<sub>2</sub> 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<sub>2</sub> content, near atmospheric pressure, high in volume, and often contaminated with other impurities (SO<sub>x</sub>, NO<sub>x</sub>, and 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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 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<sub>2</sub> Capture (SRI)



The CCP has determined that entirely new approaches will be required to reduce the cost of post-combustion CO<sub>2</sub> 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<sub>2</sub> Capture,” was a high-risk program that may be useful in retrofit and new-build applications as well as pre-combustion CO<sub>2</sub> capture. There were technical successes in preparing nanoporous materials but the activity was so low that very large systems would be required. The estimated implementation costs were about \$450/tonne CO<sub>2</sub> avoided so the study has been stopped. 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.

## Pre-Combustion Studies

Significant progress was made in pre-combustion de-carbonization technology and advancement in several key areas was achieved. Further, new insight of adopting existing technology into the CCP scenarios was achieved. The key messages from the development work are:

- Four new advanced technologies were developed to “proof-of-concept” with significant advancement in efficiency, cost and CO<sub>2</sub> capture compared to best available capture technology.
- Three of the new advanced technologies were designed for three different CCP scenarios by the technology providers. The design was checked, integrated and cost estimated by an independent contractor (Fluor) in order to assure quality of the design and consistency when comparing with the baseline technology, thus enhancing credibility of the conclusions.
- Significant advancement in hydrogen membrane material covering a wide temperature range.
- Further development is needed to advance the most promising technologies, however it is expected that new technologies can be developed and demonstrated in 2008-2015 with costs in the range of \$ 15-40 MM.
- Pre-combustion technology can be developed to meet stringent requirement on NO<sub>x</sub>, CO and SO<sub>x</sub> formation. The lowest NO<sub>x</sub> formation was predicted to 5ppm vol. from a combined-cycle gas turbine. For open-cycle gas turbines, the NO<sub>x</sub> formation was reduced by 50%. The CO and SO<sub>x</sub> formation is virtually zero.
- Pre-combustion technology can be designed as a stand-alone facility for both retrofit and new build application giving a wide application range and benefits with respect to integration in existing complex facilities, e.g. refineries
- Pre-combustion technology can be used for other application, e.g. GTL, ammonia, hydrogen and syngas production, thus increasing the economic potential of the technology and return of investment.
- Significant improvement in energy and CO<sub>2</sub> capture efficiency was obtained for several technologies, resulting in an efficiency penalty for combined-cycle gas turbines of less than 5% - point and close to 100% CO<sub>2</sub> capture.
- 15% improvement of gas turbine heat rate can be obtained when switching from natural gas to hydrogen-rich fuel, making the pre-combustion technology a strong candidate for the large numbers of open-cycle gas turbines in operation in the US.
- Demonstrated very low CO<sub>2</sub> avoided cost numbers for the Canadian scenario – CO<sub>2</sub> capture from pet coke fired IGCC – approximately 10-15 \$/ton.
- Existing Pre-combustion technology can be considered proven for a wide range of CO<sub>2</sub> capture applications including the CCP scenarios

## Oxyfuel

The principle of CO<sub>2</sub> capture by **oxyfuel** combustion is to burn fuel with oxygen rather than air so that the flue gas consists mainly of CO<sub>2</sub> and water with little nitrogen. However, oxygen combustion would result in very high combustion temperatures without the nitrogen diluent from air. 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<sub>2</sub> capture are those associated with oxygen production when new gas turbine design costs are excluded. 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 technology, 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<sub>2</sub> capture. A baseline using conventional air separation for oxygen supply was also established.

When CO<sub>2</sub> capture is not required, Oxyfiring is inherently more expensive than combustion with air using current state-of-the-art technologies. Potential advantages of oxyfiring deriving from smaller equipment size are offset by costs related to cryogenic air separation and flue gas recycle necessary to maintain acceptable temperature levels in the equipment (boiler/heater/gas turbine). When considering CO<sub>2</sub> capture, however, oxyfiring has the unique advantage to generate an effluent stream composed almost exclusively of CO<sub>2</sub> and H<sub>2</sub>O. It is very cheap and easy to capture CO<sub>2</sub> of the necessary purity for sequestration from this stream, simply by water condensation. Another unique environmental advantage of oxyfiring is the complete avoidance of NO<sub>x</sub> emissions, usually generated by high temperature reaction between nitrogen and oxygen in conventional air combustion. The potential additional benefit deriving by the elimination of NO<sub>x</sub> capture systems has not been quantified in this phase of the CCP, but should be taken into consideration for future work.

Cryogenic air separation is a mature technology, and only small, incremental improvements in oxygen cost may be expected over the next years. For this reason a large R&D effort is ongoing, outside the CCP, to develop novel technologies able to reduce consistently the cost of air separation. While this development is not driven by CO<sub>2</sub> capture considerations, their application to oxyfiring may contribute to reduce the costs of CO<sub>2</sub> capture in oxyfiring systems.

Oxyfuel technologies are basically fit both for steam generation scenarios, revamping or replacing existing heaters or boilers, like the CCP UK refinery scenario, and for gas turbine power generation

scenarios, like CCP Norwegian or Alaskan scenarios. In the latter case, modifications to current commercial machines are necessary, at least in the combustion zone, to maintain high thermodynamic efficiency.

### ***Oxyfuel Conclusions***

- Oxyfuel technologies will drastically reduce, or even eliminate, NO<sub>x</sub> emissions. This additional advantage has not been quantified in the current Phase of CCP, but should be evaluated in the light of existing and future environmental legislation.
- Oxyfiring coupled to conventional cryogenic air separation may be considered as the CCP Baseline Case, with possible application to revamping of boilers and heaters without any research activities. Demonstrative operation of oxyfiring with flue gas recycle is the only pre-requisite to commercial implementation. If a CO<sub>2</sub> avoided cost of 40-45 \$/ton, corresponding to a CO<sub>2</sub> capture cost of 35-40 \$/ton may be acceptable, this is a short-term feasible solution.
- No improvement in existing boilers may result in consistent advantage over this baseline.
- Oxyfiring application to CCGT systems with conventional air separation would require consistent and very expensive gas turbine development to maintain high energy efficiency, considering air compression and flue gas recycle costs. Vendors are not willing to engage in such activity without clear market opportunities.
- Novel membrane systems for oxygen production, currently under development and expected for commercialization by 2008-2009, do not appear to be suitable for retrofitting existing boiler systems. Application to new-built systems, including power generation in CCGT looks very promising and should be further investigated.
- Equipment integrating novel membranes in boilers or gas turbines is still at an early stage of development. Potential for reduction of capture costs is strong, but development risk is still high. Commercialization is not expected before 2009-2010.
- The Chemical Looping Project has been technically very positive and scale-up risks are reasonable, due to similarities with existing coal-fired boilers. Furthermore it produces rather pure CO<sub>2</sub> compared to the Oxyfuel Baseline. A decision to continue the project should be taken based on the results of economic evaluations. A continuation should also explore high pressure application to CCGTs and use of alternative fuels to natural gas (e.g. pulverized coal, maybe mixed with Natural Gas).

### ***The Oxyfuel Baseline***

A detailed technical/economic study for possible revamping of the Grangemouth refinery, using a conventional cryogenic system of large capacity to feed all of the existing boilers and heaters, with subsequent CO<sub>2</sub> capture, was performed by Air Products, in collaboration with Mitsui Babcock and Foster Wheeler. Air Products studied a base case and two additional options with increasing integration in the refinery. The base case has also been evaluated by the CEM Team, achieving a good agreement with the results by Air Products in terms of the “CO<sub>2</sub> avoided cost” (47 \$/ton CEM vs. 43 \$/ton AP). Additional AP cases reduced the CO<sub>2</sub> avoided cost by a further 10%. The CO<sub>2</sub> capture cost is in the 30-35 \$/ton range. The Oxyfuel Baseline is consequently technically applicable with consistent saving compared to any other available option with minor technical risk. A commercial demonstration of oxyfiring is needed and the necessary air separation unit for Grangemouth is about 20% larger than the

largest existing unit. This level of cost could make it attractive in countries applying high level of carbon tax.

**This means that the Oxyfuel baseline in the UK Scenario allows a > 40% reduction in the CO<sub>2</sub> avoided cost compared to the Post-Combustion baseline (77 \$/ton).**

### *Boiler modifications*

Boilers are more easily modified for oxyfiring than are process heaters. Process heaters often have added constraints of flux uniformity and peak temperatures that are harder to deal with. The concept of a boiler operating at higher than atmospheric pressure was studied by Mitsui-Babcock. The basic idea was that, since cryogenic air separation works under pressure, and captured CO<sub>2</sub> must be further compressed for sequestration, utility consumption and compressor costs might be reduced. It was however found that, even at the calculated optimal operating pressure of 5 Bara, potential savings were offset by the higher capital cost of the boiler.

Another approach studied with Mitsui-Babcock was the “Zero or low recycle boiler”. This had to be a boiler of new design, tailored to oxyfuel firing, based on the concept of staged combustion. Staging should allow avoiding or minimizing the recycle of flue gas. Calculations showed that flue gas recycle cannot be avoided and may only be reduced by 25% in a feasible design, resulting in possible cost saving of 10%, but double footprint compared to conventional boilers.

Praxair studied the option of designing a boiler with no flue gas recycle and no temperature mitigation, simply by using more expensive construction materials. Expected savings came from reduced boiler size and utility consumption. Again potential savings were offset by increased capital cost.

**None of the investigated options supplied results able to justify a continuation of the activities.**

### *Advanced thermodynamic cycles*

Pure oxyfiring produces flame temperatures that are well beyond current turbine capabilities. The most obvious way to moderate combustion temperature is to recycle exhaust gas, which is just CO<sub>2</sub> in the case of oxyfiring. However, between the power required for air separation and for CO<sub>2</sub> recycle, there is a large reduction in net power output from the turbine system (whether simple power cycle or combined cycle). To improve the net efficiency of oxyfiring with CO<sub>2</sub> capture, numerous power cycles proposed in the literature. With the requirement that a working fluid used to moderate temperature in the combustion turbine must also still enable simple CO<sub>2</sub> capture; the studies have generally looked at CO<sub>2</sub>, water, and combinations of those two. SINTEF performed a study to evaluate three thermodynamic cycles, applied to oxyfiring, proposed in the scientific literature: Water cycle, Graz cycle and Matiant cycle. All of the papers describing these cycles claimed much higher efficiency compared to conventional cycles. However the results of the study show that these efficiencies may only be reached at operating conditions that cannot be realized in current commercial equipment such as combustion at 1400°C or turbines discharging in high vacuum. Also, when the different cycles are compared on a consistent basis, the efficiencies were comparable.

One unique aspect of work being undertaken by Clean Energy Systems, under funding by US DOE, is an effort to develop “stoichiometric” combustion for their version of a power cycle which uses water as the moderating fluid. This addresses the fact that combustion operations generally are operated with excess air (or oxygen) to ensure complete combustion. The presence of the excess oxygen complicates CO<sub>2</sub>

capture and sequestration – often requiring additional CO<sub>2</sub> purification. CES is developing a turbine combustor that minimizes the excess oxygen.

**Direct oxyfired gas turbines are beyond the scope and timeframe of the CCP project and will not be further studied by the CCP.**

### *Novel technologies for air separation*

A very promising novel technology for air separation (ionic transport membranes) have been under development by other consortia over the past five years. These ceramic membranes, operating at high temperature (> 700°C) allow 100% selectivity to oxygen, which is transferred in anionic form using a difference in oxygen partial pressure between the two sides of the membrane as driving force. Three consortia are developing these membranes:

- led by Air Products (ITM – Oxygen Transport Membranes)
- led by Praxair (OTM – Ionic Transport Membranes)
- led by Alstom/Norsk Hydro (MCM – Mixed Conducting Membranes)

All of these consortia are targeting 2008-2009 for commercialization but the risks associated with this type of development (resistance in time to high temperature operation, mechanical problems etc.) should not be underestimated.

The CCP sponsored an engineering study by Air Products to retrofit the Grangemouth refinery to oxyfiring using an ITM system rather conventional cryogenic air separation. The particular process configuration being developed by APCI uses only a pressure differential across the ITM membrane to provide a driving force for oxygen separation, rather than use of a sweep gas on the permeate side of the membrane. As a result, the membranes may extract only about 40% of the oxygen from the air stream. Since high temperature is needed to favor oxygen transfer, a considerable export of power (446 Mw in the Grangemouth case) is necessary to balance the system. This exported power, not available with air firing could replace the current power station. It is immediately clear that this technology is not fit for the revamping of existing boilers unless there is a market for power export, but seems ideally suited for integration with large CCGT (Combined Cycle Gas Turbine) systems.

Different cases were considered by Air Products (all of them with considerable power export). The CO<sub>2</sub> avoided cost for the base case was evaluated by the CEM Team at 35.5 \$/ton (vs. 37 \$/ton by Air Products) with about 20% saving compared to the Oxyfuel Baseline. The other cases studied by Air Products allowed reduction of CO<sub>2</sub> avoided cost to the 20-30 \$/ton range.

**The most promising application for the Air Products ionic transport membrane concept that produce pure oxygen without a sweep gas seems to be in systems allowing considerable export of power.**

### *Integrated equipment*

The study described above showed that the simple substitution of an ITM system to a cryogenic air separation, while positive in a new-built perspective, may not always be applicable to revamping of existing units, due to the large associated export of power. In the new-built perspective, some Technology Providers are studying the direct integration of ionic transport membranes in boilers or gas turbine systems. Two studies were commissioned by the CCP to assess the potential for these developments.

The AZEP (Advanced Zero Emission Power) is a concept under study by Alstom/Norsk Hydro a three-year EU-funded project started in January 2002 with the aim to integrate the MCM membranes directly into a gas turbine system. A key aspect of the AZEP concept is that it can be used with conventional power turbines. In the study performed for the CCP, Alstom defined the implementation of AZEP in the Alaskan Scenario, as replacement of the current gas turbine system, using 45 MW commercial machines. The technology is also potentially applicable to the Norwegian Scenario, but the developers do not yet feel confident in evaluating such a large scale application.

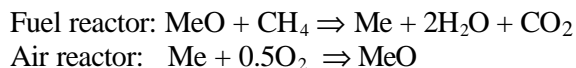
Three cycles were studied with sub-options of complete or incomplete (80-90%) CO<sub>2</sub> capture, that should minimize capture costs. It must be pointed out that, in addition to the uncertainties on the membrane development, to maximize the thermodynamic efficiency, the AZEP system includes a “High Temperature Heat Exchanger” operating at temperatures beyond present exchanger’s capability, whose development is among the targets of the Project. Alstom calculated a CO<sub>2</sub> avoided cost in the 25-35 \$/tonne range, which is an astounding result in the Alaskan Scenario (best cases evaluated by the CEM Team up to now are above 50 \$/ton).

A similar research effort is carried being out by Praxair to develop a boiler incorporating the OTM membrane system. A study co-sponsored by the CCP and the DOE was carried out by Praxair to replace one of the existing boilers in Grangemouth. Use of this boiler will be limited to the C<sub>1</sub> – C<sub>2</sub> fraction of Natural Gas, since C<sub>3</sub>-C<sub>4</sub> are coke formation precursors. The technology is still at an early stage of development, so that cost evaluation must be considered as preliminary. According to Praxair, the Advanced Boiler will be 40% more expensive than a conventional one, and cost of CO<sub>2</sub> capture in the 15-20 \$/ton range.

**These integrated equipments are promising developments, but still at an early stage with considerable uncertainties. Commercialization expected not before 2010.**

### *Chemical Looping*

The major R&D Project in the Oxyfuel field was chemical looping, developed by as a consortium formed by BP (Coordinator), Alstom Boilers, Chalmers University, CSIC, and Vienna University in a 2-year EU-cofunded project which came to a conclusion in December 2003. Chemical Looping is a new combustion technology based on oxygen transfer from combustion air to the fuel by means of a metal oxide (MeO) acting as an oxygen carrier. Central to the technology are a dual fluidized-bed reactor system with continuous circulation of solids, similar to Circulating Fluidized Boilers (CFB) used for coal combustion. The reactions are schematically:



This project has been focused on atmospheric pressure applications typical of the CCP UK Scenario, but the concept is applicable to higher pressure gas turbine systems as proven in another project outside the CCP frame and funded by the DOE. In this case the trade-off is between thermodynamic efficiency and percentage of captured CO<sub>2</sub>, since Chemical Looping Combustion takes place at relatively low temperatures (800-900°C). An additional uncertainty is the ability of the gas turbine to tolerate dust from the air separation process.

The main risk in developing the technology is the availability of a suitable material able to undergo repeated oxidation/reduction cycles maintaining both chemical activity and mechanical resistance. The “Proof-of-Feasibility” was successfully achieved by operating a pilot unit with NiO/Al<sub>2</sub>O<sub>3</sub> for a total of

about 300 hours with almost complete methane combustion (99.5% at 800°C), no gas leakage between the reactors, no significant carbon formation, no significant attrition and no chemical decay. Preliminary economic evaluation performed by the CEM Team in 2002 of replacing a boiler in the Grangemouth refinery resulted in 43% saving compared to the Post-combustion Baseline. Evaluation of the CEM Team on investment data supplied by Alstom is now ongoing.

**The Chemical Looping Project has been a technical success. The results of economic evaluations will drive the choices for continuation.**

## **Storage, Measurement, and Verification Studies**

As a commercial process, carbon dioxide sequestration includes pre-combustion decarbonization or post-combustion separation (capture), export from the production site (transportation) and long-term containment (storage). The CO<sub>2</sub> Capture Project (CCP) includes transportation and geological storage of CO<sub>2</sub> in its “Storage, Monitor and Verification” (SMV) program. Whereas the principal objective of the CCP capture program was cost reduction that of the CCP storage program was to identify efficiencies and reduce uncertainties associated with pipeline transportation and geologic CO<sub>2</sub> storage. For organizational purposes, the SMV program technical studies are grouped into four technical themes:

- **Integrity** – competence of natural and engineered systems to contain CO<sub>2</sub>
- **Optimization** – processes that improve the efficiency and economics of CO<sub>2</sub> transportation and storage
- **Monitoring** – techniques to track CO<sub>2</sub> movement within and outside of the target storage reservoir
- **Risk Assessment** – methods to identify and minimize the probability and impact of CO<sub>2</sub> leakage from storage sites

### *Integrity of geological systems*

Geological systems are complex and thus vary widely in their suitability for safe and effective CO<sub>2</sub> storage. Basic requirements include depth (pressure and temperature) sufficient to inject and maintain CO<sub>2</sub> in its supercritical state, reservoir geometry consistent with good storage capacity and structural closure, reservoir porosity and permeability distributions that permit high injection rates and fluid conformance, compatible fluids, and top seals with low permeability and high mechanical strength. There are numerous instances worldwide both of large natural CO<sub>2</sub> reservoirs that have persisted over geologic time frames and those that continuously or episodically leak. The study by ARI (Stevens) documented specific features of three natural “secure” fields in the US (McElmo Dome, CO; Jackson Dome, MS; St. Johns, AZ), the former of which are thought to have held CO<sub>2</sub> up to ~70 Ma). It is concluded that reservoir seals should be comprised of thick chemically-precipitated (carbonates, evaporates) or clastic (shales) rocks. Structural features amenable to CO<sub>2</sub> containment are characterized by lack of significant faulting and fracturing or a “self-healing” mechanism that seals those that do develop. The study by Utah State University (Evans), in contrast, investigated a natural CO<sub>2</sub>-charged geyser system in the Western Colorado Plateau of East-Central Utah to explain the “leaky” nature of the system. A 3-D structural / stratigraphic model of the study area revealed available paths for migrating fluids that ultimately erupt or bubble at the surface.

**The key message from these natural analog system assessments is that CO<sub>2</sub> accumulation and retention is a function of general geologic setting and specific local features. Such features are**

**definable and, given appropriate scenarios and models, predictable with respect to their influence on long-term CO<sub>2</sub> storage.**

Assessment of the tendency for rock and structural element failure begins with estimation of in situ stress and fault geometry as described in the University of Adelaide (Streit) study. Tools are available to simulate perturbations to the original system and thus test design limits for CO<sub>2</sub> injection. The study by GFZ-Potsdam (Schuett) showed experimentally that injection of CO<sub>2</sub>- rich fluids into reservoir rocks releases major and minor elements. The detection of ions from rock-forming minerals suggests the dissolution of rock-forming minerals which would ultimately reduce rock strength. LLNL (Johnson) applied reactive transport modeling to simulate competing geochemical and geomechanical responses of cap rocks to CO<sub>2</sub> injection. Geochemical processes driven by CO<sub>2</sub> injection tend to result in dissolution / precipitation reactions that reduce permeability of the cap rock. This process appears to be independent of key reservoir (permeability and lateral continuity) and CO<sub>2</sub> influx (rate, focality and duration) parameters. In contrast, increase of cap rock permeability due to geomechanical effects is controlled by reservoir and CO<sub>2</sub> influx parameters that control the magnitude of the pressure perturbation. These studies highlight the need to evaluate elements of prospective storage sites at various scales assisted by experiments and models.

Multiple mechanisms are available for immobilizing injected supercritical CO<sub>2</sub> in the subsurface. Principal among these is solubility and relative permeability trapping. The latter mechanism, which was recently identified and simulated for natural gas reservoirs, has now been adapted to CO<sub>2</sub> flooding in clastic aquifers and the CO<sub>2</sub> EOR water-alternating-gas (WAG) process. Other possible mechanisms of CO<sub>2</sub> immobilization include buoyant flow, brine density convection and mineralization. The fate of CO<sub>2</sub> in a fifty year aquifer injection project was simulated for the 1000 year time frame by the University of Texas (Pope). Given appropriate injection strategy (base of the reservoir) and reservoir characteristics and conditions, ~95% of the CO<sub>2</sub> is expected to be immobilized, mostly as residual gas (capillary trapping) over this time frame. Indeed, as substantial portion might be immobilized by the end of the injection period. Mineral trapping is predicted to be significant on the 10000 year time frame. A simulation by SINTEF (aimed at testing well failure scenarios) using CO<sub>2</sub> dissolution as the principal trapping mechanism, showed similar results over the 1000 year timeframe. Our understanding of CO<sub>2</sub> behavior in the subsurface backed by independent simulations, show that CO<sub>2</sub> immobilization can be highly effective given an appropriate reservoir. The solubility of CO<sub>2</sub> makes it likely; furthermore, that CO<sub>2</sub> leaking from the target reservoir will be assimilated or retarded in shallower aquifers.

**SMV studies related to the integrity of geologic systems show that despite their complexity, diverse venues suitable for CO<sub>2</sub> storage are available. Integrated characterization at multiple scales should be used to develop 3-D structural / stratigraphic models and hydrogeology should be well understood. Scenario development and simulations using a broad range of sensitivities and potential failure modes will give credibility to efforts to develop CO<sub>2</sub> storage facilities. It is of considerable importance that independently-run simulations using distinct software and favoring different CO<sub>2</sub> trapping mechanisms predict immobilization of most of injected CO<sub>2</sub> in the 1000 year time frame.**

#### *Integrity of engineered systems (SINTEF, GTI)*

Whereas natural systems, particularly gas reservoirs, have a proven ability to retain fluids for extended periods, modification of such systems (e.g., well bore penetration of top seal, physical-chemical changes due to fluid injection) has the potential to reduce their competence for long-term CO<sub>2</sub> retention. Foremost among the vulnerabilities of CO<sub>2</sub> storage reservoirs is leakage through old or poorly-constructed wells. A



major SMV project that addresses this issue entails cement and seal stability experiments and simulations. Highly relevant is an emerging industrial analog to CO<sub>2</sub> storage, natural gas storage.

SINTEF (Lindeberg) addressed the well integrity issue through experimental testing, at elevated temperature, standard and newly formulated cements (and cements in contact with steel) and cement sealants. The experiments showed that whereas initial contact of cement with CO<sub>2</sub>-rich fluids may “carbonate” the cement (reduce permeability); long-term exposure will deteriorate the cement via dissolution of calcium hydrogen carbonate. Simulations of the effect of CO<sub>2</sub> injection on abandoned well bores at different distances and reservoir conditions suggests that in a worse case scenario (open well bore created by complete well failure without remediation), ~60% of the CO<sub>2</sub> injected could be lost to the atmosphere over 100-200 years.

The natural gas storage industry has operated cumulatively >600 facilities in North America over the past 90 years with very few gas migration incidents. The GTI survey of the natural gas industry experience identifies principles responsible for its success and those technologies and practices applicable to CO<sub>2</sub> storage. Site selection criteria relevant to CO<sub>2</sub> storage include competent seal and broad structural closure. The latter is recommended as less faulting and fracturing is expected. The GTI study has identified siting and technology issues in natural gas storage that will be useful in developing and maintaining CO<sub>2</sub> storage facilities.

**The integrity of engineered systems used in CO<sub>2</sub> storage requires continued research. Work should continue on new materials development, particularly on cements and sealants in new installations. Options for remediation of old wells will become an issue in brown field developments (e.g., depleted oil and gas fields) and for contingency planning in green field developments (e.g., aquifers). Future well integrity simulation work might include scenario development such as progressive well failure and the efficacy of well remediation techniques. Siting and characterization of natural gas storage facilities has proceeded in the past with less rigor than that expected for CO<sub>2</sub> storage. Successful development of natural gas storage as an engineered system analog for CO<sub>2</sub> storage will progress its future application and safety.**

#### *Economic Offsets and Operational Efficiencies (NMT, Tie-Line, TTU, INEL, UT-B)*

Injection of CO<sub>2</sub> into depleted oil fields is considered an early opportunity for CO<sub>2</sub> storage given that the cost of CO<sub>2</sub> capture, transportation and storage might be partially offset (or profitable) by revenues from increased oil production. The Permian Basin of West Texas and adjacent New Mexico is the site of the bulk of CO<sub>2</sub> EOR experience in the World over the last 30 years. Storage of CO<sub>2</sub> in depleted gas field is attractive given that gas fields are by definition capable of storing gases but also because an appropriate infrastructure exists. In addition, there are concepts under development for enhanced gas production using CO<sub>2</sub>. Deep unmineable coals also present an opportunity as increased methane production is possible. The ability of the CO<sub>2</sub> storage reservoir to accommodate impurities (e.g., SO<sub>x</sub>, NO<sub>x</sub>) might reduce CO<sub>2</sub> capture costs and avoid their emission into the atmosphere.

The University of Texas (Bryant) study simulated the effects of CO<sub>2</sub> impurities (e.g., SO<sub>x</sub>, NO<sub>x</sub>) on aquifer reservoir injectivity and EOR performance. Increased acidity (sulfuric and nitric) is predicted to either temporarily enhance injectivity via mineral dissolution or have little effect via the mitigating effect of multiphase flow. Impurities present in an EOR operation are predicted to be neutral as there is a tradeoff between lowering MMP (improvement) and increasing the mobility ratio (worsening). The minimal performance effects expected by the presence of soluble, acid forming gases in injected CO<sub>2</sub> raises the potential for lowering CO<sub>2</sub> capture costs.

**Identification of operational efficiencies and economic offsets will be crucial both to project development decisions and safe and effective operation of CO<sub>2</sub> storage facilities. Simulation aimed at optimizing operational parameters, using model frameworks developed for site characterization, are quick and inexpensive to perform. Although formal economic analysis was not in the scope of the SMV program, it is evident that development of site specific parameters, tied to local tax and regulatory regimes, will be decisive factors in project approval.**

*New Paradigms in CO<sub>2</sub> Transportation (Reinertsen/SINTEF, IFE, BML)*

The Norwegian transportation studies coordinated by Reinertsen Engineering (Heggum) and supported SINTEF and IFE (Seiersten) aimed to reexamine CO<sub>2</sub> transportation in carbon steel pipelines for a “northern”, offshore setting (as oppose to the well-known US temperate, onshore setting). At issue was the maximum hydration of CO<sub>2</sub> streams permissible before corrosion and hydrates effects become significant. Using thermodynamic models based on new high pressure CO<sub>2</sub> solubility in water and corrosion data (with and without inhibitors), it was found that proposed (50 ppm, Hammerfest LNG) specifications for water content could be relaxed to the existing (600, Kinder-Morgan in the US) specifications and perhaps further (1300 ppm). These studies, in addition to adapting CO<sub>2</sub> transportation issues to a different geographic setting and operational regime, could enable projects that are economically prohibitive (i.e., default specification of expensive steel alloys) to proceed and succeed.

**The Norwegian transportation studies comprise a creative attempt to extend the utility of standard, inexpensive carbon steel into settings where gas processing capability is limited or prohibitively expensive. Integration of capture and transportation process efficiencies recommended by the study may upgrade the economics of marginal projects.**

*Diverse Techniques to Assess CO<sub>2</sub> Flood Performance and Containment (TNO-A, LLNL-P, Stanford, CalTech-1&2, PSU, U. Adelaide, LBNL-H, LLNL-N)*

The SMV “monitoring” studies encompassed multiple technologies (spectroscopic, radar, geophysical, geochemical) applied from the full range of vantage points (space / aerial, near surface atmosphere, subsurface). Two surveys on the state-of-the-art in monitoring technology were conducted early in the program. The survey of atmospheric monitoring technologies by CalTech (Tang) documented the applicability and costs of instruments useful over various time, length / area scales and sampling frequency. The remaining SMV monitoring studies addressed specific technologies applicable to selected potential and actual CO<sub>2</sub> storage venues. TNO (Arts) conducted a broad survey of geophysical and geochemical monitoring techniques aimed at recommending “optimal” techniques for various CO<sub>2</sub> storage venues and potential failure modes. (e.g., FEPs, or features, events and processes). In addition, the importance of characterizing the effects of CO<sub>2</sub> injection on rock properties and, therefore, monitoring resolution was pointed out in the GFZ-Potsdam (Shuett) experimental study and as a means of detecting effective stress in the University of Adelaide (Streit) geomechanical study.

“Hyperspectral geobotanical” surveys, processed to detect CO<sub>2</sub> leakage indirectly (effects on ecosystems and soils), were applied to the Mammoth Lake, CA natural volcanogenic release area (satellite) and to the Rangely Field, Colorado CO<sub>2</sub> EOR operation (aerial). Tree kills and other plant damage were easily detected at lushly-vegetated Mammoth Lake. At Rangely Field, pre- and post rain changes in “habitats” were noted in this arid landscape, but CO<sub>2</sub> detection is thought to require long term evaluation of such changes.

The resolution of the satellite radar interferometry (InSAR) technique to detect ground movement induced by CO<sub>2</sub> injection was investigated by Stanford (Zebker). Although the mathematical basis for

deformation signals and their detection were presented, it is not clear under what atmospheric conditions and topographical features the method would be applicable. Near-surface and atmospheric monitoring techniques were investigated for their applicability to detect CO<sub>2</sub> leakage. Caltech (Shuler) examined the efficacy of open path detection (laser spectroscopy) on field geometric and leakage rate and mode parameters under various ambient CO<sub>2</sub> levels and atmospheric conditions. The near ground techniques are established technologies whose installation will likely be required for early onshore CO<sub>2</sub> storage projects. Optimization of instruments and configuration will allow field scale CO<sub>2</sub> leakage monitoring at considerable cost savings.

Geophysical techniques, particularly time lapse 3-D seismic, have proven useful in monitoring subsurface CO<sub>2</sub> movement. Their expense and limitations on detecting CO<sub>2</sub> saturation levels, however, highlight the need for better interpretation techniques or alternative technologies. LBNL (Hoversten) evaluates the resolution of new seismic interpretation approaches (seismic amplitude and AVO to infer CO<sub>2</sub> saturation) and novel non-seismic techniques including gravity, electromagnetics (EM) and streaming potential (SP).

The single SMV geochemical monitoring study by LLNL (Nimz) assessed the utility of noble gases for detecting CO<sub>2</sub> movement out of target reservoirs. The development of tracer systems for CO<sub>2</sub> storage projects will be important for monitoring performance, leak detection and volume verification.

**The SMV assessment of technologies and techniques to monitor CO<sub>2</sub> reservoir performance and leakage / seepage is unique in its variety and scope. Remote atmosphere approaches to monitoring CO<sub>2</sub> leaks are shown to require further development. Existing near-surface atmospheric approaches to CO<sub>2</sub> detection are commercially available and adaptable to CO<sub>2</sub> storage. Seismic geophysical monitoring of CO<sub>2</sub> is available but a better understanding of rock response to CO<sub>2</sub> flooding and new processing and interpretation strategies require development (e.g., amplitude analysis and AVO). Much less expensive non-seismic geophysical approaches such as gravity, EM and SP may, under certain circumstances, have the resolution to track CO<sub>2</sub> movement in the subsurface. Geochemical techniques such as tracer gas surveys are potentially cost effective but further development is needed in elucidating and simulating subsurface transport mechanisms.**

### *Comprehensive Risk Assessment Frameworks (TNO, INEL)*

Risk assessment models, simulations and methodologies have been developed for the purpose of predicting the probability and consequences of natural and industrial hazards. Two comprehensive risk assessment methodologies for CO<sub>2</sub> storage were developed for the SMV program. These methodologies are similar in that they contain the basic elements of scenario development with an inventory of risk factors, model development and consequence analysis. Although the two methodologies were developed and tested using models of distinct geological storage venues, they can be adapted to other venues.

The TNO (Wildenborg) methodology (SAMCARDS) involved extensive scenario and model development over multiple Earth compartments. A performance assessment (PA) model involving numerous simulations over these compartments is capable of statistical analysis that predicts CO<sub>2</sub> concentrations and fluxes into the biosphere. In the combined off-/onshore model with two leakage scenarios (well and fault leakage), it was predicted that seepage of CO<sub>2</sub> into the biosphere would not occur in the 10000 year time frame simulated. This is despite a worst case scenario (no remediation) and 1000 parameter realizations. Further development of the surface components (atmosphere and hydrosphere) is needed. Benchmarking of the model will help in assessing the reliability and credibility of the methodology

The INEL (Wo) risk assessment methodology was applied to the Tiffany Field (Durango, CO), a coal bed methane development currently under N<sub>2</sub> flood. The four major elements of the methodology (hazard

identification, event and failure quantification, predictive modeling, risk characterization) are input into the six part functionality mathematical model capable of performing scenario and Monte Carlo simulation. Tested against the Tiffany Field coal several risks for CO<sub>2</sub> leakage were identified. The geomechanical study for the Tiffany Field highlights the importance of pressure effects on rock and fault stability over the entire field history (coal dewatering, methane production, N<sub>2</sub> injection, CO<sub>2</sub> injection).

**The two independent developed risk assessment methodologies are based on the same principals but differ in details and initial application. The significance of testing done to date is that leakage in a typical clastic aquifer appears unlikely (TNO) and that natural and engineered elements of the storage system that present a leakage hazard can be identified and thus redesigned. An important validation of the SMV and other methodologies will come with the formal benchmarking exercises planned under the auspices of IEA GHG.**

### *Leakage Scenarios and Remediation Strategies (LBNL-B2, LBNL-O, GTI)*

Development of leakage scenarios, early detection technologies and remediation strategies will prove essential in the siting and deployment of CO<sub>2</sub> storage facilities. The SMV program made progress on systematically addressing these issues through two LBNL studies (Hepple, Oldenburg) and lessons learned from the GTI (Perry) review of natural gas storage technologies.

The LBNL (Hepple) study outlines possible leakage scenarios from CO<sub>2</sub> storage sites via damaged injection wells and over-pressured reservoirs and the consequences of leakage, namely ground- and surface water contamination, vadose zone accumulation and surface releases. Remediation options are available from the natural gas storage, oil and gas production, groundwater / vadose zone treatment industries. HSE consequences of leaks are important for large leaks but also for persistent small leaks that might cause CO<sub>2</sub> accumulation in low lying areas and into occupied structures. When CO<sub>2</sub> concentrations in the near subsurface are high (either by primary seepage or CO<sub>2</sub> infiltration as a dissolved component of rainwater), surface layer winds act to rapidly disperse the CO<sub>2</sub> in the flux cases simulated.

**The near surface and atmosphere seepage simulations and contingency planning for remediation will play an important role in stakeholder acceptance of CO<sub>2</sub> storage. The most relevant industrial analog, natural gas storage, has developed tools (shallow gas recycling, aquifer pressure control, cap rock sealing) that are variously applicable to CO<sub>2</sub> storage but require further development. Additional remediation approaches should be sought or developed.**

### *Regulator, NGO and Public Acceptance (LBNL-B1, MSCI, GTI)*

The early SMV study by LBNL (Benson) examined HSE issues relevant to CO<sub>2</sub> handling and put into perspective the experiences of potential industrial analogs to CO<sub>2</sub> storage (oil production by CO<sub>2</sub> EOR, acid gas disposal, nuclear waste repository development, deep well hazardous waste injection). Based on this work, several SMV program studies were contracted to develop risk assessment methods and more closely examine industrial analogs.

The HSE lessons learned from industrial analogs study by LBNL (Benson) concluded that: 1) there is an abundant base of experience to draw on that is relevant and suggests that CO<sub>2</sub> can be stored safely, 2) the health effects of exposure to elevated concentrations of CO<sub>2</sub> are well understood and occupational safety regulations are in place for safe use, 3) the hazard depends more on the nature of release rather than the size of release, 4) experience from industrial analogs predicts the biggest risks from CO<sub>2</sub> storage and 5) regulatory paradigms and approaches vary and none address all of the issues that are important for CO<sub>2</sub> storage.

A set of potentially relevant industrial analogs to CO<sub>2</sub> storage were examined in the SMV program. In the CO<sub>2</sub> EOR experience survey by NMT (Grigg), it is evident that CO<sub>2</sub> leakage monitoring is not a perceived need. The nuclear waste disposal analog study by MSCI (Stenhouse) addresses protocols for site characterization and public involvement. Although the public perception of CO<sub>2</sub> storage is likely to be much more benign than that of nuclear waste disposal, the general principles are relevant. The natural gas storage experience should reflect well on CO<sub>2</sub> storage as its safety record is excellent. CO<sub>2</sub> storage may in several respects be considered a mild analog to natural gas storage as CO<sub>2</sub> is not flammable.

Environmental issues associated with CO<sub>2</sub> storage were not extensively studied in the SMV program as these are generally well understood. One study conducted by Princeton University (Onstott); however, address the effect of CO<sub>2</sub> on subsurface microbial ecosystems. The known distribution of metabolic

classes of microbes with depth was noted and a forward model was developed to predict their relative activities under CO<sub>2</sub>-rich conditions. The results demonstrated that growth of various microbial species (many of which have yet to be identified) will be impacted by CO<sub>2</sub> injection. More importantly for CO<sub>2</sub> storage operations, however, are the potential impact on reservoir quality (e.g., porosity) and conformance.

**The HSE-related studies comprise the basis for pre -injection characterization of risk, optimal injection operations and post-project abandonment. By openly communicating with regulators, NGOs and the public, critical issues identified can be addressed to advance the case for CO<sub>2</sub> storage.**

## **Communication of Results**

Dissemination of CCP results to the broader scientific community and to policy makers is a key activity. Detailed planning for that technology transfer activity is underway. Plans for integration and dissemination of CCP research results coordinating the SMV, Capture, and Economic Modeling efforts are being prepared. LBNL (Benson) has been contracted to arrange publications at the technical specialist, general scientific / engineering, government / regulator, NGO and general public levels for the SMV program. ARI (Thomas) will carry out a similar program for Capture and Economic modeling studies.

The CCP has arranged publication of a two volume set of the CCP's results in book form by Elsevier Science. The set, to be published by the end of 2004, will include virtually all the studies included in the CCP program as peer-reviewed technical papers, section summaries and analyses, and the economic modeling results for each of the cases. The set will provide a single source for all segments of the CCP regardless of funding source.

# Summary Report

CCP's agreement with the U.S. DOE includes a number of tasks that are reported upon in this document. Each summary refers to the relevant task - number in its title. The tasks covered by this agreement reported here are identified in the following Table 1. Not all the technology areas defined below are currently under study with DOE funding as noted in the technology development discussions.

**Table 1**  
**Relationship Between U.S. DOE Project Tasks and CCP Projects**

<b>Task</b>	<b>Description</b>	<b>Related Report Section</b>
<b>0.0</b>	<b>Project Definition</b>	Technology Selection
0.1	Identify Relevant Separation, Capture, and Sequestration Scenarios	Scenarios
0.2	Establish State-of-the-Art Separation and Capture	3. Technology Screening 4. Economic Modeling
0.3	Develop and Apply Common Economic Model	3. Technology Screening 4. Economic Modeling
0.4	Define Work Plan	See 0.0 Project Definition above.
0.5	Select Technology Developers	See 0.0 Project Definition above.
<b>1.0</b>	<b>Develop Post-Combustion Separation and Capture</b>	1.1 Post Combustion Studies - studies under this heading
1.1	Advanced Solvents	Not U.S. DOE funded in CCP
1.2	Advanced Absorbers/Desorber Designs	Not U.S. DOE funded in CCP
1.3	Systems Integration and Optimization	Not U.S. DOE funded in CCP
1.4	New and Novel Concepts	1.1.1.1 Radical Post-combustion technologies. 1.1.1.2 Self-Assembled Nanoporous Materials.
<b>2.0</b>	<b>Develop Pre-Combustion De-carbonization Techniques</b>	1.2 Pre-combustion De-carbonization (PCDC) Program - studies under this heading
2.1	Gas Turbine Fuels	1.2.1.2 Sorption Enhanced Water Gas Shift (SEWGS)
2.2	Fuel-Grade Hydrogen Generation	1.2.1 Membrane Studies 1.2.1.1.7 Membrane Water Gas Shift (MWGS)
2.3	Systems Integration and Optimization	1.2.3 Integration & Scale-up Studies
2.4	New and Novel Concepts	1.2.1.1 Sulfur Tolerant Water Gas Shift Reactor Systems
3.0	Develop Oxyfuel Technologies	1.2.1 Capture Studies - studies under this heading
3.1	Advanced New/Retrofit Boiler Designs	1.3.1 Advanced Boiler Study
3.2	Membrane Air Separation Units	Not U.S. DOE funded in CCP
3.3	Systems Integration and Optimization	Not U.S. DOE funded in CCP
3.4	New and Novel Concepts	Not U.S. DOE funded in CCP
<b>4.0</b>	<b>Establish Key Geologic Sequestration Controls and Requirements</b>	2. Storage, Monitoring and Verification (SMV) Studies - studies under this heading
4.1	Understanding Geologic Storage	2.1 Integrity - studies under this heading 2.2 Optimization- studies under this heading 2.3 Integrity - studies under this heading
4.2	Flexibility in CO <sub>2</sub> Purity	2.2.4 CO <sub>2</sub> Impurities Tradeoff – surface 2.2.5 CO <sub>2</sub> Impurities Tradeoff - subsurface
4.3	Maximizing CO <sub>2</sub> Sequestration	2.2 Optimization - studies under this heading 2.3 Integrity - studies under this heading
4.4	Measurement and Verification	2.4 Monitoring - studies under this heading
4.5	Risk Assessment and Mitigation Options	2.1 Risk Assessment and Analysis- studies under this heading
<b>5.0</b>	<b>Project Management, Reporting, and Technology Transfer</b>	3. Technology Screening 4. Economic Modeling Technology Advisory Board
5.1	Project Management	Technology Advisory Board
5.2	Routine Project Reporting	1.2.4 Capture Studies Integration and Reporting Integration Into Topical Reports 2.5.1 Technical Report Integration into Topical Reports
5.3	Technology Transfer	2.5 Integration and Communications - studies under this heading

# Scenarios

## Task - 0.1 Identify Relevant Separation Capture, and Sequestration Scenarios

CCP uses real plant and refinery applications rather than idealized model studies to ensure that the developed technologies and costs will represent practical circumstances. Each scenario includes all the operations necessary to:

- Capture the carbon dioxide from the combustion process,
- Separate it from other stream components (water, particulates, and other gaseous contaminants),
- Process it for further handling (cooling and compression)
- Transport it to a storage site (by pipeline)
- Provide for monitoring to assure the public and regulators that the carbon dioxide is safely stored for the required period.

The scenarios are defined by fuel type, combustion method, and the availability of storage sites. Separation technologies can be matched to the fuel type and plant configuration and the range of combustion methods represents the vast majority of systems used in industry. The four scenarios are summarized in Table 2 below:

**Table 2: Industrial Scenarios Used in CCP as Basis for Technology Comparison**

Scenario	Fuel Source	CO <sub>2</sub> Source	Geologic Sink	Location
<b>Refinery</b>	Hydrocarbon Gas & Liquids	Heaters & Boilers	Storage	European Refinery
<b>Very Large Gas Turbines</b>	Natural Gas	Large Electric Power Generation (CCGT)	Storage	Western Europe
<b>Distributed Gas Turbines</b>	Natural Gas	Small Distributed turbines	Storage	Alaska North Slope
<b>Gasification</b>	Solid via gasification (petroleum coke)	Syngas Purification Process	Storage	Western Canada

The **Geologic Sink** to be used is chosen from a reservoir type available near the CO<sub>2</sub> source and may be:

- Saline aquifers
- Depleted gas reservoir with or without potential for additional gas recovery,
- Depleted, or late stage, oil reservoirs usually with the potential for additional recovery of oil, or
- Unmineable coalbeds with or without the potential for methane recovery.

The geologic sink will be selected for its potential to ensure safe sequestration at minimum cost to the operator. It may be combined with oil or gas recovery from the target reservoir to provide cost recovery and potential economic benefits from the sequestration project.



# 1. Capture Studies

**Task - 1.0 Develop Post-Combustion Separation and Capture Scenarios**

**Task - 2.0 Develop Pre -Combustion De-carbonization 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 still in progress. These successful technologies will continue to the next stage in proof of concept determination.

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)** Capture technology. Where CO<sub>2</sub> is captured from the exhaust of a combustion process
- **Pre-combustion De-Carbonization (PCDC)**. Where a hydrogen-rich fuel is produced and CO<sub>2</sub> is captured from the produced syngas
- **Oxyfuel** Here a pure oxygen stream is produced which results in a combustion product containing only CO<sub>2</sub> 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 2004.

**Table 3: Capture Studies Status, January 2004**

Capture Category	Project Title	Principal Investigator	Co Funder*	Technology Provider	Status
Post Combustion	Self-Assembled Nanoporous Materials for CO <sub>2</sub> Capture	Malhotra Ripudaman	DOE	Stanford Research Institute	Complete
PCDC	Sorption Enhanced Shift Reaction	Allam, Rodney	DOE	Air Products Inc.	Completed to 2003 stagegate review
PCDC	Coke Gasification and Gas Separation Case Study	Reddy, Satish	DOE	Fluor	Completed to 2003 stagegate review
PCDC	Copper Palladium Membrane Research	Alptekin, Gokhan	DOE	TDA Research	Complete
PCDC	Electro-Ceramic Membrane Research	Mundschau, Michael	DOE	Eltron	Completed to 2003 stagegate review

**Table 3: Capture Studies Status, January 2004 (Cont'd)**

Capture Category	Project Title	Principal Investigator	Co Funder*	Technology Provider	Status
PCDC	Membrane WGS Reactor Development Study	Reddy, Satish	DOE	Fluor	Completed to 2003 stagegate review
PCDC	Develop Silica Membranes	Van Delft, Yvonne	DOE	ECN	Complete
PCDC	Develop Supported Copper Palladium Alloy	Way, Doug	DOE	Colorado School of Mines	Complete
PCDC	Develop Supported Silicalite Membranes	Lin, Jerry	DOE	Univ. of Cincinnati	Complete
PCDC	Membrane WGS reactor design	TBA	DOE	SOFCo	Completed to 2003 stagegate review

In addition, four Oxyfuel studies are underway within the CCP program. None are funded directly through the CCP / DOE award and are listed here for information. However two of the studies have been the subject of an economic review by the CCP economics team. The AZEP technology review was co-funded by NRC, the Advanced Boilers technology was co-funded by the DOE.

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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> emitted. Improving the economics of post-combustion capture is therefore a critical goal for the entire CO<sub>2</sub> 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<sub>2</sub> content, near atmospheric pressure, high in volume, and often contaminated with other impurities (SO<sub>x</sub>, NO<sub>x</sub>, 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> Capture,” is a high-risk program that may be applicable for both retrofit and new-build, as well as pre-combustion CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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 studying this technology any further. 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<sub>2</sub> (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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> loading
- The ‘Electrical Swing Effect’ – is it real?
- The impact of other gas components (water, NO<sub>x</sub>, SO<sub>x</sub> 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 be 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<sub>2</sub> 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,. additional cost-savings may result from integrating the low-cost plant with the power plant. The technical team recommends extension of the current program to include this review early in 2004.

## **Self-Assembled Nanoporous Materials for CO<sub>2</sub> Capture – SRI – DOE funded**

This work is investigating the ‘design’ of adsorbent materials for improved adsorption of CO<sub>2</sub> 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<sub>2</sub> 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<sup>2</sup>/g. SRI has also received 300-g of similar material from Dr. Seki of Osaka Gas, which only has 600 m<sup>2</sup>/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<sub>2</sub> and N<sub>2</sub>, which is ideal for PSA. The adsorbent reaches its equilibrium CO<sub>2</sub> 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<sub>2</sub> loading is sufficiently high for a PSA process to be 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<sub>2</sub> partial pressure) and pre-combustion (high CO<sub>2</sub> partial pressure) of CO<sub>2</sub>. 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<sub>2</sub> 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**

The CCP Post Combustion Team was to screen many new technology ideas for novel ways to capture CO<sub>2</sub> 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.

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

## 1.1.1.2 Self-Assembled Nanoporous Materials for CO<sub>2</sub> Capture

Task - 1.4 - "New and Novel" Concepts

Principal Investigator: Ripudaman Malhotra

Technology provider: Stanford Research Institute (SRI)

### Highlights

- Copper terephthalate 3-D complexes were synthesized, based on literature data by Seki (Osaka Gas). Surface area of prepared materials ranged from 20 to 1200 m<sup>2</sup>/g. Reproducibility and scale-up problems were encountered. A 450 m<sup>2</sup>/g surface area sample showed over 90% of the area in pores less than 20 Å. Surface morphology analysis by SEM showed a multi-lamellar structure.
- The samples showed high capacity for CO<sub>2</sub> adsorption with a selectivity 8 times greater than for N<sub>2</sub> adsorption. High adsorption capacity was demonstrated by CO<sub>2</sub> isotherm measurements that did not level off at 1 atm CO<sub>2</sub>, corresponding to 25 atm flue gas containing 4% CO<sub>2</sub>. The copper terephthalate material performed best at CO<sub>2</sub> pressures above 1atm or above 25 atm total pressure with a 4 % CO<sub>2</sub> flue gas. The highest CO<sub>2</sub> purity obtained in the experiments was 67.9% CO<sub>2</sub> with 34.1% recovery.
- A simulated 400MW gas-fired power plant with a atmospheric pressure adsorption and vacuum desorption system was evaluated because a high pressure system would have had a prohibitively high parasitic load (260 MW).
- Process cost estimates showed that the best material would have prohibitively high capture costs of \$ 406,51/tonne of captured CO<sub>2</sub> and a parasitic power load of about 1 GW. Work was halted on this project because other processes were more attractive in CCP's timeframe.

### Summary

SRI International, Chemical Science and Technology Laboratory, proposed and executed the title study to produce sorbent materials for CO<sub>2</sub> capture in pressure swing adsorption (PSA) processes. The overall objective of this fundamental research was to develop new nanoporous materials that will effectively capture CO<sub>2</sub> 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<sub>2</sub> by relatively weak van der Waals forces and that would have a high adsorption capacity for CO<sub>2</sub>.

Structures that could accommodate multiple CO<sub>2</sub> molecules at each site may exhibit cooperative binding of CO<sub>2</sub>. Binding is considered cooperative when subsequent molecules of CO<sub>2</sub> 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<sub>2</sub> than a non-cooperative system. The project objectives were:

- 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<sub>2</sub> 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 2003 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<sub>2</sub> from the material. Molecular structure calculations showed that a copper oxalate structure would hold one molecule of CO<sub>2</sub> while the larger copper terephthalate lattice would accommodate four molecules of CO<sub>2</sub> in a single cell.

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 complexes obtained had BET surface area measurements between 20 m<sup>2</sup>/g and 1200 m<sup>2</sup>/g. The pore size distribution of a 450 m<sup>2</sup>/g surface area sample was found to have over 90% of its pores less than 20 Å in size. Earlier molecular structure calculations indicated that cavities should be about 10Å 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 2θ = 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.

SRI prepared and reference samples from Osaka Gas were tested by a subcontractor, Adsorption Research Inc. CO<sub>2</sub> and N<sub>2</sub> adsorption isotherms for the SRI sample showed that the CO<sub>2</sub> isotherm did not level off at the highest pressures tested (1 atm. CO<sub>2</sub> which corresponds to 25 atm. flue gas containing 4% CO<sub>2</sub>). The result is consistent with a high capacity of the material to adsorb CO<sub>2</sub>. The selectivity of the material for CO<sub>2</sub> over N<sub>2</sub> was estimated to be about 8. The advantage of copper terephthalate manifests itself only at CO<sub>2</sub> pressures greater than 15 psia. Copper terephthalate is a fine powder so pellets were prepared by pressing the powder into discs followed by grinding and sieving. The procedure gave a granular material that worked well in the laboratory tests but showed significantly slower intra-particle diffusion. The laboratory measurements used a two-bed pressure swing adsorption (PSA) system. Powdered and granulated materials and a commercial silicalite, UOP Hisiv 3000 as a reference were tests.

The project goal was to design a process to capture the CO<sub>2</sub> from a 400 MW gas-fired power plant that would meet the specifications of 90% capture and 96% CO<sub>2</sub> purity. Because pressurizing the total plant exhaust (1586.1 MMSCFD (million std. cubic feet per day)) would generate a very high parasitic load (about 260 MW), SRI/ARI opted for a design in which the beds are charged at the pressure of the exhaust, and the CO<sub>2</sub> product is recovered by pulling a vacuum on the adsorbent. The highest purity obtained in the experiments was 67.9% CO<sub>2</sub> with 34.1% recovery.

A rough economic analysis using both experimental and modeling results from the study was performed. Simulations were run using the conditions specified by the CCP to simulate operation of a full-scale 400MW system (78,912 kgmole/hr at a CO<sub>2</sub> mole fraction of 0.04.) The required adsorption beds were found to be 2,880,996 kg/bed, for the powdered copper terephthalate adsorbent and 5,548,676 kg/bed for the granulated material. In contrast, a design based on the reference UOP silicalite required 1,440,498 kg/bed.

The estimated costs per tonne of CO<sub>2</sub> captured were: \$406.51 for the powdered copper terephthalate adsorbent, \$494.88 for the granulated material, and \$393.12 for the UOP silicalite. These costs included the adsorbers, vacuum pumps (which would be exceedingly large), valves, controls, other vessels, electrical power, labor, installation, and a modest profit margin. The resulting power requirements for

CO<sub>2</sub> capture were likewise enormous - about 1 GW or twice the output of the power plant which this capture system was being designed.

The reported results indicate that the copper terephthalate material under examination is not competitive for application to carbon dioxide capture in a low-pressure, low CO<sub>2</sub> partial pressure, system.

**Reports and Publications**

- SRI has produced two internal presentations (August 2002 and July 2003).
- See Appendices for the project final report under the same heading as this report.

## 1.2 Pre-Combustion Technology

### Task - 2.0 Develop Pre -Combustion De-carbonization Techniques

Significant progress was made in pre-combustion de-carbonization technology and advancement in several key areas was achieved. Further, new insight of adopting existing technology into the CCP scenarios was achieved. The key messages from the development work are:

- Four new advanced technologies was developed to “proof-of-concept” with significant advancement in efficiency, cost and CO<sub>2</sub> capture compared to best available capture technology.
- Three of the new advanced technologies were designed for three different CCP scenario by the technology providers. The design was checked, integrated and cost estimated by an independent contractor (Fluor) in order to assure quality of the design and consistency when comparing with the baseline technology, thus enhancing credibility of the conclusions.
- Significant advancement in hydrogen membrane material covering a wide temperature range.
- Further development is needed to advance the most promising technologies, however it is expected that new technologies can be developed and demonstrated in 2010-2015 with costs in the range of \$ 15-40 MM.
- Pre-combustion technology can be developed to meet stringent requirement on NO<sub>x</sub>, CO and SO<sub>x</sub> formation. The lowest NO<sub>x</sub> formation was predicted to 5 ppm vol. from a combined-cycle gas turbine. For open-cycle gas turbines, the NO<sub>x</sub> formation was reduced by 50%. The CO and SO<sub>x</sub> formation is virtually zero.
- Pre-combustion technology can be designed as a stand-alone facility for both retrofit and new build application giving a wide application range and benefits with respect to integration in existing complex facilities, e.g. refineries
- Pre-combustion technology can be used for other application, e.g. GTL, ammonia, hydrogen and syngas production, thus increasing the economic potential of the technology and return of investment.
- Significant improvement in energy and CO<sub>2</sub> capture efficiency was obtained for several technologies, resulting in an efficiency penalty for combined-cycle gas turbines of less than 5% - point and close to 100% CO<sub>2</sub> capture.
- 15% improvement of gas turbine heat rate can be obtained when switching from natural to hydrogen-rich fuel, making the pre-combustion technology a strong candidate for the large numbers of open-cycle gas turbines in operation in the US.
- Demonstrated very low CO<sub>2</sub> avoided cost numbers for the Canadian scenario – CO<sub>2</sub> capture from pet coke fired IGCC – approximately 10-15 \$/ton.
- Existing Pre-combustion technology can be considered proven for a wide range of CO<sub>2</sub> capture applications including the CCP scenarios

### *Introduction*

The CCP Pre-combustion Technology program is the largest capture program in the CCP. It is based on 13 individual projects including about 20 different technology suppliers. The studies are divided into 6 main categories as listed below:

- 1.2.1 Membrane studies
- 1.2.2 Coke Gasification
- 1.2.3 Integration and Scale-up Studies
- 1.2.4 Integrated Report and Communication
- 1.2.5 Generation of H<sub>2</sub> Fuels
- 1.2.6 Sorption Enhanced Technology

Table 4 a complete list of all sub-projects is given including, technology suppliers involved, co-funders and status per January 2004.

**Table 4 - Pre-combustion Technology Studies**  
**Status: Jan 2004**

<b>DOE Ref. Number</b>	<b>Project Title</b>	<b>Co Funder*</b>	<b>Technology Provider</b>	<b>Status</b>
1.2.1.1	Sulfur Tolerant Membrane Study	DoE	Fluor, SOFCo, Eltron, TDA Research, CSM, ECN, University of Cincinnati	Did not pass complete stage gate review in April03 Entered into phase II with reduced and revised scope. Eltron, Fluor and SOFCo were remaining technology providers. Project completed
1.2.1.2	Hydrogen Membrane Reactor	EU	BP, Norsk Hydro, KTH, Sintef, University of Twente, Institute for membrane technology, University of Zaragoza	Passed stage gate review end 2003. "proof-of-concept" tests completed. Further work planned
1.2.1.3	Compact Reformer with Advanced Pressure Swing Adsorption System for Hydrogen Fuel Production	DoE	Air Products & Chemicals, Inc.	2003 Stage gate review completed. Further work planned.
1.2.1.4	Hydrogen Membrane Reformer	Klimatek	Norsk Hydro	Passed stage gate Project completed with successful "proof-of-concept" test. Further work planned
1.2.1.5	Pre-combustion Membrane Reactor Study	CCP	Haldor Topsoe	Completed in Feb 2001
1.2.2.1	Advanced Technology for Separation and Capture of CO <sub>2</sub> from Gasifier Process Producing Electrical Power, Steam and Hydrogen	DoE	Fluor Federal	2003 Stage gate review completed, further work planned to clarify 2004.
1.2.3.1	Study of Gas Turbine Retrofit Requirements to Burn Decarbonized Fuel (Hydrogen)	DoE	General Electric	Completed Dec 2003
1.2.3.2	Standardized PCDC	Klimatek	Jacobs	Completed Dec 2003
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

1.2.3.5	Compact Reformer with Advanced Pressure Swing Adsorption System for Hydrogen Fuel Production	DoE	Davy/APCI	Compact reformer dropped for the time being Advanced PSA study completed Dec 2003
1.2.4.1	Capture Study Integrated Reports	DoE	ARI	Completed
1.2.5.1	Generation of H <sub>2</sub> Fuels	Klimatek	IFE	Completed Feb 2002
1.2.6.1	Production of Hydrogen Fuel by Sorbent Enhanced Water Gas Shift Reaction	DoE	Air Products and Chemicals	Passed phase II stage gate review. Phase III completed with “proof-of-concept” test Phase IV scale up work 2004

All the technologies have been developed to fit into real life scenarios as this gives the most insight into the economical potential and technical performance of the particular technology.

The overall pre-combustion program could, in principle, be divided into two phases:

1. Review and Evaluation. Where the CCP partners shared experience and know-how on both what could be considered best available technology and new development. Gaps in knowledge were closed by executing studies in particular areas.
2. Technology Development. Develop most promising technology to “proof-of-concept”, a stage where the technology could with further work to reduce uncertainties on scale –up and performance go on to pilot testing in the 2008 time frame.

## Review and Evaluation

Pre-combustion technology is based on well known technology that is in commercial operation for different application such as hydrogen, ammonia and syngas production. The technology comprises two main steps: reforming/conversion of fossil fuel to a mixture containing hydrogen, CO<sub>2</sub> and CO called syngas and separation of CO<sub>2</sub> and hydrogen to produce a hydrogen-rich stream.

Conversion of fossil fuel to syngas dates back several centuries to when coal was the primary energy source. The first to convert fossil fuel to syngas was the Scottish engineer William Murdoch who in 1792 used the gas to light his house. The gas was later called town gas or city gas and was widely spread over the world between 1800 and 1920. The technology developed from gasification of coal to reforming of natural gas through the use of catalysts. Steam reforming technology was introduced in the late 1930’s and remains the primary method to convert natural gas into syngas. More than 90% of current hydrogen production – 500 billion Nm<sup>3</sup>/year according to the IEA – is based on reforming of fossil fuel. This indicates that about 500 reformers with an average capacity of 100,000Nm<sup>3</sup>/h hydrogen are in operation worldwide.

The development of reforming technologies for natural gas and similar went in two directions: 1) steam methane reforming, an endothermic process (requires heat) converting a mixture of steam and natural gas to syngas at high temperature and 2) autothermal reforming, which is an exothermic (generates heat) process converting a mixture of steam, natural gas and oxygen into syngas. The improvement of steam methane reforming from its introduction in the 1930’s has been through increasing operating pressure and temperature by development of new catalyst and reactor materials.

Combining the two steps of syngas production and separation of hydrogen and CO<sub>2</sub> is a well established technology mainly used in production of syngas for ammonia production. The first system dates back to the 1940's where low pressure steam reforming followed by compression to 15 barg and separation by 20% MEA. In the mid-1950's, a technology using hot potassium carbonate was introduced and in the late 1970's, activated MDEA solvent was introduced leading to a significant improvement in energy efficiency. The largest ammonia plants produce about 2000-2200 tonne/day, which is equal to a hydrogen production of about 150,000-200,000 Nm<sup>3</sup>/h or 450-600 MW (LHV). Approximately 1,000,000 tonne/year of CO<sub>2</sub> is capture from the largest plants and compressed to 160 barg and used for Urea production.

Pre-combustion technology is a very complex process involving a number of catalytic steps, heating to high temperatures, and cooling to low temperatures. A step that improves one part of the process might be a disadvantage for another part. As an example, reforming is favored by low pressure, but separation of CO<sub>2</sub> is favored by high pressure. Also energy efficiency is favored by low steam addition but hydrogen production is favored by high steam addition.

Basically two approaches were identified to be feasible for improving pre-combustion technology.

1. System optimization of well known technologies
2. New technologies based on advanced separation combining both reaction and separation.

This above forms the basis of some important key messages:

- Pre-combustion technology is the only CO<sub>2</sub> capture technology, which is demonstrated in a large scale application at similar conditions as the CCP scenarios. Leading to credibility with respect to efficiency, lifetime, CO<sub>2</sub> capture, cost and operation.
- A large commercial market exist today for core pieces of pre-combustion technology and therefore cost advantages can be obtained in real life projects due to competition, between both technology licensors and main contractors.
- Pre-combustion technology generates a hydrogen-rich fuel, which can be used for other purposes, thus creating positive synergies.
- The increased focus on hydrogen and fuel cells in Europe, North-America and Japan have and will create a platform for new developments of reforming technology.

### **Commercial Value - Present and Future**

Pre-combustion Technology for CO<sub>2</sub> capture accommodates a broader potential than any of the three capture technologies. 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. A large gas-to-liquids plant may cost about \$ 1 billion with 60% of the cost being related to syngas technology.

Further, significant improvement in some of the technologies could form a basis for future low cost hydrogen for hydrogen fuel cell vehicles. Hydrogen production with capture and storage of CO<sub>2</sub> will "bridge-the-gap" towards the renewable hydrogen economy and make a more economical viable transition.

### **CCP Scenarios**

One key advantage of pre-combustion technology is its ability to convert all types of fossil fuels into syngas. That makes this technology the only applicable capture technology in all of the CCP scenarios. In addition, some of the scenarios also contained a retrofit case and there were some concerns as to whether



or not pre-combustion technology could be used for retrofitting gas turbines – in particular large combined-cycle gas turbines as for the Norwegian scenario. This issue was addressed in two studies: 1) GE study and 2) Standardized PCDC (see later). Another advantage is that production of the hydrogen fuel and capture of the CO<sub>2</sub> takes place at one place – that means significant economy of scale can be obtained compared to the other capture technologies. This also makes retrofit in complex plants like the EU refinery much easier.

Three of the most promising technologies were integrated into different scenarios by Fluor based on the technology provider information:

- Hydrogen Membrane Reformer for NorCap scenario
- Membrane water gas shift reactor for the UK refinery
- Sorption Enhanced water gas shift reactor for the Alaska scenario

Fluor work included integrated design, quality assurance and cost estimation. The work created a unique platform for comparison against the baseline technologies thus giving new insight on how the technologies performed in the given scenario and credibility to the cost reduction potential estimated by the CEM team.

## **Results and Conclusions**

### 1.2.1.1 - Sulphur Tolerant Membrane Study

The study objective was to develop a sulphur-tolerant membrane operating at water-gas-shift conditions. Four membrane developers were given one year to develop a membrane with significant flux and selectivity for a sour syngas. After one year none had reached the target however a promising membrane for sweet syngas conditions was identified. The pre-combustion team agreed to re-direct the program and continue the development based on sweet syngas application. The program continued with Eltron as the membrane developer, SOFCo as commercial reactor designer and Fluor as responsible for process integration. The development of a novel low-cost compact design for a membrane water gas shift reactor and improved membrane for a water gas shift reactor with selectivity and flux was achieved. This will lead to reduced reactor and membrane costs in the US DOE refinery scenario and the technology shows a potential of 30-35% reduction in CO<sub>2</sub> avoided cost when using refinery off-gas. It should be noted that a concept based on gasification of heavy fuel oil also was developed, but the CO<sub>2</sub>-avoided cost was higher than the amine post combustion baseline technology and was not pursued further. The team considered this a promising technology with medium potential with medium risk. They recommended that work be continued to explore the possibility to identify a sulphur tolerant hydrogen membrane that would improve the concept in a future CCP program

An alternative approach to the separation of CO<sub>2</sub> from sweet syngas was explored in the EU program. A consortium of European membrane developers was created with a common task of developing a novel hydrogen membrane that could be used in pre-combustion applications – the real life scenario being the EU refinery. The membrane types were ultra-thin Pd-membranes, silica based ceramic membranes, and Pd coated zeolites. The most promising membrane was the dense Pd/Ag membrane where a 1 µm film was manufactured by a method developed by SINTEF. The film is then transferred to a porous stainless steel support tube. Significant advancement was also achieved in the silica-based ceramic membrane area where a selectivity of 1000 was obtained.

A reactor concept incorporating the Pd-membrane was developed with an associated process scheme for production of a hydrogen fuel mix for heater and boilers. The technology demonstrates high energy and CO<sub>2</sub> capture efficiency and low cost CO<sub>2</sub> separation cost with a reduction of 25-30% for refinery off-gas was achieved. The team recommended continuing the work on Pd-membranes with a focus on long term testing of stability and performance.

#### 1.2.1.2 - Production of Hydrogen Fuel by Sorbent Enhanced Water Gas Shift Reaction

The leading adsorbent material ADS1-2 has a CO<sub>2</sub> removal capacity of up to 1.1% in PDU cyclic testing. However, a new material has been identified which the potential for significantly higher CO<sub>2</sub> capacities than the other adsorbents has tested. This could lead to significant improvement of the sorption enhanced water gas shift reactor scheme for gas turbine applications like the US DOE scenario for Alaska or the Norwegian Scenario. The technology demonstrated significant cost reduction – in the range 30-35% - compared to the baseline technology. The technology is considered to be at a more mature stage than the membrane technologies and with the high potential. The team has recommended continuing work on this technology.

#### 1.2.1.3 - Compact Reformer with Advanced Pressure Swing Adsorption System for Hydrogen Fuel Production

The scope of the work was reduced to only review the advanced pressure swing adsorption system since agreement with Davy could not be settled. Results showed that cycles that couple the hydrogen purification with the carbon dioxide recovery system offer higher hydrogen recovery with the same number of adsorbent columns. It was determined that a single-train adsorption system can provide 800,000 tonnes/year of carbon dioxide at up to 99.7% purity with a carbon dioxide recovery of up to 93%. The economics of the technology and integrating into a complete pre-combustion scheme is the next step.

#### 1.2.1.4 - Hydrogen Membrane Reformer

In NorCap, Norsk Hydro was selected to develop a technology based on high temperature ceramic hydrogen membranes for combined-cycle gas turbines. The principle of the technology is similar to some of the concepts in the oxyfuel team for oxygen-conducting ceramic membranes, an area where Hydro has significant experience. The first phase of the project aimed at developing a membrane that could achieve significant flux to meet CCP targets. This work was done in collaboration with the University of Oslo and SINTEF. A membrane with sufficient flux was synthesized. The membrane reformer system showed untouchable performance in the NorCap Norwegian scenario with very high energy efficiency, approximately 90-91% (LHV), low NO<sub>x</sub> formation – 5 ppm vol and a potential CO<sub>2</sub> avoided cost reduction of 50-55%. Proof-of-concept test confirmed that the hydrogen flux was above expectations. The team recommended continued work on the technology in the extended Klimatek program for 2004.

#### 1.2.1.5 - Pre-combustion Membrane Reactor Study

A small study was conducted in the review and evaluation phase to assess the potential of hydrogen membranes for pre-combustion applications. The Haldor Topsoe study established important targets for hydrogen membranes and has been a valuable tool for benchmarking the performance of hydrogen transport membranes.

#### 1.2.2.1 - Advanced Technology for Separation and Capture of CO<sub>2</sub> from Gasification, Producing Electrical Power, Steam and Hydrogen

Fluor made a complete study of pre-combustion technologies for a petroleum coke fired IGCC with production of steam, electricity and hydrogen. Un-controlled and baseline cases were established, several pre-combustion technologies were screened, and one technology was selected for detailed design and costing. The results showed that with conventional technology, a CO<sub>2</sub> avoided cost of approximately 15 \$/ton could be obtained. This again gives very little room for improvement. The screening of different pre-combustion options was based on different criteria, e.g. CO<sub>2</sub> recovery above 85%, delivering hydrogen at gas turbine pressure, sulphur tolerance, sulphur content in CO<sub>2</sub> stream etc. Based on these

criteria the CO<sub>2</sub>LDSEP was seen as the most suitable option. Due to confidentiality issues the capital cost was assessed by a sensitivity analysis – showing that the CO<sub>2</sub> avoided cost for the technology was in the range of 10-20 \$/ton.

Results indicated that very low CO<sub>2</sub> avoided cost can be obtained in US DOE Canadian scenario by adopting pre-combustion technology – in the range 10-15 \$/ton CO<sub>2</sub>.

#### 1.2.3.1 - Study of Gas Turbine Retrofit Requirements to Burn Decarbonized Fuel (Hydrogen)

A critical success factor for pre-combustion technology is that hydrogen-rich fuels can be used in conventional combustion processes. The use of hydrogen-fuel in gas turbines combustors is an area that requires special attention in terms of performance, lifetime, and cost. The leading gas turbine supplier (General Electric) for syngas fuel combustors was selected to conduct the study. The study results were very encouraging and the potential of gas turbine retrofit was confirmed. Improved heat rate of 15% was estimated which will reduce the size of the pre-combustion plant and increase overall energy efficiency. NO<sub>x</sub> formation is another issue and by changing from natural gas to hydrogen-rich fuel, GE estimated that a 50% NO<sub>x</sub> reduction could be achieved and for some hydrogen fuel mixtures single-digit NO<sub>x</sub> ppm levels can be obtained.

#### 1.2.3.2 - Standardized PCDC

The pre-combustion team initiated a study to evaluate cost reducing options for the pre-combustion baseline technology. The focus was on cost savings from repeat design, modularization, mechanical codes, pre fabrication etc. The result was somewhat disappointing only demonstrating cost savings in the order to 15-20%. Further work in this area should focus on rotating equipment, which contributed 60% to the total installed cost.

#### 1.2.3.3 - Very Large Scale Autothermal Reforming

One of the key features of pre-combustion technology is the potential of designing large capture plants in a single plant thus obtaining benefits from economy-of-scale. The study confirmed that a pre-combustion technology can be built as a single plant for the Alaska scenario – capturing over 2 million tonne/year of CO<sub>2</sub> and producing more than 750 MW of fuel. The team felt, however, that the proposed process design was not optimal for the Alaska scenario and further work should look into other alternatives. The estimates from the economic modeling showed that the CO<sub>2</sub> reduction potential was less than 15%. However, looking at the option at a similar maturity as the post combustion baseline technology – one conclusion from the work could be that pre-combustion is preferred over post combustion technology.

#### 1.2.3.4 - Advanced Syngas Study

Several technologies that are commercial or close to commercialization were studied for Integrated Reforming Combined-cycle – the pre-combustion baseline technology for the Norwegian scenario. The study result demonstrated limited potential when adopting new technology or optimizing the concept. However, the study also showed that a pre-combustion baseline was lower cost technology than post combustion bust with higher energy consumption.

#### 1.2.5.1 - Generation of H<sub>2</sub> Fuels

A process scheme was developed for the Norwegian and EU refinery scenario using CaO as an oxidant to drive the reforming reaction. The aim was to estimate CO<sub>2</sub> capture and energy efficiency for the technology. The results showed unsatisfactory energy efficiency (40% LHV) for combined-cycle gas turbines. An efficiency of approximately 83% HL V was estimated for the heaters and boilers option if an

electricity credit was included. Finally, 90% CO<sub>2</sub> capture efficiency could be obtained for both applications. Since CaO is converted into CaCO<sub>3</sub> and must be calcined back to CaO for recycle to the reforming reactor, the key challenge is to develop reactor systems that recycle solid materials efficiently. This risk associated to the development of the technology must be considered high and fundamental studies and lab testing must be conducted before pilot testing can be realized. The recommendation from the team is to study the refinery case in more detail and establish a cost estimate for the process before considering actual development work.

## 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 Membrane Studies of the CCP Pre-combustion De-carbonization Technology Program consist of three main projects and one screening study with contributions from 15 different technology providers. The membranes studies are divided into four sub-projects as listed below:

- 1.2.1.1 Sulfur Tolerant Membrane Study (DOE)
- 1.2.1.4 Hydrogen Membrane Reformer (NorCap)
- 1.2.1.5-11 Hydrogen Membrane Reactor (EU Grace)
- 1.2.1.12 Pre-combustion Membrane Reactor Study (Topsoe)

Membrane Studies are the dominating activity in the CCP Pre-combustion De-carbonization Technology Program with major activities in DOE, EU and Klimatek. This is the consequence of the very promising results achieved by the hydrogen membrane technologies in the analysis work performed during 2000 and 2001. During this phase the hydrogen membrane technologies were identified to have the best potential to achieve the CCP cost reduction target. Recently, these results were confirmed by the work of the Common Economic Model team.

All membrane development work has focused on applications that combine chemical reaction and hydrogen separation in a single step. Two fundamentally different approaches have been assumed:

- A single-step process for producing a hydrogen rich fuel stream and a separate CO<sub>2</sub> stream. Such a system is generally referred to as Hydrogen Membrane Reformer.
- A two-step approach using conventional technology such as autothermal reforming, partial oxidation or steam methane reforming to produce synthesis gas as a first step. Conventional processes would use a shift section downstream of the reformer, followed by a physical and/or chemical CO<sub>2</sub> removal system. Membrane based systems use technology that converts the remaining CO in the syngas and simultaneously separates the product gases hydrogen and CO<sub>2</sub>. Such systems are generally referred to as Membrane Water Gas Shift (MWGS) Reactors.

The major advantages of hydrogen membrane technologies are:

- Smaller equipment by combining reaction and separation in a single unit
- Above equilibrium conversion due to selective removal of hydrogen product from reactor
- Reduced compression cost due to production of CO<sub>2</sub> at elevated pressure

Major challenges related to membrane technologies are:

- Membrane manufacturing costs and reliability
- Membrane long-term stability and performance

Key results, highlights and future plans for the individual membrane projects are discussed below.

### 1.2.1.1 Sulfur Tolerant Membrane Study

The conclusions from Phase I of the project were:

- The project started with four membrane developer teams focusing on different types of hydrogen transmitting membranes (Eltron Research: ceramic-metal composites, Colorado School of Mines/TDA: palladium alloy, University of Cincinnati: zeolite, Energy Centre of the Netherlands (ECN) - microporous silica).
- The 12-month time frame for Phase I was extremely challenging for developing and testing hydrogen transfer membranes for sour MWGS service.
- Only a metal alloy membrane developed by Eltron demonstrated sufficient selectivity and potentially represents a significant improvement of the state-of-the art. Eltron was selected to continue their development work during phase II of the project.
- Process simulations have led to the conclusion that 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. None of the membranes developed during phase I performed satisfactorily under sour gas conditions. This led to the decision to modify the process flow scheme for phase II such that  $H_2S$  is removed upstream of the water gas shift section of the plant. Consequently, Eltron could focus on developing a membrane for a MWGS reactor under  $H_2S$ -free conditions in phase II.
- Process simulation work and preliminary cost analysis indicate that the concept of the membrane water gas shift reactor still has potential to reduce the  $CO_2$  avoided capture costs.

The main achievements from Phase II to date were:

- The metal alloy membranes developed by Eltron have ten times the hydrogen permeability of state-of-the-art (25  $\mu m$ ) Pd membranes at a fraction of the cost. The 127  $\mu m$  thick membranes have been tested in preliminary tests for over 300 hours under a hydrogen partial pressure of 13 bar at 673 K (400°C), and an absolute pressure on the  $H_2$  feed side of the membrane of 32 bar, with a differential pressure of 31 bar across the membrane. Membranes have successfully resisted the differential pressure without leak and have shown a steady hydrogen flux of  $220 \text{ Nml}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$  corresponding to a permeance of  $0.6 \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{bar}^{-0.5}$
- Extremely high hydrogen flux of  $346 \text{ Nml}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$  was achieved using a 90%  $H_2/He$  mixture at elevated hydrogen partial pressure of 29 bar with a 127  $\mu m$  metal alloy membrane.
- High-pressure reactors have been designed, built and tested to operate at an absolute pressure of 32 bar with a differential pressure of 31 bar across the membranes in the water-gas shift temperature range from 593-713 K. Reactors were designed to operate with gas mixture consisting of steam,  $CO_2$ , and  $CO$  to simulate conditions in industrial water-gas shift reactors.
- A conceptual innovative reactor design with a corrugated support and a multi-pass cross-flow configuration has been developed and cost estimated by SOFCo. The design was based on the results of systematic screening exercise during which a large number of possible combinations of support structure and flow configurations were assessed. Structural analysis of several different support structure alternatives was conducted, which involved consideration of pressure, gravity, and differential expansion loading. A design that satisfies stress and instability constraints for several permeate gap heights was found.
- A cost estimate of the commercial scale reactor was developed for the multi-pass cross-flow design. The estimate was partially based on information supplied by foil manufacturers, pressure vessel suppliers, and brazing technology experts. Based on a determination of the areas of high cost, four alternative designs were proposed and cost estimated. Cost reductions in the order of 40% were achieved.

- An AspenPlus process simulation model of the entire capture plant was developed by Fluor. Based on the conclusions from phase I of the project the flowsheet was based on a H<sub>2</sub>S-free feed to the MWGS reactor designed for the Eltron membrane. The thermal efficiency based on the production of hydrogen fuel was 61.4%. This was based on sequestering 2 million tonnes per year of CO<sub>2</sub>. The efficiency does not include 37 MW of exported power.
- It was readily apparent that there were severe capex and opex penalties involved in removing sulfur from the syngas. It was therefore decided to evaluate this type of MWGS reactor in an alternative scenario. Instead of starting with a sulfur-containing fuel oil, this alternative utilizes sweet natural gas as a feed. Since no sulfur removal is required, the economics are significantly improved.

#### 1.2.1.4 Hydrogen Membrane Reformer

The aim of this project was to develop dense hydrogen mixed conducting membranes (HMCM) with sufficient H<sub>2</sub> transport rates and stability under normal steam reforming conditions, and further develop a techno-economically viable Pre-combustion De-Carbonization process applying said materials.

- A total number of 40 candidate membrane materials have been synthesized and characterized and more than 35 hydrogen permeability measurements have been performed. Based on the measurements and theoretical evaluations, a main candidate materials system was selected October 2002.
- Several process alternatives have been evaluated and one process configuration was selected for the final cost evaluation. In the novel natural gas to hydrogen process the membrane reformer system replaces the traditional hydrogen production train. The hydrogen process is in this study integrated with a 390 MW gas fired combined cycle power plant.
- Thermodynamic analyses indicate that the membranes will be stable above 750°C under process conditions. Mechanical strength and creep resistance measurements reveal poor properties, which are results of inadequate sintering. It is expected that a significant improvement in these properties will be obtained when the processing is optimized.
- A method for manufacturing supported membrane tubes has been developed. The tubes consist of a porous tubular support (wall thickness 2 mm) with a thin membrane coating (50 µm). Two such membrane tubes were produced and one was tested under conditions similar to reformer operating conditions.
- The measured H<sub>2</sub> flux in the test rig was 18 Nml·min<sup>-1</sup>·cm<sup>-2</sup>, which compares favorably with model predictions and exceeds the flux target set to 5 Nml·min<sup>-1</sup>·cm<sup>-2</sup> H<sub>2</sub> flux at 1000 °C with a total pressure of 20 bar. Although the measurement is characterized by a relatively large uncertainty due to the fact that the tested membrane was not totally gas impervious, the goal of verifying target flux is considered reached.
- A conceptual monolithic membrane reformer design was developed for the material selected. The entire reactor comprises three discrete sections performing different tasks: reforming, shift conversion, and retentate combustion. The entire membrane reactor is operated at temperatures above 750°C to assure efficient H<sub>2</sub> transport through the ceramic membranes and maintain thermo-chemical stability of the membrane.
- A process scheme incorporating the membrane reformer was developed and optimized using an ASPEN flowsheet simulation model. The process simulations indicate high electric efficiency (53.1%) with a CO<sub>2</sub> capture efficiency close to 100% for the Norwegian scenario. The NO<sub>x</sub> formation was predicted to be approximately 5 ppm vol.

#### 1.2.1.5-11 Hydrogen Membrane Reactor

The main goal of the hydrogen membrane reactor project was to develop membranes for integration into a Pre-combustion De-carbonization process for H<sub>2</sub>S-free fuel gas in a heater and boiler scheme.

Four membrane developer teams had been selected to develop and test various types of hydrogen transmitting membranes:

- SINTEF: Dense palladium (Pd) alloy membranes
- University of Twente: Silica based microporous ceramic membranes
- University of Zaragoza: palladium coated zeolite membranes
- KTH: Pd nanoparticle preparation and membrane coating

The main achievements and conclusions from this project are:

- The SINTEF membrane consists of a very thin (1-5  $\mu\text{m}$ ) dense Pd/Ag film that is supported by a porous stainless steel tube. This membrane type clearly exhibited the most promising results within this project with virtually perfect selectivity and high hydrogen permeance:  $\text{H}_2$  fluxes up to  $30 \text{ Nm}^3 \cdot \text{min}^{-1} \cdot \text{cm}^{-2}$  have been achieved at a low differential hydrogen partial pressure of 0.34 bar, which corresponds to a permeance of  $0.68 \text{ mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2} \cdot \text{bar}^{-1}$  assuming linear pressure dependence or  $1.45 \text{ mol} \cdot \text{s}^{-1} \cdot \text{m}^{-2} \cdot \text{bar}^{-0.5}$  assuming Sievert's law. The novelty of the membrane is the low thickness of the dense layer, which results in reduced requirement for expensive palladium and high hydrogen fluxes corresponding to compact apparatuses.
- Twente produced silica membranes with very promising performance data towards the end of the project ( $\text{H}_2/\text{CH}_4$  selectivity up to 1000 at a reasonable permeance of  $0.2 \text{ mol}/\text{sm}^2\text{bar}$  at  $250^\circ\text{C}$ ). Due to time constraints these could not be considered in the reactor design or reactor testing.
- Pd coated zeolite were improved during the course of the project but fell behind the other membranes both with respect to selectivity and permeability.
- SINTEF was the only membrane developer to reproducibly produce tubular membranes with sufficient permeability and selectivity at the time when the process and reactor design was developed. Long term stability and cost efficiency has not been proven.
- Pd-alloy membranes developed by SINTEF and silica based membrane developed by Twente achieved higher than equilibrium CO conversion at temperatures above  $250^\circ\text{C}$  (up to 95% CO conversion at  $280^\circ\text{C}$ ) in water gas shift reactor tests performed by ITM. Unfortunately, ITM did not succeed in operating the membrane reactor at a pressure realistic for industrial applications (typically  $>25 \text{ bar}$ ) due to limitations in the reactor design and limited strength of the support tubes used by the membrane developer teams.
- Reactor tests focused on water gas shift reaction as it offers less severe operating conditions to the membranes, resulting in a higher chance of success. No attempts have been made to test the membranes developed during the project in a membrane reformer.
- Based on a mathematical membrane reactor model provided by SINTEF and experimental data measured by SINTEF and ITM a process scheme was developed and optimized using HYSYS software. From initially six different process options one option has been identified as most suited and selected for further optimization. The selected process is based on an oxygen-blown ATR and incorporates the use of discrete reaction and membrane stages rather than a single membrane reactor unit, which was found to give flexibility in the membrane arrangement, permitting tubular or planar schemes and allowing high surface areas per unit volume. To reduce the membrane area required, a nitrogen sweep stream is added on the permeate side. The key performance parameters of the selected process are:
  - Overall energy efficiency on LHV basis: 75.6%
  - Power balance closed
  - 99%  $\text{CO}_2$  capture efficiency (79% if natural gas consumption for power generation is considered)
  - 91% purity in  $\text{CO}_2$  capture stream (+ 9%  $\text{N}_2$ )
- A tubular reactor design using the SINTEF membranes has been developed. The design builds on commercial experience with tubular sintered membrane supports for liquid applications. The process design selected requires a total of nine identical membrane units distributed over three discrete stages. The total surface area is  $8000 \text{ m}^2$  for a plant sequestering 2 million tonnes per year of  $\text{CO}_2$



### 1.2.1.12 Pre-combustion Membrane Reactor Study

The study was designed to assess the potential of membrane reactors for use in producing a low pressure hydrogen fuel gas for use in boilers or fired heaters on a typical refinery or petrochemicals site. The target was to capture 90% of the carbon in the feed, with CO<sub>2</sub> compressed to 80 bar.

The aim was to evaluate current membrane reactor technology and to determine performance and cost characteristics of future novel membranes, which would be required to enable membrane reactors to be deployed at lower cost than conventional technology. This threshold constitutes a target for membrane development for use in membrane reactor pre-combustion de-carbonization plants. The aim was production of a nominal 230,000 Nm<sup>3</sup>/h of hydrogen as pure H<sub>2</sub> for fuel use at 1.5 bar pressure.

Two alternate base cases, steam reforming of natural gas and the gasification of coal using conventional flowsheet designs, these formed the basis for comparison with the membrane reactor schemes.

The cases developed were as follows

Natural gas fed cases:

1. Base case steam reforming (primary reformer)
2. Alternate base case (primary and secondary reformer)
3. Membrane reformer

Coal gasifier syngas fed cases:

4. Base case shift reactor and amine acid gas removal
5. Membrane shift reactor with sulphur tolerant membrane and catalyst, H<sub>2</sub>S disposed of together with the CO<sub>2</sub>.
6. Membrane shift reactor with sulphur removal upstream

Equipment sizes for balance of plant were determined from the simulation and capital cost estimates made for these equipment items using Icarus, Questimate software together with Haldor Topsoe's experience with hydrogen and syngas processes. In all cases, the process was heat integrated to maximize process efficiency.

The main conclusions from the study are listed here:

- Pd/Ag membranes offer cost savings compared to conventional technology at a thickness below 25 µm. (*NB*: membrane costs are based on very high Pd costs: 1100 \$/ozt)
- Close to 100% CO<sub>2</sub> captured and an efficiency of 75% (LHV) for the natural gas case was obtained in study
- Pd/Ag membranes at prices below \$1000/m<sup>2</sup> will be attractive, similarly a membrane with 200 Nm<sup>3</sup>·h<sup>-1</sup>·m<sup>-2</sup>·bar<sup>-0.5</sup> (or 2.5 mol·s<sup>-1</sup>·m<sup>-2</sup>·bar<sup>-0.5</sup>) would be attractive at costs up to \$10,000/m<sup>2</sup>, or three times that of the 25 µm Pd/Ag type.

### Risk Elements

The high potential of the technology should be balanced against the probability of success or the risk elements associated to the technologies. This is crucial when setting up a balanced technology development portfolio. The CCP pre-combustion team looked into three types of membrane and membrane system, which differ with respect to both economic potential and risk.

The membrane water gas shift system is considered to be a lower risk option than a membrane reformer system for different reasons:

- Lower temperature. Water-gas-shift reaction operates at 350-450°C whereas the ceramic membrane reformers need to operate at very high temperatures, i.e. 800-1000°C.
- The membrane water gas shift system can be developed without integrating the reaction and membrane, thus making a very simple system compared to membrane reformer system where reactor and membrane is fully integrated.
- Development of a sulphur tolerant membrane was not successful and it is questionable if the development of a sulphur tolerant membrane can be obtained.

A simple ranking of the different options is given below – the first being the option containing lowest risk:

1. Sweet syngas non-integrated hydrogen membrane
2. Sweet syngas integrated water-gas-shift reactor and hydrogen membrane
3. Integrated ceramic membrane reformer system
4. Sulphur tolerant hydrogen membrane

It should be noted that the risk between options 2 to 3 is significantly larger than between 1 to 2.

#### **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  $\gamma$ -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.

## 1.2.1.1 Sulfur Tolerant Membrane Water Gas Shift Reactor System

### Background

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 were:

- 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, which was used to compare the performance of the various membranes. The membrane program was developed by ECN. The membrane simulator was also integrated into an overall program (by Fluor, Inc.), which simulated the entire pre-combustion decarbonization facilities. The facilities were based on the Grangemouth refinery scenario with the feed streams consisting of fuel oil and fuel gas.

In Phase II, Eltron was selected to conduct further membrane development work and proof-of-concept testing. SOFCo was engaged to develop a preliminary design of a commercial scale MWGS reactor. Fluor was asked to provide a sized equipment list for the PCDC plant.

Phase II began on March 1, 2003 and the latest stagegate review was completed on December 31, 2003. Separate TPC summaries are also available for each technical provider.

### Phase 1 Summary

#### Eltron

The Eltron membrane is clearly the most novel. It has evolved into a metal alloy membrane 130 microns thick. The metal is considered dense and therefore, leaks are eliminated. On the both sides of the membrane, a thin layer (< 0.5 micron) of palladium catalyst is coated. This catalyst layer serves two purposes; it provides for hydrogen dissociation and reassociation, and it may protect the membrane from hydrogen embrittlement.

There are two advantages of this membrane.

- The permselectivity between H<sub>2</sub> and CO<sub>2</sub> is infinite because it is considered a dense membrane. Leaks through the membrane are eliminated. The catalyst coating does not have to be leak-free.
- The requirement for expensive palladium has 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 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 clearly apparent that the Eltron 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, later 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 6.

### **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 had 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.

### **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. 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  $H_2:CO_2$  selectivities in the 3-5 range.

### **Membrane comparison**

Each of the membrane developers were 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 Table 5.

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 were met.

It was clear that only the Eltron membrane has demonstrated sufficient H<sub>2</sub>:CO<sub>2</sub> 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 (and theoretically reducing the membrane area required) 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<sub>2</sub>S-free syngas

### **Phase II work program to date**

#### **Eltron**

Eltron was able to achieve significant improvements over results reported in Phase I. The key highlights are shown below.

- Based on Phase I results, it was decided that the Phase II work would concentrate on metal alloy dense membranes. The metal alloy foil (~130 microns thick) is coated on both sides with a 1-2 micron thick layer of palladium.
- Membrane tests were conducted with syngas compositions at differential pressures of over 30 bars. Hydrogen selectivity was essentially 100%.
- Hydrogen permeation were increased ten-fold over Phase I results. Permeance values ranged from 1.9E-3 to 2.6E-3 mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-0.5</sup> for hydrogen-helium mixtures and approached published theoretical values for the subject metal. Rates were lower for syngas mixtures.
- Numerous tests confirmed that early flux tests were limited by gas phase diffusion. The equipment test rigs were modified to reduce or eliminate this effect.
- H<sub>2</sub>S from the shift catalyst bed contaminated the membrane and reduced performance. A guard bed of Cu/ZnO was installed upstream of the membrane unit and was successful in capturing the sulfur.
- Wall contaminants also were contained by guard beds.
- Proof of concept testing showed that the use of hydrogen membranes does allow for increased conversion of CO.

- Techniques were developed to avoid hydrogen embrittlement.
- An invention disclosure was filed covering various aspects of this work.

The Eltron metal alloy membrane has several attributes.

- Very high hydrogen fluxes were achieved.
- As the metal alloy layer is dense, the thin layer of palladium does not have to be leak-free to obtain adequate H<sub>2</sub>:CO<sub>2</sub> selectivity. The H<sub>2</sub>:CO<sub>2</sub> selectivity was infinite for all of the testing.
- The membrane can be configured in a planar or tubular design.
- The minimal use of palladium reduces materials costs.
- A porous support is not required. There are no membrane support interface issues.
- Concerns about the Eltron membrane are in the following areas Gas phase diffusion – Although this was determined to be the source of the inconsistency in much of the data, Eltron feels that it has been resolved through a reconfiguration of the test rigs. It is ironic that the problem arose because the flux of the membrane was significantly higher than expected. Care should be taken in the design of the commercial reactor to avoid gas phase diffusion problems.
- Contaminants – H<sub>2</sub>S and pipe wall contaminants reduced the membrane performance significantly. Proper material selection along with the use of guard beds should adequately deal with this issue.
- Long term technology development – Eltron is a very small research and development company. The concern is that they do not have the capability (project management, financial backing, and company focus) to undertake the long term development of this MWGS concept. Eltron claims that they could undertake the overall development of the concept.

## **SOFCo**

SOFCo provided a very impressive effort in the design of a commercial MWGS reactor. The effort involved stress analysis, computational fluid dynamics and membrane modeling. In addition, outside metal foil suppliers, pressure vessel vendors, and welding and brazing experts were contacted to improve the accuracy of the cost estimate.

The initial design involved installing multiple stacks of planar membrane wafers inside of a large cylindrical pressure vessel. Cost center analysis showed that the pressure vessel added significant costs. A redesign of the reactor concept eliminated the pressure vessel requirement and reduced costs from 19 MM\$ to 12 MM\$.

Further alternative design work showed that tubular designs could also be utilized. Three different concepts resulted in costs in the 11-12 MM\$ range.

## **Fluor**

Fluor was asked to modify the Phase I process design of the gasification system to include sulfur removal upstream of the MWGS reactor. Thermal efficiency of the plant was 62% and carbon recovery was 84%. Approximately 42 MW of power is exported.

## **Phase II General Conclusions to Date**

Overall, Phase II has been very successful. Eltron was able to demonstrate significant improvements in membrane performance. They were also able to identify several performance problems and to provide

means for dealing with these problems. SOFCo developed a commercial scale MWGS reactor concept with no significant design concerns.

Because this technology was placed in a scenario where fuel oil is the feed and sulfur removal is required, the economic analysis will probably show that process concept has no advantage over the baseline case. However, if this MWGS concept is evaluated where natural gas is used as the feed and no sulfur removal is required, then the concept should show reduced avoided CO<sub>2</sub> capture costs.

#### **Recommendations for Future Work in 2004**

Eltron has provided a three task work program for the 2004 timeframe.

- Complete the performance test matrix by conducting testing with wet, syngas at high pressures
- Conduct long-term testing with syngas to verify membrane stability
- Examine alternative methods for applying the thin palladium coatings

It is also recommended that the CCP should ask Eltron to develop and file a patent covering their work.



Table 5 – Comparison of Eltron Membrane to Haldor Topsoe’s “State of the Art” Membrane

	Haldor Topsoe study	Eltron – Best Case, no H2S	Eltron – with H2S
Thickness, microns	25	0.5	0.5
Temperature, C	?	400	400
Permeance, mol/sm <sup>2</sup> Pa <sup>0.5</sup>		3.35E-04	2.61E-06
Permeance, Nm <sup>3</sup> /hm <sup>2</sup> bar <sup>0.5</sup>	20	8.6	0.07
Driving force, bar <sup>0.5</sup>	0.7	0.7	0.7
Hydrogen flow, Nm <sup>3</sup> /h	230,000	230,000	230,000
Area, m <sup>2</sup>	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 <sup>3</sup>	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 <sup>2</sup>	11610	232	232

Table 6 – Comparison of Membrane Performance

Membrane Vendor/Type	ECN - Silica	Eltron (Sweet Syngas)	Eltron (Sour Syngas)	CSM/TDA - Pd-Alloy	UCinn - Zeolite
<b>Overall Gasification Plant Performance</b>					
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 <sub>2</sub> to sequestration, MMtonnes/yr*	0.70	2.02	2.01	0.92	0.25
Expansion factor	186%	-1%	0%	117%	700%
Non-sequestered CO <sub>2</sub> , 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

\* Based on 90% on-stream factor

\*\* Includes CO<sub>2</sub> in hydrogen stream and gas turbine exhaust

Table 6 Continued

Membrane Vendor/Type	ECN - Silica	Eltron (Sweet Syngas)	Eltron (Sour Syngas)	CSM/TDA - Pd-Alloy	UCinn - Zeolite
<b>Water Gas Shift Membrane Performance</b>					
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 <sub>2</sub> 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 <sub>2</sub> , kmol/hr	11653.7	11582.9	11582.4	11883.7	12023.3
H <sub>2</sub> flux, mol/m <sup>2</sup> -sec	0.22	0.19	0.08	0.15	0.17
H <sub>2</sub> permeance, mol/m <sup>2</sup> -sec-Pascal	1.77E-07	n/a	n/a	2.38E-07	3.27E-07
H <sub>2</sub> permeance, mol/m <sup>2</sup> -sec-Pascal <sup>0.5</sup>	n/a	1.966E-04	2.650E-05	n/a	n/a
H <sub>2</sub> pre-exponential factor, mol/m <sup>2</sup> -sec-Pascal	4.93E-07	n/a	n/a	2.38E-07	1.46E-07 (Note3)
H <sub>2</sub> pre-exponential factor, mol/m <sup>2</sup> -sec-Pascal <sup>0.5</sup>	n/a	2.87E-02	7.14E+08	n/a	n/a
H <sub>2</sub> Activation Energy, J/mol	5007	24896	186000	0	-3941 2.6 (Note 3)
H <sub>2</sub> :CO <sub>2</sub> permselectivity at feed conditions	4.7	infinite	infinite	5.5	
Membrane area required, m <sup>2</sup>	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

Notes:

- (1) Cooling of fuel to 95 F was required to meet LHV requirement
- (2) H<sub>2</sub> Purity after water condensation
- (3) Permeance at 10 bar.
- (4) n/a = not available

### 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:

- We prepared thin films on ceramic supports that can separate hydrogen with a flux of  $0.36 \text{ mol/m}^2 \cdot \text{s}$  while maintaining an ideal selectivity of 70,000.
- For the first time, Pd-Cu alloy membranes were tested under Water Gas Shift (WGS) reaction conditions with high sulfur concentrations.
- The binary gas experiments with  $\text{H}_2/\text{CO}$ ,  $\text{H}_2/\text{CO}_2$  and  $\text{H}_2/\text{H}_2\text{O}$  showed that hydrogen can be separated from these mixtures without any significant degradation in the membrane performance.
- The 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  $\text{H}_2\text{S}$ -free WGS stream performed reasonably well, achieving  $\text{H}_2/\text{CO}$ ,  $\text{H}_2/\text{CO}_2$  and  $\text{H}_2/\text{H}_2\text{O}$  selectivity of 20, 12 and 18, respectively. We observed that the separation factor decreased with the addition of the mixture gases.
- $\text{H}_2/\text{H}_2\text{S}$  binary gas experiments showed that in the presence of  $\text{H}_2\text{S}$ , 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  $\text{H}_2\text{S}$  inlet concentrations. The membrane also maintained its integrity when exposed to  $\text{H}_2\text{S}$ .
- The membranes failed when exposed to WGS gases with 630 ppm  $\text{H}_2\text{S}$  (protocol conditions) in two experimental attempts. In these experiments, overall gas flux increased and the separation effectiveness decreased to Knudsen diffusion level.

#### Summary

The project objective was to develop dense palladium/copper alloy membranes for use in a water gas shift membrane reactor. 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  $\text{H}_2:\text{CO}_2$  selectivity would be infinite. The key question was whether the palladium alloy layer could be fabricated thin enough so that 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  $\text{H}_2:\text{CO}_2$  permselectivity at MWGS reactor feed conditions of 5.5 resulted in a carbon recovery of 46% versus a target of 90%. The target permselectivity was 50. The presence of  $\text{H}_2\text{S}$  reduced the permeance by 50-60 percent.

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

#### Reports and Publications

- The final project report was presented in Appendix A of an earlier report.

### **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<sub>2</sub>/CO<sub>2</sub> permselectivity measured at 350°C for standard silica membranes calcined at 400°C was 39 against a target of 50. At a H<sub>2</sub>/CO<sub>2</sub> permselectivity of 50, the hydrogen permeance is expected to be between 1 and 0.5\*10<sup>-7</sup> mol/m<sup>2</sup>sPa (= 0.01-0.02 cc (stp)/sec/cm<sup>2</sup> at dP= 1 bar). Selectivity improvement focused on higher sintering temperatures. 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 the membranes treated at 600°C cracked and further testing was not possible. The hydrogen permeance, derived from the hydrogen partial pressure driving force during gas separation testing with a dry gas mixture was well above 0.1 mol/s.m<sup>2</sup>bar, which is the target permeance for the application.
- Three days testing with H<sub>2</sub>S showed no detrimental effects on a standard silica membrane with a H<sub>2</sub>/H<sub>2</sub>S selectivity of 400. Exposure of a standard silica membrane to steam at 350°C showed, as expected, a decline in permeance and selectivity. In 15 days the H<sub>2</sub>/CO<sub>2</sub> selectivity decreased from 29.7 to 20.9 and the hydrogen permeance by a factor of 3. Thermodynamic calculations at ECN with FactSage<sup>TM</sup> show that the hydrothermal stability of zirconia and titania is not expected to be significantly better than standard silica. ECN focused on modified silica membranes for improved hydrothermal stability. A modified silica membrane has been under test 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<sub>o</sub> (permeance) and E<sub>act</sub> (activation energy) to be used as input in the software model have been obtained for the different components in the feed mixture (H<sub>2</sub>O, H<sub>2</sub>, CO<sub>2</sub>, CO and H<sub>2</sub>S) through silica membranes.
- 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. Temperature dependent hydrogen permeance and flux equations in the dense membrane model were extensively tested. A CD-ROM with the installation and sample files and the installation and operation manual of the final version of the water gas shift membrane reactor model were submitted in November 2002.

#### **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<sub>2</sub>:CO<sub>2</sub> permselectivity.

The hydrogen permeance, derived from the hydrogen partial pressure driving force during gas separation testing with a dry gas mixture, was well above the target permeance of  $0.1 \text{ mol/s.m}^2\text{bar}$ . The maximum  $\text{H}_2/\text{CO}_2$  permselectivity measured at  $350^\circ\text{C}$  for standard silica membranes calcined at  $400^\circ\text{C}$  was 39. At a  $\text{H}_2/\text{CO}_2$  permselectivity of 50 the hydrogen permeance is expected to be between 1 and  $0.5 \cdot 10^{-7} \text{ mol/m}^2\text{sPa}$  ( $= 0.01\text{-}0.02 \text{ cc (stp)/sec/cm}^2$  at  $dP= 1 \text{ bar}$ ).  $\text{H}_2/\text{H}_2\text{S}$  selectivity is 400. Three days testing with  $\text{H}_2\text{S}$  had no detrimental effect on a standard silica membrane.

Selectivity improvement research is focused on higher sintering temperatures. Increase of the  $\text{H}_2/\text{CO}_2$  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  $600^\circ\text{C}$  instead of  $400^\circ\text{C}$  did not increase selectivity. The majority of these membranes cracked and further testing was not possible.

Exposure of standard silica membranes to steam at  $350^\circ\text{C}$  showed, as expected, a decline in permeance and selectivity. In 15 days the  $\text{H}_2/\text{CO}_2$  selectivity decreased from 29.7 to 20.9 and the hydrogen permeance with a factor of 3. Thermodynamic calculations at ECN with FactSage<sup>TM</sup> 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  $Q_0$  (permeance) and  $E_{\text{act}}$  (activation energy) to be used as input in the software model have been obtained for the different components in the feed mixture ( $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{H}_2\text{S}$ ) 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  $\text{H}_2\text{S}$  did not affect 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  $\text{H}_2:\text{CO}_2$  permselectivity of 50. Permeance equations supplied by ECN showed that the expected  $\text{H}_2:\text{CO}_2$  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  $\text{H}_2:\text{CO}_2$  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**

- The project final report was presented in Appendix A of an earlier report.

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

Technology Provider: Eltron Research, Inc.

Eltron was one of four membrane developers asked to develop sulfur-tolerant hydrogen membranes for a membrane water gas shift (MWGS) reactor in Phase I (March, 2002 to March, 2003). None were successful in developing highly selective, sulfur tolerant membranes. Eltron was the only developer who demonstrated membranes having sufficient hydrogen/CO<sub>2</sub> selectivity and high hydrogen flux. For this reason, Eltron was chosen to continue developing their membrane in Phase II (March 2003 to December 2003). The objective of Phase II was to further develop dense metal-alloy membranes for use in a water gas shift membrane reactor. The focus was changed to a sulfur-free synthesis gas.

#### Highlights

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·min<sup>-1</sup>·cm<sup>-2</sup> (STP) corresponding to permeabilities for hydrogen of up to 6.4 x 10<sup>-8</sup> mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-0.5</sup> 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 to date:

- An invention disclosure was filed to protect various aspects of this research.
- Membranes were successfully tested with syngas compositions at differential pressures of over 30 bars. Hydrogen selectivity was essentially 100%. Hydrogen permeation were increased ten-fold over Phase I results. The metal alloy membrane foil (~130 microns thick) was coated on both sides with a 1-2 micron palladium layer.
- Proof of concept testing showed that the use of hydrogen membranes does allow for increased conversion of CO via the water gas shift reaction.
- Numerous tests confirmed that early flux tests were limited by gas phase diffusion. Laboratory equipment was modified to reduce or eliminate this effect.
- A guard bed of Cu/ZnO installed upstream from the membrane unit was successful in capturing sulfur from the H<sub>2</sub>S from the shift catalyst bed that contaminated the membrane and reduced performance.

- Wall contaminants also were contained by guard beds.
- Techniques were developed to avoid hydrogen embrittlement.

## Summary

### Phase I, 3/02 – 2/03

This initiative, focused on ceramic membranes was considered a long range, high-risk, alternative to 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<sub>2</sub>:CO<sub>2</sub> selectivity was essentially infinite. No stability problems were observed. Unfortunately, when subjected to H<sub>2</sub>S containing syngas, performance deteriorated significantly. For this reason, it was decided to modify the flowsheet to provide H<sub>2</sub>S-free syngas feed to the MWGS reactor.

### Phase II, 4/03 – present

Eltron was chosen to continue membrane development in Phase II because they were the only membrane developer that could demonstrate adequate H<sub>2</sub>:CO<sub>2</sub> permselectivity. Since this membrane is significantly impaired by H<sub>2</sub>S, the flowsheet was modified to eliminate H<sub>2</sub>S. Eltron has demonstrated significantly higher permeabilities than achievable with pure palladium. In addition, the metal alloy they developed is significantly less expensive than palladium.

Eltron conducted a wide variety of tests during Phase II.

**Disassociation catalysts** as alternatives to palladium as the disassociation and association catalyst were tested. Membranes coated with palladium had 2-3 orders of magnitude higher permeances than other materials tested. .



**Gas phase diffusion** tests showed that, at low hydrogen concentrations, the permeance results did not follow the expected Sievert's law and early tests showed that the hydrogen flux was independent of the metal alloy thickness. Both of these curious results were later found to be indicative of gas phase diffusion limitations. Insufficient hydrogen was reaching the palladium catalyst surface. The problems were especially acute in the high pressure reactor. These problems were eliminated by increasing the feed flow and by bringing the feed nozzle closer to the membrane.

**Temperature effects** – Bulk diffusion through the membrane should be inversely proportional to the temperature. Membranes thicknesses greater than 250 microns showed the expected inverse proportionality relationship while thinner membranes did not. The result indicated that surface effects or diffusion through the palladium was the limiting step.

**Contamination Issues** – Tests showed that steam contaminated the membrane with S, Si, Ca, Mg, Na, and Fe. This contamination from the stainless steel reactor system walls was eliminated by adding a guard bed upstream of the test reactor. When wet syngas was passed over a WGS catalyst and then to the membrane, there was an immediate degradation in membrane performance. It was found that residual sulfur leaving the shift catalyst poisoned the palladium catalyst. A guard bed of Cu/ZnO eliminated that contaminant issue.

**High pressure testing** was found to be helpful in dealing with embrittlement, gas diffusion and contamination issues. The testing also showed that the membrane could withstand differential pressures of over 30 bars. Hydrogen flux rates of  $340 \text{ mL}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$  (STP) were reported

**Proof of concept test** – One Phase II goal was to prove that integrating a hydrogen membrane into a water gas shift reactor. Eltron fabricated a system consisting of a series of water gas shift reactors and hydrogen membranes. The results shown in the following table confirm that a hydrogen membrane increases the conversion of CO beyond that expected from thermodynamic equilibrium Calculations.

**Gas Compositions (Observed and Calculated) of the WGS Mixture at Each Stage of the Integrated WGS-CMR Apparatus.**

	CO Content (vol%)		CO <sub>2</sub> Content (vol%)		H <sub>2</sub> Content (vol%)	
	Al <sub>2</sub> O <sub>3</sub>	Cu/ZnO	Al <sub>2</sub> O <sub>3</sub>	Cu/ZnO	Al <sub>2</sub> O <sub>3</sub>	Cu/ZnO
Initial dry feed	5.22		28.15		66.31	
Type of Guard bed	Al <sub>2</sub> O <sub>3</sub>	Cu/ZnO	Al <sub>2</sub> O <sub>3</sub>	Cu/ZnO	Al <sub>2</sub> O <sub>3</sub>	Cu/ZnO
After 1 <sup>st</sup> WGS, <i>(expected value)</i>	2.2 <i>(2.08)</i>	2.0	31.0 <i>(30.30)</i>	31.2	66.3 <i>(67.32)</i>	66.0
After 1 <sup>st</sup> CMR <i>(expected value)</i>	2.4 <i>(2.29)</i>	2.1	34.3 <i>(33.50)</i>	38.4	62.9 <i>(63.87)</i>	58.9
After 2 <sup>nd</sup> WGS <i>(expected value)</i>	1.8 <i>(2.00)</i>	1.6	34.8 <i>(33.69)</i>	38.4	63.4 <i>(63.97)</i>	59.2
After 2 <sup>nd</sup> CMR <i>(expected value)</i>	2.0 <i>(2.17)</i>	1.1	38.0 <i>(36.41)</i>	43.5	59.9 <i>(61.05)</i>	55.3

Key findings from Phase II were:

- Eltron has significantly improved the performance of their metal alloy membrane in Phase II. Membrane permeance increased ten-fold over Phase I testing.
- Infinite H<sub>2</sub>:CO<sub>2</sub> selectivity was achieved.
- Gas phase diffusion could be rate limiting with this high flux membrane.
- Contaminants such as sulfur, carbon, iron, and nickel significantly decrease membrane performance.
- The membrane operated under full differential pressure for over 300 hours.
- A proof of concept test demonstrated the benefit of hydrogen removal via membranes.

- An invention disclosure was filed covering various aspects of this work.

### **Reports and Publications**

- The final project report 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<sub>2</sub>:CO<sub>2</sub> 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. XRD analysis indicated that silicalite can grow well without an organic template on the surface of the silicalite seeded  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports. SEM showed a thickness of the silicalite membrane of about 5  $\mu$ m. The membranes were further characterized by pervaporation experiments with 1,3,5-triisopropylbenzene and xylene and the results indicated good quality silicalite membranes.
- H<sub>2</sub>:CO<sub>2</sub> selectivities as high as 12 were achieved at low pressures. However, at elevated pressures, the H<sub>2</sub>:CO<sub>2</sub> selectivity decreased significantly. Based on results from the MWGS reactor model, the expected H<sub>2</sub>:CO<sub>2</sub> permselectivity at feed conditions would be only 2.6. This is far below the target permselectivity of 50.
- For the simple gas mixture under dry conditions, the ideal separation factors of H<sub>2</sub>/CO and H<sub>2</sub>/CO<sub>2</sub> are as high as 6 at 500°C with hydrogen permeance of  $1.2 \times 10^{-6}$  mol/m<sup>2</sup>.s.Pa. The ideal separation factor of H<sub>2</sub>/CO and H<sub>2</sub>/CO<sub>2</sub> for the silicalite membranes under wet conditions are as high as 9.4 and 8.8, respectively with a hydrogen permeance around  $10^{-7}$  mol/m<sup>2</sup>.s.Pa. Using the protocol syngas as the feed, separation factors for H<sub>2</sub>/CO and H<sub>2</sub>/CO<sub>2</sub> as high as 11.6 and 12, respectively, were obtained using the silicalite membrane. The separation factor decreases at the higher feed side pressure, especially for H<sub>2</sub>/CO<sub>2</sub>.
- The silicalite membranes are chemically very stable. Temperature dependency for the permeability for the linear flux equation was obtained for H<sub>2</sub>, CO and CO<sub>2</sub> for the silicalite membrane prepared in this project.

#### Summary

Prior to the start of the project, the main concern was the H<sub>2</sub>:CO<sub>2</sub> 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  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> supports. SEM showed that the silicalite membranes were about 5  $\mu$ m 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. 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.

Under dry conditions, the ideal separation factors of H<sub>2</sub>/CO and H<sub>2</sub>/CO<sub>2</sub> were as high as 6 at 500°C with hydrogen permeance of 1.2×10<sup>-6</sup> mol/m<sup>2</sup>.s.Pa. At lower temperatures the separation factors of H<sub>2</sub>/CO and H<sub>2</sub>/CO<sub>2</sub> are not so high. The ideal separation factors of H<sub>2</sub>/CO and H<sub>2</sub>/CO<sub>2</sub> 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<sup>-7</sup> mol/m<sup>2</sup>.s.Pa. With the proposed syngas as the feed in the separation experiments, separation factors for H<sub>2</sub>/CO and H<sub>2</sub>/CO<sub>2</sub> 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<sub>2</sub>/CO<sub>2</sub>. H<sub>2</sub>:CO<sub>2</sub> selectivities as high as 12 were achieved at low pressures. However, at elevated pressures, the H<sub>2</sub>:CO<sub>2</sub> selectivity decreased significantly. Results from the MWGS reactor model yield an expected H<sub>2</sub>:CO<sub>2</sub> permselectivity at feed conditions of 2.6. This is far below the target permselectivity of 50.

The silicalite membranes are chemically very stable. Temperature dependency for the permeability for the linear flux equation was obtained for H<sub>2</sub>, CO and CO<sub>2</sub> for the silicalite membrane prepared in this project.

### **Reports and Publications**

- The project final report was presented in Appendix A of an earlier report.

### 1.2.1.1.6 Design, Scale Up and Cost Assessment of Membrane Shift Reactor for Use in Gasification Process for Decarbonizing Fossil Fuel

Technology Provider: SOFCo-EFS

The objective of this project was to design and estimate the cost of a commercial-scale water gas shift membrane reactor. This Phase II work period started in April, 2003 and extended through November of 2003. SOFCo did not participate in Phase I

#### Highlights

- A spreadsheet based model of the membrane reactor was created to study alternative reactor configurations. The ECN model was restricted to a counter-current configuration.
- Four different reactor configurations were evaluated: counter-flow, baffled counter-flow, cross-flow, and multi-pass cross-flow
- Four different membrane/support designs were evaluated
- The proposed membrane/support design was evaluated for the effect of pressure loading, thermal loading, gravity loading, elastic instability, and natural frequency
- Deflection tests by Eltron were used to confirm that a conservative stress value was being used in the design.
- A preliminary, detail design was developed for the multi-pass cross-flow configuration.
- A cost estimate of the commercial scale reactor was developed for the multi-pass cross-flow design. The estimate was partially based on information supplied by foil manufacturers, pressure vessel suppliers, and brazing technology experts.
- Based on a determination of the areas of high cost, four alternative designs were proposed and cost estimated. Cost reductions in the order of 40% were achieved.

#### Summary of results

##### Structural analysis

Structural analysis of several different support structure alternatives was conducted. The analysis involve consideration of pressure, gravity, and differential expansion loading. Designs that satisfy stress and instability constraints for several permeate gap heights were found.

Concept	Ease of Membrane Manufacture	Ease of Support Manufacture	Ease of Assembly	Stability	Membrane Utilization (Fluxing / Total Area)
<i>Flat Membrane</i>					
Straight Support	Good	Good	Poor	Poor	Good
Corrugated Support	Good	Poor	Good	Good	Good
<i>Curved Membrane</i>					
Straight Support	Fair	Good	Poor	Poor	Good
Corrugated Support	Fair	Fair	Good	Good	Fair

The above table summarizes an early analysis of several support and membrane configurations.

Based on this investigation, the curved membrane with corrugated support option was chosen for detailed analysis.

Two dimensional, plane-stress (i.e., no out-of-plane stress) finite element analyses of the membranes and support structure were accomplished. Two different models were considered: 1) a detailed model of a repeat unit and 2) a coarse model of an entire wafer (multiple repeat units).

The repeat unit model was utilized for the detailed pressure and differential thermal expansion loading analysis. The wafer model was utilized for gravity loading, stability, and natural frequency analyses. A design was achieved that satisfied previously selected stress limits.

### Membrane performance estimation

A model of the MWGS reactor was developed to facilitate design activities and sensitivity studies of important design parameters. The model included:

- Membrane kinetics based on Phase I results
- Catalyst kinetics for a commercially available bulk catalyst
- Heat transfer between the feed and permeate streams

A comparison of the output from this model (SOFCo) was compared to the output from the ASPEN based model developed in Phase I of the program. The results, summarized in the following table, show the agreement is adequate for design purposes.

	Baseline 315°C			400°C Case 1			400°C Case 2		
	Aspen	SOFCo	% Diff	Aspen	SOFCo	% Diff	Aspen	SOFCo	% Diff
<b>Operating Conditions</b>									
Membrane Area, m <sup>2</sup>	17,325	17,325		11,410	11,410		11,780	11,780	
Catalyst Volume to Area, m <sup>3</sup> /m <sup>2</sup>	0.100	0.100		0.005	0.005		0.005	0.005	
Nitrogen Sweep Gas, kmol/hr	9,100	9,100		9,100	9,100		9,100	9,100	
Steam Sweep Gas, kmol/hr	8,800	8,800		8,800	8,800		10,200	10,200	
Feed Side Pressure, bara	35.00	32.20		32.20	32.20		32.20	32.20	
Sweep Side Pressure, bara	3.00	3.35		3.35	3.35		3.35	3.35	
<b>Performance Comparisons</b>									
Average H <sub>2</sub> Flux (mol/m <sup>2</sup> -sec)	0.186	0.185	<b>-0.4%</b>	0.275	0.277	<b>0.7%</b>	0.272	0.274	<b>0.6%</b>
H <sub>2</sub> Recovery, %	95.3%	95.0%	<b>-0.3%</b>	93.3%	93.9%	<b>0.7%</b>	95.2%	95.7%	<b>0.5%</b>
CO <sub>2</sub> Purity (dry)	90.2%	88.90%	<b>-1.3%</b>	86.86%	86.84%	<b>0.0%</b>	90.04%	89.97%	<b>-0.1%</b>
CO Out, PPM	995	1,000	<b>-0.5%</b>	3,000	4,077	<b>-35.9%</b>	2,000	3,063	<b>-53.1%</b>
Permeate Outlet Temp, °C	347.5	346.5	<b>0.3%</b>	419.9	417.3	<b>0.6%</b>	421.9	420.4	<b>0.4%</b>
Retentate Outlet Temp, °C	327.7	329.0	<b>-0.4%</b>	421.8	422.7	<b>-0.2%</b>	418.0	418.9	<b>-0.2%</b>

### Reactor configuration selection

The reactor model was used to estimate membrane area, catalyst volume, total volume for four different flowpath configurations

- Counter-flow
- Baffled counter-flow
- Cross-flow
- Multi-pass cross-flow

Based on the perceived advantages and disadvantages of each configuration shown in the following table, the multi-pass cross-flow configuration was chosen for further development.

Option	Advantages	Disadvantages
Counter-Flow	<ul style="list-style-type: none"> <li>Minimum membrane required</li> </ul>	<ul style="list-style-type: none"> <li>Large wafer plates difficult to braze</li> <li>Catalyst packing between plates</li> </ul>
Baffled Counter-Flow	<ul style="list-style-type: none"> <li>Minimum membrane required</li> </ul>	<ul style="list-style-type: none"> <li>Large wafer plates difficult to braze</li> <li>Baffle plates</li> </ul>
Cross Flow	<ul style="list-style-type: none"> <li>Assembly of manifolds</li> <li>Smallest wafer package</li> </ul>	<ul style="list-style-type: none"> <li>22% more membrane than counter-flow option</li> </ul>
Multi-Pass CrossFlow	<ul style="list-style-type: none"> <li>Assembly of manifolds</li> </ul>	<ul style="list-style-type: none"> <li>8% more membrane than counter-flow option</li> </ul>

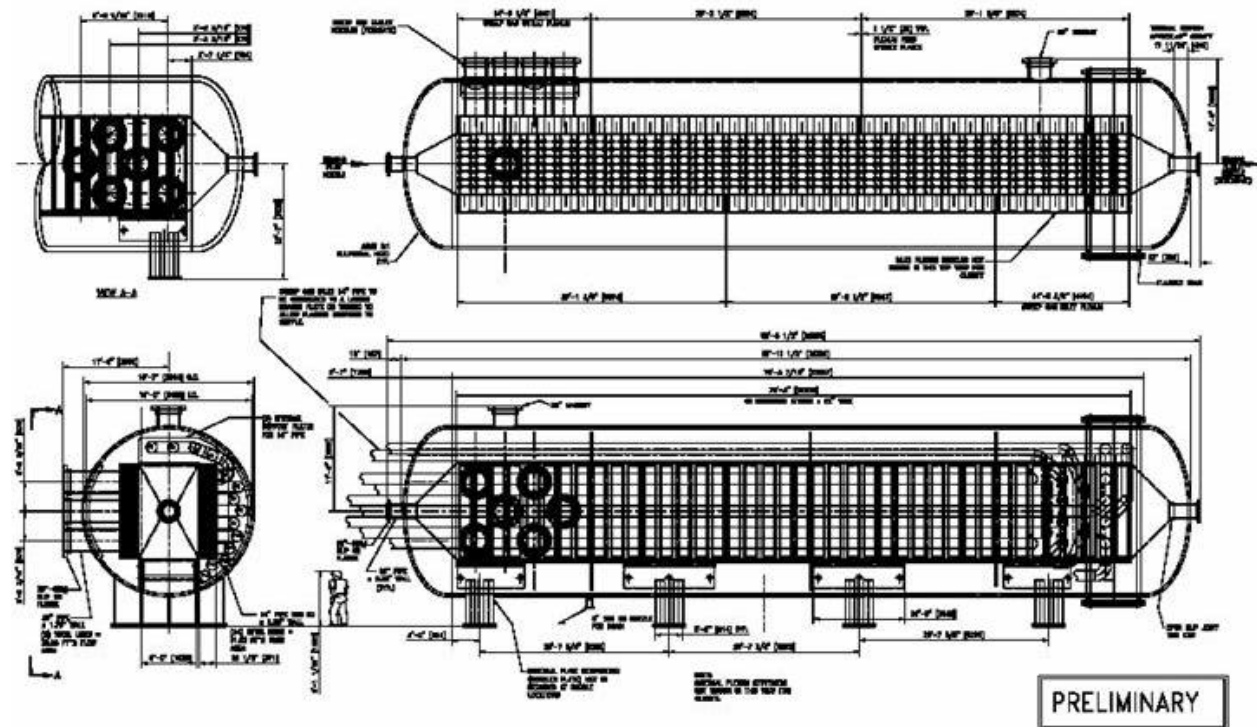
### Final reactor design

Computational fluid dynamics analysis was used to estimate retentate side and permeate side pressure drops and to design the inlet gas diffuser. Further structural analysis was used to design the stack assemblies, including the spacer bars, stay bars, and stiffeners.

### *Overview*

The reactor is a horizontally oriented steel pressure vessel resting on four saddle supports, as illustrated in the drawing below. Characteristics of the vessel are as follows:

- Length is approximately 88 feet
- Inside diameter is 18 feet
- Welded construction
- Designed according to Section VIII, Division 1 of the ASME Boiler and Pressure Vessel Code.
- The vessel is designed for an internal pressure of 600 psig at a vessel metal temperature of 850°F.



The 600 psig design condition provides for a safety margin above the nominal operating process pressure of 450 psi. The external surface of the vessel is insulated to maintain the 440°C process operating temperature, thus establishing the 850°F metal temperature design condition for the vessel.

The vessel houses 40 stacks of planar (corrugated) membrane panels. Each stack is comprised of 159 membrane panels which are aligned and spaced vertically apart to permit syngas to flow over the outer surfaces of the membrane panels along the longitudinal axis of the vessel. The 40 stacks are arranged in line along the longitudinal axis of the vessel, and are each separated by a 6 inch thick bed of catalyst. Flow manifolds attached to the sides of the 40 stacks direct sweep gas through the inside of the membrane panels in a cross-flow direction, normal to the axial direction of syngas flowing over the panels. Divider plates inside the flow plenums are located such that sweep gas passes through the panels of a group of eight stacks at a time in five alternating cross-flow paths across the 40-stack membrane panel assembly.

### Reactor cost estimate

The estimated cost to fabricate the reactor vessel is approximately \$19 million. The estimate is based on input from various suppliers of materials and services, as well as manufacturers specializing in the fabrication of components specified for the reactor. In part, the estimates developed by these vendors were based on detail information provided to them, such as drawings or written processes and specifications. In many cases, where detail information is not yet developed, rough cost estimates were provided by vendors based on similar work and standard cost models. As such, the \$19 million estimate represents an order-of-magnitude cost to fabricate the reactor.

The reactor fabrication cost estimate is broken down into four major cost categories:

- 1) Membrane panel stack assemblies, \$4.3 million
- 2) Assembly of the reactor internals, \$6.0 million
- 3) Reactor pressure vessel, \$7.7 million
- 4) Catalyst beds and vessel external insulation, \$1.0 million

### **Alternative reactor designs**

Two alternative designs were considered after completion of the initial baseline design and estimate:

- An externally stayed rectangular pressure vessel in which the internals of the vessel are designed to be the primary pressure boundary and the cylindrical pressure vessel is eliminated.
- A tubular membrane vessel in which the high pressure syngas is contained within thin membrane tubes which are sized accordingly to meet the pressure requirements. The tubes are packaged in a pressure vessel in a U-tube arrangement which resembles standard shell-and-tube construction.

### Rectangular vessel arrangement

This design is based on the same functional concept and arrangement of in-line membrane panel stacks and catalyst beds as the baseline horizontal planar membrane reactor presented above. The principal difference is that the 40 membrane panel stack assemblies and the syngas inlet and outlet flow diffusers are designed to contain the full syngas pressure, thus eliminating the need for an outer vessel to serve as the primary syngas pressure boundary. To contain the full syngas internal pressure, the top and bottom cover plates along the membrane panel stacks are thicker than the cover plates in the baseline design. Likewise, the thicknesses of the syngas inlet and outlet flow diffusers are increased. In addition, 3-inch thick reinforcing plates (external stay plates) are welded to the stack top and bottom cover plates at regular intervals along the row of membrane panel stacks to stiffen the rectangular cross-section of the



membrane panel stack assemblies. The top and bottom edges of these C-shaped reinforcing plates are welded to continuous 1-inch thick tie plates along the length of the vessel to provide lateral stability and further stiffen the rectangular pressure boundary. Other design aspects of the panel stack assemblies remain the same as the baseline concept, i.e., the membrane panel geometry, materials, and method of construction, the number of membrane panels in each stack and the vertical spacing between panels. Likewise, as in the baseline concept, the 40 stacks are arranged in line to form the longitudinal axis of the rectangular vessel, and are each separated by a 6 inch thick bed of catalyst.

The estimated cost to fabricate the externally-stayed, rectangular reactor vessel is approximately \$12 million. This represents a reduction in cost of about \$7 million compared to the cost of the baseline reactor concept. The reduced cost is primarily attributed to eliminating the conventional outer pressure vessel required for the baseline design. The estimate does not include the cost for process piping and connections to the vessel, nor does it include fabrication development functions, such as for forming of corrugated membrane panels, brazing and other joining processes, tooling, building prototypes and assembly trials.

#### Tubular (U-tube) vessel arrangement

This design is fashioned after a standard U-tube type shell and tube heat exchanger, in which the membranes are of a tubular form and are an integral part of U-tube assemblies. The ends of the U-tube assemblies are joined to a single tubesheet with syngas flowing inside the tubes (high pressure tube-side of the reactor). Sweep gas flows across the outside of the membrane tubes in the lower pressure shell side of the reactor.

Four membrane reactors are required to achieve the hydrogen separation capacities of the program. However, unlike the baseline concept in which syngas catalyst beds are an integral part of the reactor, the U-tube membrane reactor concept does not include a provision for containing catalyst. As such, the catalyst beds are contained in four separate catalyst reactor vessels external to the membrane reactors. These catalyst reactor vessels are interstaged with the membrane reactor vessels.

The estimated cost to fabricate and assemble four single U-tube membrane reactors and four catalyst reactors required for the tubular membrane plant concept is approximately \$12 million. This estimate does not include the cost for interconnecting piping between the eight vessels, nor does it include fabrication development functions, such as for membrane tube forming, brazing and other joining processes, tooling, building prototypes and assembly trials.

### **Conclusions**

Three feasible MWGS reactor designs have been developed which use either a planar or a tubular hydrogen separation membrane. Two reactor designs use a planar membrane composed of a curved membrane supported by a corrugated Type 430 stainless steel sheet. Finite element analysis which considered the pressure, gravity, and differential thermal expansion loadings indicates that it is structurally adequate for 41.1 bar (600 psid) pressure loading at 450°C (842°F). A third MWGS reactor concept is based on a tubular membrane sized appropriately to contain high pressure inside the tubes.

The following additional investigations are recommended for the membrane design:

- 1) Re-evaluation of the membrane stress (or allowable tube diameter) when mechanical properties of the membrane material alloy are available and final membrane thickness is selected.
- 2) Acceptability of Type 430 stainless steel considering operating environment and interaction with membrane material.

3) Vibration testing of the wafer panel assembly or tube bundle.

An analysis tool was developed to permit examination of different arrangements for the MWGS reactor and bench-marked against the model developed in Phase 1. This analysis tool determined the membrane area required for the planar and tubular reactor concepts. Four different flow arrangement options were examined and sized to meet the performance and pressure drop requirements.

### **Reports and Publications**

The final project report 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<sub>2</sub> Capture” Technology Provider: Fluor Federal**

The project objective was to develop a process flowsheet incorporating a based on gasification and incorporating a membrane water gas shift reactor into a gasification process. .

#### **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<sub>2</sub> 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 in 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.

The original work 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<sub>2</sub>:CO<sub>2</sub> selectivity, it was decided that only one flowsheet (for the Eltron membrane) was required. The savings were used for various sensitivity studies.

The calculated thermal efficiency based on the production of hydrogen fuel was 61.4% with sequestration of 2 million tonnes per year of CO<sub>2</sub>. The efficiency does not include 37 MW of exported power.

#### Phase II

Fluor modified the Phase I flowsheet to provide a H<sub>2</sub>S-free feed to the MWGS reactor and developed a equipment specifications list for cost estimation purposes. Flowsheet development and equipment sizing was completed on schedule. A summary of the overall performance of the gasification plant is shown below.

<b>Gasification Plant Performance</b> Metal Alloy Membrane	
Gasifier feed (41% fuel oil/59% refinery fuel gas)	3802.8 GJ/hr (LHV)
Natural gas for power generation	755.8 GJ/hr (LHV)
Total fuel to plant	4558.6 GJ/hr (LHV)
Hydrogen fuel return to existing boilers	2812.3 GJ/hr (LHV)
Overall thermal efficiency for hydrogen fuel	62%
Pure carbon dioxide to sequestration	1.98 million tonnes/yr
Total carbon recovery (including power generation)	84%
Power Generation	MWe
Combustion Turbine	72
Steam Turbine	45
Auxiliary Power Consumption	76
Net Power Export	42

### Reports and Publications

- The final project report 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<sub>2</sub> capture from gas turbines, and 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<sub>2</sub> capture for geologic sequestration. A combined shift reaction and CO<sub>2</sub> 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 thermogravimetric 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<sub>2</sub> 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 °C), this is believed to be due to desorption rate increase with temperature compensating for the reduction in equilibrium CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>x</sub> 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<sub>2</sub> 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 Production

Task 2.3 Systems Integration and Optimization

Technology Provider: Davy Process Technology  
Air Products, Ltd.

#### Highlights

- The work scope was reduced to only evaluate Air Products' Gemini advanced pressure swing adsorption system since agreement with Davy could not be settled.
- Results showed that cycles that couple the hydrogen purification with the carbon dioxide recovery system offer higher hydrogen recovery with the same number of adsorbent columns.
- A single-train adsorption system can provide 0.8 million tonnes per annum of carbon dioxide at up to 99.7% purity with a carbon dioxide recovery of up to 93%.

#### Summary

Pre-Combustion De-carbonization (PCDC) technology for the direct and simultaneous production of CO<sub>2</sub>, suitable for sequestration, and hydrogen, for chemical and fuel applications, is a key technology area of interest to the CCP. The CCP requested Air Products and Davy Technology to undertake a study combining, in an optimal way, two established technologies that could (in combination) considerably reduce the cost of CO<sub>2</sub> capture.

The aim of the study was 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<sub>2</sub> within scenario 3 (Refinery heaters and boilers). The study was to be set within the Grangemouth Refinery and Petrochemical plant scenario established by the CCP to facilitate easy comparison with competing technologies. The goal is to capture 2.0 million tonnes/year of CO<sub>2</sub> 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<sub>2</sub>, captured as a pressurized product from the Gemini PSA unit, would be further compressed for export for use in an offshore enhanced oil recovery scheme.

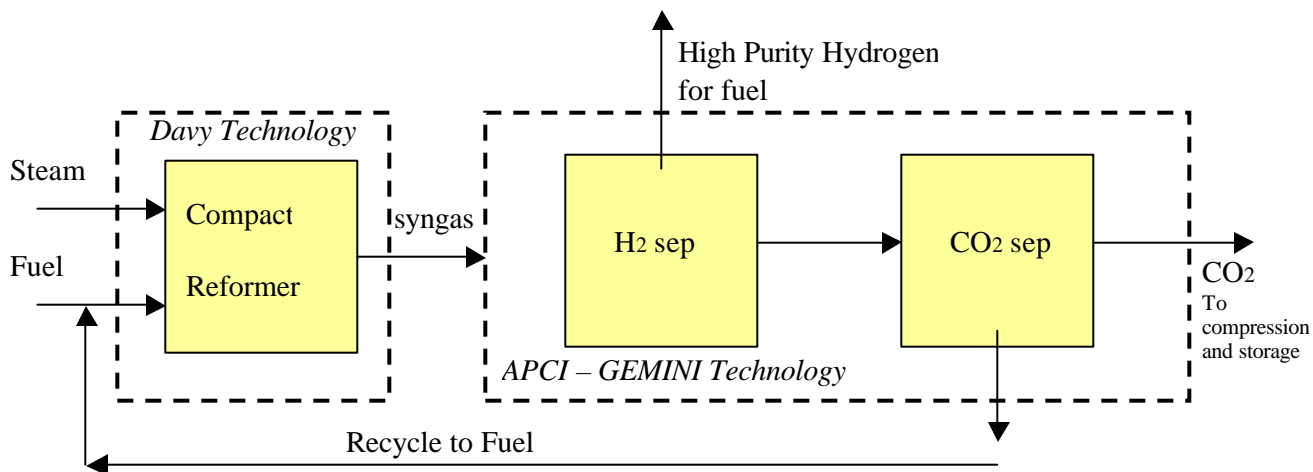
This study Compact Reformer study was to incorporate the following two distinctive technologies:

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

Compact Reforming is licensed by Davy Process Technology and has been used by BP at its Nikiski Gas-to-Liquids demonstration plant. The technology achieves high thermal performance by avoiding the requirement for large-scale steam production normally associated with traditional reforming units.

Gemini PSA (Pressure Swing Adsorption) technology was developed in the 1970's and operating plants have been running since the 1980's in the U.S.A. The technology utilises traditional PSA cycles for high purity Hydrogen production, and compliments this with additional cycle stages for the production of a high purity CO<sub>2</sub> product.

The overall schematic for the combination is as follows;



Due to difficulties with Davy accepting the terms of the DOE/CCP contract the Compact Reformer element of the work was not undertaken. Davy's Compact Reforming technology is being actively licensed and they had concerns about the transfer of key data and other background information that may have been implicit under the standard DOE terms. APCI carried out the GEMINI part of the program that focused on building an understanding of the potential trade-offs between the number of beds (a surrogate for capex) and the purity of the CO<sub>2</sub> product. They used an estimated reformer effluent composition and recycled the residual gas stream for unit feed/fuel. This was not optimized in any way due to the absence of actual compact reformer effluent composition data.

Although this study reached no firm conclusion about the potential for the proposed technology combination, it did develop ideas around the shape and size of the GEMINI process unit and will provide a valuable lead-in to future work (under CCP2), where we hope to circumvent the previous contract difficulties by offering a separate CCP contract to Davy to execute the compact reformer work, and then to optimize the combination by using only the output of that study to allow APCI to complete the GEMINI integration.

Using this approach we hope to clearly be able to 'Black Box' the Davy Technology input, which will then enable the result to be shared by all parties (CCP, DOE, APCI and Davy).

### Reports and Publications

- The final project report is in Appendix A under the same heading as this summary.



## 1.2.2 Coke Gasification

### 1.2.2.1 Advanced CO<sub>2</sub> 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<sub>2</sub> avoidance cost can be calculated for a world-scale Integrated Gasification Combined-cycle (IGCC) facility designed to capture CO<sub>2</sub> 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<sub>2</sub> capture, uncontrolled release, case: \$870million USD
  - 90% CO<sub>2</sub> 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 CO<sub>2</sub> with less than 30 ppmv of H<sub>2</sub>S
  - Ability to produce CO<sub>2</sub> at greater than 97 mol %
  - H<sub>2</sub> produced at pressure to minimize compression costs
  - Sulfur tolerant process
- Qualitative screening exercise identified CO<sub>2</sub>LDSEp as the most promising advanced technology for reducing CO<sub>2</sub> capture costs as compared to the controlled baseline

#### Summary

This work evaluates advanced (i.e. not yet commercially available or commercially demonstrated) CO<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> capture and a controlled case in which where 90% of the CO<sub>2</sub> 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<sub>2</sub> capture and the Controlled Baseline Case represents currently available commercial technologies to capture CO<sub>2</sub>, these base cases represents the reasonable estimates of the costs industry would incur if they were required to capture CO<sub>2</sub> 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<sub>2</sub> 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 by Fluor Daniel.

#### **Reports and Publications**

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

## 1.2.3 Integration and Scale-up Studies

### Task 2.3 Systems Integration and Optimization

The CCP Pre-combustion Technology Integration and Scale-up Study program is based on 5 individual studies :

1.2.3.1 Study of Gas Turbine Retrofit Requirements to Burn Decarbonized Fuel (Hydrogen)

1.2.3.2 Standardized PCDC

1.2.3.3 Very Large Scale Autothermal Reforming

1.2.3.4 Advanced Syngas Technology

1.2.1.3 Compact Reformer with Advanced Pressure Swing Adsorption System for Hydrogen Fuel Production

The objective in the integration and scale-up studies is to apply commercial or close to commercial available Pre-combustion technology into the CCP scenarios. By system integration, optimization and value engineering it is expected that a significant cost reduction can be obtained at very low risk.

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

#### 1.2.3.1 Study of Gas Turbine Retrofit Requirements to Burn Decarbonized Fuel (Hydrogen)

This study contracted with GE and co-funded by the US Department of Energy was designed to establish that the use of hydrogen fuels is a feasible option for these gas turbines, that satisfactory performance is retained and to that the conversion is economic, not adding an unacceptable cost to that of the capture process. Three hydrogen fuel mixtures based on composition derived from different pre-combustion technologies developed or assessed in the CCP. The key result was:

- The feasibility of retrofitting Alaska Case Study Frame 5 and 6 Gas Turbines to fire decarbonized (hydrogen rich) fuels was confirmed
- Machine output is increased by decarbonization and retrofit by around 16% at typical operating conditions
- The fuel firing rate per MWH output for decarbonized fuel is typically around 9-18% lower on a LHV basis than for natural gas
- NO<sub>x</sub> emission can be reduced to between 42 and 20ppm by firing the selected fuel, a 50-80% reduction on current operation.
- Costs of retrofits estimated at \$3.3 million for first machine of each type and \$2.5-3.0 million for subsequent machines, this will not significantly increase the cost of capture for this case study
- GE Frame 5-2C or Frame 6B industrial gas turbines are good candidates for retrofit for demonstration of CO<sub>2</sub> capture by fuel decarbonization.

#### 1.2.3.2 Standardized PCDC

**The study by Jacobs Consulting was carried out in collaboration with IEA GHG program under the Annex 16 subtask A. The focus was pre-combustion technology for large natural gas fed 400 MW combined cycle power plants, i.e. the Norwegian CCP scenario. The objective was to assess if further cost reduction of a PCDC technology could be obtained by standardization and modularization.**

Some of the highlights from the study were:

- Screening of previous studies shows that efficiency varies from 43 to 49% (LHV) and cost for the PCDC technology is ranging from 250 \$/kW to 500 \$/kW.
- The benefits from standardization showed the following potential
  - Repeat design (10 per year): 15-20% saving on capital cost
  - Modularization: Only minor savings < \$ 2 MM
- The optimization study indicated that the following items would improve the concept by 10 \$/t CO<sub>2</sub> avoided
  - Air extraction from gas turbine
  - Fuel gas heating and saturation
  - Single shaft air compressor/steam turbine drive rather than electrical motor and steam driven generator

For future work emphasize should be put on bringing cost down for rotating equipment. According to the Jacobs study 50-60% of the capital cost for the PCDC originates from compressors and steam turbines.

#### 1.2.3.3 Very Large Scale Autothermal Reforming

This study by Jacobs Consulting evaluated the use of pre-combustion decarbonization technology based on the relatively conventional approach of autothermal reforming (ATR) of the gas followed by shift reaction and wet scrubbing for CO<sub>2</sub> removal for the BP's Prudhoe Bay central gas facility in Alaska. A particular focus for the study was an evaluation of the potential to decarbonize all the fuel gas in a single process, generating economies of scale. This necessitated consideration of individual unit operations with respect to maximum throughput and issues with the construction and transportation of these systems to the Alaskan North slope.

The conclusion from the study was:

Single train VLS ATR is feasible for the Alaska case study.

This approach is a relatively low risk capture route as all the technologies are proven, the only design issues are those of scaling up to world-scale plants and design for the challenging environment.

A simple ATR without gas-heated reformer is likely to be a more cost effective solution, but the ability to design a single train plant using this technology would require evaluation.

In the event that the VLS ATR route appears to be a leading contender for capture from the Alaska case study, there is likely to be some merit in evaluation of the alternative arrangements discussed above, i.e. conventional ATR and oxygen blown ATR

#### 1.2.3.4 Advanced Syngas Technology

This study by Foster-Wheeler compared several pre-combustion decarbonization (PCDC) schemes producing a fuel mixture, comprising mainly hydrogen and nitrogen, for a 350 - 400 MW combined cycle power plant, based on the GE Frame 9351FA machine with a carbon capture of 90%. A conventional autothermal reforming plant with shift, followed by CO<sub>2</sub> removal and compression was defined as the base case. Then several further advanced syngas generation concepts were derived, including gas heated reforming, gas-gas exchangers and high pressure operation. For each the capital cost and net power output was compared against the base. In all cases the carbon capture from the overall PCDC/power system was greater than 90%.

Not surprising one of the clearest conclusions is that the level and quality of CO<sub>2</sub> capture directly affects the efficiency of the scheme. This is mainly due to the energy intensive nature of CO<sub>2</sub> removal processes.

Of the schemes which comply to the base case definition of CO<sub>2</sub> removal and purity the Gas/Gas Exchange case is the best performer. This is not surprising as this scheme is arguably the best heat integrated of the cases under consideration. Similar comments apply to the Gas Heated reformer case.

Power recovery from hot syngas is shown to have some potential, but the cost of this scheme shows that this is of interest only when the feed gas is of sufficient pressure.

Perhaps the most interesting conclusion is that high pressure operation appears to offer no benefit, even when the feed gas is at sufficient pressure to enable this (i.e. no compression required).

The results showed no significant improvement over the base case thus no further work was recommended in this area.

### 1.2.1.3 Compact Reformer with Advanced Pressure Swing Adsorption System for Hydrogen Fuel Production

The scope of the work was reduced to only look into the advanced pressure swing adsorption system since agreement with Davy could not be settled.

In the 1980's Air Products developed Gemini™ pressure swing adsorption process for the separation of syngas streams into two products: carbon dioxide and hydrogen. In this work, Air Products' in-house dynamic adsorption simulation program was used to determine the capabilities, evaluate new adsorbents, and identify preferred operating conditions of Gemini™ processes in the recovery of carbon dioxide from high-pressure syngas. Results showed that Cycles that couple the hydrogen purification with the carbon dioxide recovery system offer higher hydrogen recovery with the same number of adsorbent columns. It was determined that a single-train adsorption system can provide 0.8 million tonnes per annum of carbon dioxide at up to 99.7% purity with a carbon dioxide recovery of up to 93%.

### 1.2.3.1 Gas Turbine Retrofit Requirements to Burn Decarbonized Fuel (H<sub>2</sub>)

Task 2.3 Systems Integration and Optimization  
Technology Provider: General Electric

The CCP Alaska Scenario is intended to evaluate CO<sub>2</sub> capture processes in a gas compression facility in Alaska's North Slope oilfields. The facility 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 study evaluated retrofit of these generic GE Frame-5 and GE Frame-6 Gas turbines to burn a range of hydrogen fuel mixtures. Fuel compositions will be selected to cover the composition range anticipated from PCDC capture technologies.

The study covered issues of hydrogen firing feasibility and its effects on the performance and emissions expected from the turbines. Key system design considerations of the overall capture scheme such as fuel temperature and steam content were studied.

#### Highlights

- The feasibility of retrofitting Alaska Case Study Frame 5 and 6 Gas Turbines to fire decarbonized (hydrogen rich) fuels was confirmed
- Machine output is increased by de-carbonization and retrofit by around 16% at typical operating conditions
- The fuel firing rate per MWH output for decarbonized fuel is typically around 9-18% lower on a LHV basis than for natural gas
- NO<sub>x</sub> emission can be reduced to between 42 and 20ppm by firing the selected fuel, a 50-80% reduction on current operation.
- Costs of retrofits estimated at \$3.3 million for first machine of each type and \$2.5-3.0 million for subsequent machines, this will not significantly increase the cost of capture for this case study
- GE Frame 5-2C or Frame 6B industrial gas turbines are good candidates for retrofit for demonstration of CO<sub>2</sub> capture by fuel de-carbonization.

#### Summary

The CCP elected to study the feasibility and cost of CO<sub>2</sub> capture using a range of technologies from four different cases studies, one of which was BP Prudhoe Bay Central gas compression facility in Alaska. This study centered on the capture of CO<sub>2</sub> from 11 gas turbines driving gas compressors on the Alaskan North Slope, which together emit 2.2 million tonnes of CO<sub>2</sub> per year.

Pre-combustion de-carbonization (PCDC) was identified as an attractive option to capture CO<sub>2</sub> from the gas turbines, benefiting from the possibility of using a central de-carbonization facility to supply fuel to all the machines, gaining economy of scale. Several technologies have been developed by the CCP, which are suited to the de-carbonization of gas turbine fuels and the costs of these processes have been evaluated in the Alaskan and other case studies. A key requirement for the application of these systems to existing gas turbines is that the machines can be adapted to accept the fuel without adversely affecting the critical performance characteristics such as power output, efficiency, emissions, reliability or flexibility.

This study contracted with GE and co-funded by the US Department of Energy was designed to establish that the use of hydrogen fuels is a feasible option for these gas turbines, that satisfactory performance is retained and to that the conversion is economic, not adding an unacceptable cost to that of the capture process. The study was conducted in two phases.

Phase 1: A performance evaluation of fuels produced by three different de-carbonization processes was made. Three fuels were selected as representing the range of decarbonized fuel types likely to be considered for gas turbine firing, listed in Table 7. The gasifier case is not likely to be directly applicable to Alaska, there are however opportunities to retrofit existing IGCC processes from coal or oil feedstock for CO<sub>2</sub> removal, hence the results provide a valuable insight into these options. The Phase 1 work-scope included requirements definition, condition assessment, combustion assessment and performance predictions.

Table 7

		Composition Mol %			
	Fuel Process	Hydrogen	Nitrogen	Water	Other
A	Sorption Enhanced WGS	53	37	7	3
B	Gasification baseline	66	<1	29	4
C	Hydrogen Membrane Reformer	42	37	20	0

Phase 2: A single fuel was selected for as the basis for design of the modifications and equipment changes required to burn the selected fuel. The phase 2 work-scope comprised conversion requirements, i.e. bill of materials and budgetary estimate for the conversion work. The fuel selection was made on the basis performance data generated in phase 1 and applicability to the Alaska case study.

### Study Methodology and Findings

The requirements definition and condition assessment was undertaken using data provided by BP including study definition, fuel compositions, machine-identification and key performance requirements, combined with GE's data on the gas turbines.

GE undertook performance analysis for the individual machines using in-house computer simulations to predict combustor conditions, which indicates combustion stability, turndown capability, combustor life and emissions. These parameters were evaluated at a range of ambient temperatures representing the extreme conditions experienced on the Alaskan North Slope. Key results are summarized in Table 8 for the three fuels at the ambient temperature of 32 °F.

Table 8

Parameter	Model 6B			Model 5-2C		
	Fuel A	Fuel B	Fuel C	Fuel A	Fuel B	Fuel C
Change in Maximum Output % relative to current	<b>+15.7</b>	+17.5	+15.8	<b>+17.3</b>	+13.5	+25.3
Change in Fuel Rate per KW (LHV)	<b>-13.8</b>	-9.1	-13.8	<b>-12.7</b>	-8.6	-18.2
NO <sub>x</sub> Emission without steam injection	<b>44</b>	79	7	<b>45</b>	79	<10
NO <sub>x</sub> Emission with steam blend	<b>24</b>	22	NA	<b>23</b>	25	NA
Injected Steam/Gas mass ratio	<b>0.1</b>	0.5	NA	<b>0.1</b>	0.5	NA
Cost for first unit retrofit	<b>\$3.32 million</b>			<b>\$3.39 million</b>		
Cost for subsequent units	<b>\$3.02 million</b>			<b>\$2.49 million</b>		

These results indicate a significant increase in maximum power output relative to natural gas firing and a reduction in fuel firing rate for all the decarbonized fuels. A significant reduction of NO<sub>x</sub> emission is possible from current typical operation for fuels A and C. Fuel C offers exceptionally low values of <10ppm. Fuel A could achieve the CCP proposed target of 25ppm with a small steam injection of 10% by mass.

The maximum turndown load for the Frame 5-2C model for fuel A was estimated at 90% corresponding to a firing temperature of 1500 °F, this is an improvement on natural gas operation where the unit is fixed at full load. The CO emission from very low carbon syngas fuels on this combustor has not been studied and the turndown limitation may be further relaxed subject to experimental measurement of CO slip. The model 6B machine can be turned down to 60% of maximum load and remain in CO compliance.

The scope of retrofit work was determined by the study, with regard to operability, safety, reliability and other issues addressed.

### **Conclusions**

- Firing of fuels A, B and C can be readily accomplished on Frame 5-2C and Frame 6B machines.
- Fuels A & C give significant performance and emission improvements over current operation.
- Maximum output is higher on decarbonized fuels except at the lowest operating temperatures of minus 40 °F. For most of the year the machine capacities would be increased by use of decarbonized fuel.
- Fuel A gives a NO<sub>x</sub> emission of 42ppm falling to 25ppm with steam addition of 10% by weight.
- Fuel C can give exceptionally low NO<sub>x</sub> emissions of <10 ppm with no additions
- Costs for retrofitting these machine is \$3.3 million for the first of each model falling to \$2.5-3 million for subsequent units.

### **Recommendations for Further Work**

No additional technical of development work is considered necessary in this field. The next logical step will be to demonstrate CO<sub>2</sub> free power generation by firing of decarbonized fuel gas on an industrial gas turbine such as the GE Frame 5 or 6B. This study provides data, which will be invaluable in assessing demonstration options including retrofit of existing machines possibly using existing sources of hydrogen such as refinery hydrogen sources, ammonia plants and IGCC plants.

### **Reports and Publications**

Wotzak et Al, "Study of Gas Turbine Retrofit Requirements to burn decarbonized Fuel (Hydrogen): Conversion Evaluation for Gas Turbines at BP Prudhoe Bay Facility", Dec 2003



## **1.2.4 Capture Studies Integration and Reporting**

### **1.2.4.1 Capture Study Integrated Reports**

**Technology Provider: Advanced Resources International.**

Elsevier Science has agreed to publish a two volume set of results from the full CCP program. The coordinated volumes on capture, separation, storage, monitoring, and verification are being edited now. Approximately 70 papers comprising the key results from the full study are being written, peer-reviewed, and edited with a target publication date of 1 November 2004.

## 1.3 Oxyfuel Technology

### Introduction

Investigating the potential savings that combustion using pure oxygen (oxyfiring) may give in CO<sub>2</sub> capture, compared to conventional combustion with air, is the mission of the CCP Oxyfuel Team. This involved monitoring and sponsoring R&D activities whose results may contribute to further reduction of CO<sub>2</sub> capture costs by the year 2010.

When CO<sub>2</sub> capture is not required, Oxyfiring is inherently more expensive than combustion with air using current state-of-the-art technologies. Potential advantages of oxyfiring deriving from smaller equipment size are offset by costs related to cryogenic air separation and flue gas recycle necessary to maintain acceptable temperature levels in the equipment (boiler/heater/gas turbine).

When considering CO<sub>2</sub> capture, however, oxyfiring has the unique advantage to generate an effluent stream composed almost exclusively of CO<sub>2</sub> and H<sub>2</sub>O. It is very cheap and easy to capture CO<sub>2</sub> of the necessary purity for sequestration from this stream, simply by water condensation.

Another unique environmental advantage of oxyfiring is the complete avoidance of NO<sub>x</sub> emissions, usually generated by high temperature reaction between nitrogen and oxygen in conventional air combustion. The potential additional benefit deriving by the elimination of NO<sub>x</sub> capture systems has not been quantified in this phase of the CCP, but should be taken into consideration for future work.

For fuel combustion using pure oxygen, the temperature is much higher than with air. In many applications, it is advantageous to utilize this high quality heat, which results in increased thermal efficiency. However, advanced materials have not yet been discovered to enable such applications. As a result, nearer term efforts have focused in use of various diluents to moderate the combustion temperature, while still enabling ease of CO<sub>2</sub> capture. Depending on the diluent, and the degree of temperature moderation, it is possible to retrofit combustion equipment for oxyfiring. Previous studies have concluded that the major cost center for oxyfiring is the production of pure oxygen.

Cryogenic air separation is a mature technology, and only small, incremental improvements in oxygen cost may be expected over the next years. For this reason a large R&D effort is ongoing, outside the CCP, to develop novel technologies able to reduce consistently the cost of air separation. While this development is not driven by CO<sub>2</sub> capture considerations, their application to oxyfiring may contribute to reduce the costs of CO<sub>2</sub> capture in oxyfiring systems.

Oxyfuel technologies are basically fit both for steam generation scenarios, revamping or replacing existing heaters or boilers, like the CCP UK refinery scenario, and for gas turbine power generation scenarios, like CCP Norwegian or Alaskan scenarios. In the latter case, modifications to current commercial machines are necessary, at least in the combustion zone, to maintain high thermodynamic efficiency..

The Oxyfuel Team performed its work according to the following guidelines:

1. Definition of an Oxyfuel baseline, potentially applicable “today”: CO<sub>2</sub> capture with state-of-the-art air separation technology and flue gas recycle to moderate temperature increase, applied to the UK Scenario (revamping of existing boilers and heaters in the Grangemouth refinery).
2. Investigation of novel technological solutions for boiler revamping or new-building, maintaining conventional air separation.

3. Investigation of advanced thermodynamic cycles for power generation systems, involving turbine modification.
4. Investigation of novel air separation technologies (e.g. ionic transport membranes for oxygen) for application to conventional boilers/heaters.
5. Investigation of novel technologies integrating steam or power generation system and novel techniques for oxygen supply (e.g. Chemical Looping , AZEP).

### The Oxyfuel Baseline

A detailed technical/economic study for possible revamping of the Grangemouth refinery, using a conventional cryogenic system of large capacity to feed all of the existing boilers and heaters, with subsequent CO<sub>2</sub> capture, was performed by Air Products, in collaboration with Mitsui Babcock and Foster Wheeler.

Air Products studied a base case and two additional options with increasing integration in the refinery. The base case has also been evaluated by the CEM Team, achieving a good agreement with the results by Air Products in terms of the “CO<sub>2</sub> avoided cost” (47 \$/ton CEM vs. 43 \$/ton AP). Additional AP cases reduced the CO<sub>2</sub> avoided cost by a further 10%. The CO<sub>2</sub> capture cost is in the 30-35 \$/ton range.

**This means that the Oxyfuel baseline in the UK Scenario allows a > 40% reduction in the CO<sub>2</sub> avoided cost compared to the Post-Combustion baseline (77 \$/ton).**

The Oxyfuel Baseline is consequently technically applicable with consistent saving compared to any other available option with minor technical risk. A commercial demonstration of oxyfiring is needed and the necessary air separation unit for Grangemouth is about 20% larger than the largest existing unit. This level of cost could make it attractive in countries applying high level of carbon tax.

### Boiler modifications

A few studies were commissioned to different Technology Providers to investigate potential savings deriving by optimization of the boilers for oxyfiring. According to equipment vendors, boilers are more easily modified for oxyfiring than are process heaters. Process heaters often have added constraints of flux uniformity and peak temperatures that are harder to deal with.

The concept of a boiler operating at higher than atmospheric pressure was studied by Mitsui-Babcock. The basic idea was that, since cryogenic air separation works under pressure, and captured CO<sub>2</sub> must be further compressed for sequestration, utility consumption and compressor costs might be reduced. It was however found that, even at the calculated optimal operating pressure of 5 bara, potential savings were offset by the higher capital cost of the boiler.

Another approach studied with Mitsui-Babcock was the “Zero or low recycle boiler”. This had to be a boiler of new design, tailored to oxyfuel firing, based on the concept of staged combustion. Staging should allow avoiding or minimizing the recycle of flue gas. Calculations showed that flue gas recycle cannot be avoided and may only be reduced by 25% in a feasible design, resulting in possible cost saving of 10%, but double footprint compared to conventional boilers.

Praxair studied the option of designing a boiler with no flue gas recycle and no temperature mitigation, simply by using more expensive construction materials. Expected savings came from reduced boiler size and utility consumption. Again potential savings were offset by increased capital cost.

**None of the investigated options supplied results able to justify a continuation of the activities.**

### Advanced thermodynamic cycles

As noted in the Introduction, pure oxyfiring produces flame temperatures that are well beyond current turbine capabilities. The most obvious way to moderate combustion temperature is to recycle exhaust gas, which is just CO<sub>2</sub> in the case of oxyfiring. However, between the power required for air separation and for CO<sub>2</sub> recycle, there is a large reduction in net power output from the turbine system (whether simple power cycle or combined cycle). To improve the net efficiency of oxyfiring with CO<sub>2</sub> capture, there have been numerous power cycles proposed in the literature. With the requirement that a working fluid used to moderate temperature in the combustion turbine must also still enable simple CO<sub>2</sub> capture, the studies have generally looked at CO<sub>2</sub>, water, and combinations of those two.

SINTEF performed a study to evaluate three thermodynamic cycles, applied to oxyfiring, proposed in the scientific literature: Water cycle, Graz cycle and Matiant cycle. All of the papers describing these cycles claimed much higher efficiency compared to conventional cycles. However the results of the study show that these efficiencies may only be reached at operating conditions that cannot be realized in current commercial equipment such as combustion at 1400°C or turbines discharging in high vacuum. Also, when the different cycles are compared on a consistent basis, the efficiencies were comparable.

One unique aspect of work being undertaken by Clean Energy Systems, under funding by US DOE, is an effort to develop “stoichiometric” combustion for their version of a power cycle which uses water as the moderating fluid. This addresses the fact that combustion operations generally are operated with excess air (or oxygen) to ensure complete combustion. The presence of the excess oxygen complicates CO<sub>2</sub> capture and sequestration – often requiring additional CO<sub>2</sub> purification. CES is developing a turbine combustor that minimizes the excess oxygen.

Some turbine vendors were contacted to evaluate their willingness to work in the development of turbines able to operate in the conditions described by the SINTEF report. No positive answers were received since turbine development is a very expensive and time consuming activity. It was estimated that the development costs for an oxyfiring gas turbine would be in the range of tens of millions of US Dollars. **This type of development cannot be carried out in the CCP frame.**

#### Novel technologies for air separation

A very promising novel technology for air separation (ionic transport membranes) have been under development by other consortia over the past five years. These ceramic membranes, operating at high temperature (> 700°C) allow 100% selectivity to oxygen, which is transferred in anionic form using a difference in oxygen partial pressure between the two sides of the membrane as driving force.

Three consortia are developing these membranes:

- led by Air Products (ITM – Oxygen Transport Membranes)
- led by Praxair (OTM – Ionic Transport Membranes)
- led by Alstom/Norsk Hydro (MCM – Mixed Conducting Membranes)

All of these consortia are targeting 2008-2009 for commercialization but the risks associated with this type of development (resistance in time to high temperature operation, mechanical problems etc.) should not be underestimated.

The CCP sponsored a study by Air Products to revamp the Grangemouth refinery to oxyfiring using an ITM system rather conventional cryogenic. The particular process configuration being developed by APCI uses only a pressure differential across the ITM membrane to provide a driving force for oxygen separation, rather than use of a sweep gas on the permeate side of the membrane. As a result, the membranes may extract only about 40% of the oxygen from the air stream. Since high temperature is needed to favor oxygen transfer, a considerable export of power (446 Mw in the Grangemouth case) is

necessary to balance the system. This exported power, not available with air firing could replace the current power station. It is immediately clear that this technology is not fit for the revamping of existing boilers unless there is a market for power export, but seems ideally suited for integration with large CCGT (Combined Cycle Gas Turbine) systems.

Different cases were considered by Air Products (all of them with considerable power export). The CO<sub>2</sub> avoided cost for the base case was evaluated by the CEM Team at 35.5 \$/ton (vs. 37 \$/ton by Air Products) with about 20% saving compared to the Oxyfuel Baseline. The other cases studied by Air Products allowed reduction of CO<sub>2</sub> avoided cost to the 20-30 \$/ton range.

**Most promising application of the Air Products implementation of ionic transport membranes that produce pure oxygen without a sweep gas to CO<sub>2</sub> capture seems to be in systems allowing considerable export of power.**

#### Integrated equipment

The study described above showed that the simple substitution of an ITM system to a cryogenic air separation, while positive in a new-built perspective, may not always be applicable to revamping of existing units, due to the large associated export of power. In the new-built perspective, some Technology Providers are studying the direct integration of ionic transport membranes in boilers or gas turbine systems. Two studies were commissioned by the CCP to assess the potential for these developments. The AZEP (Advanced Zero Emission Power) is a concept under study by Alstom/Norsk Hydro a three-year EU-funded project started in January 2002 with the aim to integrate the MCM membranes directly into a gas turbine system. A key aspect of the AZEP concept is that it can be used with conventional power turbines. In the study performed for the CCP, Alstom defined the implementation of AZEP in the Alaskan Scenario, as replacement of the current gas turbine system, using 45 MW commercial machines. The technology is also potentially applicable to the Norwegian Scenario, but the developers do not yet feel confident in evaluating such a large scale application.

Three cycles were studied with sub-options of complete or incomplete (80-90%) CO<sub>2</sub> capture, that should minimize capture costs. It must be pointed out that, in addition to the uncertainties on the membrane development, to maximize the thermodynamic efficiency, the AZEP system includes a “High Temperature Heat Exchanger” operating at temperatures beyond present exchanger’s capability, whose development is among the targets of the Project. Alstom calculated a CO<sub>2</sub> avoided cost in the 25-35 \$/tonne range, which is an astounding result in the Alaskan Scenario (best cases evaluated by the CEM Team up to now are above 50 \$/ton).

A similar research effort is carried being out by Praxair to develop a boiler incorporating the OTM membrane system. A study co-sponsored by the CCP and the DOE was carried out by Praxair to replace one of the existing boilers in Grangemouth. Use of this boiler will be limited to the C<sub>1</sub> – C<sub>2</sub> fraction of Natural Gas, since C<sub>3</sub>-C<sub>4</sub> are coke formation precursors. The technology is still at an early stage of development, so that cost evaluation must be considered as preliminary. According to Praxair, the Advanced Boiler will be 40% more expensive than a conventional one, and cost of CO<sub>2</sub> capture in the 15-20 \$/ton range.

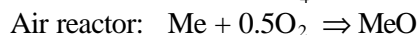
**These integrated equipments are promising developments, but still at an early stage with considerable uncertainties. Commercialization expected not before 2010.**

#### **Chemical Looping**

The major R&D Project (actually the only one directly funded) in the Oxyfuel field has been the Chemical Looping, developed by as a consortium formed by BP (Coordinator), Alstom Boilers, Chalmers

University, CSIC, and Vienna University in a 2-year EU-cofunded project coming to a conclusion by December 2003.

Chemical Looping is a new combustion technology based on oxygen transfer from combustion air to the fuel by means of a metal oxide (MeO) acting as an oxygen carrier. Central to the technology are a dual fluidized-bed reactor system with continuous circulation of solids, similar to Circulating Fluidized Boilers (CFB) used for coal combustion. The reactions are schematically:



This project has been focused on atmospheric pressure applications, typical of the CCP UK Scenario, but the concept is also applicable to higher pressure gas turbine systems as proven in another project outside the CCP frame and funded by the DOE. In this case the trade-off is between thermodynamic efficiency and percentage of captured CO<sub>2</sub>, since Chemical Looping Combustion takes place at relatively low temperatures (800-900°C). An additional uncertainty is the ability of the gas turbine to tolerate dust from the air separation process.

The main risk in developing the technology is the availability of a suitable material able to undergo repeated oxidation/reduction cycles maintaining both chemical activity and mechanical resistance. The screening activity performed during the first year of the project identified a restricted number of materials for further development. In the meantime, with the support of hydrodynamic testing on cold units, a pilot unit was designed and built to achieve "Proof-of-Feasibility" of the technology - the main target of this Project. The pilot unit at Chalmers is composed by two fluid bed reactors (bubbling fuel reactor and fast riser air reactor) with continuous circulation of solids maintaining the solid flux foreseen for larger units. The "Proof-of-Feasibility" was successfully achieved by operating the pilot unit with NiO/Al<sub>2</sub>O<sub>3</sub> for a total of about 300 hours with almost complete methane combustion (99.5% at 800°C), no gas leakage between the reactors, no significant carbon formation, no significant attrition and no chemical decay. Preliminary economic evaluation performed by the CEM Team in 2002 of replacing a boiler in the Grangemouth refinery resulted in 43% saving compared to the Post-combustion Baseline. Evaluation of the CEM Team on investment data supplied by Alstom is now ongoing.

In case of positive results of the economic evaluations, the CCP should consider co-funding a subsequent phase of the Project, which could achieve Demonstration of the Technology by the end of 2006, in the perspective of a commercialization by 2008. Inclusion of a catalyst manufacturer in the Partnership to drive the scale-up of the solid material production is necessary.

**The Chemical Looping Project has been a technical success. The results of economic evaluations will drive the choices for continuation.**

### Conclusions

- Oxyfuel technologies will drastically reduce, or even eliminate, NO<sub>x</sub> emissions. This additional advantage has not been quantified in the current Phase of CCP, but should be evaluated in the light of existing and future environmental legislation.
- Oxyfiring coupled to conventional cryogenic air separation may be considered as the CCP Baseline Case, with possible application to revamping of boilers and heaters without any research activities. Demonstrative operation of oxyfiring with flue gas recycle is the only pre-requisite to commercial implementation. If a CO<sub>2</sub> avoided cost of 40-45 \$/ton, corresponding to a CO<sub>2</sub> capture cost of 35-40 \$/ton may be acceptable, this is a short-term feasible solution.
- No improvement in existing boilers may result in consistent advantage over this baseline.

- Oxyfiring application to CCGT systems with conventional air separation would require consistent and very expensive gas turbine development to maintain high energy efficiency, considering air compression and flue gas recycle costs. Vendors are not willing to engage in such activity without clear market opportunities.

- Novel membrane systems for oxygen production, currently under development and expected for commercialization by 2008-2009, do not appear to be suitable for retrofitting existing boiler systems. Application to new-built systems, including power generation in CCGT looks very promising and should be further investigated.

- Equipment integrating novel membranes in boilers or gas turbines is still at an early stage of development. Potential for reduction of capture costs is strong, but development risk is still high. Commercialization is not expected before 2009-2010.

- The Chemical Looping Project has been technically very positive and scale-up risks are reasonable, due to similarities with existing coal-fired boilers. Furthermore it produces rather pure CO<sub>2</sub> compared to the Oxyfuel Baseline. A decision to continue the project should be taken based on the results of economic evaluations. A continuation should also explore high pressure application to CCGTs and use of alternative fuels to natural gas (e.g. pulverized coal, maybe mixed with Natural Gas).

#### Team Recommendations for Future Studies:

- Based on the economic analysis results of the Oxyfuel Baseline evaluation, the CCP should evaluate the option of funding revamping and operation of a small boiler for a demonstration of oxyfiring with a goal to remove the remaining concerns to commercial application.

- In case of positive evaluation of Chemical Looping, the Team recommends that a second phase be funded. The Partnership should be including a commercial catalyst manufacturer to handle scale-up of the production methodology. Two options may be considered:

1. Aggressive development: A 3-year project targeting a demonstration unit operating by the beginning of 2006 (revamping an existing Demo-CFB unit, as suggested by Alstom). The first half of the project should be devoted to optimization of the solid material and definition of the scale-up.
2. Paced development: A 2-year project focused on the solid material issues and exploration of the whole range of possible applications that leaves demonstration to a third phase starting in 2006.

- Low-cost oxygen production is a powerful driver independently from greenhouse gas issues. Oxyfuel capture may benefit from any advance in the various technologies under study. The Team recommends periodic monitoring and reevaluation of these technologies. A study on application of ITM to a new-built CCGT could be funded as part of the 2004 CCP activities.

- The Team recommends funding a project to quantify the advantages derived from reduction of NO<sub>x</sub> emissions by oxyfuel combustion as compared air combustion.

- The Team recommends investigation of the synergism between Oxyfuel and PCDC technologies such as integration of oxyfiring and steam reforming.

## 1.3.1 Advanced Boiler Study

Task 3.1 Advanced New/Retrofit Boiler Designs  
Technology Provider: Praxair

### Highlights

- A cost and feasibility study of the Praxair Advanced Boiler applied to the CCP Refinery Scenario was completed.
- Capital cost savings are estimated to be greater than 60%, and the CO<sub>2</sub> capture energy cost savings are approximately 80% when compared to the baseline case.

### Summary

Praxair, Inc. is leading a consortium supported by the US Department of Energy to develop a novel Advanced Boiler which incorporates a membrane to separate oxygen from the air, which is then used for combustion. The flue gas will consist essentially of CO<sub>2</sub> and water from which the CO<sub>2</sub> can easily be separated. The technology promises to reduce the cost of capturing CO<sub>2</sub> from new boilers and possibly process heaters.

Praxair has produced an outline design and feasibility study and provided conceptual capital and operating cost estimates for a plant incorporating a Praxair Advanced Boiler designed to:

- (i) match the performance of a specified boiler in the CCP's Refinery Scenario (Grangemouth, Scotland) and
- (ii) to capture the CO<sub>2</sub> emissions, delivering them with a specified product quality for storage.

The study provided cost and performance data for a new conventional boiler with the same output and air as oxidant, without CO<sub>2</sub> capture as a baseline so that a net capture cost per ton of CO<sub>2</sub> can be calculated.

### Results

One effective approach to produce a CO<sub>2</sub> rich flue gas from a combustion process is to use pure oxygen rather than air as the oxidant stream. Oxygen-fuel fired combustion systems offer a number of advantages over air fired systems. Praxair has demonstrated that oxy-fuel fired processes offer

- (i) increased fuel efficiency,
- (ii) reduced pollutant emissions (e.g., NO<sub>x</sub>), and
- (iii) improved productivity/throughput.

These advantages coupled with the fact that the exhaust products contain high concentrations of CO<sub>2</sub> make oxy-fuel fired systems ideal candidates for high efficiency boilers with CO<sub>2</sub> sequestration. To date, the primary issue limiting the application of oxy-fuel fired systems to a greater market is the cost of producing oxygen (separating O<sub>2</sub> from other gases present in air). Systems with high thermal efficiencies have typically not been candidates for oxy-fuel conversion as the incremental improvements in thermal efficiency are typically not enough to offset the cost of oxygen production.

Praxair is currently developing a new method of oxygen production that is expected to significantly improve the cost of oxygen production. This technology utilizes an oxygen transport membrane (OTM) that selectively transports O<sub>2</sub> across a ceramic membrane. The driving force for transport is a concentration gradient across the membrane. Development work at Praxair has identified a target operating temperature of the membranes of approximately 800-1000 °C (1500-2000 °F). In low temperature processes, or standalone systems, the energy required to maintain this operating temperature



must be supplied for an external source. However, in high temperature exothermic systems the integration of the OTM components with the heat generation system can offer many advantages. Combustion systems, in particular boilers, are ideal candidates for this integration. Integration of the OTM materials into the firebox of a boiler offers several inherent advantages. The flux of O<sub>2</sub> through the OTM material is driven by the gradient of the O<sub>2</sub> partial pressure across the membrane. Supporting the combustion process on the surface of the OTM tube effectively creates a sink for O<sub>2</sub> on the process side of the tube, thereby allowing significant O<sub>2</sub> fluxes to be achieved. Heat generated by the combustion process can be utilized to maintain the OTM materials at the desired operating temperature. Steam tubes placed among the OTM materials capture the balance of the heat generated by the combustion process.

Integration of OTM technology into a boiler represents a method that will allow the benefits of oxy-fuel combustion to be extended to fired processes that have to date not been suitable candidates for conversion to oxy-fuel. More importantly, this will facilitate the integration of CO<sub>2</sub> sequestration in a technically compelling and economically competitive manner. Figures (a) and (b) illustrate the basic configuration of an OTM boiler system with CO<sub>2</sub> capture and a conventional air-fired system with CO<sub>2</sub> capture. Because of the low concentration of CO<sub>2</sub> in the exhaust of the air-fired system, a chemical absorption process is required to remove the CO<sub>2</sub>, thus adding to the cost and complexity of the system.

The Praxair Advanced Boiler design consists of a furnace in which the fuel and exhaust gas products pass over oxygen transport membranes (OTMs) arranged perpendicular to the flow direction. The OTMs are supported on tubes and manifold together so that each tube is fed from a common air source. Steam tubes run parallel to the OTM tubes and are placed so that the OTM tube surfaces are maintained at a constant tube temperature down the length of the furnace. The exhaust then moves on to a heat recovery system to preheat the incoming air and feed water. Finally, the exhaust gases are purified and compressed through a series of compressors and coolers to produce a purified CO<sub>2</sub> product.

The current Advanced Boiler design requires approximately 13 MW (43 MMBTU/hr) less fuel than the equivalent conventional air-fired boiler. Maintaining the pressure drop across the OTM manifold requires a large blower to feed air to the Advanced Boiler. Even though the blower requires about 4 MW (14 MMBTU/hr) of additional energy, the Advanced Boiler still shows an advantage in efficiency over the conventional boiler. The addition of the CO<sub>2</sub> capture system requires another 4.2 MW (14 MMBTU/hr) of energy and 0.3 m<sup>3</sup>/s (5000 gpm) of cooling water. This case requires significant amounts of added cooling water due to the incoming temperatures of the air and water feed to the boiler. The addition of the CO<sub>2</sub> capture system to the Advanced Boiler also shows an energy efficiency gain over the conventional boiler.

The economic analysis prepared for this study showed that a boiler with integrated ceramic membranes has the potential for substantial capital and operating cost savings when CO<sub>2</sub> capture is required. The capital cost savings are estimated to be greater than 60%, and the CO<sub>2</sub> capture energy cost savings are approximately 80%. In the case of a more conventional boiler without CO<sub>2</sub> capture, the energy savings can potentially pay for the incremental cost of the OTM boiler in ~ two years.

## **Reports and Publications**

- The final project report is in Appendix A under the same heading as this summary.

## 2. Storage Monitoring And Verification (SMV) Studies

### Task - 4.0 - Establish Key Geologic Controls & Requirements

#### Introduction

As a commercial process, carbon dioxide sequestration includes pre-combustion decarbonization or post-combustion separation (capture), export from the production site (transportation) and long-term containment (storage). The CO<sub>2</sub> Capture Project (CCP) includes transportation and geological storage of CO<sub>2</sub> in its “Storage, Monitor and Verification” (SMV) program. Whereas the principal objective of the CCP capture program was cost reduction that of the CCP storage program was to identify efficiencies and reduce uncertainties associated with pipeline transportation and geologic CO<sub>2</sub> storage. For organizational purposes, the SMV program technical studies are grouped into four technical themes:

- **Integrity** – competence of natural and engineered systems to contain CO<sub>2</sub>
- **Optimization** – processes that improve the efficiency and economics of CO<sub>2</sub> transportation and storage
- **Monitoring** – techniques to track CO<sub>2</sub> movement within and outside of the target storage reservoir
- **Risk Assessment** – methods to identify and minimize the probability and impact of CO<sub>2</sub> leakage from storage sites

Summaries of the objectives, results and CCP assessment of some 30 projects distributed over the four technical themes appear elsewhere in the SMV section. In the present section, the findings of these studies will be presented in précis form with **key messages** identified. From this, an assessment is made on the present status of and further science and technology needs for safe and effective geological CO<sub>2</sub> storage.

#### *Integrity of geological systems (ARI, USU, UT-P, SINTEF, INEL)*

Geological systems are complex and thus vary widely in their suitability for safe and effective CO<sub>2</sub> storage. Basic requirements include depth (pressure and temperature) sufficient to inject and maintain CO<sub>2</sub> in its supercritical state, reservoir geometry consistent with good storage capacity and structural closure, reservoir porosity and permeability distributions that permit high injection rates and fluid conformance, compatible fluids, and top seals with low permeability and high mechanical strength. The SMV program included two studies that directly address the competence of natural systems (natural analogs) to retain CO<sub>2</sub>. Additional studies addressed the need for characterization of prospective CO<sub>2</sub> storage sites for long-term suitability at the sub-basinal, field and reservoir / cap rock scales. Reservoir simulations of the physical-chemical behavior of CO<sub>2</sub> also show that CO<sub>2</sub> is amenable to retention in natural systems by multiple mechanisms.

There are numerous instances worldwide both of large natural CO<sub>2</sub> reservoirs that have persisted over geologic time frames and those that continuously or episodically leak. The study by ARI (Stevens) documented specific features of three natural “secure” fields in the US (McElmo Dome, CO; Jackson Dome, MS; St. Johns, AZ), the former of which are thought to have held CO<sub>2</sub> up to ~70 Ma). It is concluded that reservoir seals should be comprised of thick chemically-precipitated (carbonates, evaporates) or clastic (shales) rocks. Structural features amenable to CO<sub>2</sub> containment are characterized by lack of significant faulting and fracturing or a “self-healing” mechanism that seals those that do develop. The study by Utah State University (Evans), in contrast, investigated a natural CO<sub>2</sub>-charged geyser system in the Western Colorado Plateau of East-Central Utah to explain the “leaky” nature of the system. A 3-D structural / stratigraphic model of the study area revealed available paths for migrating fluids that ultimately erupt or bubble at the surface. Geochemical sampling and analysis was used to

describe in time and space the origin (clay-carbonate reactions at 1-1.5 km), subsurface movement (up faults conduits to a temporary reservoir at 300-500m) and leakage to the surface (phase change pressure-induced migration through minor faults and fractures). Storage of CO<sub>2</sub> in the system as travertines and porosity / vein fills is estimated to be a maximum of ~10%. **The key message from these natural analog system assessments is that CO<sub>2</sub> accumulation and retention is a function of general geologic setting and specific local features. Such features are definable and, given appropriate scenarios and models, predictable with respect to their influence on long-term CO<sub>2</sub> storage.**

Assessment of the tendency for rock and structural element failure begins with estimation of in situ stress and fault geometry as described in the University of Adelaide (Streit) study. Tools are available to simulate perturbations to the original system and thus test design limits for CO<sub>2</sub> injection. The study by GFZ-Potsdam (Schuett) showed experimentally that injection of CO<sub>2</sub>- rich fluids into reservoir rocks releases major and minor elements. The detection of ions from rock-forming minerals suggests the dissolution of rock-forming minerals which would ultimately reduce rock strength. LLNL (Johnson) applied reactive transport modeling to simulate competing geochemical and geomechanical responses of cap rocks to CO<sub>2</sub> injection. Geochemical processes driven by CO<sub>2</sub> injection tend to result in dissolution / precipitation reactions that reduce permeability of the cap rock. This process appears to be independent of key reservoir (permeability and lateral continuity) and CO<sub>2</sub> influx (rate, focality and duration) parameters. In contrast, increase of cap rock permeability due to geomechanical effects is controlled by reservoir and CO<sub>2</sub> influx parameters that control the magnitude of the pressure perturbation. These studies highlight the need to evaluate elements of prospective storage sites at various scales assisted by experiments and models.

Multiple mechanisms are available for immobilizing injected supercritical CO<sub>2</sub> in the subsurface. Principal among these is solubility and relative permeability trapping. The latter mechanism, which was recently identified and simulated for natural gas reservoirs, has now been adapted to CO<sub>2</sub> flooding in clastic aquifers and the CO<sub>2</sub> EOR water-alternating-gas (WAG) process. Other possible mechanisms of CO<sub>2</sub> immobilization include buoyant flow, brine density convection and mineralization. The fate of CO<sub>2</sub> in a fifty year aquifer injection project was simulated for the 1000 year time frame by the University of Texas (Pope). Given appropriate injection strategy (base of the reservoir) and reservoir characteristics and conditions, ~95% of the CO<sub>2</sub> is expected to be immobilized, mostly as residual gas (capillary trapping) over this time frame. Indeed, as substantial portion might be immobilized by the end of the injection period. Mineral trapping is predicted to be significant on the 10000 year time frame. A simulation by SINTEF (aimed at testing well failure scenarios) using CO<sub>2</sub> dissolution as the principal trapping mechanism, showed similar results over the 1000 year timeframe. Our understanding of CO<sub>2</sub> behavior in the subsurface, backed by independent simulations, show that CO<sub>2</sub> immobilization can be highly effective given an appropriate reservoir. The solubility of CO<sub>2</sub> makes it likely; furthermore, that CO<sub>2</sub> leaking from the target reservoir will be assimilated or retarded in shallower aquifers.

**SMV studies related to the integrity of geologic systems show that despite their complexity, diverse venues suitable for CO<sub>2</sub> storage are available. Integrated characterization at multiple scales should be used to develop 3-D structural / stratigraphic models and hydrogeology should be well understood. Scenario development and simulations using a broad range of sensitivities and potential failure modes will give credibility to efforts to develop CO<sub>2</sub> storage facilities. It is of considerable importance that independently-run simulations using distinct software and favoring different CO<sub>2</sub> trapping mechanisms predict immobilization of most of injected CO<sub>2</sub> in the 1000 year time frame.**

*Integrity of engineered systems ( SINTEF, GTI)*

Whereas natural systems, particularly gas reservoirs, have a proven ability to retain fluids for extended periods, modification of such systems (e.g., well bore penetration of top seal, physical-chemical changes due to fluid injection) has the potential to reduce their competence for long-term CO<sub>2</sub> retention. Foremost among the vulnerabilities of CO<sub>2</sub> storage reservoirs is leakage through old or poorly-constructed wells. A major SMV project that addresses this issue entails cement and seal stability experiments and simulations. Highly relevant is an emerging industrial analog to CO<sub>2</sub> storage, natural gas storage.

SINTEF (Lindeberg) addressed the well integrity issue through experimental testing, at elevated temperature, standard and newly formulated cements (and cements in contact with steel) and cement sealants. The experiments showed that whereas initial contact of cement with CO<sub>2</sub>-rich fluids may “carbonate” the cement (reduce permeability), long-term exposure will deteriorate the cement via dissolution of calcium hydrogen carbonate. Permeabilities increase faster by 2-3 orders of magnitude for standard cement compared to new cements (e.g., silica flour added) but are all within the microdarcy range. Simulations of the effect of CO<sub>2</sub> injection on abandoned well bores at different distances and reservoir conditions suggests that in a worse case scenario (open well bore created by complete well failure without remediation), ~60% of the CO<sub>2</sub> injected could be lost to the atmosphere over 100-200 years. The study provides useful protocols for testing the performance of cements formulations in a CO<sub>2</sub>-rich environment.

The natural gas storage industry has operated cumulatively >600 facilities in North America over the past 90 years with very few gas migration incidents. The GTI (Perry) survey of the natural gas industry experience identifies principles responsible for its success and those technologies and practices applicable to CO<sub>2</sub> storage. Site selection criteria relevant to CO<sub>2</sub> storage include competent seal and broad structural closure. The latter is recommended as less faulting and fracturing is expected. Modified pump testing might be suitable for seal competency testing in prospective CO<sub>2</sub> storage sites. The GTI study has identified siting and technology issues in natural gas storage that will be useful in developing and maintaining CO<sub>2</sub> storage facilities.

**The integrity of engineered systems used in CO<sub>2</sub> storage requires continued research. Work should continue on new materials development, particularly on cements and sealants in new installations. Options for remediation of old wells will become an issue in brown field developments (e.g., depleted oil and gas fields) and for contingency planning in green field developments (e.g., aquifers). Future well integrity simulation work might include scenario development such as progressive well failure and the efficacy of well remediation techniques. Siting and characterization of natural gas storage facilities has proceeded in the past with less rigor than that expected for CO<sub>2</sub> storage. Successful development of natural gas storage as an engineered system analog for CO<sub>2</sub> storage will progress its future application and safety.**

#### *Economic Offsets and Operational Efficiencies (NMT, Tie-Line, TTU, INEL, UT-B)*

Injection of CO<sub>2</sub> into depleted oil fields is considered an early opportunity for CO<sub>2</sub> storage given that the cost of CO<sub>2</sub> capture, transportation and storage might be partially offset (or profitable) by revenues from increased oil production. The Permian Basin of West Texas and adjacent New Mexico is the site of the bulk of CO<sub>2</sub> EOR experience in the World over the last 30 years. Storage of CO<sub>2</sub> in depleted gas field is attractive given that gas fields are by definition capable of storing gases but also because an appropriate infrastructure exists. In addition, there are concepts under development for enhanced gas production using CO<sub>2</sub>. Deep unmineable coals also present an opportunity as increased methane production is possible. The ability of the CO<sub>2</sub> storage reservoir to accommodate impurities (e.g., SO<sub>x</sub>, NO<sub>x</sub>) might reduce CO<sub>2</sub> capture costs and avoid their emission into the atmosphere.

The survey of CO<sub>2</sub> EOR operations experience in the Permian Basin by NMT (Grigg) revealed aspects of the process which went well and identified those needing further research. Slow or less than expected oil response was the biggest concern followed by gas breakthrough / production. Remediation to improve injectivity and thus oil response were usually unsuccessful and monitoring of performance and leakage is considered inadequate. Poor pre-injection reservoir characterization is identified as the major factor in difficulties experienced. The other SMV study relevant to CO<sub>2</sub> EOR is that by Tie-Line Technology (Stenby). Models and software are available for screening CO<sub>2</sub> effects on MMP and MME and dispersion indicators for large scale simulations. Calculations of the timing and gas composition at breakthrough can be used to design surface facilities. The CO<sub>2</sub> EOR studies identify the major reservoir and fluid character issues that need to be addressed before large scale CO<sub>2</sub> EOR with storage can be effectively applied.

The tools necessary to make CO<sub>2</sub> storage in depleted gas and gas condensate fields, and possibly their enhanced production was examined by TTU (Lawal). Experiments and simulations showed that gas compressibility and phase behavior are important factors in optimizing CO<sub>2</sub> storage in such reservoirs. The highly compressible nature of CO<sub>2</sub> indicates that up to five times the volume of CO<sub>2</sub>, relative to original gas, may be stored under appropriate conditions. Hydrocarbon and CO<sub>2</sub> gas PVT experiments predict the phase behavior of gas mixtures in reservoirs. A “CO<sub>2</sub> Sequestration Parameter” was developed for quickly assessing the suitability for and capacity of reservoirs for CO<sub>2</sub> storage. The key implication of the study is that prospective gas field storage sites may have better or worse than expected capacity and ease of operation than thought using conventional evaluations. Global estimates of depleted gas field storage capacity might be revisited using the tools developed by this study.

The University of Texas (Bryant) study simulated the effects of CO<sub>2</sub> impurities (e.g., SO<sub>x</sub>, NO<sub>x</sub>) on aquifer reservoir injectivity and EOR performance. Increased acidity (sulfuric and nitric) is predicted to either temporarily enhance injectivity via mineral dissolution or have little effect via the mitigating effect of multiphase flow. Impurities present in an EOR operation (e.g., WAG) are predicted to be neutral as there is a tradeoff between lowering MMP (improvement) and increasing the mobility ratio (worsening). The minimal performance effects expected by the presence of soluble, acid forming gases in injected CO<sub>2</sub> raises the potential for lowering CO<sub>2</sub> capture costs. The modeling framework established should be useful for testing the effects of other gases such as N<sub>2</sub>, hydrocarbons and O<sub>2</sub>.

**Identification of operational efficiencies and economic offsets will be crucial both to project development decisions and safe and effective operation of CO<sub>2</sub> storage facilities. Simulation aimed at optimizing operational parameters, using model frameworks developed for site characterization, are quick and inexpensive to perform. Although formal economic analysis was not in the scope of the SMV program, it is evident that development of site specific parameters, tied to local tax and regulatory regimes, will be decisive factors in project approval.**

#### *New Paradigms in CO<sub>2</sub> Transportation (Reinertsen/SINTEF, IFE, BML)*

The Norwegian transportation studies coordinated by Reinertsen Engineering (Heggum) and supported SINTEF and IFE (Seiersten) aimed to reexamine CO<sub>2</sub> transportation in carbon steel pipelines for a “northern”, offshore setting (as oppose to the well-known US temperate, onshore setting). At issue was the maximum hydration of CO<sub>2</sub> streams permissible before corrosion and hydrates effects become significant.

Using thermodynamic models based on new high pressure CO<sub>2</sub> solubility in water and corrosion data (with and without inhibitors), it was found that proposed (50 ppm, Hammerfest LNG) specifications for water content could be relaxed to the existing (600, Kinder-Morgan in the US) specifications and perhaps further (1300 ppm). Specifications for inhibitor (MEG) content and pipeline protection to lower

corrosion rates to acceptable levels and prevent hydrates formation are documented. These studies, in addition to adapting CO<sub>2</sub> transportation issues to a different geographic setting and operational regime, could enable projects that are economically prohibitive (i.e., default specification of expensive steel alloys) to proceed and succeed.

**The Norwegian transportation studies comprise a creative attempt to extend the utility of standard, inexpensive carbon steel into settings where gas processing capability is limited or prohibitively expensive. Integration of capture and transportation process efficiencies recommended by the study may upgrade the economics of marginal projects.**

*Diverse Techniques to Assess CO<sub>2</sub> Flood Performance and Containment (TNO-A, LLNL-P, Stanford, CalTech-1&2, PSU, U. Adelaide, LBNL-H, LLNL-N)*

The SMV “monitoring” studies encompassed multiple technologies (spectroscopic, radar, geophysical, geochemical) applied from the full range of vantage points (space / aerial, near surface atmosphere, subsurface). Two surveys on the state-of-the-art in monitoring technology were conducted early in the program. The survey of atmospheric monitoring technologies by CalTech (Tang) documented the applicability and costs of instruments useful over various time, length / area scales and sampling frequency. The remaining SMV monitoring studies addressed specific technologies applicable to selected potential and actual CO<sub>2</sub> storage venues. TNO (Arts) conducted a broad survey of geophysical and geochemical monitoring techniques aimed at recommending “optimal” techniques for various CO<sub>2</sub> storage venues and potential failure modes (e.g., FEPs, or features, events and processes). In addition, the importance of characterizing the effects of CO<sub>2</sub> injection on rock properties and, therefore, monitoring resolution was pointed out in the GFZ-Potsdam (Shuett) experimental study and as a means of detecting effective stress in the University of Adelaide (Streit) geomechanical study.

“Hyperspectral geobotanical” surveys, processed to detect CO<sub>2</sub> leakage indirectly (effects on ecosystems and soils), were applied to the Mammoth Lake, CA natural volcanogenic release area (satellite) and to the Rangely Field, Colorado CO<sub>2</sub> EOR operation (aerial). Tree kills and other plant damage were easily detected at lushly-vegetated Mammoth Lake. At Rangely Field, pre- and post rain changes in “habitats” were noted in this arid landscape, but CO<sub>2</sub> detection is thought to require long term evaluation of such changes. An independent soil gas survey by Ron Klusman of the Colorado School of Mines shows that most CO<sub>2</sub> seepage in the area is diffuse and originates from near-surface microbial activity and that methane may be the relevant gas to monitor. The ability of the hyperspectral geobotanical technique to detect CO<sub>2</sub> from storage projects is probably limited to heavily vegetated areas or awaits new processing and interpretation methods to examine bands influenced by “groundtruthed” microbial activity or soil alteration.

The resolution of the satellite radar interferometry (InSAR) technique to detect ground movement induced by CO<sub>2</sub> injection was investigated by Stanford (Zebker). Although the mathematical basis for deformation signals and their detection were presented, it is not clear under what atmospheric conditions and topographical features the method would be applicable.

Near-surface and atmospheric monitoring techniques were investigated for their applicability to detect CO<sub>2</sub> leakage. As a follow-up their earlier literature review, Caltech (Shuler) examined the efficacy of open path detection (laser spectroscopy) on field geometric and leakage rate and mode parameters under various ambient CO<sub>2</sub> levels and atmospheric conditions. The spreadsheet application developed can be used to screen the feasibility of specific instruments and optimize field configurations. The eddy covariance method, which is above ground (10 m) laser spectroscopic technique used for CO<sub>2</sub> ecosystems flux determinations, is theoretically tested for CO<sub>2</sub> leakage detection under various scenarios. The near ground techniques are established technologies whose installation will likely be required for early onshore

CO<sub>2</sub> storage projects. Optimization of instruments and configuration will allow field scale CO<sub>2</sub> leakage monitoring considerable cost savings.

Geophysical techniques, particularly time lapse 3-D seismic, have proven useful in monitoring subsurface CO<sub>2</sub> movement. Their expense and limitations on detecting CO<sub>2</sub> saturation levels, however, highlight the need for better interpretation techniques or alternative technologies. LBNL (Hoversten) evaluates the resolution of new seismic interpretation approaches (seismic amplitude and AVO to infer CO<sub>2</sub> saturation) and novel non-seismic techniques including gravity, electromagnetics (EM) and streaming potential (SP). Gravity detection (calibrated with ground movement detection such as tiltmeters) is feasible but more appropriate as a down hole application. The EM technique is inexpensive, well understood and would be most applicable to CO<sub>2</sub> / brine systems. SP has been modeled in 2-D and tested experimentally. Unlike gravity and EM, however, further development of instrumentation, testing and interpretative methods are required. The novel geophysical applications, if successful in meeting acceptable CO<sub>2</sub> detection resolution specifications may provide considerable cost savings over time lapse seismic.

The single SMV geochemical monitoring study by LLNL (Nimz) assessed the utility of noble gases for detecting CO<sub>2</sub> movement out of target reservoirs. The Xe noble gas “system” (ten isotopes) was selected based on cost, availability and distinctiveness (relative to native and atmospheric noble gases) for the model Mabee CO<sub>2</sub> EOR oil field of W. Texas. Given the volume of CO<sub>2</sub> injected and instrumental detection limits, the cost of the Xe system applied to Mabee is estimated at \$0.18/tonne. As the subsurface transport features of Xe were not addressed, however, it is not known how well this tracer of CO<sub>2</sub> movement would perform. The development of tracer systems for CO<sub>2</sub> storage projects will be important for monitoring performance, leak detection and volume verification.

**The SMV assessment of technologies and techniques to monitor CO<sub>2</sub> reservoir performance and leakage / seepage is unique in its variety and scope. Remote atmosphere approaches to monitoring CO<sub>2</sub> leaks are shown to require further development. Existing near-surface atmospheric approaches to CO<sub>2</sub> detection are commercially available and adaptable to CO<sub>2</sub> storage. Seismic geophysical monitoring of CO<sub>2</sub> is available but a better understanding of rock response to CO<sub>2</sub> flooding and new processing and interpretation strategies require development (e.g., amplitude analysis and AVO). Much less expensive non-seismic geophysical approaches such as gravity, EM and SP may, under certain circumstances, have the resolution to track CO<sub>2</sub> movement in the subsurface. Geochemical techniques such as tracer gas surveys are potentially cost effective but further development is needed in elucidating and simulating subsurface transport mechanisms.**

#### *Comprehensive Risk Assessment Frameworks (TNO, INEL)*

Risk assessment models, simulations and methodologies have been developed for the purpose of predicting the probability and consequences of natural and industrial hazards. Two comprehensive risk assessment methodologies for CO<sub>2</sub> storage were developed for the SMV program. These methodologies are similar in that they contain the basic elements of scenario development with an inventory of risk factors, model development and consequence analysis. Although the two methodologies were developed and tested using models of distinct geological storage venues, they can be adapted to other venues.

The TNO (Wildenborg) methodology (SAMCARDS) involved extensive scenario and model development over multiple Earth compartments. A performance assessment (PA) model involving numerous simulations over these compartments is capable of statistical analysis that predicts CO<sub>2</sub> concentrations and fluxes into the biosphere. In the combined off-/onshore model with two leakage scenarios (well and fault leakage), it was predicted that seepage of CO<sub>2</sub> into the biosphere would not occur in the 10000 year time frame simulated. This is despite a worst case scenario (no remediation) and 1000 parameter realizations. The SAMCARDS risk assessment methodology is comprehensive but flexible in terms of applicable scenarios and data needed. Further development of the surface components

(atmosphere and hydrosphere) is needed. Benchmarking of the model will help in assessing the reliability and credibility of the methodology

The INEL (Wo) risk assessment methodology was applied to the Tiffany Field (Durango, CO), a coal bed methane development currently under N<sub>2</sub> flood. The four major elements of the methodology (hazard identification, event and failure quantification, predictive modeling, risk characterization) are input into the six part functionality mathematical model capable of performing scenario and Monte Carlo simulation. Tested against the Tiffany Field coal several risks for CO<sub>2</sub> leakage were identified. Predictive quantitative modeling shows that elevated pressure from N<sub>2</sub> injection caused coal fractures to extend from the injectors to producers. The risk of early gas (N<sub>2</sub> and CO<sub>2</sub>) breakthrough and elevated cut are predicted to increase if injection wells are placed within three miles of an outcrop. The geomechanical study for the Tiffany Field (provided by LBNL), highlights the importance of pressure effects on rock and fault stability over the entire field history (coal dewatering, methane production, N<sub>2</sub> injection, CO<sub>2</sub> injection). Further testing of the model on other CO<sub>2</sub> storage venues and benchmarking will demonstrate the broader applicability of the methodology.

**The two independent developed risk assessment methodologies are based on the same principals but differ in details and initial application. The significance of testing done to date is that leakage in a typical clastic aquifer appears unlikely (TNO) and that natural and engineered elements of the storage system that present a leakage hazard can be identified and thus redesigned. An important validation of the SMV and other methodologies will come with the formal benchmarking exercises planned under the auspices of IEA GHG.**

#### *Leakage Scenarios and Remediation Strategies (LBNL-B2, LBNL-O, GTI)*

Development of leakage scenarios, early detection technologies and remediation strategies will prove essential in the siting and deployment of CO<sub>2</sub> storage facilities. The SMV program made progress on systematically addressing these issues through two LBNL studies (Hepple, Oldenburg) and lessons learned from the GTI (Perry) review of natural gas storage technologies.

The LBNL (Hepple) study outlines possible leakage scenarios from CO<sub>2</sub> storage sites via damaged injection wells and over-pressured reservoirs and the consequences of leakage, namely ground- and surface water contamination, vadose zone accumulation and surface releases. Remediation options are available from the natural gas storage, oil and gas production, groundwater / vadose zone treatment industries. HSE consequences of leaks are important for large leaks but also for persistent small leaks that might cause CO<sub>2</sub> accumulation in low lying areas and into occupied structures. The coupled model developed by LBNL (Oldenburg) simulates CO<sub>2</sub> flow in the shallow subsurface and atmosphere. When CO<sub>2</sub> concentrations in the near subsurface are high (either by primary seepage or CO<sub>2</sub> infiltration as a dissolved component of rainwater), surface layer winds act to rapidly disperse the CO<sub>2</sub> in the flux cases simulated.

**The near surface and atmosphere seepage simulations and contingency planning for remediation will play an important role in stakeholder acceptance of CO<sub>2</sub> storage. The most relevant industrial analog, natural gas storage, has developed tools (shallow gas recycling, aquifer pressure control, cap rock sealing) that are variously applicable to CO<sub>2</sub> storage but require further development. Additional remediation approaches should be sought or developed.**

#### *Regulator, NGO and Public Acceptance (LBNL-B1, MSCI, GTI)*

The early SMV study by LBNL (Benson) examined HSE issues relevant to CO<sub>2</sub> handling and put into perspective the experiences of potential industrial analogs to CO<sub>2</sub> storage (oil production by CO<sub>2</sub> EOR, acid gas disposal, nuclear waste repository development, deep well hazardous waste injection). Based on



this work, several SMV program studies were contracted to develop risk assessment methods and more closely examine industrial analogs.

The HSE lessons learned from industrial analogs study by LBNL (Benson) concluded that: 1) there is an abundant base of experience to draw on that is relevant and suggests that CO<sub>2</sub> can be stored safely, 2) the health effects of exposure to elevated concentrations of CO<sub>2</sub> are well understood and occupational safety regulations are in place for safe use, 3) the hazard depends more on the nature of release rather than the size of release, 4) experience from industrial analogs predicts the biggest risks from CO<sub>2</sub> storage and 5) regulatory paradigms and approaches vary and none address all of the issues that are important for CO<sub>2</sub> storage. These findings are elaborated upon with examples and needs for further research.

A set of potentially relevant industrial analogs to CO<sub>2</sub> storage were examined in the SMV program. In the CO<sub>2</sub> EOR experience survey by NMT (Grigg), it is evident that CO<sub>2</sub> leakage monitoring is not a perceived need. Anecdotally, this may result from the absence of fatalities attributed to CO<sub>2</sub> leakage over the 30+ years of CO<sub>2</sub> EOR operation. The nuclear waste disposal analog study by MSCI (Stenhouse) addresses protocols for site characterization and public involvement. Although the public perception of CO<sub>2</sub> storage is likely to be much more benign than that of nuclear waste disposal, the general principals are clearly relevant. The natural gas storage experience should reflect well on CO<sub>2</sub> storage as its safety record is excellent. CO<sub>2</sub> storage may in several respects be considered a mild analog to natural gas storage as CO<sub>2</sub> is not flammable (although it is harmful at high concentrations) and its high solubility allows better retention in aqueous systems. The siting (deeper and away from populated areas) and characterization (more thorough and confirmed by simulations) standards for CO<sub>2</sub> storage are also likely to be more rigorous.

Environmental issues associated with CO<sub>2</sub> storage were not extensively studied in the SMV program as these are generally well understood. One study conducted by Princeton University (Onstott), however, address the effect of CO<sub>2</sub> on subsurface microbial ecosystems. The known distribution of metabolic classes of microbes with depth was noted and a forward model was developed to predict their relative activities under CO<sub>2</sub>-rich conditions. The results demonstrated that growth of various microbial species (many of which have yet to be identified) will be impacted by CO<sub>2</sub> injection. More importantly for CO<sub>2</sub> storage operations, however, are the potential impact on reservoir quality (e.g., porosity) and conformance.

**The HSE-related studies comprise the basis for pre -injection characterization of risk, optimal injection operations and post-project abandonment. By openly communicating with regulators, NGOs and the public, critical issues identified can be addressed to advance the case for CO<sub>2</sub> storage.**

## 2.1 Risk Assessment and Analysis

### Task - 4.5 Risk Assessment and Mitigation Options

#### 2.1 Risk Assessment

The SMV risk assessment studies have evolved from earlier “lessons learned” analyses of natural and industrial analogs to scenario development and modeling of specific elements of systems to whole system comprehensive methodologies.

#### *Comprehensive and Multi-Compartment Methodologies (TNO, INEL, LBNL)*

TNO (Wildenborg) has developed a comprehensive methodology for long-term safety assessment of underground CO<sub>2</sub> storage (SAMCARDS) that is available for application. The three basic components of the methodology are: 1) scenario analysis which includes a comprehensive inventory of risk factors, or FEPs (features, events and processes) that are selected as appropriate to a given venue, 2) model development which enables a quantitative safety assessment in the 3) consequence analysis. A performance assessment (PA) model based on the large number of simulations with physical models comprised of multiple compartments has been developed. The PA model is capable of a statistical analysis that predicts CO<sub>2</sub> concentrations and fluxes into the biosphere, and therefore established whether or not they are likely to exceed acceptable levels. The methodology has been applied to a reference scenario (combined on-and offshore case, The Netherlands) and two leakage scenarios (well and fault leakage). The scenarios were run without mitigation efforts and therefore represent worst case scenarios. The results showed that seepage of CO<sub>2</sub> to the biosphere would not occur in the 10000 year timeframe simulated (this was true for all 1000 parameter realizations considered) so statistical analysis was not necessary. The SAMCARDS approach to risk assessment is comprehensive and flexible in terms of applicable scenarios and the quantity of data needed. Further development of the surface (hydrosphere and atmosphere) components and benchmarking with other risk assessment models will improve its reliability and acceptance by regulators, NGOs and the public.

INEL (Wo) has developed a mathematical model for probabilistic risk assessment for the Tiffany Field, CO which is presently under N<sub>2</sub> flood for enhanced coal bed methane (ECBM) production. The risk assessment methodology includes four major elements (hazard identification, event and failure quantification, predictive modeling, risk characterization) and the mathematical model includes six functional constituents (initiators, processes, failure modes, consequences, indicators and inference queries). To demonstrate the applicability of the methodology and model, a prototype application, capable of performing scenario and Monte Carlo simulations, was developed in Microsoft Access<sup>TM</sup>. The geomechanical study revealed processes that lead to risks of developing leakage paths at each step of CO<sub>2</sub> storage in coal beds. It was found that risk of leakage is higher for old wells that were converted to injectors and that the most likely mechanism of leakage path formation is slip on preexisting discontinuities cross-cutting coal seams. Predictive quantitative modeling demonstrates that elevated pressure resulting from N<sub>2</sub> injection caused the coal fractures on the preferred permeability trends to expand and extend from injectors to producers. The risk of early gas (N<sub>2</sub> plus CO<sub>2</sub>) breakthrough and high non hydrocarbon gas cut during gas injections are increased if CO<sub>2</sub> injection is placed within three miles of an outcrop. The importance of evaluating the effects of processes employed prior to CO<sub>2</sub> injection (e.g., coal bed depressurization and dewatering, N<sub>2</sub> injection) on CO<sub>2</sub> movement is highlighted. Further testing of the methodology on additional, candidate CO<sub>2</sub> storage venues and benchmarking with other risk assessment models will strengthen the application and make it more universally accepted by regulators and the public.

A coupled modeling framework has been developed by LBNL (Oldenburg) to simulate CO<sub>2</sub> leakage and seepage in the subsurface and atmosphere for risk characterization. The methodology and structure of the

coupled modeling framework are based on the concepts that 1) the primary HSE risk is in the near-surface where humans, animals and plants live, 2) that leakage and seepage flow process are coupled and 3) the main risk drivers are CO<sub>2</sub> flux and concentration. The coupled model framework is built on integral finite difference multiphase and multi-component reservoir simulator (TOUGH2) and models CO<sub>2</sub> and air in both subsurface and atmospheric surface-layer regions simultaneously. The model is demonstrated for a coupled subsurface-surface layer system and shows that seeping CO<sub>2</sub> can reflux into the subsurface as a dissolved component in infiltrating rainwater. Whereas CO<sub>2</sub> concentrations in the subsurface might be high, surface layer winds act to reduce CO<sub>2</sub> concentrations via dilution to low levels for the fluxes investigated (e.g., the Rio Vista area which is characterized by strong persistent winds). High CO<sub>2</sub> levels persisting in the vadose zone, however, are a threat to ecosystems and for humans occupying poorly ventilated, low lying structures. The coupled subsurface-surface leakage and seepage modeling framework is likely to attract the attention of stakeholders in proposed CO<sub>2</sub> storage projects as the behavior of CO<sub>2</sub> at the surface is of the most immediate concern.

#### *Mitigation and Remediation (LBNL)*

Early detection and remediation of CO<sub>2</sub> leakage from storage sites is an understudied topic that LBNL (Hepple) has addressed. The objective of this scoping study was to identify 1) monitoring approaches for early detection of CO<sub>2</sub> leakage, 2) remediation options that could be used to eliminate or manage risks after leakage has been detected and 3) additional information and R&D necessary to develop new remediation approaches. Scenarios for CO<sub>2</sub> leakage from storage sites include damaged injection wells, over-pressured reservoirs and accumulation in groundwater. The consequences of leakage include groundwater and surface water contamination by acidification and toxic element mobilization, vadose zone accumulation and surface releases. Remediation options applicable to leaking CO<sub>2</sub> storage projects are available from natural gas storage, oil and gas production, groundwater remediation and soil gas / vadose zone clean up experience. HSE concerns become relevant for large leaks but also for chronic small leaks that may accumulate CO<sub>2</sub> in structures. The study establishes a framework from which CO<sub>2</sub> leakage scenarios can be developed for specific storage sites and outlines available versus needed technologies necessary to manage such leaks and lessen their consequences. A site-specific plan that includes such contingencies will be essential for acceptance of CO<sub>2</sub> storage by NGOs, regulators and the public.

#### *Environmental / Regulatory / Public Perception (LBNL, MSCI, Princeton)*

LBNL (Benson) produced a comprehensive compendium of information relevant to CO<sub>2</sub> sequestration (directly or by analog) via experiences with deep well injection of industrial wastes, natural gas storage, geologic repositories for nuclear waste and other information. Human health and ecosystem responses to various levels of CO<sub>2</sub>, which are the most immediate concerns associated with CO<sub>2</sub> capture, transportation, injection and leakage, are also addressed. The lessons learned:

- 1) There is an abundant base of experience to draw on that is relevant and suggests that CO<sub>2</sub> can be stored safely (natural gas storage, SCUBA, deep injection of liquid and hazardous waste, enhanced oil recovery),
- 2) The health effects of exposure to elevated concentrations of CO<sub>2</sub> are well understood and occupational safety regulations are in place for safe use (confined spaces, SCUBA, transportation, food additive, pipeline transportation),
- 3) The hazard depends more on the nature of the release rather than the size of the release (volcanic eruptions, ecosystem fluxes, fire suppression, limnic releases),
- 4) Experience from industrial analogs predicts that the biggest risks from CO<sub>2</sub> storage (leakage from poor quality or aging injection wells, leakage up abandoned wells, leakage through poorly characterized cap rocks, inconsistent or inadequate monitoring) and

- 5) Regulatory paradigms and approaches vary and none address all of the issues that are important for CO<sub>2</sub> storage (leakage between geologic units, performance versus practice based requirements, state versus federal regulatory oversight, short versus long- term monitoring).

Recommendations for risk management approaches include development of a single set of consistent regulations, identification and investigation of the effectiveness of multi-barrier concepts, develop well completion, abandonment procedures and methods and develop a risk management strategy that couples monitoring requirements with performance confirmation. Risk mitigation and remediation methods should also be developed. The “lessons learned” study was an early SMV contribution that guided selection of subsequent risk assessment projects.

The “lessons learned” study by Monitor Scientific (MSCI) examined the relevance to CO<sub>2</sub> storage of past efforts towards nuclear waste disposal. Details of the siting, permitting and installation process, completed to various extents in six countries, were examined. The assessment found that conducting risk assessment, engaging with the public in a transparent manner and gas migration studies are most relevant of the lessons learned to CO<sub>2</sub> storage. Although the potential hazard levels associated with CO<sub>2</sub> storage are not in the same league with that of high level nuclear waste disposal, this detailed study is very perceptive. Recommendations to avoid pitfalls in project development are detailed and sound. There is also a good technical review of gas migration.

The objective of the study by Princeton University (Onstott) was to assess potential impacts of CO<sub>2</sub> injection on subsurface organisms. The deep biosphere extends to ~3.5 km with decreasing number of organisms with depth. These organisms are primarily by methanogens, sulfur reducers, fermentative anaerobes. Genetic testing (16S rDNA) suggests that only about one third of these subsurface organisms have been identified. By defining microbial assemblages and determining “microbial power” (free energy of redox reactions and availability of nutrients) a forward model is used to predict the impact of CO<sub>2</sub> injection on microbes in different environments (reservoir lithologies, ground water types) over three reservoir temperatures and constrained pCO<sub>2</sub> and pH/Eh. Fe (III) reducers and fermentative anaerobes are not favored by the presence of CO<sub>2</sub> but there is an increase in methanogenesis and acetogenesis. Considering chemical changes induced by CO<sub>2</sub> presence and microorganism response, several implications to CO<sub>2</sub> storage operation and performance are noted. In general, the impact on microorganism growth in carbonate systems is expected to be most significant. Dolomitic systems may increase in porosity by 0.3%. For clastic systems of any given salinity, a 20% reduction in porosity might result (precipitation of clays such as kaolinite). This study, originally commissioned to address NGO concerns, identified important CO<sub>2</sub> storage performance issues such as porosity changes, methane gas production and bacterial growth near gas water contacts.

## 2.1.1 Safety Assessment Methodology for Carbon Dioxide Sequestration (SAMCARDS)

Task - 4.5 - Risk Assessment and Mitigation Options

Principal Investigator: Ton Wildenborg

Technology Provider: TNO-NITG

### Highlights

- An *overall* methodology for long-term safety assessment of underground CO<sub>2</sub> sequestration has been developed and can be readily applied. The three individual basic components of the method, i.e. scenario analysis, model development and consequence analysis, were developed and tested successfully.
- Detailed *process models* have been constructed for the different earth / atmosphere compartments. Simplifications of these models have been made using results obtained with the full-scale detailed models. These simplified models gave results in terms of CO<sub>2</sub> fluxes comparable to the fluxes obtained with the detailed models. Carrying out Monte Carlo simulations with the simplified compartment models did not pose major problems.
- The methodology has been applied to a reference scenario (combined on- and offshore case) and two leakage scenarios, i.e. a well leakage and a fault leakage scenario. The leakage scenarios were run without mitigation measures and therefore represent worst case scenarios. The results for the reference scenario showed that seepage of CO<sub>2</sub> to the biosphere would not occur within the period simulated (10,000 years). This was true for all (1000) parameter realisations considered. Statistical analysis was therefore not necessary. For both the well leakage and the fault leakage scenarios, CO<sub>2</sub> concentrations and fluxes showed a large variation as a result of parameter uncertainty in the compartment models.

### Summary

The objective of the project Safety Assessment Methodology for Carbon Dioxide Sequestration (SAMCARDS), conducted by TNO-NITG of the Netherlands, was to develop a methodology and computational tools for HSE risk assessment of geological CO<sub>2</sub> sequestration in various geological media of the North Sea region. The main deliverable, consisting of risk assessment method and computational tools, will be suitable for site-specific assessment of geological sequestration projects, in particular storage in an offshore aquifer and storage in an onshore gas field. The methodology was to be applied in a generic performance assessment of two European sequestration scenarios, one defined by CCP JIP and one introduced by TNO-NITG. The results of the generic safety assessment will provide building blocks for site characterization, risk mitigation, remediation and monitoring of the storage facility. The two scenarios were originally an onshore depleted gas field in the Netherlands and an offshore aquifer trap in the SW UK sector of the North Sea. As a result of budget cuts, these two scenarios differ only in the impacts in the biosphere.

The developed methodology consists of three main parts

- scenario analysis
- model development
- consequence analysis

The *scenario analysis* is focused on a comprehensive inventory of risk factors (Features, Events and Processes or FEPs) and subsequent selection of the most critical factors that will be grouped into discrete CO<sub>2</sub> leakage scenarios. *Models* developed will enable a quantitative safety assessment of the scenarios in the *consequence analysis*. At the very beginning of the safety assessment, the *assessment basis* should be

defined. It sets the scope of the assessment through determination of the safety criteria, the concept and the setting of the sequestration facility.

A scenario describes a potential future state or evolution of the sequestration facility that could lead to leakage of CO<sub>2</sub>. A scenario element refers to a specific spatial compartment of the sequestration domain, like reservoir, seal overburden or biosphere and the risk factors that operate in a compartment. A dedicated database of more than 600 individual risk factors or FEPs has been developed in SAMCARDS. The database is the starting-point for ranking and screening of the FEPs in different categories, viz. likely to occur, uncertain to occur or irrelevant. The FEPs may be grouped into scenario-elements, which in turn can be assembled into discrete scenarios. Tools have been developed to analyze the FEPs in terms of interactions, relations and grouping, which is required for assembling them consistently into discrete scenarios. However, even though these tools are a necessity, analysis of the FEPs and grouping them into scenario defining elements cannot be done without expert judgment.

Physical models for the different compartments have been developed. These models include geomechanics, geochemistry and the marine biosphere. An atmospheric compartment that was originally planned was omitted due to budget cuts. It is included in another CCP Risk Assessment (RA) project by Lawrence Berkeley National Laboratory (LBNL). Coupling of the models is through calculated CO<sub>2</sub> fluxes. In order to be able to account for parameter uncertainty in these models, simplified versions had to be developed to allow for Monte Carlo simulations. Results of the Monte Carlo simulations in terms of CO<sub>2</sub> concentrations as a function of space and time have been defined approximately to minimise the amount of data needing analysis. Sensitivity analyses were carried out to identify the main dimensionless parameters that control the transport of CO<sub>2</sub> to the biosphere.

A Performance Assessment (PA) model based on the results of a large number of simulations with the physical models for the different compartments has been developed. The PA model is capable of a statistical analysis of CO<sub>2</sub> concentrations and fluxes in the biosphere, and is therefore able to predict probabilities of CO<sub>2</sub> concentrations and fluxes to exceed certain standards. This allows a detailed analysis of the consequences in terms of risks to human health and the environment, of failure of the containment of CO<sub>2</sub> stored in the deep subsurface.

Other RA methods are also available, including FEP databases. Benchmarking of these methods and integration of the databases (e.g. Weyburn and CO<sub>2</sub>CRC), as well as placing the common database on a public web-site (IEA Greenhouse Gas R&D Programme) is desirable and should be considered for further work. This could lead to the development of a standard/guideline for risk assessment and, ultimately, for underground CO<sub>2</sub> storage.

The SAMCARDS approach to risk assessment is comprehensive and flexible in terms of applicable scenarios and the quantity of data needed. Further development of the surface (hydrosphere and biosphere) components and benchmarking with other RA models will improve its reliability and acceptance by regulators, NGOs and the public.

## **Publications**

- Kreft, E., P.J.P. Egberts, A.F.B. Wildenborg and F. van Bergen (2003). Risk Assessment using FEPs, no 1540, EAGE Conference, Stavanger.
- Wojcik, R. and Torfs, P. (2003a) Fitting multidimensional Parzen densities with the use of a Kullback-Leibler penalty. Journal of the American Mathematical Society.
- Wojcik, R. and Torfs, P. (2003b) Manual for the use of the PARDENS tool. Wageningen University and Research Centre

- CCP workshop in Potsdam, October 31, 2001: Safety Assessment Methodology for Carbon Dioxide Sequestration (SAMCARDS)
- Risk Assessment Workshop in Nottingham, May 29, 2002: SAMCARDS
- CCP workshop in Santa Cruz, CA, October 22, 2002: SAMCARDS Status and outlook.
- Expert seminar on Building a Common FEP Database, London February 25, 2003: SAMCARDS FEP Database Activities
- CCP workshop in Dublin, Ireland, September 22-24, 2003: SAMCARDS.
- The final project report is in Appendix A under the same heading as this report.

## 2.1.2 Probability Risk Assessment Methodology for CO<sub>2</sub> Injection into Coalbeds

### Task - 4.5 - Risk Assessment And Mitigation Options

Principal Investigators: Jenn-Tai Liang and Shaochang Wo

Technology Provider: INEEL

### Highlights

- A mathematical model for probabilistic risk assessment of CO<sub>2</sub> storage in coal beds was developed. To demonstrate the applicability of this model, a prototype application was developed. The application is capable of performing scenario simulations and Monte Carlo simulations.
- The geomechanical study revealed processes that lead to risks of developing leakage paths for CO<sub>2</sub> at each step in the process of CO<sub>2</sub> sequestration in coal beds. Risk of leakage is higher for old wells that are converted to injectors. The most likely mechanism for leakage path formation is slip on pre-existing discontinuities cross cutting coal seams.
- Predictive quantitative modeling demonstrates that elevated pressure resulting from N<sub>2</sub> injection caused the coal fractures on the preferred permeability trends to expand and extend from injectors to producers. The risk of early inert gas (N<sub>2</sub> plus CO<sub>2</sub>) breakthrough and high inert gas cut during gas injections are increased if CO<sub>2</sub> injection is placed within a three miles of an outcrop.

### Summary

To evaluate the geomechanical issues in CO<sub>2</sub> sequestration in coal beds, it is necessary to review each step in the project development process and evaluate potential geomechanical impacts. Wellbore stability is a geomechanical problem that can be encountered during drilling of the well. Weak shale and coal layers, overpressure, and fault zones are common vulnerabilities. Rock failure and displacements associated with wellbore instability generate potential leakage paths in the vicinity of the well. Risks of leakage are much higher for open cavity completions than for cased well completions. Careful selection of fracturing technology for well completion that takes into account specific coal properties should minimize the risk of propagating hydrofractures. Techniques to monitor fracture height need further development.

The processes of depressurization during dewatering and methane production, followed by repressurization during CO<sub>2</sub> injection, lead to risks of leakage path formation by failure of the coal and slip on discontinuities in the coal and overburden. The most likely mechanism for leakage path formation is slip on pre-existing discontinuities which cut across the coal seam. The relationship between the amount of slip and the increase in flow (if any) along a discontinuities needs further development.

The focus of quantitative modeling (simulation) was placed on a sensitivity study of key coal reservoir properties and CO<sub>2</sub> seepage from outcrops. The main conclusions from this simulation study are:

- Reservoir models that match the primary production history may not be accurate in forecasting CO<sub>2</sub> or N<sub>2</sub> injection because of the response of coal structure to gas injection.
- The simulated early inert gas (N<sub>2</sub> plus CO<sub>2</sub>) breakthrough and high inert gas cut during future gas injections suggests that the future gas injection and CO<sub>2</sub> sequestration may be restricted to only one third of the total available pay.
- Isotherm data are the most important data in coalbed methane related simulations. Laboratory measured isotherms on dry coals should be rescaled by matching field history performance. Without rescaling, the simulation forecast of CO<sub>2</sub> or N<sub>2</sub> injection may not be accurate.
- Any CO<sub>2</sub> injection within three miles of outcrop should be considered with high risk.



Assuring environmental acceptability and safety is an essential prerequisite for the selection of a potential CO<sub>2</sub> storage in coalbeds as well as in other geological traps. Conceptual and descriptive risk characterization is necessary and helpful in providing the baseline for quantitative risk assessments. Probability-based risk assessment is considered to be one of the most effective methods for dealing with uncertainties and the nature of stochastic phenomena.

The risk assessment methodology developed in this project includes four major elements: hazard identification, event & failure quantification, predictive modelling, and risk characterization.

A mathematical model for probabilistic risk assessment was developed. The model consists of six functional constituents: initiators, processes, failure modes, consequences (effects), indicators, and inference queries. Features of the model include generality and transparency, design for implementation on a relational database, inference rules that can be converted to and verified by set operations, and quantified indicators as model outputs. To demonstrate the applicability of the mathematical model, a prototype application was developed in Microsoft Access. The application consists of several modules that reside in the database as functional combinations of tables, forms, and stored procedures. An intuitive main user interface and its pop-up interfaces are created to facilitate the data input and risk assessment process. The application can perform both scenario simulations and Monte Carlo simulations.

Other RA methods are also available, including FEP databases. Benchmarking of these methods and integration of the databases (e.g. Weyburn and CO<sub>2</sub>CRC), as well as placing the common database on a public web-site (IEA Greenhouse Gas R&D Programme) is desirable and should be considered for further work. This could lead to the development of a standard/guideline for risk assessment and, ultimately, for underground CO<sub>2</sub> storage.

### **Publications**

- S. Wo and J.-T. Liang, (2004) "Simulation Assessment of N<sub>2</sub>/CO<sub>2</sub> – Coal Contact Volume and Its Impact on Outcrop Seepage in N<sub>2</sub>/CO<sub>2</sub> Injection to Enhance Coalbed Methane Recovery," To be presented at the SPE/DOE Fourteenth Symposium on Improved Oil recovery, April 17-21, Tulsa, Oklahoma.
- Coal-Seq II Forum, 2003, Methodology for Conducting Probabilistic Risk Assessment of CO<sub>2</sub> Sequestration in Coal Beds. Washington D.C. (March 6-7)
- CCP workshop in Potsdam, October 31, 2001: Methodology for Conducting Probabilistic Risk Assessment of CO<sub>2</sub> Storage in Coal Beds.
- Risk Assessment Workshop in Nottingham, May 29, 2002: Methodology for Conducting Probabilistic Risk Assessment of CO<sub>2</sub> Storage in Coal Beds.
- CCP workshop in Santa Cruz, CA, October 22, 2002: Methodology for Conducting Probabilistic Risk Assessment of CO<sub>2</sub> Storage in Coal Beds.
- CCP workshop in Dublin, Ireland, September 22-24, 2003: Methodology for Conducting Probabilistic Risk Assessment of CO<sub>2</sub> Storage in Coal Beds.
- The final project report for this project is in Appendix A under the same heading as this summary.

## 2.1.3 HSE Risk Assessment of Deep Geological Storage Sites

Task - 4.5 - Risk Assessment and Mitigation Options

Principal Investigator: Curt Oldenburg

Technology Provider: LBNL

### Highlights

The injection of carbon dioxide (CO<sub>2</sub>) into deep geologic carbon sequestration sites entails the risk that CO<sub>2</sub> will leak away from the primary storage target formation and migrate upwards where it can seep out to the near-surface or atmosphere. A coupled modeling framework has been developed for simulating CO<sub>2</sub> leakage and seepage in the subsurface and in the atmospheric surface layer for risk characterization. The results of model simulations can be used to quantify the two key health, safety, and environmental (HSE) risk drivers, namely CO<sub>2</sub> seepage flux and near-surface CO<sub>2</sub> concentrations.

- The methodology and structure of the coupled modeling framework are based on the concepts that (1) the primary HSE risk is in the near-surface environment where humans, animals, and plants live, (2) leakage and seepage flow processes are coupled, and (3) the main risk drivers are CO<sub>2</sub> flux and concentration.
- The coupled modeling framework is built on the integral finite difference multiphase and multicomponent reservoir simulator TOUGH2 and models CO<sub>2</sub> and air in both subsurface and atmospheric surface-layer regions simultaneously.
- The model is demonstrated for a coupled subsurface–surface-layer system and shows that seeping CO<sub>2</sub> can reflux into the subsurface as a dissolved component in infiltrating rainwater. Whereas CO<sub>2</sub> concentrations in the subsurface are high, surface-layer winds reduce CO<sub>2</sub> concentrations to low levels for the fluxes investigated.

### Summary

A coupled modeling framework for modeling CO<sub>2</sub> fluxes and concentrations for risk characterization has been demonstrated. This work is relevant and important to the development of geologic carbon sequestration because it provides a rigorous modeling capability for simulating CO<sub>2</sub> flow and transport from the deep CO<sub>2</sub> storage site all the way to the atmosphere. The approach is built on the assumption that the near-surface environment is the main region in which HSE risks will arise. In this region, CO<sub>2</sub> flux and concentration are the main risk drivers. The coupled model handles subsurface and atmospheric surface-layer flow and transport assuming that dispersion in the surface-layer is passive and that the wind is described by a logarithmic velocity profile.

Model results show limited unsaturated zone attenuation of leakage flux, with correspondingly large CO<sub>2</sub> concentrations possible in the shallow subsurface. These results show that if leakage leads to CO<sub>2</sub> migrating as far as the vadose zone, high CO<sub>2</sub> concentrations can occur in the root zone of the shallow subsurface with potentially harmful effects on plants, as well as on humans or other animals in poorly ventilated subsurface structures such as basements.

Coupled subsurface–surface-layer demonstration simulations show the large degree of dilution that occurs in the surface layer, and the possible reflux of CO<sub>2</sub> to the subsurface that occurs when CO<sub>2</sub> dissolves in infiltrating rainwater. Although no leakage of stored CO<sub>2</sub> would be expected at the Rio Vista Gas Field given its record of natural gas accumulation and production, preliminary application of the model to the site

under an assumed seepage scenario suggests that the high and steady winds at Rio Vista are a very favorable feature insofar as they have the potential to disperse CO<sub>2</sub> seepage flux

## Reports and Publications

- Oldenburg, C.M., A.J.A. Unger, R.P. Hepple, and P.D. Jordan, On Leakage and Seepage from Geologic Carbon Sequestration Sites, Task 1 Report, Lawrence Berkeley National Laboratory Report *LBL-51130*, July 2002a.
- Oldenburg, C.M., T.E. McKone, R.P. Hepple, and A.J.A. Unger, Health Risks from Leakage and Seepage of CO<sub>2</sub> Sequestered in the Subsurface: Requirements and Design of a Coupled Model for Risk Assessment, Task 2 Report, Lawrence Berkeley National Laboratory Report *LBL-51131*, July 2002b.
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- Oldenburg, C.M., and A.J.A. Unger, Coupled Modeling Framework for CO<sub>2</sub> Leakage and Seepage Risk Assessment, Task 4 Report, Lawrence Berkeley National Laboratory Report *LBL-53009*, June 2003b.
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- Oldenburg, C.M., and A.J.A. Unger, Coupled subsurface-surface layer gas transport and dispersion for geologic carbon sequestration seepage simulation, Proceedings of the TOUGH Symposium 2003, Lawrence Berkeley National Laboratory, May 12–14, 2003, and Lawrence Berkeley National Laboratory Report *LBL-52477*, May 2003a.
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- Oldenburg, C.M., and A.J.A. Unger, Coupled subsurface-surface layer gas transport and dispersion for geologic carbon sequestration seepage simulation, *Vadose Zone Journal*, submitted, 2003d.

## **2.1.4 Synthesis Of Nuclear Waste Disposal Experience**

**Task - 4.1 Understanding Geologic Storage**

**Task - 4.5 Risk Assessment and Mitigation Options**

**Principal Investigator: Mike Stenhouse**

**Technology Provider: Monitor Scientific**

### **Highlights**

- The experience of efforts to site, evaluate and deploy high level nuclear waste disposal in six countries is documented with elements relevant to a much less potentially hazardous process, CO<sub>2</sub> storage, highlighted.
- A well-planned risk assessment, openly communicated to the public, is cited as critical to acceptance of nuclear waste disposal and, by extension, geological CO<sub>2</sub> storage. The key technical issue that needs to be addressed in planning for CO<sub>2</sub> storage is gas migration.

### **Summary**

The study detailed the approach and results in six countries where attempts have been made to site, assess and deploy nuclear disposal sites. Elements of these efforts parallel the situation likely to be encountered in future geological CO<sub>2</sub> storage projects but are likely to differ in detail and the level of technical rigor necessary and are less controversial as the handling of CO<sub>2</sub> is recognized as much less of a potential threat to humans and ecosystems.

Performance / Safety Assessment (PA) aims to demonstrate the suitability or acceptability of a site for radioactive waste disposal (i.e., demonstration of the required isolation requirement). Applications of PA include concept development, siting criteria, repository design, site characterization, system optimization and licensing (each with necessary research priorities). PA calculations require appropriate input (source team) defining the nature and quantity of the hazardous component. The output from the calculations is in the form of suitable 'end-points' which are relevant to the system being modeled. In the nuclear disposal case, a common end-point is the maximum dose, per radionuclide, to a member of the critical group (maximally exposed subset of the population). The way PA is carried out can be affected by certain considerations, and these considerations are also relevant to CO<sub>2</sub> sequestration: the underlying regulations which may drive assessment, end-points to be evaluated, timescales to be considered and the target audience for assessment results. Various approaches and techniques are available for organizing and analyzing information for repository PAs. A general theme, however, is the need to follow a systematic procedure in order to develop a defensible train of argument. The main components of a comprehensive assessment (some of which can be omitted or reduced in scope depending on the purpose of assessment) are: scenario development, conceptual model development, mathematical model development, uncertainty and sensitivity analysis and confidence building. The processes associated with these assessment elements and how and where they have been applied are discussed in detail in the report. Some of the points about scenario development that have relevance to public perception issues are listed below (NEA, Nuclear Energy Agency, 1991) are:

- Take a broad perspective
- Provide a logical and consistent framework which can encompass alternative methodologies and regulations.
- Document the reasons for analyzing some scenarios in detail and rejecting others in an understandable and traceable way.
- Allow the judgment and reasoning power of experts and generalists to be integrated with more quantitative considerations.

- Involve people with a wide variety of expertise.
- Provide a systematic way of compiling a comprehensive list of potentially important events, features and processes.
- Result in a manageable number of representative scenarios through a well-define screening procedure.
- Be a practical tool rather than just an intellectual framework.
- Be of use to regulators and developers, and be communicable to decision makers and the public.

In addition to the assessment process and public perception experiences described, included in the report is a technical assessment of gas migration phenomena develop applicable to CO<sub>2</sub> sequestration.

### **Reports and Publications**

- The final project report was attached in Appendix A of an earlier report.

## 2.1.5 Reactive Transport Model: Caprock Integrity

Task - 4.1 - Understanding Geologic Storage

Principal Investigator: Jim Johnson

Technology Provider: LLNL

### Highlights

Reactive transport modeling was used to predict long-term cap rock integrity during natural and engineered CO<sub>2</sub> storage:

- A new interface between LLNL's reactive transport simulator (NUFT) and distinct-element geomechanical model (LDEC) was developed.
- A series of integrated reactive transport and geomechanical simulations designed to evaluate the dependence of cap-rock integrity on key reservoir and CO<sub>2</sub>-influx parameters that distinguish natural and engineered storage sites was completed.
- A new conceptual framework that permits inter-comparison of geochemical and geomechanical contributions to long-term cap rock integrity was developed. This framework reveals that ultimate counterbalancing of geochemical and geomechanical effects is feasible, which suggests that shale cap rocks may *evolve* into effective hydrodynamic seals—in both natural and engineered storage sites—as a function of progressive geochemical alteration that attends some degree of initial CO<sub>2</sub> leakage. It further suggests that the secure cap rock of a given natural CO<sub>2</sub> accumulation may be incapable of providing an effective seal in the context of an engineered injection.
- Received the 2003 AAPG DEG (Division of Environmental Geosciences) “Best Paper—Oral Presentation” award for our abstract entitled “CO<sub>2</sub> reservoirs: are they natural analogs to engineered geologic storage sites?”, which was presented at the AAPG annual meeting.

### Summary

The objective was to assess the integrated effect of geochemical and geomechanical contributions to long-term cap rock integrity, which represents the single most important constraint on the long-term isolation performance of natural and engineered geologic CO<sub>2</sub> storage sites.

CO<sub>2</sub> influx that forms natural accumulations and CO<sub>2</sub> injection for EOR/sequestration or saline-aquifer disposal both lead to concomitant geochemical alteration and geomechanical deformation of the cap rock, enhancing or degrading its seal integrity depending on the relative effectiveness of these interdependent processes.

Using the reactive transport simulator (NUFT), supporting geochemical databases and software (SUPCRT92), and distinct-element geomechanical model (LDEC), it was shown that:

- Influx-triggered mineral dissolution/precipitation reactions within typical shale cap rocks continuously reduce microfracture apertures, while pressure and effective-stress evolution first rapidly increase then slowly constrict them.
- For a given shale composition, the extent of geochemical enhancement is nearly independent of key reservoir properties (permeability and lateral continuity) that distinguish saline aquifer and EOR/sequestration settings and CO<sub>2</sub> influx parameters (rate, focality, and duration) that distinguish engineered disposal sites and natural accumulations.
- In contrast, the extent of geomechanical degradation is highly dependent on these reservoir properties and influx parameters because they effectively dictate magnitude of the pressure perturbation; specifically, initial geomechanical degradation has been shown inversely proportional to reservoir permeability and lateral continuity and proportional to influx rate.

While the extent of geochemical alteration is nearly independent of filling mode, that of geomechanical deformation—which invariably results in net aperture opening for compartmentalized reservoirs—is

significantly more pronounced during engineered injection. This result limits the extent to which natural CO<sub>2</sub> accumulations and engineered disposal sites can be considered analogous.

## Reports and Publications

- Johnson, J.W., Nitao, J.J., Morris, J.P., 2004, Reactive transport modeling of long-term cap rock integrity during CO<sub>2</sub> injection for EOR or saline-aquifer storage, in CO<sub>2</sub> Capture Project Summary Volume 2: “Geologic Storage of Carbon Dioxide with Monitoring and Verification”, Benson S.M., ed. (in prep.).
- Johnson, J.W., Nitao, J.J., Morris, J.P., and Blair, S.C., 2003, Reactive transport modeling of geohazards associated with offshore CO<sub>2</sub> injection for EOR and geologic sequestration: *invited paper*, *Proceedings Offshore Technology Conference 2003*, Houston, TX, May 5-8, 2003, 9 p.
- Johnson, J.W., Nitao, J.J., and Morris, J.P., Reactive transport modeling of cap rock integrity during natural and engineered CO<sub>2</sub> storage: Seventh Intl. Conf. Greenhouse Gas Control Technologies, Vancouver, Canada, September 5-9, 2004 (abstract submitted December 31, 2003).
- Johnson, J.W., Nitao, J.J., and Morris, J.P., Reactive transport modeling of cap rock integrity during natural and engineered CO<sub>2</sub> sequestration: American Chemical Society National Meeting, New York, NY, September 7-11, 2003 (oral presentation).
- Johnson, J.W., Nitao, J.J., Blair, S.C., and Morris, J.P., CO<sub>2</sub> reservoirs: are they natural analogs to engineered geologic storage sites?: Special Session on Geological Sequestration of CO<sub>2</sub>, AAPG Annual Meeting, Salt Lake City, UT, May 11-14, 2003 (abstract and oral presentation). *NOTE: we received the 2003 AAPG DEG (Division of Environmental Geosciences) “Best Paper—Oral Presentation” award for this presentation.*
- Johnson, J.W., Nitao, J.J., and Morris, J.P., Reactive transport modeling of long-term cap rock integrity during CO<sub>2</sub> injection for EOR or saline-aquifer storage: Second National Conference on Carbon Sequestration, Alexandria, VA, May 5-8, 2003 (abstract and poster presentation).
- Johnson, J.W., Nitao, J.J., Blair, S.C., and Morris, J.P., Reactive transport modeling of geohazards associated with offshore CO<sub>2</sub> injection for EOR and geologic sequestration: Special Session on Geohazards (Fred Aminzadeh, organizer), Offshore Technology Conference 2003, Houston, TX, May 5-8, 2003 (invited abstract and oral presentation).
- Johnson, J.W., Nitao, J.J., and Morris, J.P., Reactive transport modeling to predict long-term cap-rock integrity, Third Annual JIP CO<sub>2</sub> Capture Project Workshop, Dublin, Ireland, Sep 22-24, 2003 (oral presentation).
- Johnson, J.W., Nitao, J.J., Blair, S.C., and Morris, J.P., Reactive transport modeling to predict long-term cap-rock integrity, JIP CO<sub>2</sub> Capture Project Workshop: “Leveraging the SMV Family of Technology Providers”, Santa Cruz, CA, Oct 21-23, 2002 (oral presentation).
- Johnson, J.W., Nitao, J.J., and Blair, S.C., Reactive transport modeling to predict long-term cap-rock integrity, JIP CO<sub>2</sub> Capture Project Workshop: “Building the SMV Family of Technology Providers”, Potsdam, Germany, Oct 31-Nov 2, 2001 (oral presentation).

## 2.1.6 Early Detection and Remediation of Leakage from CO<sub>2</sub> Storage Projects

**Principal Investigator: Sally M. Benson**

**Technology Provider: Lawrence Berkeley National Laboratory**

### Highlights

- Scenarios for CO<sub>2</sub> leakage from storage sites include damaged injection wells, overpressured reservoirs and accumulation in shallow groundwater. The effects of leakage include ground water and surface water contamination by acidification, vadose zone and soil gas accumulation and surface releases.
- Remediation options applicable to leaking CO<sub>2</sub> storage projects are available from natural gas storage, oil and gas production, groundwater remediation and soil gas / vadose zone clean up experience.
- HSE concerns become relevant for large leaks but also for chronic small leaks that may accumulate CO<sub>2</sub> into structures. Remediation plans for a range of eventualities are necessary for public assurance of CO<sub>2</sub> capture and storage efforts.

### Summary

The need for methods of early detection and remediation of leakage from CO<sub>2</sub> storage projects is a recurrent theme in discussions with environmental NGO's about the acceptability of geologic storage of CO<sub>2</sub> as an approach to carbon management. To date, little, if any, research has been done that addresses this concern. The purpose of this scoping paper is to identify 1) monitoring approaches for early detection of leakage, 2) remediation options that could be used to eliminate or manage risks after leakage has been detected and 3) additional information and R&D that is needed to develop the remediation approaches identified. The overarching goal of the study is to begin to develop approaches that can be used to manage human health and environmental risks to an acceptable level in the event that a storage project leaks. The approach taken in this study is as follows:

- Identify and develop the leakage scenarios and consequences that are most likely to occur in geologic storage projects (e.g. leakage up abandoned wells, leakage up undetected faults or fractures in the reservoir seal, etc...).
- Calculate a range of hypothetical leakage rates from prototypical storage projects, including those performing effectively and those leaking at unacceptable rates.
- Identify monitoring approaches that could be used for early detection of leakage in each of the scenarios (e.g. seismic imaging, satellite or air-borne imaging, surface IR detectors, etc...)
- Survey and document remediation practices currently used in natural gas storage, oil and gas production, groundwater and vadose zone remediation, dam construction and maintenance and acid gas disposal.
- Evaluate how and the extent to which existing remediation practices could be employed to remediate leakage in geologic storage projects.
- Identify potential new approaches for remediation of geologic storage projects for scenarios where existing remediation approaches are not sufficient.
- Identify additional knowledge or information needed to develop and build confidence in the effectiveness of new or improved remediation approaches.

This study established a framework from which CO<sub>2</sub> leakage scenarios can be developed for specific storage sites and outlines the available versus needed technologies needed to manage such leaks and remediate their possible effects. A site specific plan that includes such contingencies and their solution will be essential for acceptance by NGOs regulators and the public.



## **Reports and Publications**

- CCP-SMV 2003 Workshop, Dublin

## 2.1.7 Impact of CO<sub>2</sub> Injection On Subsurface Microbes and Surface Ecosystems

**Task - 4.1 - Understanding Geologic Storage**

**Technology Provider: Princeton University**

**Principal Investigator: T. C. Onstott**

### Highlights

Lab tests and calculations were made to evaluate the potential effects of injected CO<sub>2</sub> on microorganisms that might be present in the deep subsurface.

- Based upon the calculated potential microbial power for microbial redox reactions, the most readily identified impact of CO<sub>2</sub> injection was a reduction of pH in ground water by one unit in siliciclastic reservoirs. CO<sub>2</sub> injection should cause a short term stimulation of Fe(III) reducing communities.
- Dolomitic or carbonate aquifers may be more severely impacted by the CO<sub>2</sub> injection because the dissolution of the carbonate fails to restore the pH to a range the organisms can tolerate. Guidelines for choosing reservoirs where this will not occur are presented.
- Overall CO<sub>2</sub> injection should increase the availability of N and P to microbial communities.
- For shallow aquifers where organic acids are more abundant, the impact of CO<sub>2</sub> injection should be less pronounced.
- For long term sequestration of CO<sub>2</sub> in siliciclastic reservoirs, the short term enhancement of Fe(III) reducing microorganisms will increase the pH and most likely lead to the precipitation of various carbonates.

### Summary

Environmental assessment of subsurface CO<sub>2</sub> injection requires an understanding of impact on microbial communities both in the subsurface as well as surface. The project provides an estimate of the present-day distribution and composition of deep microbial communities using literature review and compilation of current research. Thermodynamic and kinetic modeling was used to project the outcome of CO<sub>2</sub> injection into these ecosystems. A variety of parameters including CO<sub>2</sub> concentration, carbonate versus clastic reservoirs, type of bacteria, and ground water salinity were varied to observe the outcome in a range of scenarios covering the possible locations for CO<sub>2</sub> injection being considered by the CCP Consortium. Organisms are known to exist at depths of at least 3.5 km, although the number of organisms per ml of groundwater becomes less with depth, as does their genetic diversity. In the deep subsurface, four physiological types or microbes dominate: methanogens, sulfate or sulfur reducing bacteria, fermentative anaerobes and Fe(III) reducing bacteria. Genetic testing is now capable of identifying such organisms and thus inferring their metabolic pathways. Based on the metabolic pathways, it appears that these communities are self sufficient in nutrient and energy resources so that they do not rely on growth substrates from the surface photosphere, but are biologically and chemically isolated.

Several potential effects of microbial populations favored by changed chemical regime are noted. For dolomitic systems, there can be a net increase in porosity of 0.3%. For low, moderate, and high salinity clastic systems, there can be a 20% reduction in porosity (clay precipitation such as kaolinite). Dolomitic reservoirs are more severely impacted by CO<sub>2</sub> injection – dissolution of aquifer minerals fails to restore pH. Injection of H<sub>2</sub> would stimulate CO<sub>2</sub> reduction in methanogens, raising the pH. During long term CO<sub>2</sub> sequestration, Fe(III) reducing microbes will increase the pH, precipitating carbonates. Microbial biomass may become concentrated at the gas/water boundary. For aquifers with high initial pH (8 or 9), injection of CO<sub>2</sub> and lowering of pH will make proton pumping reactions across the cell membrane more

favorable, enhancing microbial growth. (For aquifers that already have a lower pH, the impact is negligible.)

In addition to providing a basis for evaluating environmental effects of CO<sub>2</sub> injection, the study is useful for anticipating untoward reservoir engineering problems,

### **Reports and Publications**

- Tullis C. Onstott, Impact of CO<sub>2</sub> injections on Deep Subsurface Microbial ecosystems, CCP SMV International Meeting, Dublin, Ireland, September 21, 2003.
- The final project report is included in Appendix A until the same heading as this report.

## 2.2 Optimization

### Task - 4.1 - Understanding Geologic Storage

The SMV “optimization” studies aimed to realize operational efficiencies or cost savings that might make CO<sub>2</sub> storage a technical and economic success.

#### *Cost reduction in CO<sub>2</sub> capture, transportation and injection (BMI, UT, Reinertsen, IFE)*

The Battelle (Gupta) study on CO<sub>2</sub> impurities tradeoffs serves as a link between storage studies proper and those examining transportation and capture issues. The substantial cost savings potential in CO<sub>2</sub> capture of delivering CO<sub>2</sub> contaminated with impurities such as SO<sub>x</sub>, NO<sub>x</sub> and others (e.g., N<sub>2</sub>, O<sub>2</sub>, hydrocarbons, Hg) is balanced with potential operational complications and damage to surface facilities such as compressors, pipelines and injection systems. Absorption and regeneration characteristics of amines and other solvents used for CO<sub>2</sub> capture are adversely affected by acid gas impurities. Compression of gas mixtures may be complicated by the presence of higher boiling constituents, which may limit the ability to achieve adequate interstage cooling and may damage compressors and related processing equipment. Materials used in separation, compression and transmission are subject to corrosion by carbonic, sulfuric, nitric and nitrous acids. Although corrosion mechanisms and their effects are fairly well understood, further work needs to be done on phase behavior of gas mixtures their effects on compression and piping. Once likely gas composition ranges from the capture process are defined, experiments and thermodynamic modeling can proceed to better predict possible adverse effects of impure gas streams and approaches devised to prevent them.

The Reinertsen Engineering (Heggum) project focused on designing safe and cost-effective systems and operational parameters for the compression and transportation of CO<sub>2</sub> under various conditions (e.g., offshore vs. onshore, distance, presence of cooling water, CO<sub>2</sub> impurities). The principal goal of the study is to assess the utility of inexpensive carbon steel in settings, such as offshore Norway (hydrated, cool) as opposed to the better known US situation (dehydrated, onshore). Based on water solubility in supercritical CO<sub>2</sub> experiments (by IFE; see below), it is suggested that the proposed dehydration level specification for Hammerfest LNG (50 ppm) might easily be relaxed to 600 ppm (the existing US Kinder-Morgan specification). Thermodynamic calculations of free water precipitation from supercritical CO<sub>2</sub> indicate that the specification might be further relaxed to 1300 ppm. The effect of CO<sub>2</sub> impurities such as N<sub>2</sub> and CH<sub>4</sub> will have significant effects on water solubility in CO<sub>2</sub>.

The IFE (Seiersten) study provided experimental results that were used in the Reinertsen Engineering study. Existing models and mechanisms for CO<sub>2</sub> corrosivity to carbon steel were found to be inadequate at pressures above 20 bar. Experimental data obtained at higher pressure (up to 50 bar) showed that CO<sub>2</sub> systems containing water and those containing water and MEG inhibitor are considerably lower than existing corrosion models predict, particularly at low temperatures typical for sub-sea pipelines in northern waters. The study provides the basis for operational constraints for CO<sub>2</sub> transport in inexpensive carbon steel pipelines which may improve the economics of CO<sub>2</sub> storage offshore.

#### *Leveraging natural resources to offset CO<sub>2</sub> storage costs (NMT, TTU, Tie-Line Tech)*

The New Mexico Tech (Grigg) study surveys the performance of Permian Basin (West Texas, Southeast New Mexico) CO<sub>2</sub> EOR operations over the past 30 years to assess what can be learned from the projects (successes / failures) and where further research is needed. Data from operator surveys and the literature were tabulated by reservoir / seal type and performance issues such as injectivity, oil response and gas breakthrough and containment. Oil response, which is often related to injectivity, is the principal concern although the poor and good responses were about even. Early gas breakthrough, which occurred more often than expected, is also an important concern. Other issues of concern include scaling, solids

deposition and corrosion. Remediation of wells has met with some success except for improving injectivity. Although most of the injected CO<sub>2</sub> is thought to remain in the target reservoir (and in the subsurface), monitoring programs necessary to make such determinations appear not to have been in widespread use (although H<sub>2</sub>S is apparently monitored). Many of the problems encountered could have been avoided with better pre-injection reservoir characterization. The need for performance and leak monitoring is recognized. Although data on safety was not included as a deliverable, the author noted that there are no apparent official or anecdotal reports of fatal mishaps. The Permian Basin CO<sub>2</sub> EOR survey is a valuable 'lessons learned' exercise for CO<sub>2</sub> storage efforts given the extensive and unique collective experience of such operations.

The feasibility of CO<sub>2</sub> storage in depleted gas and gas condensate reservoirs and possible enhanced gas condensate recovery is examined by the Texas Tech University (Lawal) study. Experimental determination of Z factors (gas compressibility) and simulations of phase behavior (with gas, gas condensate, retrograde condensates) were conducted. In addition, a "CO<sub>2</sub> Sequestration Parameter" tool for optimal CO<sub>2</sub> storage is ready for testing. It was determined that CO<sub>2</sub> compressibility is much higher (lower Z factor) than that of hydrocarbon gases, indicating that CO<sub>2</sub> storage capacity might be up to five times higher than that of the original hydrocarbons. Dry gas with high %CO<sub>2</sub> exhibits wet gas phase behavior whereas retrograde gases become dryer in behavior (retrograde liquid is vaporized). The "CO<sub>2</sub> Sequestration Parameter" tool will assess for a given reservoir the UCSV (ultimate CO<sub>2</sub> sequestered volume) and a material balance approach will assist project design and surveillance. The study has added much needed data on CO<sub>2</sub> and hydrocarbon phase behavior and the tools for rapid screening of candidate gas and gas condensate reservoirs for safe, effective and economic CO<sub>2</sub> storage.

Tie-Line Technology (Stenby) developed models and software for screening CO<sub>2</sub> effects on gas-oil minimum miscibility pressure (MMP), minimum miscibility enrichment (MME) and dispersion indicators for large scale simulations. The calculation tool can be used for various gas mixtures to construct "solvent design" diagrams. The 1-D "dispersion-free" simulation gives rapid estimates of gas composition at breakthrough or as a function of time after breakthrough. The calculations and simulations are important to run prior to CO<sub>2</sub> EOR as CO<sub>2</sub> storage miscibility delays breakthrough and maximizes storage. Prediction of post breakthrough gas composition is essential for surface facility design.

#### *Improving CO<sub>2</sub> injection and reservoir performance (UT-Pope)*

The aquifer CO<sub>2</sub> injection simulation study by the University of Texas (Pope) was aimed at improving understanding of physico-chemical behavior of CO<sub>2</sub> in reservoirs, particularly gas / brine transfer, multiphase flow and chemical reactions. The modeled scenario was for a 50 year injection at along the total height and at the base of the reservoir. Post-injection, dissolution, gravity driven flow and mineralization reduce the proportion of mobile CO<sub>2</sub>. The time required for CO<sub>2</sub> immobilization depends on petrophysical properties (residual gas saturation, average permeability and relative permeability, including hysteresis) and anisotropy. Injection at the base of the formation prevents CO<sub>2</sub> migration to the top of the formation. Immobilization of about half of the CO<sub>2</sub> injected occurs by the cessation of the 50 year injection period and >95% is immobilized in the 10<sup>3</sup> year timeframe. CO<sub>2</sub> mineralization rates depend on reservoir mineralogy and are expected to be significant on the 10<sup>5</sup> timeframe. The assumptions about various CO<sub>2</sub> interactions are basic although the effects of residual saturation and relative permeability are important and well-developed. Mineralization rate and extent is poorly known due to lack of kinetics data. The significant determination of the study is that with appropriate reservoir and injection point selection, CO<sub>2</sub> is largely immobilized over the 10<sup>2</sup>-10<sup>3</sup> year timeframe.

The University of Texas (Bryant) study examined the possible subsurface implications of injecting CO<sub>2</sub> with impurities (e.g., SO<sub>x</sub>, NO<sub>x</sub>) into aquifer (dissolution / precipitation affecting injectivity) and CO<sub>2</sub>

EOR (MMP and fluid displacement) reservoirs. It was found that injecting CO<sub>2</sub> with impurities is unlikely to degrade injectivity even in a worst case scenario (rapid reaction equilibrium and carbonate mineral precipitation) as multiphase flow would be a mitigating mechanism. Increased acidity from the nitric or sulfuric acid might even improve injectivity (temporarily). Impurities in CO<sub>2</sub> EOR injection are unlikely to affect performance as there is a tradeoff between lowering MMP (improvement) and increasing the mobility ratio (worsen). The study confirms the hypothesis that CO<sub>2</sub> impurities (particularly soluble species such as SO<sub>x</sub> and NO<sub>x</sub>) are not of particular concern in aquifer injectivity or EOR performance. Other gases such as N<sub>2</sub>, however, would present operational difficulties and degrade performance.

## 2.2.1 Depleted Gas and Gas Condensate Reservoirs for the Geologic Storage of CO<sub>2</sub>

### Task - 4.1 - Understanding Geologic Storage

Principal Investigator: Scott Frailey; Akanni S. Lawal

Technology Provider: Texas Tech University

### Highlights

- The analyses of results show that irrespective of the CO<sub>2</sub>/hydrocarbon gas mixture's reservoir composition, dry and wet gas reservoirs remain as a vapor phase in the reservoir as well as at surface conditions, thereby showing no phase change in these reservoirs due to CO<sub>2</sub> storage. The same trend has been confirmed by our laboratory measurement of Z-factor for retrograde gas condensate reservoirs.
- The analysis of results shows that a developed Material Balance Model and volumetric equation provide estimates of CO<sub>2</sub> sequestered CO<sub>2</sub> in gas reservoirs.

### Summary

This research project used laboratory measurements of the physical properties of carbon dioxide-hydrocarbon gas mixtures to investigate the phase behavior to be encountered by using depleted gas reservoirs for CO<sub>2</sub> storage; and the use of material balance reservoir model and volumetric equation to develop guidelines for selecting depleted gas reservoirs for CO<sub>2</sub> storage.

To quantify the volume of sequestered CO<sub>2</sub>, enhanced gas recovery (EGR) and enhanced condensate recovery (ECR), a material balance model and volumetric equations are developed to determine how much CO<sub>2</sub> can be stored in the respective dry gas, wet gas and retrograde gas reservoirs. This material balance model and volumetric model include fundamental fluid and petrophysical properties of gas reservoirs.

The purpose of this project is to investigate the use of a depleted gas reservoir for the geologic storage of CO<sub>2</sub>. Furthermore, a benefit exists for the recovery of hydrocarbon gas and condensate that formed in the reservoir that includes re-vaporized condensate in the case of retrograde gases below their dew point pressure. The idea is to quantify the geologic storage of CO<sub>2</sub> for reservoir pressure, reservoir temperature, hydrocarbon gas composition, water and condensate saturation. The three main objectives of the project are as follows:

- Study the feasibility of geologic storage of CO<sub>2</sub> in depleted or abandoned gas reservoirs.
- Determine EGR and EOR benefits of geologic CO<sub>2</sub> storage in dry gas, wet gas, and retrograde reservoirs.
- Develop guidelines for selecting candidate reservoir for CO<sub>2</sub> storage.

The methodology used towards proving a reliable and resourceful means of validating the use of depleted gas reservoirs for CO<sub>2</sub> storage follows these steps:

- Collect group of candidate gas reservoirs.
- Classify gases as dry, wet, or retrograde based on TTU gas identification chart.
- Estimate potential CO<sub>2</sub> storage using material balance or volumetric models with variables derived for specific gas types and reservoir rock properties.
- Estimate gas and condensate recovery by material balance or volumetric models with variables derived for specific gas types and reservoir rock properties.

Two approaches to estimating EGR, ECR, and USCV are investigated: volumetrics and material balance methods. Volumetrics can be used for a gas reservoir with minimal production and pressure records; however, petrophysical ( $h$ ,  $\phi$ , and  $S_w$ ) and PVT data ( $Z$ -factors, gas-type, liquid drop-out) are required. Material balance does not require petrophysical data, but  $P$ ? $T$ , gas production, and reservoir pressure data are required. On the basis of the availability of adequate data, both methods (volumetrics and material balance methods) are useful for estimating EGR, ECR, and USCV.

The highlight of the volumetric equation is the development of guidelines for selecting gas reservoir candidates in terms of USCV, EGR and ECR. Consequently, gas reservoir selection guidelines are to maximize USCV, EGR, and ECR. Most are straightforward and follow basic reservoir engineering theory and principles. The volume of USCV is controlled by the parameters in the volumetric equation. The larger the hydrocarbon pore volume,  $Ah\phi(1-S_w)$ , the greater is the USCV. Likewise, the volume of sequestered  $CO_2$  in the depleted gas reservoir is greater for lower initial pressure and higher MaSP (Maximum Sequestration Pressure). Lower reservoir temperature yields greater USCV, but this effect may be offset by the lower pressures that accompany low temperature reservoirs, unless at temperatures less than the cricondentherm of  $CO_2$ , the  $CO_2$  saturation pressure is exceeded such that liquid  $CO_2$  is possible. Under liquid  $CO_2$  conditions the volume of  $CO_2$  sequestered would be very high. This project also demonstrates EGR and ECR benefit of sequestering  $CO_2$  in gas reservoirs due to re-vaporization of retrograde condensate in the reservoir. The results our laboratory experiments show that re-vaporized condensate can range from 5.7% to 35% of the initial retrograde volume. Stated in different ways, as much as one-third of the condensate liquid in a depleted gas reservoir can be produced as hydrocarbon gas after  $CO_2$  is sequestered. This result confirms the trend seen through our theoretical developments.

This research focuses on using laboratory investigation and computer simulation to analyze phase behavior and enhanced gas and condensate recovery by  $CO_2$  storage in depleted gas reservoirs. The laboratory measured  $CO_2$  compressibility factor (or  $Z$ -factor) is much lower than hydrocarbon gas mixtures at the specified temperatures and pressures. Therefore, that offers the opportunity to store larger surface volumes of  $CO_2$  than hydrocarbon gases. Five times the storage is possible depending on pressure, temperature and hydrocarbon gas composition.

### Reports and Publications

- Sobers, L. E., "Phase Behavior of  $CO_2$  Sequestration in Depleted Gas Reservoirs," MS Thesis, Department of Petroleum Engineering, Texas Tech University, Lubbock, Texas (August 2003).
- Sobers, L., Frailey, S. M. and Lawal, A. S., "Geological Sequestration of Carbon Dioxide in Depleted Gas Reservoirs," Paper SPE/DOE 89345 presented at the 2004 SPE/DOE Fourteenth Symposium on Improved Oil Recovery held in Tulsa, Oklahoma 17-21 April, 2004.
- Adisoemarta, P., Frailey, S. M. and Lawal, A. S., "Experimental Data of  $CO_2$ -DryGas/WetGas/Gas Condensates for Sequestering  $CO_2$  in Depleted Gas Reservoirs," Paper SPE/DOE 89466 presented at the 2004 SPE/DOE Fourteenth Symposium on Improved Oil Recovery held in Tulsa, Oklahoma 17-21 April, 2004.
- The final project report is in Appendix A under the same heading as this summary.



## **2.2.2 Screening Tool for CO<sub>2</sub> Miscibility Determination**

**Task - 4.1 - Understanding Geologic Storage**

**Principal Investigator: Erling Stenby**

**Technology Provider: Tie-Line Technology**

### **Highlights**

- This project has been completed and the final report delivered.

### **Summary**

The result of the project is a software product that can be used to predict the Minimum Miscibility Pressure (MMP) for an injection gas - e.g. CO<sub>2</sub> - in a reservoir oil. Also it can be used to calculate the effect on the MMP of mixing two gases. Furthermore a dispersion free, semi analytical, one-dimensional compositional simulator was made available that is useful for prediction of the composition of the gas phase that will be produced during the gas injection process. The simulation tool will be of significant importance in evaluation of CO<sub>2</sub> injection into oil reservoirs. A favorable license for the software will be available to the CCP partners.

The product is a Windows based tool for prediction of phase behavior and the conditions for which multicontact miscibility will develop when a gas is injected into a reservoir oil. The user must specify the critical properties of the reservoir fluid in question. When the fluid system is specified, several tasks are available for the reservoir engineer. These are a PT-flash, bubble/dew point calculation, phase envelope, MMP calculation including indicator for sensitivity towards numerical dispersion if finite difference compositional simulation, a conceptual slimtube simulator, swelling test and a MME simulation tool.

### **Reports and Publications**

- The final project report was presented in Appendix A of an earlier report.

## 2.2.3 Reservoir Simulation of CO<sub>2</sub> Storage

Task - 4.5 - Risk Assessment and Mitigation Options

Technology Provider: University of Texas

Principal Investigator: Gary Pope

### Highlights

Over the range of parameters investigated, simulation results from this study showed that

- The bulk of the CO<sub>2</sub> injected is stored in CO<sub>2</sub>-saturated brine and CO<sub>2</sub>-rich residual gas phases.
- Although temperature, salinity, aquifer dip, and residual gas saturation significantly affect the distribution of CO<sub>2</sub> in the aquifer, residual gas saturation has the greatest effect on the distribution and immobilization of CO<sub>2</sub> in the aquifer.
- Injecting CO<sub>2</sub> only into the lower half of an aquifer is likely to prevent free gas from ever reaching the upper seal of the aquifer so well completion strategies are critical.
- By the end of a 50 year injection period, most (~75%) of the CO<sub>2</sub> is rendered immobile and >95% is immobile after a few centuries. Mineralization resulted in 2 – 3% of the CO<sub>2</sub> stored after 10<sup>3</sup> years this figure may be more significant on the 10<sup>5</sup> year time frame.

### Summary:

This project involved modeling and simulation of a CO<sub>2</sub> storage project in a deep saline aquifer. The objective of the project was to develop a better understanding of the chemical and physical phenomena associated with the storage of CO<sub>2</sub> in deep saline aquifers and to quantify these phenomena. Specifically, the effects of dissolving CO<sub>2</sub> in the brine and of geochemical reactions resulting in mineralization were to be determined quantitatively. Experimental data shows that the density of brine increases due to dissolved CO<sub>2</sub>. Storing CO<sub>2</sub> in a denser, CO<sub>2</sub>-rich aqueous phase should reduce the risk of CO<sub>2</sub> escaping from the aquifer by reducing the potential for upward migration. Mineralization is another possible sink for CO<sub>2</sub>. The CO<sub>2</sub>-rich aqueous phase is acidic and can react with the minerals present in the aquifer. The injected CO<sub>2</sub> is consumed in the production of secondary minerals. By this mechanism, CO<sub>2</sub> can be permanently trapped in the form of carbonate minerals. UTComp and CMG's GEM compositional simulators were used to model and simulate the storage of CO<sub>2</sub> in a deep saline aquifer.

The project consisted of three tasks. The first task was to establish a base case simulation. Representative characteristics were selected to model a generic aquifer. Fluid property models were calibrated against experimental data as a first step in establishing the input to the simulator. Experimental data for brine density, brine viscosity, and the solubility of CO<sub>2</sub> in brine at different temperatures, pressures, salinities, and CO<sub>2</sub> concentrations were obtained from the literature.

The second task was to quantify the effect of CO<sub>2</sub> on the brine density. The impact of some of the most important aquifer parameters on the storage of CO<sub>2</sub> in the aqueous phase was then examined. Aquifer properties evaluated included permeability, the ratio of vertical to horizontal permeability, residual gas saturation, salinity, temperature, and aquifer dip. Simulation results showing the effect of residual gas saturation suggested that well completion strategies could significantly impact the amounts of CO<sub>2</sub> trapped in the residual gas phase and in the brine. To determine the impact of well completion strategy on CO<sub>2</sub> storage, additional simulations were run using alternative CO<sub>2</sub> injection schemes.

The third task was to estimate the capacity for CO<sub>2</sub> storage by mineralization as a function of the amount and distribution of the minerals in an aquifer. The first step was to identify a limited set of relevant geochemical reactions. Simulations were then run coupling these chemical reactions with fluid flow

through the aquifer. Additional simulations were run where water was injected either sequentially or simultaneously with the CO<sub>2</sub>.

Simulations were run injecting pure supercritical CO<sub>2</sub> through a single, centrally located injection well. CO<sub>2</sub> was injected for 10 years at which time the injector was shut in. The simulation was then continued with only density differences driving fluid flow. Total simulation time was 1000 years. Total simulation time for the mineralization studies was increased to 10,000 years. For the simulations studying well completion strategy, CO<sub>2</sub> was only injected into the lower half of the aquifer and CO<sub>2</sub> injection was increased to 50 years to see how injecting greater amounts of CO<sub>2</sub> affected storage. Total simulation time for these runs was 100,000 years.

Residual gas saturation may be the most significant aquifer parameter affecting CO<sub>2</sub> storage. Simulation results showed that the bulk of the CO<sub>2</sub> was stored in a CO<sub>2</sub>-saturated brine and in a residual CO<sub>2</sub>-rich gas phase with the largest percentage of CO<sub>2</sub> being stored as an immobile, residual gas. In most cases, only a few percent of the CO<sub>2</sub> remained as a free, mobile gas. Gravity-driven flow after CO<sub>2</sub> injection is stopped is the primary mechanism that leads to the conversion of free CO<sub>2</sub> to trapped forms. Movement of mobile CO<sub>2</sub> leads to contact with unsaturated water. More CO<sub>2</sub> dissolves in the unsaturated brine and some of the CO<sub>2</sub> is left behind in an immobile, residual gas phase. Aquifer dip and vertical to horizontal permeability ratio both had a significant effect on gas migration. The simulations show that about 75% of CO<sub>2</sub> is immobilized by the end of the 50 year injection period and that more than 95% may be immobilized after a few centuries. The magnitude and variation of the immobilization effects need to be further studied. Additional work needs to be done to determine the effect of varying other aquifer properties on CO<sub>2</sub> storage mechanisms, magnitudes and time scales.

Well completion strategy can play an important role in increasing the amount of CO<sub>2</sub> stored in immobile forms. Results from simulations injecting CO<sub>2</sub> into only the lower half of the aquifer indicated that with time all the gas will be trapped in various forms and free CO<sub>2</sub> will never reach the top of the aquifer. The simulation results showed that, for the reservoir properties studied, reduction of CO<sub>2</sub> to trapped forms required on the order of a few centuries.

The amount of CO<sub>2</sub> trapped as precipitated carbonate minerals was only 2 – 3% during the 1000 year span of the base case simulation. This amount was increased to 4.5% by injecting fresh water during CO<sub>2</sub> injection. The simulation results showed that the amount of CO<sub>2</sub> trapped by mineralization is highly dependent on the amount and type of minerals present in the aquifer and that trapping of CO<sub>2</sub> by mineralization occurs over a much longer time frame than does trapping in brine or a residual gas phase.

### **Reports and Publications:**

- CCP-SMV 2003 Workshop, Dublin
- The final project report is in Appendix A under the same heading as this summary.

## 2.2.4 CO<sub>2</sub> Impurities Tradeoff – Surface (SO<sub>x</sub>/NO<sub>x</sub>) Impurities Study)

**Principal Investigator: Neeraj Gupta**

**Technology Provider: Battelle Memorial Institute**

### Highlights

- A status review of existing technologies used for CO<sub>2</sub> gas separations addressing major issues affecting the industry and offers suggestions for potential research areas.

### Summary

Battelle undertook a preliminary assessment of the effects of impurities in the CO<sub>2</sub> streams on the aboveground processing equipment. The study, which focuses on SO<sub>x</sub> and NO<sub>x</sub> impurities in flue gas, is based on an assessment of existing literature. The three main components of the work include:

- Impact of impurities on the performance of amine separation systems.
- Evaluation of the phase behavior of multi-component gas mixtures on multi-stage compressors.
- Literature review of compressed gases to determine the corrosivity of pipeline materials in contact with CO<sub>2</sub>, SO<sub>x</sub>, and NO<sub>x</sub> species with moisture present.

Flue gas impurities such as SO<sub>x</sub> and NO<sub>x</sub>, as well as arsenic and mercury present in solid fuels, have the potential of interacting unfavorably with capture, compression, and pipeline transmission of CO<sub>2</sub>. Absorption and regeneration characteristics of amines and other solvents used to separate CO<sub>2</sub> are affected adversely by acid gas impurities. Compression of gas mixtures is subject to condensation of the higher boiling constituents, which may limit the ability to achieve adequate interstage cooling and may damage the compressor and other related processing equipment. Finally, materials used in separation, compression, and transmission are subject to corrosion by acids which include carbonic, sulfuric, sulfurous, nitric, and nitrous acids.

### Recommendations:

- What is lacking is a sufficient understanding of the mechanisms for amine degradation in the presence of contaminants typically found in flue gases at flue gas scrubber conditions and what is necessary to minimize these effects.
- There is a clear need for more detailed information regarding CO<sub>2</sub> streams and the influence of NO<sub>x</sub> and SO<sub>x</sub> impurities on fluid properties and compressor performance. It is not possible to conclude from this study whether multiphase conditions should be expected during compression stages, or whether the impurities would cause substantial increases in energy consumption, other operating costs, or capital costs. It is recommended that research and development be undertaken in this area to clarify these issues. An experimental program may be needed to measure all important properties as a function of temperature and pressure.
- SO<sub>2</sub> and NO<sub>2</sub> have high solubility in water/moisture. It is not clear to what degree they will lower the pH of any aqueous phase in pipeline condensate; however, this is an area that should be studied further to understand its effect on internal corrosion rates. There is a need to understand the interaction of SO<sub>x</sub> and NO<sub>x</sub> with CO<sub>2</sub> under pressurized wet conditions. A fundamental approach is suggested to qualitatively evaluate the effect of small amounts of SO<sub>x</sub> and NO<sub>x</sub> in CO<sub>2</sub> on corrosion properties of pipeline material.

This study provides a general overview of the state of knowledge of technical issues associated with CO<sub>2</sub> impurities tradeoffs. Once a range of CO<sub>2</sub> stream concentration possibilities is specified by those

working on CO<sub>2</sub> separation processes, the reported information can be used to constrain an experimental and thermodynamic research program to predict adverse effects.

### **Reports and Publications**

- CCP-SMV 2003 Workshop, Dublin.
- The project final report is presented in Appendix A under the same heading.

## 2.2.5 CO<sub>2</sub> Impurities Tradeoff – Subsurface

Technology Provider: University of Texas

Principal Investigator: Steven Bryant

### Highlights

- Presence of CO<sub>2</sub> impurities (e.g., SO<sub>x</sub>/NO<sub>x</sub>) in injected CO<sub>2</sub> may, by increasing acidity, result in mineral dissolution near the well bore. This is not expected to change the gross mineralogy, thus significant injectivity performance changes are unlikely.
- Correlations of MMP with solvent compositions that allow tradeoffs between CO<sub>2</sub> capture cost and CO<sub>2</sub> EOR performance indicate that a reasonable SO<sub>x</sub>/NO<sub>x</sub> content would be in the 1 mole % range. The presence of other impurities in larger abundances may slightly degrade or improve performance.
- The overall effect of impurities in CO<sub>2</sub> on well injectivity and the EOR recovery process is deemed small to negligible at the likely levels of impurity occurring in CO<sub>2</sub> streams.

### Summary

This project had two goals. The first one was to examine the potential effect of highly reactive impurities (SO<sub>x</sub>, NO<sub>x</sub>) on well injectivity into clastic aquifers during large-scale CO<sub>2</sub> sequestration. The second goal is to perform a literature review to determine whether impurities might adversely affect enhanced oil recovery processes.

Assuming continuous injection of CO<sub>2</sub> (as opposed to, say, alternating water and CO<sub>2</sub>), the primary influence on well injectivity is expected to be geochemical alteration of the near-well formation. Simulations of a “worst-case” scenario (in which mineral reactions go to thermodynamic equilibrium instantaneously) indicate that the *net change* in mineral volume is likely to be small, even though extensive changes in mineralogy may occur. Thus the effect on injectivity is unlikely to be significant. The presence of impurities in their likely concentrations (less than 1 mole percent) may speed up the reactions due to increased acidity, but otherwise should have little incremental effect on the injectivity. These findings are also “worst-case” in that brine is assumed to flow co-currently with the CO<sub>2</sub>. Such flow will occur for a relatively short time in the near-well region, further limiting the extent of precipitation/dissolution reactions.

Minimum miscibility pressure (MMP) is generally regarded as one of the primary determinants to the success of an oil-recovering CO<sub>2</sub> flood. Miscibility implies the total suppression of capillary forces and excellent oil recovery efficiency on the small scale. However, it is important to recall that other factors also contribute to flood efficiency, including WAG (water-alternating-gas) ratio, well productivity, and several reservoir-specific quantities such as heterogeneity and well spacing. Miscibility develops in most cases because the CO<sub>2</sub> will extract intermediate components from the crude into the CO<sub>2</sub> - rich phase. The extraction depends strongly on the purity of the solvent. CO<sub>2</sub>-N<sub>2</sub> mixtures are poorer extractors than CO<sub>2</sub> alone, whereas CO<sub>2</sub>-H<sub>2</sub>S mixtures are better extractors. MMP generally decreases as the solvent becomes more “oil-like”. Thus, impurities in a CO<sub>2</sub> stream which behave more like the oil than CO<sub>2</sub> generally decrease the MMP, whereas impurities that are less like the oil typically increase the MMP.

Most of the data on MMP have been captured through correlation, most commonly as statistical correlations. The report discusses various correlations available and selects one for further study. Applying this correlation to a typical range of impurity concentrations suggests that the MMP should

decrease slightly as the impurity concentration increases. The effect is relatively small; for example, a 5 mol% concentration of SO<sub>2</sub> reduces the MMP only 10%. The presence of NO would counteract this effect, so the net change in MMP because of the presence of flue-gas type impurities should not be large.

For immiscible displacements, the mobility ratio and the gravity number are the principal factors influencing recovery. Impurities of SO<sub>x</sub>/NO<sub>x</sub> generally reduce the viscosity of the solvent, thereby increasing the mobility ratio. These impurities would also reduce the density of the solvent, thereby decreasing the gravity number. Both effects reduce the effectiveness of the process. For the small concentrations of impurities likely to be encountered, these effects are quite small and should not significantly influence the process. Thus the presence of flue-gas type impurities should not reduce the effectiveness of an EOR application, whether the process is miscible or immiscible.

The study results indicate that injection of minor quantities (<1 mole % base case) of CO<sub>2</sub> stream contaminants is unlikely to adversely affect injection rates into clastic aquifers or the performance of CO<sub>2</sub> EOR operations (e.g., WAG). Larger concentrations of some components (e.g., 5% SO<sub>2</sub>) may have only a slight adverse effect on the EOR process. Thus capture processes that yield less than pure CO<sub>2</sub> at considerable cost savings may be possible. The model set up can be used to quickly screen larger (>1 mole %) and more varied contaminants specified by separation plant operators.

### **Reports and Publications**

- CO<sub>2</sub> Impurities Tradeoffs (Subsurface) – 2003 CCP-SMV Workshop Presentation, Dublin
- The final project report is presented in Appendix A under the same heading.

## 2.3 Integrity

### Task - 4.1 - Understanding Geologic Storage

### Task - 4.4 – Measurement and Verification

The SMV “integrity” theme studies are directed towards better understanding elements of natural (reservoir and cap rocks, overburden, faults, etc.) and engineered (well materials) features that permit safe and effective geological storage of CO<sub>2</sub>.

#### *Defining geological features responsible for competent vs. ineffectual CO<sub>2</sub> storage (ARI, USU)*

The ARI (Stevens) study on “competent” systems examined features of three large US CO<sub>2</sub> reservoirs: 1) McElmo Dome, CO (30 Tcf OCO<sub>2</sub>IP at 2300 m; 800 MMcfd production; carbonate reservoir with thick halite cap rock), 2) Jackson Dome, MS (2 Tcf at 4700 m; 185 MMcfd production; sandstone with some carbonate reservoir with carbonate cap rock) and 3) St. Johns, AZ (14 Tcf at 500 m; 1 MMcf production; sandstone reservoir and anhydrite cap rock). These natural CO<sub>2</sub> accumulations vary in CO<sub>2</sub> state (supercritical in McElmo and Jackson domes), origin (carbonate metamorphism and / or volcanic for McElmo Dome and St. Johns; Jackson Dome cited as volcanic but more likely from thermochemical sulfate reduction, TSR) and length of storage (~70 Ma in McElmo and Jackson Domes; ~ 0-6 Ma in St. Johns). Production operation data was gathered for each of the sites. Key finding of the study include:

- CO<sub>2</sub> storage is a natural process.
- Reliable reservoir seals require evaporites or shales as the cap rock.
- Natural analog CO<sub>2</sub> production practices provide insights for CO<sub>2</sub> storage.
- Efficient CO<sub>2</sub> storage operations will require specialized practices and technologies.

Recommendations include further analogs studies including general site suitability classification, specific elements characterization, modeling of injection process and monitoring. Future work will benefit from comparison of US fields with other natural CO<sub>2</sub> analogs (e.g., Australia).

The Utah State University (Evans) study on ineffectual natural CO<sub>2</sub> storage systems focuses on CO<sub>2</sub>-charge geysers from Western Colorado Plateau (East Central Utah). A 3D structural / stratigraphic and fluid hydrology / geochemistry assessment documented the origin, history and escape paths of CO<sub>2</sub> to the surface. The CO<sub>2</sub> originates in the 1-1.5 km depth range from clay carbonate reactions. The Little Grand Wash and Salt Wash faults deliver supercritical CO<sub>2</sub> from depth to a shallow, temporary reservoir at 300-500 m where a phase change to CO<sub>2</sub> vapor provides the pressure necessary for CO<sub>2</sub> charged water to erupt or bubble at the surface. Detailed structural analysis and hydrologic studies indicate that it is not the major faults, but their associated minor faults and fractures that serve as conduits for CO<sub>2</sub> charged water arriving at the surface. Over time, as these conduits are sealed by mineralization, new conduits become available for fluid transport. The system of travertine terraces and void fillings indicate that this geyser system has persisted before historical and perhaps into the geologic time frame. It is estimated that a maximum of 10% of the CO<sub>2</sub> brought to the surface was “fixed” or stored as travertine. Anthropogenic activity, such as drilling through faults, appears to have altered the location and episodicity of CO<sub>2</sub> charged eruptions in the area. No untoward ecological or human health effects attributed to CO<sub>2</sub> release to the surface have been recorded. The study demonstrates the utility of constructing a 3-D geological and fluid history model to assess the suitability of geologic systems for CO<sub>2</sub> storage. The fluid sampling techniques and the modeling of water and CO<sub>2</sub> origin are an important contribution of this study.

#### *Assessment of reservoir and cap rock response to CO<sub>2</sub> injection (ASP, LLNL, GFZ)*

The University of Adelaide (Streit) provided a state-of-the-art review of geomechanical effects on rock and faults stability with subsurface CO<sub>2</sub> injection and outlines techniques used to monitor rock stress /



strength and CO<sub>2</sub> leakage. Increases in formation fluid pressure due to CO<sub>2</sub> injection decreases effective rock stress thereby increasing the likelihood of fault reactivation or rock failure. Assessment of the geomechanical stability of reservoir rocks and top seals and faults requires predictions of in situ stresses, fault geometries, and rock frictional strength. Commercial tools exist to predict the maximum sustainable fluid pressure for rocks and faults (e.g., FAST™ or TrapTester™). Fault stability is also predicted by mapping fault geometry and constructing fault failure plots. In assessing the suitability of a CO<sub>2</sub> storage site in a depleted oil or gas field, it is necessary to analyze for the effects of both depletion (from production) and recharging (from injection). Stress-seismic velocity relationships are used to detect poroelastic changes in rocks due to fluid injection. Recent development of new waveforms and data processing techniques may improve the accuracy of stress-seismic techniques. Installation of downhole seismic monitoring instruments may provide rapid, early detection of faulting or fracturing induced by effective stress changes. The importance of geomechanical considerations for CO<sub>2</sub> storage has only recently received significant attention. The present study brings together theoretical, experimental and field models from several leading scientists and engineers to integrate findings and identify research needs. A particularly acute need is experimental data on seal and fault-associated rocks.

The LLNL (Johnson; cross reference Risk Assessment) study used reactive transport geochemical and distinct element geomechanical models to infer long-term effects of CO<sub>2</sub> injection on cap rocks. It was shown that CO<sub>2</sub> influx-triggered mineral dissolution / precipitation reactions in typical shale cap rocks continuously reduce microfracture apertures whereas pressure and effective stress evolution first rapidly increase and then slowly decrease them. For a given shale composition, the extent of geochemical alteration (to reduce permeability) appears nearly independent of key reservoir properties (permeability and lateral continuity) and CO<sub>2</sub> influx parameters (rate, focality and duration). In contrast, the extent of geomechanical degradation (to increase permeability) is highly dependent on the reservoir and influx parameters as they control the magnitude of pressure perturbation, i.e., initial geomechanical degradation has been shown to be inversely proportional to reservoir permeability and lateral continuity and proportional to influx rate. A major implication of the study is the limiting extent to which natural CO<sub>2</sub> accumulations and engineered CO<sub>2</sub> storage sites can be considered analogous given that geomechanical effects will be more pronounced with engineered injection. This may be ameliorated to some extent by abatement of injection-induced pressure with time as CO<sub>2</sub> dissolves in water, particularly in large, unconfined reservoirs.

Changes in geophysical attributes and mineral stability with CO<sub>2</sub> injection is the subject of the GFZ-Potsdam (Schuett) experimental study. Using a triaxial cell and autoclaves to reproduce reservoir PT conditions, fluids with varying supercritical CO<sub>2</sub> saturation levels (e.g., WAG) were injected into rock samples to assess how suitable existing geophysical models are for predicting rock changes (e.g., strength) and whether or not ions are released from rock forming minerals during CO<sub>2</sub> injection. The *in situ* geophysical measurements (V<sub>p</sub>, V<sub>s</sub>, electrical resistivity, stress-strain, flow rates) show that some effects are predicted quantitatively by standard models (e.g., Gassmann and Voigt). Discrepancies noted may be attributed to laboratory measurement artifacts or fluid front instabilities. Improvements in the standard models using these data may have implications for imaging CO<sub>2</sub> reservoir performance and containment. The geochemical results suggest that major elements essential for rock stability and minor elements of importance to water quality are mobilized by CO<sub>2</sub> injection. This work is the most comprehensive such laboratory study concluded to date. Collection of such data on reservoir and cap rocks from a candidate CO<sub>2</sub> storage site will assist in developing seismic monitoring protocols and assessing environmental impact.

#### *Engineered systems competence to contain CO<sub>2</sub> (SINTEF, GTI)*

SINTEF (Lindeberg and Akervoll) has addressed the well integrity issue, perhaps the most critical issue relevant to successful CO<sub>2</sub> storage, through experimental testing (at elevated T) of standard and newly

formulated cements (and cement in contact with steel) and cement sealants. Using the data generated, simulations of well material degradation with time and potential loss of CO<sub>2</sub> from storage reservoirs were conducted. Experimental data on corrosion / erosion of cements and inference of chemical mechanisms involved show that initial CO<sub>2</sub> contact will first “carbonate” the cement (reduce permeability via carbonate precipitation) but over the long-term the cement will deteriorate due to dissolution of calcium hydrogen carbonate. Permeabilities will increase by 2 to 3 orders of magnitude depending on the cement type (Portland cement vs. newer formulations, respectively) but will still be in the microdarcy range. Modifying cements (e.g., adding silica flour) or epoxies may improve the longevity of cements in the CO<sub>2</sub>-rich regime. A reservoir simulation of CO<sub>2</sub> leakage from an abandoned leaky cemented well showed that even in a worse case scenario (unremediated open borehole), not all CO<sub>2</sub> will leak from the reservoir (e.g., 60% over 100-200 years). More typically, dissolution of CO<sub>2</sub> in water can be expected to immobilize the vast majority of CO<sub>2</sub> over the 1000-2000 year time frame. The study provides an essential experimental data baseline on existing widely used well bore cements and the basis for developing new cement formulations and sealants. The results of the simulation work (typical case) are comparable to other such studies (e.g., University of Texas - Pope; see “optimization”), but future work should incorporate more recently developed CO<sub>2</sub> immobilization mechanisms (e.g., residual gas trapping) and scenario development.

In the GTI (Perry) survey of the natural gas storage industry operational experience in North America and Europe, important parallels to a future CO<sub>2</sub> storage industry are drawn. Through operation of ~600 natural gas storage facilities over the past 90 years, only nine gas migration incidents are recorded. These include three cap rock failures, five well bore failures and one case of poor reservoir selection. The review of natural gas storage technologies with possible implications for CO<sub>2</sub> storage includes:

- Field integrity determination – This involves selecting a structure that has a competent seal and structurally adequate closure. Broadly structured sites are favored because those with tight structuring have often developed faults and fractures. Pump testing of structures to ensure caprock integrity is often performed. The same selection principals are applicable to CO<sub>2</sub> storage. A modified pump test may be feasible for CO<sub>2</sub> cap rock testing.
- Monitoring and leak detection – Involves monitoring via observation wells the occurrence of gas above and lateral to the structure. Similar approaches may be used for CO<sub>2</sub> storage although gas migration may not be as readily detected.
- Response to leakage – Leak mitigation measures for natural gas leaks include shallow gas recycle, aquifer pressure control and cap rock sealing. For CO<sub>2</sub> storage, the former approaches are relevant but the latter approach needs further development.

The natural gas storage experience is a useful if not a more extreme analog to CO<sub>2</sub> storage. Regulation and public scrutiny will dictate CO<sub>2</sub> storage operations further from populated areas. To take advantage of the increased storage capacity of supercritical CO<sub>2</sub>, storage depths will be deeper and thus remote from near surface conduits and potable water resources. Although CO<sub>2</sub> can be harmful in high concentrations, which may occur in low lying areas with calm atmospheric conditions, it is not flammable.

## 2.3.1 Evaluation of Natural CO<sub>2</sub> Charged Systems for CO<sub>2</sub> Sequestration

Task - 4.1 - Understanding Geologic Storage

Principal Investigator: James Evans

Technology Provider: Utah State University

### Highlights

- A 3D structural / stratigraphic and fluid hydrology/geochemistry study was conducted on natural CO<sub>2</sub> seeps and geysers in East-Central Utah (Colorado Plateau) to infer features of geologic system that are prone to CO<sub>2</sub> leakage.
- The geologic and geochemical data constrains the origin of CO<sub>2</sub> and the mechanisms by which it reaches the surface through time. Originating in the 1-1.5 km depth range from clay-carbonate reactions, CO<sub>2</sub> is temporarily stored at depths of 300-500 m and released through permeability fracture zones associated with faults.
- Carbonate mineral precipitation in porous rocks, veins and in surface terraces are evidence for long-term CO<sub>2</sub> leakage to the surface (~10% of leaked CO<sub>2</sub> may be fixed in these features). Although specific localities of leakage points has changed over time as old conduits are mineralized and new ones become available, the fundamental character of the leaking fluids has not.
- A viable protocol for evaluating prospective CO<sub>2</sub> storage sites in this or other settings (e.g., North Sea) has been developed. The study area itself is an ideal laboratory for testing monitoring instruments and protocols.

### Summary

Natural CO<sub>2</sub> reservoir system analogs provide useful information on geologic features that govern the integrity of prospective engineered CO<sub>2</sub> storage venues. This “leaky” analogues study, focusing on CO<sub>2</sub>-charged geysers and seeps in the Colorado Plateau (Paradox Basin) of East-Central Utah, complements the study of competent natural systems conducted by ARI (some of which are also located in the same geological province). The approach to the study, construction of a 3D geological model and fluid history analysis, might be used in the future as standard methodology to evaluate the relative competence of geological systems to store anthropogenic CO<sub>2</sub>.

The East-Central Utah geysers and seeps studied are situated on the western rim of the Colorado Plateau where the Little Grand Wash and Salt Wash faults deliver fluids from the Paradox Basin to the surface. Because the erupting or bubbling CO<sub>2</sub>-charged waters are cool (~18°C) and have isotopic indications of meteoric origin, a relatively shallow reservoir (300-500 m) is indicated. The mechanism of release to the surface, therefore, is pressure build up from expansion of CO<sub>2</sub> into the free phase and not from pressure exerted by superheated water as is the case in better known geyser systems. Although the CO<sub>2</sub> does not have a unique isotopic signal, geothermometry and He isotope analyses suggest an origin consistent with clay-carbonate reactions occurring at moderate depth (1-1.5 km) as opposed to organic, microbial, metamorphic or mantle origin.

The persistence of the leaking CO<sub>2</sub> system is evident from the calcite veins and travertine mound and terrace deposits associated with the major faults. Hydrologic studies show that the faults act as a barrier to fluid movement, probably by the mechanism of clay gouge formation and cataclasis. Fine scale structural, lithologic and petrographic studies indicate that fluid movement is facilitated by minor faults and fractures associated with the major faults (fault damage zone). Rerouting of seepage points occurred when these conduits were cemented in by mineral precipitation. A preliminary mass balance

study of CO<sub>2</sub> flux versus carbonate precipitation suggests that about 10% of the CO<sub>2</sub> arriving at the surface over time has been “stored” as travertine. Anticipated data from U-dating of travertine deposits might give an indication of how long the leaking system has been operational.

Drilling of wells in the area appears to have influenced the location, cyclicity and magnitude of CO<sub>2</sub> seepage, possibly by relieving reservoir pressure and evening out leakage point distribution. Although the CO<sub>2</sub> leakage system has persisted through historical times (and likely long before), no incidence of harm to humans or ecosystems has been noted. Indeed, saltbush present in the area may rely on the briny water type left after CO<sub>2</sub> seepage.

Implications of the study for CO<sub>2</sub> storage are noted by the authors. Foremost among these is the necessity of conducting integrated structural / stratigraphic, hydrology and geochemistry assessments on prospective geological CO<sub>2</sub> storage sites. Recommendations for future research relate to determining CO<sub>2</sub> flux in space and time. The duration of CO<sub>2</sub> leakage might be inferred from travertine dating. The present day absolute CO<sub>2</sub> flux can be estimated using systematic sampling and monitoring. The area is offered as an ideal locality for testing monitoring instruments and methodologies.

The success of the “leaky” analogue study can be attributed to its systematic and multidisciplinary methodology. Obvious individual clues to CO<sub>2</sub> origin, subsurface movement and surface venting were abandoned and replaced when needed with those more consistent with the larger body of data. The geochemical sampling techniques perfected will be useful for assessing other CO<sub>2</sub> storage venues as well as in environmental science in general. Where considerable uncertainty about the system remained, the researchers developed the tools necessary to resolve issues (e.g., origin of CO<sub>2</sub> inferred from geochemical modelling). The study would have benefited from collaboration with the competent systems natural analogue (ARI) and reactive transport modelling (LLNL) studies.

### **Reports and Publications**

- 2003 CCP-SMV Workshop Presentation, Dublin
- The final project report is presented in Appendix A under the same heading.

## 2.3.2 Long Term Sealing Capacity Of Cemented Petroleum Wells

### Task - 4.1 - Understanding Geologic Storage

Principal Investigator: Erik Lindeberg

Technology Provider: SINTEF

#### Highlights

- Project is complete. Technical SINTEF Report no. 54.5232.00/01/03 entitled “Report January 2003: The long term sealing capacity of cemented petroleum wells in a CO<sub>2</sub> storage project” was submitted and accepted.
- Abandoned wells have been identified as potential leakage pathways from underground CO<sub>2</sub> storage reservoirs. A completely open well, however, will never leak more than a fraction of the CO<sub>2</sub> stored in the reservoir.
- When the CO<sub>2</sub> from the storage formation has migrated/diffused to the cement layer around the casing of a well, the cement will first “carbonate” (reduce permeability via carbonate precipitation). Over the long-term, however, the cement will deteriorate due to dissolution of calcium hydrogen carbonate. This will increase permeability by 2 to 3 orders of magnitude.
- Special cements/cementing materials with less reactivity are presently available and new ones are under development in this project.
- CO<sub>2</sub> rich pore water is also corrosive to steel casings in the short but they are normally protected by the encasing cement.

#### Summary

The objective of this study was to investigate the long-term integrity of wells to prevent CO<sub>2</sub> leakage from underground storage reservoirs and to make recommendations for well plugging and treatment prior to field abandonment to avoid such leakage. Experiments on cement and cement in contact with steel were conducted at elevated pressure and temperature to assess long-term cement erosion rates.

Experience in the use of carbon steels in pipelines transportation of supercritical CO<sub>2</sub> demonstrates that this material is suitable for dry CO<sub>2</sub>. However, if water is present the corrosion rates are high. The report summarizes relevant chemical reactions among CO<sub>2</sub> and steel and CO<sub>2</sub> and cement and cement in contact with steel.

When the carbon dioxide from a CO<sub>2</sub> storage formation has migrated/diffused to the cement layer around the casing of a well, the cement first will precipitate carbonate but eventually will deteriorate due to dissolution of calcium hydrogen carbonate. In the present report possible means of isolating the well construction from stored CO<sub>2</sub> and brine in the near well bore region are presented. Special CO<sub>2</sub> resistant cements have been developed that have better resistance against CO<sub>2</sub> compared to standard cements. Adding silica flour and other additives in various proportions increase the durability of the cement and its resistance to a CO<sub>2</sub> rich environment. Other alternatives such as epoxy also exist, however, but there is no information about the long-term durability and CO<sub>2</sub>/brine resistance for this product.

A reservoir simulation model has been run to estimate the amount of CO<sub>2</sub> expected to escape from a leaky abandoned well and to quantify the escape rate as an emission profile. The simulations show that an important factor regarding CO<sub>2</sub> escape from the reservoir is the erosion process of the well cement. The

long-term rate of cement erosion with and without contact of steel was assessed by laboratory experiments performed at elevated temperature (200 °C) and pressure (1200 bar) in an autoclave. The results show that accelerated cement erosion with CO<sub>2</sub> exposure increases the permeability of standard cements by 2 to 3 orders of magnitude. The absolute level of permeability nevertheless is still in the microdarcy range.

The well integrity study addresses in a realistic fashion what is probably the most vulnerable link in geological CO<sub>2</sub> storage. The development of new cement formulations and sealants will markedly increase the useful life and thereby longevity of CO<sub>2</sub> storage.

### **Reports and Publications**

- Mid-term report June 2002: The Long Term Sealing Capacity of Cemented Petroleum Wells in a CO<sub>2</sub> Storage Project. Presented at the Santa Cruz, CA, workshop October 21-23, 2002.
- Presentation: SMV Santa Cruz, CA, Workshop October 21-23, 2002: Well materials, leakage and experiments.
- SINTEF Report no. 54.5232.00/01/03 entitled “Report January 2003: The long term sealing capacity of cemented petroleum wells in a CO<sub>2</sub> storage project”.
- CCP-SMV 2003 Workshop, Dublin, Ireland.
- The final project report is in Appendix A under the same heading as this summary.

### 2.3.3 Geomechanical Effects of CO<sub>2</sub> Storage With Emphasis on the Effects of Stress on Seal Integrity

Technology Provider: APCRC

Principal Investigator: Andy Rigg, Jurgen Streit, Milovan Urosevic, D. Sherlock

#### Highlights

- This project reviewed the current state of the art in geomechanical analysis and its application to predicting the effects of subsurface fluid injection on rock integrity.
- Integration of laboratory and field measurements are required to adequately characterize subsurface reservoirs intended for CO<sub>2</sub> storage.
- Key laboratory work still needs to be done to create the appropriate numerical models to interpret field data.

#### Summary

The report summarizes the effects of CO<sub>2</sub> storage on rock stresses and seal integrity in deep saline formations and depleted hydrocarbon fields. Geological storage of CO<sub>2</sub> is optimized when CO<sub>2</sub> is in supercritical state and has relatively high liquid-like densities that usually occur at depths greater than approximately 800m. The supercritical state of CO<sub>2</sub> delivered to the reservoir maximizes the storage volume and the CO<sub>2</sub> column height that can be retained by top seals.

Increases in formation fluid pressure due to CO<sub>2</sub> injection decrease the effective stresses in the rock. Low effective stresses can lead to fault reactivation or rock failure which could lead to seal breaching and thus unwanted CO<sub>2</sub> migration. Assessments of the geomechanical stability of faults, reservoir rock, and top seal in potential CO<sub>2</sub> storage sites requires the determination of in situ stresses, fault geometries, and frictional strengths of reservoir and seal rock. Such information is essential when estimating maximum sustainable pore fluid pressures in the storage formation. This can be accomplished using the FAST™ technique or TrapTester (Badley Geoscience Ltd) software. In pressure-depleted reservoirs and fields, in situ stresses and seal integrity need to be determined after depletion to estimate maximum sustainable pore fluid pressures.

Since seismic wave attributes (velocity, frequency, and amplitude) are sensitive to changes in effective stress, time-lapse seismic methods could be applied to detect pore pressure changes resulting from CO<sub>2</sub> injection. Detection of microseismic events arising from injection-induced shear failure of faults, fractures and intact rock is possible with geophone and accelerometer installations, and can be used for real-time adjustment of injection pressures. While the analysis of wave velocities from 3D time-lapse seismic data can be used to detect and monitor CO<sub>2</sub> accumulations in a reservoir and its overburden, multi-component seismic methods and shear-wave splitting analysis are useful for detecting the opening of extensive fracture arrays due to CO<sub>2</sub> infiltration. The minimum change in fracture width resulting from CO<sub>2</sub> infiltration and the minimum number of opened fractures that can possibly be detected using time-lapse seismic methods needs further study.

The application of geomechanics to CO<sub>2</sub> storage is well-developed theoretically but little tested by experiments and in the field. Considerable further work, much of which is underway, is required make useful characterizations and predictions.

1. Little is known about the compaction trends in low-effective stress mud. These represent the “seal of last resort” for CO<sub>2</sub> which has escaped from deeper reservoirs, and is migrating upward to the sea bottom. Unfortunately, these sediments are rarely cored and rarely logged. Laboratory

measurements of muds undergoing compaction for permeability, porosity,  $V_p$ ,  $V_s$ , and anisotropic seismic parameters, such as are being collected by Kurt Nihei at LBL, are critical to understanding the whole system.

2. Most work on the Biot effective stress parameter, which controls the efficiency with which pore pressures reduce effective stress, have been performed on sandstones. Since the seals are shales, it is imperative to have measurements of the effective stress parameter in these seal lithologies. Work on the sandstone system has already been performed by Dewhurst and Siggins at CSIRO.
3. Related to (2), but as a separate question: Under which conditions will top seals fail by hydraulic fracture rather than capillary entry as  $\text{CO}_2$  is injected into depleted reservoirs or virgin brine aquifers? How is this related to the rate of injection?
4. What are the practical limits to using shear-wave splitting to detect changes in the stress field? The 3D seismic datasets from Weyburn should be further analyzed to determine viability of method.
5. Can microseismic events be detected when the input fluid pressures of injected  $\text{CO}_2$  are small? The best documented use of microseismic s in the past was for monitoring hydro-fracturing, where the pressures input were large.
6. Will  $\text{CO}_2$  act to chemically lubricate fault planes and produce seismicity out of proportion to the pressure reduction due to higher pore pressures? i.e. if the fault plane sediments have high carbonate content, how will the strength of the faults be influenced by  $\text{CO}_2$ ?

The importance of geomechanical considerations for  $\text{CO}_2$  storage has only recently received significant attention. The report brings together theoretical and experimental data and applications from several leading geologist, geophysicists and engineers into a single document with an excellent effort to integrate findings and identify research needs. Advancement of geomechanical studies requires testing of rocks (particularly shales) in the laboratory and active and passive seismic  $\text{CO}_2$  leak detection in the field. Reservoirs that have been depleted by hydrocarbon production are of particular interest as *in situ* stress and seal integrity may be compromised before  $\text{CO}_2$  injection.

## Reports and Publications

- CCP-SMV 2003 Workshop, Dublin
- Streit, J.E. and Siggins, A.F., Predicting, monitoring and controlling geomechanical effects of  $\text{CO}_2$  injection, submitted for presentation at the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7); Vancouver, Sept. 5-9, 2004.



## 2.4 Monitoring

### Task - 4.4 - Measurement and Verification

The SMV “Monitoring” projects were intended to examine the efficacy of a wide range of techniques, commercially available and under development, applied remotely, near the surface or in the subsurface.

#### *Remote Techniques (Satellite and Aerial) (LLNL, Stanford)*

The “hyperspectral geobotanical” remote sensing study by LLNL (Pickles) entails satellite and aerial data acquisition and processing to detect indirect effects of CO<sub>2</sub> leakage on plants and soils. Case studies include a satellite survey of Mammoth Lake, CA where substantial volcanogenic leakage is known to have caused tree kills and an aerial survey of Rangely Field, CO where low CO<sub>2</sub> leakage due to EOR operations is postulated. The satellite imagery of Mammoth Lake correlated well with ground-based CO<sub>2</sub> measurements and observations of vegetation effects. The Rangely Field surveys included pre- and post-rain images that showed marked differences in the (sparse) vegetation patterns (i.e., habitats) but no obvious indications of CO<sub>2</sub> leakage. Detection of CO<sub>2</sub> leakage at Rangely Field will require further development and be mindful of the results of an independent Colorado School of Mines soil gas survey that showed little to no CO<sub>2</sub> leakage from the EOR operation (however, a possibly significant methane flux was detected). Additional processing and interpretation might reveal soil changes due to long-term CO<sub>2</sub> leakage and the location of hidden faults.

The feasibility of satellite radar interferometry (InSAR) technique for detecting ground movements due to CO<sub>2</sub> injection was investigated by Stanford University (Zebker). Pressure profiles for an injection model were used to produce surface deformation maps. The sensitivity of the InSAR digital images versus noise level will determine sensitivity requirements and how local topography will affect detectability. Although the mathematical basis for deformation signatures and their detectability were presented, it is not clear how the results addressed the objectives of the study. The study was terminated due to lack of progress,

#### *Near-Surface and Atmospheric Techniques (CalTech, Penn State)*

A state-of-the-art survey of currently available and developing detection equipment for CO<sub>2</sub> atmospheric monitoring was conducted by CalTech (Tang and Shuler) early in the SMV program. The applicability and costs of instruments useful over various time, length / area scales and sampling frequencies was outlined. Established CO<sub>2</sub> detection systems include fixed point detectors and portable personal detectors. Costs are reasonable for small areas of know risk. More recently developed “open path” detectors that might be applied over larger scales are mentioned in this study and examined in detail in a follow up study (see below). Remote sensing technology can cover considerable area but has low vertical resolution. Some remote satellite and airborne techniques under development by NASA might address this. The study was a practical and thorough evaluation of available and emerging technologies. A follow up study was commissioned to take a closer look at some of the more promising technologies and their applicability to field size and leakage type and magnitude.

In the follow up Caltech (Shuler and Tang) study, the capability of various ground-based instruments to detect CO<sub>2</sub> leakage was examined in detail. The target detectable leak rate of 1% over 100 years (0.01% / year) was given as a base case. The detectability of leaks depends on the amount of leakage with time (flux), size of the affected area, mode of leakage (diffuse or point source) and atmospheric conditions but should be detectable if atmospheric CO<sub>2</sub> concentration increases >10ppm over background. Nomograms are used to predict the “excess” CO<sub>2</sub> present in the atmosphere for a given situation. Open path instruments (laser spectrometers) may be a cost effective means of detecting small CO<sub>2</sub> leakage over a field-sized area (a few km<sup>2</sup>). A spreadsheet application produced for the study permits matching of analytical instruments suitable for detecting CO<sub>2</sub> under various leakage scenarios.

The “eddy covariance” method, a technology used to establish baseline CO<sub>2</sub> flux from plant photosynthesis and respiration cycles, was evaluated for its applicability to CO<sub>2</sub> leak detection at the field scale. The technology is based on laser spectrometers mounted on towers (10 m) that could be set up in an array at the field scale. The magnitude of CO<sub>2</sub> leakage that can be detected given natural variation might typically be 2.5% of 1000MT stored of 1000 years for a reservoir leak, 10<sup>-1</sup>kgm<sup>-2</sup>s<sup>-1</sup> for a diffuse leak (injection well failure) and 10<sup>-5</sup>kgm<sup>-2</sup>s<sup>-1</sup> for a “diffuse” leak (fault). This technology has been widely applied and is considered reliable and robust. Its applicability and expense should be compared with similar ground-base detection given field size and the type and magnitude of CO<sub>2</sub> leakage.

#### *Geophysical & Geochemical Techniques (TNO, LBNL, LLNL)*

TNO (Arts) conducted a broad survey of geophysical and geochemical monitoring techniques for the purpose of recommending “optimal” techniques for various CO<sub>2</sub> storage venues (COMM). Monitoring well technologies include P&T control, electrical resistivity, TDT, microseismic, VSP, crosswell seismic and fluid sampling. Surface geophysical methods include 4-D seismic, subbottom profiling and sonar (marine), gravity, electromagnetics, gravity, InSAR and tiltmeters. Geochemical monitoring includes groundwater sampling, tracer surveys, atmospheric detection and geobotanical hyperspectral remote sensing. The applicability of the various monitoring techniques were matched to specific FEPs (features, events and processes) such as those related to seal, casing / cement or well failure. Additional seismic modeling work to assess the resolution of 4-D seismic detection of CO<sub>2</sub> presence in a Sleipner-type case was included. The study provides a useful assessment of available technologies to monitor CO<sub>2</sub> leakage in a variety of settings and potential failure modes.

The “novel geophysical” monitoring study conducted by LBNL (Hoversten) evaluates the resolution and applicability of seismic and non-seismic geophysical techniques to detecting CO<sub>2</sub> leakage. The Schrader Bluff and Liberty reservoirs were used to model the spatial resolution of various geophysical CO<sub>2</sub> detection techniques. The significant changes in water with increasing CO<sub>2</sub> saturation might be detectable using seismic amplitude and AVO analysis. Ground-based gravity modeling shows that resolution is insufficient but might be improved with permanent sensor emplacement coupled with surface deformation measurements. Borehole gravity instrumentation emplaced up to 1200 feet above the reservoir might be sufficient to directly map the areas of net density changes caused by injecting CO<sub>2</sub> into water. The electrical resistivity changes attending CO<sub>2</sub> dissolution in water are easily detectable using electromagnetic (EM) techniques. This technique is currently available, inexpensive compared to seismic and most applicable to CO<sub>2</sub> / brine systems. The streaming potential (SP) method has been successfully modeled in 2-D for the Liberty Field and experimental results show promise. Unlike the other techniques, however, further development in instrumentation and interpretation are needed. The novel geophysical techniques show considerable technical promise for CO<sub>2</sub> performance and leakage modeling whether by adding value to lapse seismic data or by development of inexpensive non-seismic techniques

The utility and cost of using noble gas additives to monitor CO<sub>2</sub> movement and leakage in subsurface was conducted by LLNL (Nimz). The West Texas Mabee Field was used as a model for the study. Among the factors considered in selecting noble gases are cost, availability, subsurface transport characteristics and “distinctiveness” relative to the atmosphere and noble gases native to the reservoir. The Xe “system” (10 isotopes) was considered to meet these criteria. Given the volume of CO<sub>2</sub> injected into the reservoir and the detectability limits of the Xe isotopes, it is calculated that it would cost ~\$0.18 / tonne CO<sub>2</sub> stored to adopt this monitoring system for the Mabee field. The transport properties of Xe were not worked out (just literature references to a He and SF<sub>6</sub> system for Yucca Mountain proposed nuclear waste disposal facility). The theory behind using noble gases to monitor CO<sub>2</sub> movement in the reservoir and leakage out reservoir is sound but work progress in the present project has been unimpressive.

## 2.4.1 Atmospheric CO<sub>2</sub> Monitoring Systems – A Critical Review of Available Techniques and Technology Gaps

**Technology Provider: CalTech**

**Principal Investigator: Yongchun Tang & Patrick J. Shuler**

**Task - 4.4 - Measurement and Verification**

### Highlights

- Calculations are made to estimate the resolution of various ground-based instruments to detecting CO<sub>2</sub> leakage at a rate of 1% of total CO<sub>2</sub> stored over 100 years (0.01% / yr.). A spreadsheet tool was included to facilitate such calculations with inputs of reservoir dimensions and leak characteristics (volume, size and nature of leak; background CO<sub>2</sub> variations and atmospheric conditions).
- Local, increased concentration of CO<sub>2</sub> over a site depends greatly on the magnitude and type (diffuse, point source) of leak and atmospheric conditions but should be detectable if CO<sub>2</sub> levels exceed a few ppmv over background concentrations.
- A considerable array of leak detection equipment is available but newer, “open path” (laser spectrometer) instruments may be more cost effective over a substantial “field-sized” area (a few km<sup>2</sup>).

### Summary

The report considers detection methods ranging from personal monitors that might be worn to warn a project employee of very high local concentrations of carbon dioxide, to instruments mounted in satellites to detect over many square miles any subtle increases in CO<sub>2</sub> that might be associated with a leakage of the injected greenhouse gas back to surface.

The greatest challenge and probably most important application is the long-term, continuous measurement of CO<sub>2</sub> near ground level across the several square miles of a project area, and the immediate surrounding area. Options include

- 1) Remote sensing from satellites or aircraft,
- 2) Development of new open path instruments that can sample over significant distances, or
- 3) A large network of conventional fixed point detectors.

NASA indicates satellite surveys might be useful for a “global” view of CO<sub>2</sub> although they may be limited to two-dimensions (satellites do not sample at ground level, but over the entire air column, from the surface to the stratosphere). Aircraft surveys may be an efficient means to collect data near ground level, but this is only practical in an infrequent basis.

Novel instruments located on the ground that are based on open path sampling appear to offer a good compromise. They could have the capability to detect increases of just a few percent of CO<sub>2</sub> from normal background, over a sample path of tens of meters, and, importantly, continuously and with unattended operation. Potentially, just a few such instruments could provide efficient long-term monitoring over a large area.

Many different commercial fixed-point units suitable for networking are available, but this is probably an impractical approach to monitor more than a small area. These detectors are better suited for deployment

to monitor sensitive, high-risk points of leakage. Infrared spectroscopy detection based methods are the most common technical approach for CO<sub>2</sub> measurement in ambient air.

The report also discusses other novel approaches to carbon dioxide monitoring. For example, one technology development in progress is the real-time measurement of carbon and oxygen isotopes via laser spectroscopy. This technique could aid in pinpointing the source of the measured CO<sub>2</sub>. Another example is the efforts by NASA to use satellite data to determine the changes in the biomass (e.g. changes in forest cover) over large areas. These observations provide a method to monitor carbon sinks over a wide area, and also are related at least indirectly to changes in greenhouse gas concentrations. CCP is sponsoring at LLNL a similar approach where remote sensing is used to monitor changes in local fauna as indicators of elevated CO<sub>2</sub> concentrations.

In the case of diffuse leakage, the study approaches the problem systematically using a series of calculation steps: 1) CO<sub>2</sub> injection (mass = volume x time), 2) leakage of a portion of injected CO<sub>2</sub> to the surface (1% / 100 years as default), 3) CO<sub>2</sub> flux rate at the surface (volume / area x time), 4) addition of CO<sub>2</sub> to a specific volume at the surface (10 ft. "box"), 5) dilution of CO<sub>2</sub> in "box" by air and 6) CO<sub>2</sub> monitor detection of increased CO<sub>2</sub>. Given a particular diffuse leakage setting (leakage flux with atmospheric dilution); therefore, detection of CO<sub>2</sub> leakage is simply a matter of identifying atmospheric concentrations of CO<sub>2</sub> above the normal background (seasonal and diurnal photosynthesis and respiration cycles; other sources) within the constraints of instrument uncertainty.

The second type of calculation uses Gaussian distribution analysis for dispersion of a contaminant plume to model CO<sub>2</sub> venting from a single point (e.g., wellbore). Selection of site specific parameters including CO<sub>2</sub> leakage rate and time, wind speed and horizontal and vertical dispersion coefficients (read from plots of downwind distance from source versus Pasquill atmospheric stability classifications) are input into an equation from which "additional" CO<sub>2</sub> due to leakage is quantified. This quantity is then compared to instrument resolution.

The third calculation uses a spreadsheet application to test the performance of open path monitoring instruments (laser spectrometer) given a leakage flux scenario (diffuse versus point with atmospheric conditions). The open path CO<sub>2</sub> detectability is a function of distance x concentration. Thus the number and array design of these instruments (and thereby cost) can be determined.

Several example calculations are used to illustrate the level of increased atmospheric CO<sub>2</sub> concentration from leakage and thereby instrument detectability. In a diffuse leakage case (10MM m<sup>3</sup>/day/20 years injected with 1% leakage over 100 years) with an atmospheric dilution factor of 25x, CO<sub>2</sub> concentration would be 24 ppmv over an area of 10 km<sup>3</sup>. Given a sample instrument uncertainty of 9 ppmv and background variation of 5 ppmv, the excess atmospheric CO<sub>2</sub> due to leakage would be easily detected. In contrast, leakage over a 100km<sup>3</sup> area would not be resolvable from background CO<sub>2</sub> and instrument uncertainty.

In a similar case but with leakage from a point source, the distances at which CO<sub>2</sub> could be detected from the source can be estimated assuming a wind speed (e.g., 3 m/s) and assigning a Pasquill stability class. At the 15 ppmv level (assuming the background and instrument uncertainty level considered in the previous example), CO<sub>2</sub> might be detectable from 0.2 to 1.2 km from the source depending unstable versus stable (respectively) atmospheric conditions.

In the case of an open path laser spectrometer instrument (cumulative CO<sub>2</sub> distance x concentration), CO<sub>2</sub> might be detected in the 1000-10000 ppmv range for a 1 m path or 0.1- 1 ppmv range for a 10000

m path. It is estimated that a suitable open path system serviceable to a field might cost \$50000-500000 (based on similar monitoring systems for other gases in use).

The study comprises a simple but very useful approach to examine CO<sub>2</sub> leak detection in a wide variety of settings. The applicability of conventional and new detection equipment to CO<sub>2</sub> detection in individual settings can be quickly screened using the spreadsheet application. One of the biggest unknowns in planning CO<sub>2</sub> storage projects is cost estimation for monitoring. The Tang Associates study addresses this in a tangible way. For example, baseline and early monitoring done by ground-based instruments could guide the design of much more expensive field scale “tower” systems. Ground-based instruments could evolve into very reliable, sensitive and inexpensive approaches to monitoring that might obviate the need for other monitoring techniques (e.g., subsurface imaging, soil gas collection and remote an aerial).

### **Recommendations:**

The authors recommend:

- Development of reliable, lower cost, open path laser spectrometer detection systems customized to measure CO<sub>2</sub>
- Testing of instrumentation at sites where CO<sub>2</sub> flux to the surface is active either from natural processes (e.g., Mammoth Mountain) or CO<sub>2</sub> EOR operations (e.g., Weyburn).

### **Reports and Publications**

- CCP-SMV Workshop, Dublin
- The project final report is in Appendix A under the same heading as this summary.

## 2.4.2 Novel Geophysical Techniques To Monitor CO<sub>2</sub> Movement

Task - 4.4 - Measurement and Verification

Principal Investigator: Mike Hoversten

Technology Provider: LBNL

### Highlights

- It is confirmed that standard P-wave seismic is effective in monitoring CO<sub>2</sub> movements in the subsurface and suggestive that offset attributes of seismic data should also be useful for this purpose also.
- Gravity work requires either borehole application or, if on the surface, permanent instrumentation, in order to reliably detect CO<sub>2</sub> movements
- Further work in resistivity and streaming potentials technologies is justified because these techniques could be result in lower resolution but cost effective CO<sub>2</sub> monitoring techniques alone or as supplements to conventional techniques.

### Summary

The Schrader Bluff model was chosen as a numerical test bed for quantitative comparison of the spatial resolution of various geophysical techniques being considered for CO<sub>2</sub> sequestration monitoring. The difference in the vertical component of gravity caused by CO<sub>2</sub> injection over a 20-year period is on the order of 2  $\mu$ Gal, which is in the noise level of the field survey. Just as with  $G_z$ , the magnitude of  $dG_z/dz$  measured at the surface is above the gradiometer accuracy, but the difference between initial conditions and 20 years into CO<sub>2</sub> injection is too small to resolve with current technology. These results suggest future analysis to determine the maximum sensitivity of  $G_z$  and  $dG_z/dz$  that could be obtained by permanent emplacement of sensors with continuous monitoring coupled with surface deformation measurements to reduce noise levels.

In addition to surface gravity measurements, borehole gravity measurements have been modeled. Measurements done in boreholes just above (1,200 m depth) the reservoir interval would produce measurable changes in  $G_z$  that would directly map the areas of net density changes caused by injected CO<sub>2</sub> and water within the reservoir.

There is a significant change in seismic amplitude associated with the reservoir caused by the changes in water and CO<sub>2</sub> saturation as sequestration proceeds. In addition, there is a large change in the AVO response from the reservoir interval. Both seismic amplitude and AVO can be exploited to make quantitative estimates of saturation changes. Forward calculations using the Zoeppritz equation for both five and twenty years into injection show significant changes in both the zero-offset amplitude and the gradient of the response with angle.

The electrical resistivity of reservoir rocks is highly sensitive to changes in water saturation. This high sensitivity to water saturation in a reservoir can be exploited by electromagnetic (EM) techniques where the response is a function of reservoir electrical resistivity. There is a direct one-to-one correspondence with the change in  $S_w$  and the change in the electric field amplitude. While this signal level is low, it can be measured given the signal-to-noise ratio of the data. While this represents a potential low-cost monitoring technique it is best suited for CO<sub>2</sub> – brine systems where there is a one-to-one correlation

between the change in water saturation and the change in CO<sub>2</sub> saturation (since  $S_w + S_{CO_2} = 1$ ). The equipment and service providers exist to apply this technique for monitoring in the future.

The streaming potential method has the potential to be a low-cost low-resolution method of large scale reservoir monitoring. Compared to other geophysical techniques, relatively little quantitative work has been done on the SP technique. The response of a CO<sub>2</sub> sequestration scenario in 2D has been simulated, based both on the Liberty Field and Sleipner CO<sub>2</sub> injection tests. Modeling results show that injection of CO<sub>2</sub> to the Liberty Field formation would produce a response, which is easily measured with the SP method. The Sleipner results are less encouraging, however, as a number of key parameters are poorly defined and definitive statements about the potential of SP as a monitoring tool cannot yet be made.

### **Reports and Publications**

- Hoversten, G. M., Gritto, R., Washbourne, J., Daley, T., M., 2003, Pressure and Fluid Saturation Prediction in a Multicomponent Reservoir, using Combined Seismic and Electromagnetic Imaging. Geophysics, (In Press Sept-Oct 2003). LNBL - 51281
- Hoversten. G. M., Gritto, R., Washbourne, J., Daley, T., ,“Non-seismic geophysics for CO<sub>2</sub> Sequestration Monitoring”, 2002 SEG Workshop on CO<sub>2</sub> sequestration Oct. 10, 2002, SEG Annual Convention
- Hoversten. G. M., Gritto, R., Washbourne, J., Daley, T., “CO<sub>2</sub> gas/oil ratio prediction in a multi-component reservoir by combined seismic and electromagnetic imaging”, 2002, LBNL report # 51408
- Hoversten, G. M., Myer, L., Daley, T., “Crosswell seismic and electromagnetic monitoring of CO<sub>2</sub> sequestration”, 2002, GHGT-6 conference, Kyoto, Japan.

## 2.4.3 Optimum Monitoring Technology

### Task - 4.4 - Measurement and Verification

Principal Investigator: Rob Arts

Technology Provider: TNO-NITG

#### Highlights

- The project was completed yearend 2002 and a final report was delivered.
- The study provides a comprehensive roadmap of potential monitoring technologies that may be useful in future projects.

#### Summary

The Optimum Monitoring Technology project completed by TNO-NITG reviews the benefits of currently available monitoring techniques and provides a best practice manual for CO<sub>2</sub> sequestration and monitoring. The present work was directed to the improvement of long-term monitoring & verification for sequestration of CO<sub>2</sub> in various geological media. The experience from other projects (SACS, RECOPOL, Coal and Gas Thermie B, NASCENT, Dutch NOVEM study) was used to set guidelines for an optimum monitoring strategy for the different geological options. Baseline measurements prior to CO<sub>2</sub> injection are needed so that sequestration induced changes can be observed. This implies that monitoring techniques must be selected at the earliest stage of each sequestration project to provide the “base case.” This study gives “best practice” guidelines for such a selection by defining the key geological parameters and circumstances required for the different techniques and an estimation of the accuracy obtained.

The objectives of monitoring underground CO<sub>2</sub> storage are:

- To ensure the sustainability of the CO<sub>2</sub> reduction target and
- To ensure the safety requirements for subsurface activities during and after the operational phase

The first objective is focused on tariffs and legislation, whether the agreed quota as originally planned for CO<sub>2</sub> sequestration are met and maintained. The second objective is more important focusing on the safety issues of the storage site. The main risks as a consequence of underground CO<sub>2</sub> sequestration can be categorized as:

- Leakage to the surface or other geological formations with possible groundwater contamination or escape to the atmosphere as a consequence.
- Uplift due to injection of CO<sub>2</sub> or subsidence due to production or leakage of CO<sub>2</sub> can cause damage to constructions at the surface.

A secondary goal of monitoring is research and development regarding underground CO<sub>2</sub> sequestration. Gaining more understanding of the processes going on in the reservoir is important for the optimization of future storage sites.

CO<sub>2</sub> sequestration has to be monitored so that the operators and public will know that the CO<sub>2</sub> is not leaking to the surface (or overburden) where it is migrating in the reservoir. In this report a broad approach has been chosen taking into account as many monitoring techniques as possible. Globally three areas of investigation for monitoring can be identified:

- Reservoir integrity: Pressure, temperature, spreading and long-term fate of the CO<sub>2</sub>.
- Seal integrity: Fractures, faults, wells, heterogeneous permeability.



- Migration pathways in the overburden and the atmosphere.

The first and especially the second are probably the most important areas in terms of an early warning system for possible leakage. In the ideal case one would expect to “see nothing” in the third area.

Monitoring techniques have been divided into 3 categories:

- Instrumentation in a well (monitoring well)
- Instrumentation at the (near) surface (surface geophysical methods)
- Sampling at the (near) surface measuring CO<sub>2</sub> concentrations (geochemical sampling techniques)

The final report describes each of the available monitoring techniques and gives direction on which are likely to be successful in CO<sub>2</sub> storage applications.

### **Reports and Publications**

- CO<sub>2</sub> Optimum Monitoring Methodology, R.J.Arts & P. L. A. Winthagen, Netherlands Institute of Applied Geosciences TNO, Report NITG-02-229-B, 23 December 2002.
- The final report was presented in Appendix A of an earlier report.

## 2.4.4 Hyperspectral Geobotanical Remote Sensing for CO<sub>2</sub> Storage Monitoring

**Task - 4.4 - Measurement and Verification**

**Principal Investigator: William Pickles**

**Technology Provider: LLNL**

### Highlights

- A remote hyperspectral monitoring technique, which uses the reflectance of sunlight from plants and geological formations to detect changes induced by CO<sub>2</sub> leaks, has been tested at two localities: 1) Mammoth Lake., CA (satellite detection of natural volcanic CO<sub>2</sub> emanations) and 2) Rangely Field, CO (aerial detection of CO<sub>2</sub> leakage from a 15 year CO<sub>2</sub> EOR operation).
- At the heavily vegetated Mammoth Lake locality CO<sub>2</sub>-stressed plants including tree kills mapped remotely by the hyperspectral technique are corroborated by ground-based observations.
- At high desert Rangely oilfield locality, there are indications that potential CO<sub>2</sub> leakage might be monitored by repeated surveys of “habitat” distributions (assemblages of two or more plant species with associated soil types). The prospects for remote detection of CO<sub>2</sub> leakage from Rangely may be limited, however, as soil gas surveys show that such leakage is negligible.
- The principle utility of this large area coverage technique appears to be detection of long term, low level CO<sub>2</sub> leakage that subtly changes “habitat” or short term or high level CO<sub>2</sub> leakage rates that result in plant stress or mortality.

### Summary

The objective of this project was to develop a remote (satellite or aerial) method of mapping for CO<sub>2</sub> leaks indirectly by detecting changes in plants or by mapping hidden faults that serve as pathways for potential CO<sub>2</sub> leaks, over the entire area above an underground formation being injected with CO<sub>2</sub>. Hyperspectral geobotanical remote sensing was applied by satellite to Mammoth Lake, CA and the Rangely Oil Field, CO. Detailed maps developed of soil types, plant species, plant health, water conditions, and human activities were used in attempts to infer the location and magnitude of CO<sub>2</sub> leakage.

- These maps established an environmental and ecological baseline against which any future CO<sub>2</sub> leakage effects on the plants soils and water conditions could be detected and verified.
- Signatures that may be subtle hidden faults were noted. If confirmed these faults might provide pathways for upward CO<sub>2</sub> migration.
- Analysis of the detailed maps allowed the identification of plant types and plant ecologies which could be used to detect long term, low level CO<sub>2</sub> leaks by changes in ecological balance as well as short term, high concentration leaks that would be noted by changes in plant health.
- The technique uses commercially available remote sensing technology and newly developed analytical techniques to provide a reliable and reasonable cost method of long term monitoring.

It is not known what concentrations of CO<sub>2</sub> in the vadose zone and over what time frame the reflectance of various plants will be affected. This was cited as the basis of future work.

The hyperspectral geobotanical satellite and aerial surveys identified current interpretive limits for the application of this technology to CO<sub>2</sub> leak detection. The high cumulative flux of CO<sub>2</sub> at the well-

vegetative Mammoth site was easily qualified using plant stress indicators. The Rangely Field is located in an arid region and has been shown by soil gas surveys to have a very low to nil net CO<sub>2</sub> flux. The hyperspectral method could not, therefore, directly detect CO<sub>2</sub> leakage but the potential exists for long term detection of “habitat” changes due to CO<sub>2</sub> leakage through repeat surveys. Further interpretive work on hyperspectral bands sensitive to soil microbe changes (from CO<sub>2</sub> and methane) and their direct corroboration with soil gas survey data might be a more economical and time saving approach to this problem.

### **Reports and Publications**

- William L. Pickles, Geobotanical hyperspectral remote sensing of Vegetation Responses to CO<sub>2</sub> Leakage From Underground storage formations, CCP SMV International Meeting, GFZ, Potsdam, Germany, October 31, 2001
- William L. Pickles, Finding hidden faults above and Vegetation Responses to CO<sub>2</sub> Leakage from Underground storage formations, CCP SMV International Meeting, University of California Santa Cruz, October 21, 2002,
- William L. Pickles, LLNL, Wendy A. Cover, UCSC, Donald C. Potts, UCSC, Brigitte A Martini, HyVista Corp, Possible CO<sub>2</sub> Leakage Monitoring and Verification. Finely Detailed Habitat Mapping Using High Resolution Hyperspectral Imagery At the Rangely CO, USA, EOR field, CCP SMV International Meeting in Dublin Ireland, September 21, 2003
- William L. Pickles, Hyperspectral Geobotanical Remote Sensing for CO<sub>2</sub> Storage Monitoring, CO<sub>2</sub> Capture Project - An Integrated, Collaborative Technology Development Project for Next Generation CO<sub>2</sub> Separation, Capture and Geologic Sequestration, Semi-Annual Report, 2.4.4, July 14, 2003
- The project finalreport is in Appendix A under the same heading as this summary.

## 2.4.5 Long Term Monitoring And Verification Using Noble Gas Isotopes

### Task - 4.4 - Measurement and Verification

Principal Investigator: Greg Nimz

Technology Provider: LLNL

#### Highlights

- Initiated noble gas isotopic analyses on samples obtained from the Mabee EOR field.
- Based on the initial Mabee analyses, the quantities of noble gas tracers required for an actual CO<sub>2</sub> storage setting were calculated. Cost estimates relative to total CO<sub>2</sub> storage costs and CO<sub>2</sub> “taxes” were derived.
- The distinct elemental and isotopic composition of the noble gases present in the injected CO<sub>2</sub> can be used as noble gas tracers of the EOR process. The 15 samples collected from the Mabee field show a good spread in CO<sub>2</sub> noble gas contributions in the recovered casing gas.
- Literature survey was completed to obtain satisfactory rock properties for incorporation into a NUFT-C model of gas transport through the shallow crust. This includes obtaining data on porosity-permeability relationships, mineralogy and lithological heterogeneity.
- Initial simulations of noble gas transport were produced. These form the basis of a noble gas monitoring strategy.
- This project is faced with major funding issues. Discussions are underway with the principal investigator to try and resolve the issues. Work scope reductions will likely be required.

#### Summary

The objective of this project is to develop the technological foundation for using noble gas isotopes to:

- 1) Create a mechanism for long-term monitoring of CO<sub>2</sub> storage sites;
- 2) Test EOR reservoirs for CO<sub>2</sub> leakage caused by production-related changes in caprock integrity (thereby screening for their suitability for long-term large volume CO<sub>2</sub> storage);
- 3) Screen brine aquifers or similar formations for suitability for CO<sub>2</sub> storage; and
- 4) Provide a mechanism for fingerprinting injected CO<sub>2</sub> so that the source and ownership of leaking or migrating CO<sub>2</sub> can be identified.

The project is comprised of three basic components:

- Collecting and analyzing noble gas isotopes accompanying both injected and recycled CO<sub>2</sub> at an operating Enhanced Oil Recovery (EOR) field in the Permian Basin of West Texas.
- Initiate a noble gas tracer test at an active EOR field. Injected CO<sub>2</sub> will be spiked with identifiable noble gas isotopes; recycled CO<sub>2</sub> will be monitored for recovery of spike signals. This and the previous component will provide a proof of principle and “debugging” of techniques for noble gas/CO<sub>2</sub> injection.
- Develop a NUFT-C computer model of noble gas tracers migrating upward through the crust from a leaking CO<sub>2</sub> storage site. This component will form the basis for the design of a monitoring strategy.

Activities during this reporting period included:

- Began compilation of geologic and hydrologic data relevant to the Permian basin (especially the Mabee EOR field) for the purpose of development of a NUFT-C prototype numerical model of noble gas migration in crustal media. This will form the basis of a monitoring strategy for CO<sub>2</sub> leakage.
- Initiated noble gas isotopic analyses on samples obtained from the Mabee EOR field.
- Analyses of neon and argon from samples of well casing gases from the Mabee EOR field, west Texas, were completed, and preliminary helium and xenon data were obtained.
- Based on the work at the Mabee EOR field, it is clear that the distinct elemental and isotopic composition of the noble gases present in the injected CO<sub>2</sub> can be used as noble gas tracers of the EOR process. The 15 samples collected from the Mabee field show a good spread in CO<sub>2</sub> noble gas contributions in the recovered casing gas. While the neon and argon components from the injected CO<sub>2</sub> give similar results, the signal at xenon (fission xenon - primarily <sup>134</sup>Xe and <sup>136</sup>Xe) appears to be depleted relative to neon and argon, possibly suggesting preferential partitioning of the xenon into a hydrocarbon liquid phase.
- Literature survey was completed to obtain satisfactory rock properties for incorporation into a NUFT-C model of gas transport through the shallow crust. This includes obtaining data on porosity-permeability relationships, mineralogy and lithological heterogeneity. Although the first model will incorporate a simplified stratigraphy, these data will provide the basis for constructing that first model in such a way as to allow expedient incorporation of heterogeneity in the second set of model runs.
- Initial simulations of noble gas transport were produced. These form the basis of a noble gas monitoring strategy.

### **Reports and Publications**

- Nimz, G.J., Hudson, G.B., and Glassley, W.E., Noble gas isotopes for screening, verification, and monitoring at CO<sub>2</sub> storage sites, JIP CO<sub>2</sub> Capture Project Workshop: "Building the SMV Family of Technology Providers", Potsdam, Germany, Oct 31-Nov 2, 2001. (presentation)
- Nimz, G.J., Hudson, G.B., and Glassley, W.E., Noble gas isotopes for screening, verification, and monitoring at CO<sub>2</sub> storage sites, JIP CO<sub>2</sub> Capture Project Workshop: "Building the SMV Family of Technology Providers", Santa Cruz, California, Oct 21-23, 2002. (presentation)

## **2.4.6 Monitoring Geologic Sequestration with Satellite Radar Interferometry**

### **Task 4.4 Measurement and Verification**

**Principal Investigator: Howard Zebker**

**Technology Provider: Stanford University**

### **Highlights**

- The applicability of satellite radar interferometry (InSAR) to detecting ground movement (deformation) due CO<sub>2</sub> injection (sequestration) was investigated. Deformation modeling was used to produce surface deformation maps that could be tested against InSAR sensitivity. The advantages of InSAR detection relative to tiltmeters and GPS are compared.
- Given ERS radar system parameters and allowing for atmospheric “noise”, a sensor baseline was derived. InSAR resolution is expected to be in the 1 cm range (compared to tiltmeter < 0.1 rad, GPS < 1cm). Atmospheric effects may diminish this resolution by 10 mm.

### **Summary**

This study investigated the theoretical resolution of satellite radar interferometry (InSAR) in detecting small ground movements induced by CO<sub>2</sub> injection into reservoirs. The advantages of this technology would include high spatial coverage (20 m postings over a large area), continuous data collection and ease of data collection. The approach is compared to the resolution of other technologies such as tiltmeters (<0.1 rad) and GPS (<1 cm). Influences that can diminish the resolution of the InSAR technique include atmospheric and topographic effects.

Using a model reservoir (2000 m depth, 4000 m radius, 100 m thickness, 6CPa shear modulus, 0.25 Poisson's Ratio, 20% porosity, 10 mD permeability, hydrostatic pore pressure and standard geothermal gradient) and injection protocol (supercritical CO<sub>2</sub>, 12 months, constant 30kg/s) injection swelling (deformation) was modeled and mapped. An expected deformation detection of the InSAR method using the model reservoir and injection properties is thought to be ~ 1 cm. Modeling of noise due to atmospheric effects was calculated at 10 mm. Modeling of the topography influence was mentioned but no numerical figure was put forward.

The authors concluded that given the ERS radar system parameters a sensor baseline could be established. Differential InSAR can be used to detect small surface deformation signals due to CO<sub>2</sub> sequestration. Future work proposed identifying CO<sub>2</sub> sequestration or oil and gas reservoirs to test the InSAR data and inversion of InSAR measurements for pressure changes at depth.

This study was terminated at the 2002 SMV Meeting (Santa Cruz) with lack of progress. Resolution was considered insufficient to give meaningful measurements. The study was terminated in September 2002 due to high technical risk for deployment.

## 2.4.7 Measurement Techniques For the Detection of Leaks From Underground CO<sub>2</sub> Reservoirs: Evaluation and Summary of Capabilities

Task - 4.4 - Measurement and Verification

Technology Provider: Penn State University

Principal Investigators: K. J. Davis, J. C. Wyngaard

### Highlights

- Major atmospheric CO<sub>2</sub> fluxes are easily detectable by the eddy covariance method if they are less than a few kilometers upwind of the measurement tower.
- Minor CO<sub>2</sub> fluxes (1% of 100 million tons of CO<sub>2</sub> lost evenly over 100 years through a 0.1 square km patch) may also be detectable by the current generation of equipment.
- Minor CO<sub>2</sub> flux emissions are of the order of biological CO<sub>2</sub> flux variability (related to diurnal photosynthetic and respiration cycles) and so require knowledge of the background biological signal in order to properly assess the CO<sub>2</sub> flux readings.
- The method depends on the presence of substantial atmospheric turbulence (which occurs about 75% of the time) and so is appropriate for long-term monitoring but cannot replace point concentration monitors near wellheads to warn of sudden major leaks.

### Summary

The eddy covariance technique involves continuous atmospheric measurements of both CO<sub>2</sub> mixing ratio and atmospheric winds from a tower platform. Equipment is robust and commercially available, and the methodology is well-established.

The upwind distance sensed is typically 10-100  $z_m$ , where  $z_m$  is the measurement height, and the cross-wind extent of the measurements is of the order of the upwind distance. Thus a 10 m high tower would detect fluxes from an upwind distance of 100 to 1000 m, and an area of order 0.1 to 1 km<sup>2</sup>. Typical applications of this methodology result in fairly continuous hourly or half-hourly measurements of ecosystem-atmosphere exchange over these areas. The measurement works best under well-mixed atmospheric conditions, which occur on a daily basis, often for a majority of the day.

The ability to detect leaks from geologic CO<sub>2</sub> reservoirs is assessed by comparing expected leakage rates to typical ecological flux rates. While the character and magnitude of ecological fluxes are well established, reservoir leakage rates are uncertain. Fairly conservative estimates based on ensuring the economic viability of CO<sub>2</sub> sequestration are constructed. It is shown that the leakage rates under these assumptions would range from 1 to 10<sup>4</sup> times the magnitude of typical ecological fluxes. The flux measurement areas can readily encompass the assumed leakage areas (10 to 10<sup>5</sup> m<sup>2</sup>). Thus we conclude that this approach shows promise for the monitoring of leakage from underground CO<sub>2</sub> storage facilities.

Future work should include active tests of the eddy covariance method for detecting release-related CO<sub>2</sub> fluxes. For example, once a site is characterized with respect to its biological CO<sub>2</sub> flux variability, a planned CO<sub>2</sub> release could then be initiated and the response by the eddy covariance measurement towers determined. This portion of the assurance process should be performed at a well-characterized site remote from human populations.

### Reports and Publications

- CCP-SMV 2003 Workshop, Dublin

- Davis, K. J., P. S. Bakwin, C. Yi, B. W. Berger, C. Zhaos, R. M. Teclaw, and J. G. Isebrands, 2003: The annual cycles of CO<sub>2</sub> and H<sub>2</sub>O exchange over a northern mixed forest as observed from a very tall tower. *Glob. Change Biol.*, **9**, 1278–1293.



## 2.5 Integration and Communications

The SMV program of CCP has funded and managed ~30 projects over the last three years. These projects are grouped into four technology areas: Integrity, Optimization, Monitoring and Risk Assessment. Research results were submitted in the form of presentations, reports and software. The results of most of these studies so far has met expectations. There is a concern, however, that these research products might be filed away and thus not be made available to promote CO<sub>2</sub> storage technology. To publicize SMV efforts to a broad range of audiences, LBNL (Benson) was contracted to develop a plan for “Publication and Dissemination of Research Results” to be conducted in parallel with the larger CCP integration and communication effort. Five categories of publications are envisioned:

- 1) A large compilation of high quality, technical papers covering all areas of SMV research by a respected scientific society (e.g., AGU). The target audience includes technical specialists interested in geological sequestration of CO<sub>2</sub> and the IPCC.
- 2) A technical review article focusing on the principal technology areas of SMV (integrity, optimization, monitoring and risk assessment) (e.g., JPT, Oil & Gas Journal). The target audience includes scientists and engineers being introduced to CO<sub>2</sub> sequestration.
- 3) A technical review article similar to 2) but with more introductory treatment (e.g., Scientific American). The target audience includes NGOs, Regulators, government officials with an interest in science and technology.
- 4) A short, high impact “state-of-the-art” article (e.g., Science, Nature). The target audience includes government officials, scientific policymakers, NGOs and scientific press.
- 5) Brochure or pamphlet on geologic storage that highlights the accomplishments of the SMV (hard copy or web-based). The target audience includes general public, educators and regulators being introduced to the technology.

The CCP has arranged publication of a two volume set of the CCP’s results in book form by Elsevier Science. The set, to be published by the end of 2004, will include virtually all the topics included in the CCP program as peer-reviewed technical papers, section summaries and analyses, and the economic modeling results for each of the cases. The set will provide a single source for all segments of the CCP irregardless of funding source.

The 2003 SMV Workshop will be held in Dublin, Ireland September 22-25. Most of the projects are expected to be complete or nearly so by that time. The workshop will offer an opportunity for TP PIs to vet their work among themselves and before the SMV team and external experts. This will allow modest adjustments to be made before project completion. The workshop will also offer the opportunity to encourage the participants to contribute to the publication efforts and to engage them on possible future CCP efforts.

## 2.5.1 Technical Report Integration Into Topical Reports

### Task - 5.2 - Routine Project Reporting

#### Highlights

Contract has been executed and work is underway.

#### Summary

The purpose of this task is to develop a book (edited volume) and several overview articles based on results from the SMV team of the CO<sub>2</sub> Capture Project. We will develop a series of reports and publications that will be used to communicate the results of the SMV team's work to a variety of audiences that would benefit from this information. Target audiences include the staff of the member companies of the CCP JIP, technical specialists interested in geologic sequestration, NGO's, regulators, government officials, opinion makers, and the general public. The overview publications will be submitted between by November 30, 2003 with publication expected by mid-2004. The edited volume will be submitted by March 31, 2004 and published before October 2004. This effort is being coordinated with the overall CCP integration and communications plan.

The CCP SMV team has contracted Lawrence Berkeley National Laboratory to implement a publication strategy that will disseminate the results of the ~30 SMV studies to diverse audiences ranging from technical specialists to the public. Table 9 matches the audience to the type of publication.

**Table 9**  
**Suggested products from the SMV Team for dissemination of results.**

<b>Audiences</b>	<b>Product</b>	<b>Description</b>
<ul style="list-style-type: none"> <li>• Technical staff from the member companies of the JIP</li> <li>• Technical specialists interested in geologic sequestration</li> </ul>	Publication #1. Large compilation of technical papers (20-30 pages each) from all of the projects in the SMV; prefaced by an executive summary.	Peer reviewed, high quality technical document. Suitable for citation by the IPCC special study. Published as a book from a widely respected scientific society.
<ul style="list-style-type: none"> <li>• Scientists and engineers being introduced to geologic sequestration, regulators</li> </ul>	Publication #2. Technical review article, 20-30 pages long. Focused on major areas of the SMV, risk assessment, storage optimization, storage integrity and monitoring and verification.	Technical article to be published in widely distributed technical journal (e.g. JPT, Oil and Gas Journal).
<ul style="list-style-type: none"> <li>• NGOs, regulators, government officials, public with an interest in science and technology, press</li> </ul>	Publication #3. Technical review article, 20-30 pages long. Introduction to geologic storage followed by a description of the major areas of the SMV project, risk assessment, storage optimization, storage integrity and monitoring and verification	Article for a broad audience published in a widely read journal such as Scientific American or the equivalent.
<ul style="list-style-type: none"> <li>• Government officials, scientific opinion makers, NGOs, scientific press</li> </ul>	Publication #4. Short "State of the Technology Article" (3-5 pages) for highly influential scientific audience and government leaders.	Short article for high impact scientific journal (e.g. Science or Nature).
<ul style="list-style-type: none"> <li>• General public, NGOs, press, educators, regulators being introduced to the technology</li> </ul>	Publication #5. Brochure or pamphlet on geologic storage that highlights the contributions of the CCP JIP.	Hard copy & web-based description of geologic storage targeted to a non-tech audience. Emphasis on contributions of the CCP to geologic storage. Emphasize benefits of technology.

The following outlines the deliverables for the project:

1. Publication #1. Prepare an executive summary, introduction and conclusions that would introduce and summarize a compilation of all of the papers for each of the SMV projects. Organize and oversee a peer review for all of the final papers delivered to the SMV team.
2. Publication #2. In consultation with the SMV team, prepare a review article (approximately 30 pages) of the results from the SMV teams work. Submit to a widely available journal for technical specialists interested in geologic sequestration (e.g. JPT, Oil and Gas Journal, or others at the suggestion of the SMV team).
3. Publication #3. In consultation with the SMV team and the SMV team's communications consultant, prepare a review article (approximately 30 pages) of the results from the SMV teams work. Submit to a widely available journal for broad audience (e.g. Scientific American or others at the suggestion of the SMV team).
4. Publication #4. In consultation with the SMV team, prepare a short "State of the Technology" paper (approximately 35 pages) based on the results of the SMV teams work. Submit to a highly prestigious journal (e.g. Science or Nature).
5. Publication #5. Provide technical assistance to the SMV team's communications consultant to prepare a brochure or short pamphlet for the general public about Geologic Sequestration and the SMV team's projects.

### **Reports and Publications**

None.

## 2.5.2 SMV Workshop – Dublin, Ireland, September 22-24, 2003.

### Highlights

- The fourth annual CCP-SMV Workshop, held in Dublin, Ireland on September 22-24, 2003, drew 45 CCP members and researchers and external experts and JIP representatives.
- The presentations, organized by SMV categories “integrity”, “optimization”, “monitoring” and “risk assessment”, were given over five half day sessions. The final half day session entailed breakout groups discussing research and collaborative needs in geosciences, engineering, risk assessment, monitoring & verification, inter-JIP collaboration & benchmarking and policies & incentives / economics.
- The presentations were of good quality and opportunities were made available for the participants to offer feedback. The breakout sessions were useful in identifying technology gaps and tentatively establishing collaboration relationships.

### Summary

The 2003 CCP-SMV Workshop, held in Dublin (September, 22-24), drew 45 participants including contracted researchers, CCP representatives and leaders of other JIPs. The CCP program is co-funded by the US DOE (NETL), The EC and the Norwegian Research Council (Klimatek program).

The research presentations were of high quality and for the most part showed excellent progress towards the final deliverables. With the "integrity" studies, a framework is now in place for assessing the suitability of prospective CO<sub>2</sub> storage sites. With the "optimization" studies, CCP has documented specific operational data and models that can be applied to pilot, demonstration and commercial CO<sub>2</sub> storage projects. The “monitoring” technologies presented, although unconventional, will likely complement more conventional approaches with further development. Risk assessment has advanced to where systematic datasets are available to test selected scenarios.

In addition to the research reports, the Workshop included overviews of other JIPs (IEA Weyburn and CO<sub>2</sub>CRC) and presentations on active and planned CO<sub>2</sub> sequestration projects (Sleipner, Weyburn, In Salah, Gorgon and US pilots). In the half day topical session, breakout groups addressed issues in geosciences, engineering, monitoring & verification, risk assessment and inter-JIP collaboration.

The conference was viewed by many as a unique opportunity to build collaborative relationships among major CO<sub>2</sub> sequestration JIPs. For the SMV team, the conference was essential to assess needed work to complete the CCP-SMV project and to identify needs for future research.

Among the recommendations received, the following is excerpted from Vello Kuuskraa’s (President ARI and CCP Technical Advisory Board Chair):

*1. Implementing a Formal "Peer Review" Process in Addition to the Information Exchange Workshop. A true "peer review" function would provide an opportunity for more in-depth examination of the research findings and results, beyond what can be accomplished by a Workshop or by limited SMV project management. In the capture portion of the CCP, such "peer review" is provided by the several Carbon Capture Team Leaders as well as by the Technical Advisory Board.*

*2. Creating Additional Sub-Teams for Distinct SMV Areas/Each With a Formal*

*Team Leader.* The SMV area is much more diverse and specialized than originally assumed. At least four distinct areas have emerged, including: (1) Reservoir Integrity; (2) Storage Optimization; (3) Monitoring and Verification; and, (4) Risk Assessment. (These four topics served as an excellent organizing structure for the recent SMV Workshop.) As such, the SMV structure could begin to resemble to CCP CO<sub>2</sub> Capture structure where a company-designated Team Leader would head each of the four distinct SMV areas. This structural approach would also provide greater management oversight for individual projects and would lead to greater project-to-project coordination.

3. *Achieving Greater Coordination Among the Capture and SMV Teams.* A number of approaches could be used to achieve this highly desirable and valuable objective, eventually leading to lower overall CO<sub>2</sub> capture and storage costs. One approach would be periodic meetings among the Capture and Storage Team Leaders to discuss CO<sub>2</sub> purity specifications as well as the cost impact of capturing and storing co-pollutants (i.e., SO<sub>x</sub>, NO<sub>x</sub>). Another approach would be to include a capture and storage optimization function within the common economic model to address the issue of CO<sub>2</sub> purity and co-products.

4. *Including Resources for Workshop Attendance and PI Presentations in Future Research Contracts.* Future research contracts between SMV Technology Providers and the CCP should specify a line item budget for attending SMV Workshops and should require that the PI provide the SMV presentation at these Workshops. This would preclude some of the "budget tightness" problems common at the end of a project.

5. *Installing a More Rigorous "Before the Fact" Planning and Priority Process for Future SMV Projects.* The current SMV Program evolved from a combination of CCP-identified gaps in SMV technology and research and from the "good ideas" in the proposals from the SMV Technology Providers. This process served the initial phase of SMV research reasonably well. Now, however, the research and knowledge process is further advanced, enabling new SMV research to focus on priorities and not just gaps. The three high priorities identified during the "breakout session" (listed previously) and the suggestion for a highly instrumented field storage site (field laboratory) are steps in the right direction toward planning for high impact SMV research for Phase II of the CCP.

### **3. Technology Screening**

#### **Task - 0.3 - Develop & Apply Common Economic Model**

##### **Highlights:**

The technology screening process continues to be used by the technology teams in their work.

##### **Summary:**

Early in the technology development program, it became obvious that the best way to derive a truly consistent comparison of all technologies and all scenarios is to fully design each complete system and estimate costs to a high standard. The cost of using the independent cost estimation contractor to complete that work for every combination of technology and scenario would be prohibitively expensive and would detract from the technology development effort. Furthermore, the technology development effort could be best focused if the CCP was able to choose high potential technologies early in the program and focus resources on those most likely to succeed.

The CCP formed a Technology Screening Task - Force (TSTF), comprising representatives from all the technical teams and a cross-section of the participating companies. For each case, a preliminary process design and description was prepared that included estimates of the key process variables (fuel, power, CO<sub>2</sub> captured & emitted etc.). Capital and operating expense estimates for each case were prepared as input to and analysis by the Common Economic Model (see below). Design and costs were benchmarked against the baselines established for each scenario by the common cost estimation contractor. Twelve cases were completed in 2002 All of the economic and screening work to date was funded directly by the CCP.

##### **Reports and Publications:**

None.

## **4. Economic Modeling**

### **Task - 0.3 - Develop & Apply Common Economic Model**

#### **Highlights:**

- Economic modeling results from all the engineering studies performed under the CCP project are being consolidated in a report and are receiving intense scrutiny by team members.
- The final economic modeling results will be issued with the next progress report (August 2004) and final project report (October 2004).

#### **Summary:**

A primary objective of the CCP is to develop technologies that can be applied in various commercial applications. Business investments require accurate estimates of the costs to build, commission, and operate the resulting plant. At the outset, the team found that there was little consistency in the way that the cost of CO<sub>2</sub> mitigation was estimated. Wildly varying numbers were published and used throughout the CO<sub>2</sub> mitigation community. Consequently, CCP set an early goal to develop a transparent and straightforward way to estimate the full cost of CO<sub>2</sub> mitigation by the subject technologies. The resulting common economic model has been used by the CCP team to evaluate technologies for further development and is used to help the teams judge the potential of new technologies.

The Common Economic Model (CEM), developed by a small CCP team, is a multi-technology economic screening tool that uses a set of economic assumptions and high-level technology and scenario input data. The objective of the model is to establish best estimates of CO<sub>2</sub> avoidance costs to enable economic decision-making. All CO<sub>2</sub> costs are calculated as normalized differentials between the capture and non-capture cases. The target for each model run is to establish the lowest cost per tonne of CO<sub>2</sub> avoided and to calculate the cost of CO<sub>2</sub> captured. The definitions of those two terms are:

**Captured CO<sub>2</sub> Cost** = total capture-related cost (capital expense, operating expense, energy) per tonne of CO<sub>2</sub> directly captured by the process.

**Avoided CO<sub>2</sub> Cost** = Captured CO<sub>2</sub> Cost (above) adjusted for the volume of CO<sub>2</sub> associated with imported energy (i.e. indirect CO<sub>2</sub>).

The first version of the model was peer reviewed by two independent advisers (Ed Rubin, Carnegie Mellon University, and Howard Herzog, MIT.) Following that peer review, a simplified version of the model (CEM Compact) was developed and was used to support the technology screening effort.

**Early cost estimation:** The basic approach was to test CO<sub>2</sub>-capture technologies for application in the CCP scenarios. The resulting Scenario-Technology (S-T) matrix contains S-T cases to be evaluated for cost to allow fair and consistent economic comparisons. The CCP technology program includes a large number of technologies completed by numerous suppliers. As each project is completed, the external technology suppliers established cost estimates for their technologies. CCP is evaluating new capture technologies for application in the CCP scenarios that include costs of all integration activities such as: energy/ utility supplies, transportation/ logistics, various site costs, etc. The CEM team uses the results from the technology provider reports in the common economic model to make its estimates of overall CO<sub>2</sub> capture cost.

**Final Cost Estimation:** The dilemma facing the team and the reason that its results are delayed is that the technology development projects were finished in the past month (January 2004). The economic team

must receive, enter, calculate, evaluate, and iterate with the technology development teams to ensure that the results are being used correctly. A very necessary internal peer review is completed with additional adjustments and corrections following. This process, intended to ensure excellent results, is time consuming. As this report is being written, certain results are being hotly debated within the team and are not yet resolved. In general, the largest cost reduction potential is being found in the pre-combustion decarbonization (PCDC) area and in the oxyfuel chemical looping area.

### **Reports and Publications**

None.



## 4.10 Cost Evaluation of Selected Scenario Technologies

Task 5.0 - Project Management, Reporting, and Technology Transfer  
Technology Provider: Fluor Federal Services.

### Highlights

Three selected pre-combustion technology/scenario combinations were evaluated by Fluor acting as a common cost estimator to allow for consistent economic evaluation by the Common Economic Modeling Team.

### Summary

The technology-scenario combinations were:

- Membrane Water Gas Shift(WGS) for a UK refinery. Technology scope supplied by Eltron Research, SOFCo and Fluor;
- Ceramic Hydrogen Membrane Reformer for a Norwegian power plant. Technology scope supplied by Norsk Hydro;
- Sorption Enhanced WGS for a distributed gas turbine gas compression plant in Alaska. Technology supplied by APCI.

Three cases were cost evaluated, two supplied by external technology providers, one supplied by Fluor's process department. The sequence was determined by the availability of the technical data. The first draft report was thoroughly discussed for content and allowed Fluor to revise a few assumptions and improve on the cost-consistency of one of the cases. Direct communication between Fluor and CCP cost estimate experts on cost attributing factors and in particular on the breakdown of specific equipment costs contributed to the consistency and understanding of the cost evaluations that are so useful in the early stages of technology development.

### Reports and Publications

- Two draft reports were received and are under evaluation.

## **5. Technology Advisory Board**

### **Task - 5.1 - Project Management**

#### **Highlights:**

The Technology Advisory Board (TAB) met to review CCP progress on Economic Modeling on May 9, 2003.

#### **Summary:**

The CCP is advised by a group of independent external experts formed into a Technology Advisory Board (TAB). The TAB is an integral part of the CCP program management process and serves to assure the funding government organizations that the CCP leadership are proper stewards of public funds and to providing assurance to the Executive Board on the technical soundness of the projects.

The roles of the TAB are to provide:

- Advice on, and oversight of, the technology development projects to the Executive Board.
- Provide assurance that the technology development work is in keeping with the project goals and objectives.
- Independent challenge to the technology directions of the teams.
- Assurance that best technical practices have been used in delivery of the project.
- Review of a High Level Plan for the process
- Selection of Peer Review participants
- Advise on external benchmarking that will serve to give assurance that the technology work is at the forefront of technology.

TAB members are:

- Vello Kuuskraa, Chairman (Advanced Resources International)
- Maarten van der Burgt (Independent Consultant)
- Dale Simbeck (SFA Pacific)
- Sally Benson (Lawrence Berkeley National Lab)
- Pierpaolo Garibaldi (Independent Consultant)
- Arnie Godin (Independent Consultant)
- Hans Roar Sorheim (Norway, Klimatek)
- Dave Beecy (USA, Department of Energy)
- Vassilios Kougionas (EU, DG TREN)
- Dennis O'Brien (EU, DG RES)

The CCP Technical Advisory Board held a technical review meeting at on May 9, 2003. The primary purpose of the meeting was to review the Common Economic Model (CEM) and its application to a select number of CO<sub>2</sub> pre-combustion cases. An update was provided to the TAB on the chemical looping

process. Based on the discussion during the meeting and the materials provided, the TAB offered the following observations, comments and recommendations.

The TAB finds that the structure and design of the Common Economic Model (CEM) is appropriate and when completed will provide an excellent tool for technology evaluators and R&D planners:

- The model provides a common, transparent and relatively simple framework for evaluating alternative CO<sub>2</sub> capture technologies.
- It provides the ability to perform sensitivity analyses on the impact of key variables, such as the future price of oil, natural gas or electricity, the cost of capital and assumptions on the expected performance of key technology components.
- It provides one important output measure for cross-technology comparisons, namely the cost per ton of net carbon avoided.

The TAB recommends that for each promising capture technology that the Technology and CEM Teams identify the points of “high leverage” and “high uncertainty” in process performance. This would help R&D funding and technology evaluators to quickly focus on the portion of the process that would benefit from future R&D. The TAB recommends that all of the capture technologies that are considered as promising should be subject to cost review. Detailed review should be directed at the two most mature and potentially most widely applicable technologies, namely: (1) advanced gasification for the petroleum residues “case study”; and, (2) the sorption enhanced water gas shift reactor for the natural gas power “case study.” Cost consistency review, limited to checking the cost of major components and verifying the factors used for instrumentation, piping, etc. (the *f*-factor), should be directed at the remaining technologies.

The TAB found the presentation, research and progress to date on Chemical Looping Combustion to be most promising. Successful implementation of chemical looping combustion, with the promise of a 43% cost reduction in the oxyfuel technology, could introduce a most valuable CO<sub>2</sub> emissions avoided technology to the portfolio of capture options. A formal “stage gate” review of this technology should be conducted in midsummer to establish the likelihood that the pilot testing and cold flow modeling, plus work on particle testing, would bring the technology to a status ready for a full feasibility and CEM study. The use of iron oxide as the oxygen transfer agent appears promising because it is cheap and has been used previously in bulk processes for the production of hydrogen.

The TAB recommends that the CCP management and the technology teams define what technologies will not be completed within CCP. This would set the stage for the following options:

- Include the most promising “unfinished” technologies follow on to the CCP.
- Enable the participating companies the opportunity to consider their alternatives.

The TAB recommends that early attention be given to the nature, structure and contents of the Final CCP Report and that significant emphasis be given to prompt communication of the major accomplishments and results of the CCP to the funding bodies.

## **Reports and Publications**

None

## **Conclusions**

Subproject reports reported in the summaries above and included in the attached Appendices do draw conclusions for their segment of the project, where appropriate. The reader is directed to those attachments for interim conclusions stated therein.

## **References**

Each subproject report includes appropriate references for the work being discussed. The summaries in this report refer the reader forward to the actual work documents included in the appendices to find the literature references.