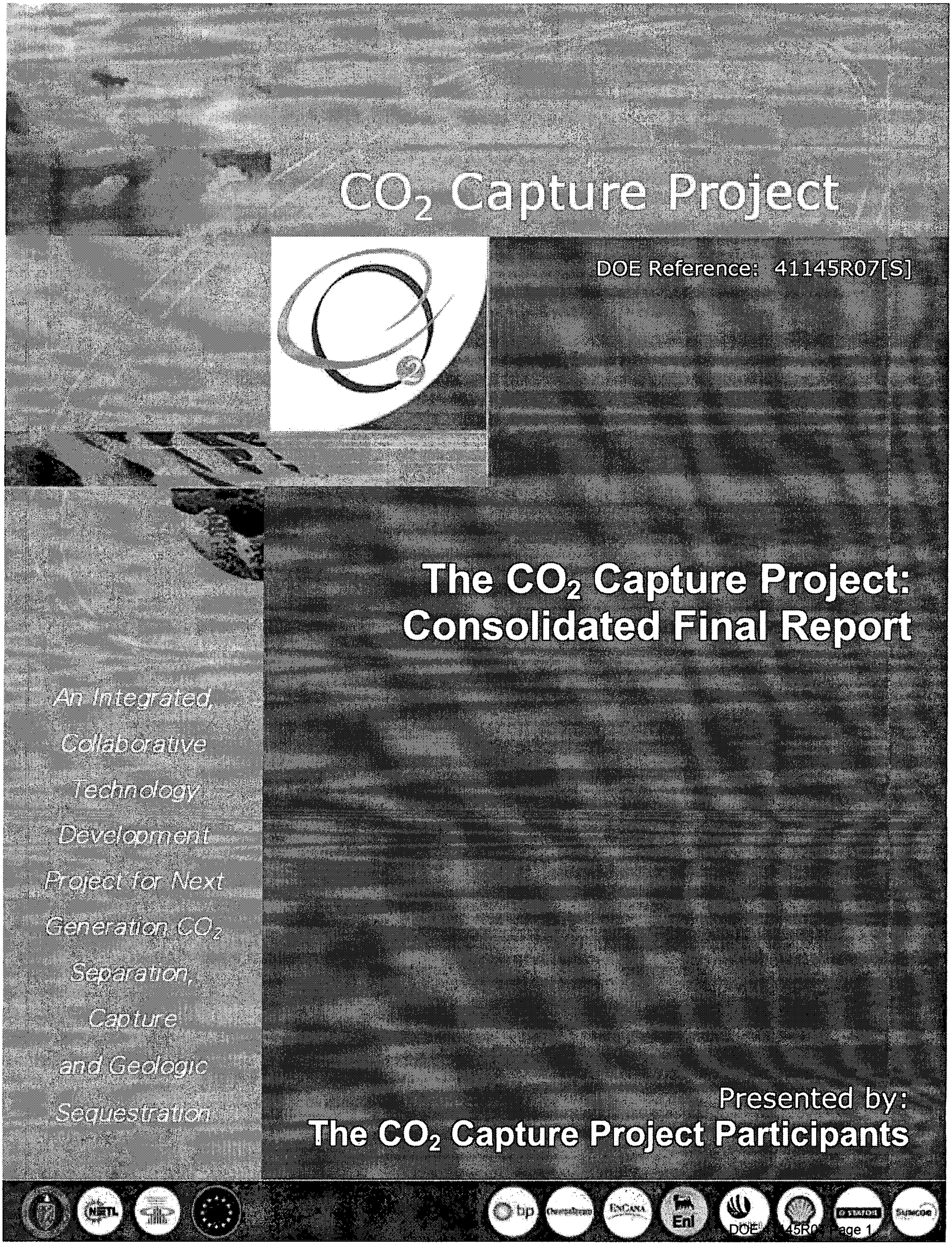

CO_2 Capture Project

DOE Reference: 41145R07[S]

The CO_2 Capture Project: Consolidated Final Report

An Integrated,
Collaborative
Technology
Development
Project for Next
Generation CO_2
Separation,
Capture
and Geologic
Sequestration

Presented by:
The CO_2 Capture Project Participants

CO_2 Capture Project - An Integrated, Collaborative Technology Development Project for Next Generation CO_2 Separation, Capture and Geologic Sequestration

Consolidated Final Report to Funding Agencies

Funding Agencies:

- CO_2 Capture Project Participants
- European Union – Directorate General – TREN
- European Union – Directorate General – RES
- Norwegian Research Council – Klimatek Program
- U. S. Department of Energy – NETL

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Editor's Note:

This report describes the results of a complex multi-company, multi-funder, and multi-provider study. I have attempted to provide both a comprehensive and readable report to the reader. The report is organized to allow you to read and study these results to the level of detail that meets your needs. It includes:

- **Executive Summary:** multi-page summary that brings together the key results of each technology and study area.
- **Major topic summaries:** More detailed summaries and analysis of the work at a relatively high level so that the reader can see an overview of each technology area. e.g. Capture Studies and Storage, Measurement and Verification (SMV) Studies
- **Sub-topic summaries:** Discussions of each sub-topic in both overview and project-by-project summaries. E.g. Post-combustion, pre-combustion, oxyfuel, monitoring, integrity, optimization, risk assessment. This level includes 1-2 page project-by-project summaries of the full reports.
- **Appendices:** Complete final reports as presented by the technology providers to the CCP.

Abstract

The CO_2 Capture Project (CCP) was 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}, the Norwegian Research Council {Klimatek Program} and the U.S. Department of Energy {NETL.}) The project **objective** was to develop new technologies that could reduce the cost of CO_2 capture and geologic storage by 50% for retrofit to existing plants and 75% for new-build plants. Technologies were to be developed to "proof of concept" stage by the end of 2003. Certain promising technology areas were increased in scope and the studies extended through 2004. The project budget was approximately $26.4 million over 4 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_2.
- **Capture Technology, Post Combustion**: technologies, which can remove CO_2 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_2 for storage.
- **Capture Technology, Pre-Combustion**: in which, natural gas and petroleum cokes are converted to hydrogen and CO_2 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_2 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_2 capture and storage.

Pre-combustion De-carbonization (hydrogen fuel) technologies showed excellent results and may be able to meet the CCP's aggressive cost reduction targets for new-build plants. Chemical looping to produce oxygen for oxyfuel combustion shows real promise. Post-combustion technologies emerged as higher cost options that may only have niche roles. Storage, measurement, and verification studies suggest that geologic sequestration will be a safe form of long-term CO_2 storage.

Economic modeling shows that options to reduce costs by 50% exist. A rigorous methodology for technology evaluation was developed.

Public acceptance and awareness were enhanced through extensive communication of results to the stakeholder community (scientific, NGO, policy, and general public. Two volumes of results have been published and are available to all. Well over 150 technical papers were produced.

All funded studies for this phase of the CCP are complete. The results are summarized in this report and all final reports are presented in the attached appendices.

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Executive Summary

The CO_2 Capture Project (CCP) was 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 **objectives** were to 1) develop new technologies, which could reduce the cost of CO_2 capture by 50% for retrofit to existing plants and 75% for new-build plants and 2) evaluate technologies and protocols to assure safe and effective geological storage of CO_2..

Technologies were to be developed to "proof of concept" stage by the end of 2003.

Cost reductions were 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** petroleum coke facility in **Canada**.

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

- **Common Economic Model - Baseline Design and New Technology Cost Estimation.** For each of the four applications baseline designs were developed. These define the uncontrolled emissions from each facility, developed a design for CO_2 abatement using the current best available technology (BAT), and estimated the current cost of abatement in $/tonne CO_2. Technology advances made by CCP were benchmarked against the best available technology on a consistent basis. New Technology Cost Estimation – costs were compared on a consistent basis to the baseline to demonstrate cost reductions.

- **Post Combustion CO_2 Capture Technology:** Technologies that can remove CO_2 from exhaust gases after combustion in conventional systems of boilers, heaters, turbines, and power plants.

- **Oxyfuel Combustion - CO_2 Capture Technology:** Oxygen is separated from air and then burned with a carbonaceous fuel to produce an exhaust with high CO_2 for storage.

- **Pre-Combustion CO_2 Capture Technology.** Carbonaceous fuels, like natural gas and petroleum coke, are converted to hydrogen and CO_2 in a reformer/gasifier. The CO_2 is compressed for storage and the hydrogen is mixed with air for combustion, emitting only nitrogen and water.

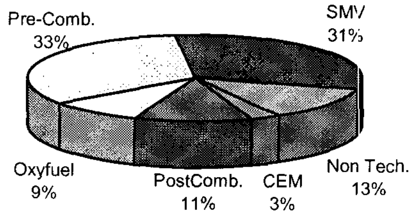
- **Geologic Storage Monitoring and Verification (SMV)**: Technologies and protocols to provide long-term assurance for safe and effective CO_2 storage in geologic formations through studies addressing the integrity of geologic and engineered systems, optimization of processes, cost-effective monitoring technologies and risk assessment.

- **Non-Technical Activities**: These included communication of results to the stakeholders, interactions with NGO organizations, participation in world-wide symposia, and preparation of a review of current policies and incentives governing CO_2 capture and storage.

The two charts (Figure 1) illustrate spending over the life of the project, split by technology and funder.

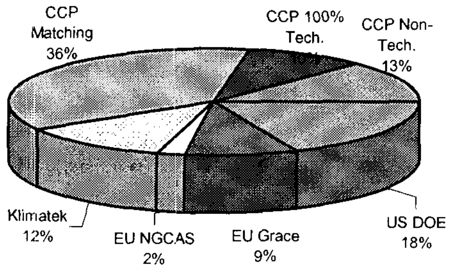
Figure 1. CCP Spending By Technology and by Funding Organization

$24 Million Project Budget Forecast - By Technology



CEM	$743K
PostComb.	$2,972K
Oxyfuel	$2,455K
Pre-Comb.	$8,715K
SMV	$8,155K
Baseline Cost Est.	$0K
Non Tech.	$3,348K
Total	**$26,388K**

$24 Million Project Budget Forecast - Direct Funding



US DOE	$4,848K
EU Grace	$2,319K
EU NGCAS	$575K
Klimatek	$3,187K
CCP Matching	$9,594K
CCP 100% Tech.	$2,518K
CCP Non-Tech.	$3,348K
Total	**$26,388K**

During 2001, the teams completed a critical analysis of existing commercial technologies and new technologies under development from which the team identified high-potential technologies for further study. The four base scenarios were finalized and used to evaluate the cost reduction potential of the technologies studied. 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 developed and used to evaluate technologies in the CCP scenarios with and without CO_2 capture as well as key capture technologies that showed promise.

During 2002 and 2003, intensive technology development took place. Since the CCP was such a large program and combined a broad range of experts from around the world, it was necessary to use transparent and consistent processes to ensure that all comparisons were fair and complete. It became apparent that the cost of performing rigorous cost estimation for every technology in every scenario would be prohibitive, so a **Technology Screening Task - Force** was formed to provide early indications of abatement costs and help to choose the technologies most likely to meet CCP objectives. 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 produced a comprehensive review of existing governmental regulations and expected policies governing CO_2 Capture & Storage. **Outreach to stakeholders** combined workshops, participation in numerous technical meetings and symposia, over 150 technical papers were presented and the whole CCP program was the subject of a two volume book published by Elsevier Science in late 2004. This book is expected to be a reference for researchers and policy makers for many years. The CCP also manages a public website that receives over 5000 visitors monthly. It is available at the following URL:

http://www.co2captureproject.org/

Post Combustion CO_2 Capture Technology:

In post-combustion capture, CO_2 is recovered from the exhaust gases of large sources such as boilers, heaters, and turbines. These sources are present everywhere throughout refineries, power plants, gas processing plants and chemical plants of the world. Post-combustion sources of CO_2 are the biggest CO_2

emitters in the USA, with power plants contributing roughly 1.7 billion tonnes/year of CO_2. Improving the economics of post-combustion capture was a critical goal for the CO_2 Capture Project (CCP).

Current post-combustion capture practice uses an amine separation unit at the flue-gas source primarily to provide the CO_2 used in food and refrigeration. This is a very difficult separation because the exhaust gases are hot, dilute in CO_2 content, near atmospheric pressure, high in volume, and often contaminated with other impurities (SO_x, NO_x, and ash). Residual oxygen in the flue gas is especially troublesome for conventional amine plants because of oxidative degradation of the amine. Collectively, these factors would result in enormous amine circulation rates, large equipment, and large energy requirements in CO_2 sequestration service. In the case of CO_2 capture from power plants, the heat duty of the amine stripper places a substantial burden on the low-pressure steam supply.

Post-combustion capture of CO_2 from flue gas has been researched for over 30 years, resulting in fewer opportunities to significantly reduce the cost of capture relative to conventional amine technology. However a small stream of potential ideas emerged. Thus, the CCP Post-Combustion team took a balanced approach with regards to maturity and technical risk in technology selection. We sought to reduce the cost of CO_2 capture through:

- Step-change cost reduction through improving existing amine technology (e.g., better solvents, better solvent contactors, cost-effective plant design).
- High-risk, entirely novel approaches to post-combustion capture

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

Despite the maturity of this approach, the CCP was able to identify, in the Nexant "Cost Efficient Design" study with co-funding by the Norwegian Research Council's Klimatek program, ample opportunities for substantial improvements. Nexant studied a generalized "low-cost" design for amine plants to be integrated into a power generation plant. This activity led to the definition of the Best Integrated Technology (BIT), with potential saving in capture costs >50% compared to state-of-the-art technologies. The main features of BIT are:

- Partial recycle of flue gas to the combustion chamber to increase CO_2 concentration reducing the size of the amine plant.
- Integration of stripping reboiler in the HRSG system of the power plant.
- Use of novel solvents requiring less heat for regeneration.
- Use of structured rather than random packing in the absorber.
- Relax of metallurgy and standards compared to chemical plant applications.
- Use of plate and frame heat exchangers rather than tube and sheet.

Extensive studies and tests are still needed to assess the technical feasibility of BIT.

The other studies performed in the Post-Combustion program did not identify technologies with potential to achieve the CCP targets in terms of cost reduction opportunities. The CCP will continue to monitor novel ideas in this field with special attention on novel solvents that may also contribute to further improvement of BIT.

Pre-Combustion CO_2 Capture Technology

Pre-combustion CO_2 capture is based on well known commercial technology being applied in such areas as hydrogen, ammonia and syngas production. There are two main unit operations: conversion of fossil fuel to syngas (a mixture of H_2, CO_2, and CO) and separation of CO_2 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 known as **town gas** and was used worldwide 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^3/year – is based on reforming of fossil fuel. This indicates that about 500 reformers with an average capacity of 100,000Nm^3/h hydrogen are in operation worldwide.

Combining the two steps of syngas production and separation of hydrogen and CO_2 is a well established technology mainly used in ammonia production. Activated MDEA solvents are used in the separation process. The largest ammonia plants produce about 2000-2200 tonne/day, which is equal to a hydrogen production of about 150,000-200,000 Nm^3/h or 450-600 MW (LHV). Approximately 1,000,000 tonne/year of CO_2 is captured from the largest plants and compressed to 160 barg for use in 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_2 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 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_2 capture technology, which is used in large scale applications at similar conditions as the CCP scenarios. It has credibility with respect to efficiency, lifetime, CO_2 capture, cost and operation.
- A large commercial market exists today for core pieces of pre-combustion technology and cost advantages can be obtained in commercial projects through competition between both technology licensors and contractors.
- Pre-combustion technology generates a hydrogen-rich fuel that can be used for other purposes, thus creating positive synergies.
- The focus on hydrogen for use in fuel cells in Europe, North-America, and Japan will create a platform for new developments of reforming technology.

Commercial Value - Present and Future

Pre-combustion Technology for CO_2 capture has a broader potential for application than any other capture technology. It is widely applicable for syngas production as a precursor for methanol, synfuel, ammonia and hydrogen production. Thus technology improvements made by the CCP can be adopted as well in these areas. 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_2 will "bridge-the-gap" towards the renewable hydrogen economy and make a more economical viable transition.

The CCP contributed to significant progress in pre-combustion de-carbonization technology in several key areas. 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 potential of significant advancement in efficiency and cost compared to best available capture technology.
- Three of the new advanced technologies were engineered for three different CCP case studies 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.
- Significant advancement achieved in membrane materials for selective hydrogen permeation, covering a wide temperature range.
- Pre-Combustion technology can be developed to meet stringent requirements on NOx and SOx formation. The lowest NOx formation was predicted to be 5 ppm vol. from a combined cycle gas turbine. For open-cycle gas turbines NOx formation may be reduced by 50%. SOx formation is virtually zero.
- Pre-combustion technology can be designed as a stand-alone facility for both retrofit and new built application giving a wide application range and benefits with respect to integration in existing complex facilities, e.g. refineries.
- Novel pre-combustion technology has potential for use in other applications, e.g. GTL, ammonia synthesis, hydrogen and syngas production, thus increasing the economic potential of the technology and return on investment.
- Significant improvement in energy and CO_2 capture efficiency was envisaged for several technologies, resulting in efficiency penalty for combined cycle gas turbines of less than 5 percentage points and close to 100% CO_2 capture.
- 15% improvement of gas turbine heat rate can be obtained when switching from natural gas to a hydrogen-rich fuel, making pre-combustion technology a strong candidate for the large numbers of open-cycle gas turbines in the US.
- Existing Pre-combustion technology can be considered proven for a wide range of CO_2 capture applications including the CCP scenarios.

Other Pre-Combustion activities:

One of the CCP case studies is related to a coal gasification unit in Canada. The application of pre-combustion techniques for CO_2 removal in this scenario was studied by Fluor with DOE co-funding. Fluor studied the application of state-of-the-art amine washing and of their CO_2LDSEP technology based on separation by refrigeration. The CCP is considering the option to study this application further, considering possible synergies and cost reductions by novel separation technologies, like, for instance, Sorption Enhanced Water Gas Shift or Membrane Water Gas Shift.

Oxyfuel Combustion – CO_2 Capture Technology

The principle of CO_2 capture by **oxyfuel** combustion is to burn fuel with oxygen rather than air so that the flue gas consists mainly of CO_2 and water. Oxygen combustion results 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. 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. 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_2 capture. A baseline using conventional air separation for oxygen supply was also established.

When CO_2 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_2 capture, however, oxyfiring has the unique advantage of generating an effluent stream composed almost exclusively of CO_2 and H_2O. It is easy to capture CO_2 of the necessary purity for sequestration from this stream by water condensation. Another unique environmental advantage of oxyfiring is the elimination of NO_x 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_x 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_2 capture considerations, their application to oxyfiring may contribute to reducing the costs of CO_2 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 scope of work carried out by the Oxyfuel Team in the 2001-2003 timeframe included:

1. Definition of an Oxyfuel baseline, potentially applicable "today": CO_2 capture with state-of-the-art cryogenic 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 boiler and heater designs which take advantage of Oxyfuel firing to reduce equipment size (and hopefully, cost) and increase efficiency compared to conventional fired equipment, maintaining conventional air separation.
3. Investigation of advanced thermodynamic cycles for power generation systems, most of which involve 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).

For commercial application by 2008-2010, oxyfuel technologies under development show promising potential for a very broad range of applications. Current state-of-the-art technology allows retrofit of existing heaters and boilers with the lowest CO_2 capture costs among currently available technologies.

Oxyfiring with flue gas recycle may be considered as a CCP Baseline Case, with possible application to revamping of boilers and heaters without any research activities. A demonstration of oxyfiring with flue gas recycle is the only pre-requisite to commercial implementation. In case a CO_2 avoided cost of 40-45 \$/ton, corresponding to a CO_2 capture cost of 35-40 \$/ton may be acceptable, this is a short-term feasible solution.

No improvement in boiler design was identified that would result in consistent savings over the Oxyfuel Baseline. Oxyfuel use in gas turbine (CCGT) systems with conventional air separation would require very expensive gas turbines developments to maintain high energy efficiency. Vendors are not willing to engage in such activity without clear market perspectives.

Novel membrane systems for pure oxygen production, currently under development and expected for commercialization by 2008-2009, will produce oxygen at substantially lower cost than conventional cryogenic separation. 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 Combustion** Study was technically very positive and scale-up risks are reasonable because of its similarity to existing coal fired boilers (CFBs.) Furthermore it produces rather pure CO_2 compared to the Oxyfuel Baseline. A decision on the opportunity 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).

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

Fuel reactor: $MeO + CH_4 \Rightarrow Me + 2H_2O + CO_2$
Air reactor: $Me + 0.5O_2 \Rightarrow MeO$

This project focused on atmospheric pressure applications, typical of the CCP UK Scenario, but the concept is applicable to higher pressure gas turbine systems being studied outside the CCP. In gas turbine applications, the trade-off is between thermodynamic efficiency and percentage of captured CO_2, since Chemical Looping Combustion takes place at relatively low temperatures (800-900°C).

The main risk in Chemical Looping is the availability of a suitable oxygen transport material capable of undergoing repeated oxidation/reduction cycles while maintaining both chemical activity and mechanical resistance. Ni-based oxygen carriers were successfully tested in a pilot unit funded by the CCP. "Proof-of-Feasibility" was successfully achieved by operating the pilot unit with a Ni-based oxygen carrier 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 loss of activity by the carrier.

Storage, Monitoring and Verification Studies

As a commercial process, **CO_2 sequestration** will include **capture** from combustion systems, **separation** from associated impurities, **compression** and **transportation** to the storage site, and long-term **containment (storage)**. The CO_2 Capture Project (CCP) includes transportation and geological storage of CO_2 in its Storage, Monitoring and Verification (SMV) program. While 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 transportation and geologic CO_2 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_2
- **Optimization** – processes that improve the efficiency and economics of CO_2 transportation and storage
- **Monitoring** – cost-effective techniques to track CO_2 movement within and outside of the target storage reservoir
- **Risk Assessment** – methods to identify and minimize the probability and impact of CO_2 leakage from storage sites

Integrity of geological systems

Geological formations are complex and, thus, vary widely in their suitability for safe and effective CO_2 storage. Basic requirements include:

1) depth (pressure and temperature) sufficient to inject and maintain CO_2 in its supercritical state,
2) reservoir geometry and porosity consistent with good storage capacity,
3) a sealing mechanism to ensure containment,
4) permeability distributions that permit high injection rates and conformance, and
5) compatible fluid properties

The SMV program included studies that contrasted the competence of natural systems (natural analogs) to retain CO_2. Additional studies (NGCAS) addressed the need for characterization of prospective CO_2 storage sites for long-term suitability at the sub-basinal, field and reservoir / cap rock scales.

There are numerous instances worldwide of large natural CO_2 reservoirs that have persisted over geologic time frames and those that leak. The study by ARI 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_2 up to ~70 million years). It is concluded that reservoir seals should be comprised of thick chemically-precipitated (carbonates, evaporates) or clastic (shales) rocks. Structural features amenable to CO_2 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_2-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_2 in the system as travertines and porosity / vein fills is estimated to be a maximum of ~10%.

The NGCAS project (EU-funded) demonstrated how petroleum systems modeling tools applied at multiple scales (sub-basin to reservoir) can be used to assess the integrity of geological systems to CO_2 storage. The study, applied to the UK North Sea Forties Field, found that long-term CO_2 storage is likely effective, principally due to the lack of faults (wells were not considered) and slow ground water movement.

Assessment of the tendency for seal rock failure begins with estimation of in situ stress and fault geometry. The ASP study evaluated such tools for simulating perturbations to the original system from pressure draw down (during production) to pressurization to test design limits for CO_2 injection. Experimental studies by GFZ-Potsdam showed that CO_2 injection may affect reservoir mechanical strength (and thus seismic response) of reservoir rocks via pressure effects and dissolution of rock forming minerals. Mineral dissolution may release elements that have a deleterious effect on water quality should fluids migrate from the injection zone. The "reactive transport modeling" applied by LLNL to simulate competing geochemical and geomechanical responses of cap rocks to CO_2 injection suggested that geomechanical-driven opening of seal rock apertures may be offset by geochemical processes via dissolution / precipitation reactions. The status of the injection aquifer (i.e., volume; confined vs. unconfined) strongly influences pressure profiles with time, which may be predictive of storage security over project lifecycle.

Results from coupled reservoir – geomechanical modeling studies on cap rocks conducted by LBNL using the TOUGH-FLAC simulator indicate that conventional seismic techniques should be able to detect changes in the rock elastodynamic properties resulting from contact with injected CO_2. Induced hydraulic fracturing and shear reactivation would likely be contained in the lower portion of the caprock so the sealing mechanism would still function. Changes detected in mechanical properties of the caprock could be addressed by operational changes to minimize the potential for any leakage.

Multiple mechanisms can immobilize injected supercritical CO_2 in the subsurface. Principal among these are solubility and relative permeability trapping. Other possible mechanisms of CO_2 immobilization include buoyant flow, brine density convection and mineralization. The fate of CO_2 after a fifty year aquifer injection project was simulated by UT for the 1000 year time frame. Given appropriate injection strategy (base of the reservoir) and reservoir characteristics and conditions, ~95% of the CO_2 is expected to be immobilized, mostly as residual gas (capillary trapping) over this time frame. Indeed, a 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. These studies showed that CO_2 immobilization can be highly effective in an appropriate reservoir and that injection positioning and operating conditions can be optimized to avoid CO_2 movement to vulnerable features such as wells and faults. The solubility of CO_2 makes it likely; furthermore, that CO_2 leaking from the target reservoir will be assimilated or retarded in shallower saline aquifers. A matrix of operational and geological parameters was developed that indicates the sensitivity of certain characteristics of long-term storage to specific aquifer properties. The matrix can serve as a screening tool to help an operator qualitatively assess the impact of aquifer properties on CO_2 storage project objectives. A preliminary economic analysis of the sensitivity of CO_2 storage project operating costs to aquifer properties concluded that operating costs are fairly insensitive to aquifer properties.

SMV studies related to the integrity of geologic systems show that despite their complexity, diverse venues suitable for CO_2 storage are available. Integrated characterization to develop 3-D structural / stratigraphic models and hydrogeology should be well understood before implementation. The key message from these natural analog system assessments is that CO_2 accumulation and retention is a function of general geologic setting and specific local features. Such features are definable through 3D structural / stratigraphic and fluid history construction and, given appropriate scenarios and models, predictable with respect to their influence on long-term CO_2 storage. It is significant that independent studies (UT and SINTEF, see below) using different methods and favoring different CO_2 trapping *mechanisms predict immobilization of most of injected CO_2 for the 1000 year time frame. Adequate reservoir – caprock characterization and simulation of injection, furthermore, can be used to establish operational parameters that will optimize CO_2 flood performance and minimize leakage.*

Integrity of engineered systems

Whereas natural systems, particularly gas reservoirs, have a proven ability to retain gaseous 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_2 retention. Foremost among the vulnerabilities of CO_2 storage reservoirs is leakage through old or poorly-constructed wells. The natural gas storage industry provides a useful, if not extreme in terms of potential hazards, analog to CO_2 storage with respect to site characterization, operations and leakage detection / intervention.

Cement degradation in active or abandoned well bores is a primary concern in CO_2 storage as well materials are vulnerable to attack by water acidified by CO_2 dissolution. SINTEF addressed the issue through experimental testing, at elevated temperature, of 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_2-rich fluids may "carbonate" the cement (reduce permeability); long-term exposure will deteriorate the cement via dissolution of calcium hydrogen carbonate. Tests did not indicate any significant change in the mechanical properties of cement plugs following exposure to CO_2. Modeling studies indicated that the amount of CO_2 that escapes from a leaking well depends on the thickness of the interval and on the proximity of the leaking well to the injection point. Simulations of the effect of CO_2 injection on abandoned well bores at different distances from injection and variable reservoir conditions suggests that in a worse case scenario (open well bore created by complete well failure without remediation), ~60% of the CO_2 injected could be lost to the atmosphere over 100-200 years. This simulation, however, omitted permeability trapping, which is widely regarded as a primary mechanism for CO_2 immobilization. More recent work using an upgraded reservoir simulation (including hysteresis effects over various Kv & Kh realizations) demonstrates that CO_2 is movement is more constrained. Further cement testing and XRD analysis has identified cement mineral dissolution and precipitation reactions that are not detectable using imaging methods. The study provides useful protocols for testing the performance of cements formulations in a CO_2-rich environment.

The natural gas storage industry has operated cumulatively over 600 facilities in North America and Europe over the past 90 years with very few untoward gas migration incidents. A survey of the natural gas industry experience by GTI identified principles responsible for its success and those technologies and practices applicable to CO_2 storage. Site selection criteria relevant to CO_2 storage include competent seal and broad structural closure. Modified pump testing might be suitable for seal competency testing in prospective CO_2 storage sites. Comparisons of geologically secure versus leaking facilities will be key to understanding the importance successful site selection protocols and in quantification of gas leakage. A comparative study could provide the data necessary to (1) geologically describe leakage pathways, (2) identify and characterize leak points, faults, and other structures, (3) quantify leakage volumes into shallow formations and identify zones of accumulation, (4) establish criteria for determination of potential leaky fields, and (5) form recommendations for mitigation of leakage or sealing of leakage where possible. GTI established criteria for selecting active leaking and geologically secure gas storage fields for a comparison study. Candidate fields were identified and ranked based on the screening criteria. Operators of the highest ranking candidate fields were contacted for participation in further studies. Siting and technology issues in natural gas storage will be useful in developing and maintaining CO_2 storage facilities.

The integrity of engineered systems associated with prospective CO_2 storage venues is a research priority as wells appear considerably more vulnerable to leakage than geologic features and the gas storage industry offers a vast information base for site selection, operation and leakage detection / intervention.

Options for remediation of old wells will become an issue in depleted oil and gas fields) and for contingency planning in aquifers. Siting and characterization of natural gas storage facilities has proceeded in the past with less rigor than that expected for CO_2 storage despite the high mobility of hydrocarbon gases and the hazards they present. Development of natural gas storage as an "extreme" engineered system analog for CO_2 storage will put into perspective that latter's risk level.

Optimization of Economic Offsets and Operational Efficiencies

Injection of CO_2 into depleted oil fields is considered an early opportunity for CO_2 storage given that the cost of CO_2 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_2 EOR experience in the World since the early 1970s. Storage of CO_2 in depleted gas fields is attractive given that gas fields are by definition capable of storing gases for geologic time periods and infrastructure is available yet not as extensive as in depleted oil fields (i.e., fewer vulnerable wells). Deep unmineable coals also present an opportunity as increased methane production is possible. The ability of the CO_2 storage reservoir to accommodate impurities (e.g., SOx, NOx) might reduce CO_2 capture costs and avoid their emission into the atmosphere.

The NMT survey of CO_2 EOR operations experience in the Permian Basin revealed aspects of the process which went well and identified those needing further research. Remediation to improve injectivity and oil response was 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 CO_2 EOR studies identified the major reservoir and fluid character issues that need to be addressed before large scale CO_2 EOR with storage can be effectively applied. Merchant Consulting compiled a summary of current CO_2 flooding knowledge, the history of the development of CO_2 flooding, an explanation of the applicability of various CO_2 flooding techniques, and a discussion of the technical and economic issues that are important to making a CO_2 EOR project profitable. Many of the issues highlighted as key for CO_2 EOR floods are also important for CO_2 sequestration projects in non-hydrocarbon bearing formations. Reservoir properties will influence what CO_2 EOR method is best suitable for a particular reservoir and this can have significant implications for the amount of CO_2 that can be sequestered. Merchant Consulting simulated the conventional water alternating gas (WAG) and non-conventional gravity stabilized and double displacement approaches to EOR on western US reservoirs. The results lend insight into the economic basis converting an EOR project into a CO_2 storage project.

Tools necessary to make CO_2 storage in depleted gas and gas condensate fields possible were examined by TTU. Experiments and simulations showed that gas compressibility and phase behavior are important factors in optimizing CO_2 storage in such reservoirs. Due to its high compressibility it is predicted that up to five times the volume of CO_2, relative to original hydrocarbon gas, may be stored under appropriate conditions. Hydrocarbon and CO_2 gas PVT experiments predict the phase behavior of gas mixtures in reservoirs. A "CO_2 Sequestration Parameter" was developed for quickly assessing the suitability for and capacity of reservoirs for CO_2 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.

The effects of CO_2 impurities such as SO_x and NO_x on aquifer reservoir injectivity and EOR performance were evaluated by UT. Increased acidity (sulfuric and nitric) is predicted to 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 in effect. The minimal performance effects expected by the presence of soluble, acid forming, gases in injected CO_2 raises the potential for lowering CO_2 capture costs. The modeling framework established should be useful for testing the effects of other gases such as N_2, hydrocarbons and O_2. A companion study examining the effects of CO_2 impurities on "surface" facilities was conducted by Battelle. Corrosion effects, particularly with hydrated fluids are well understood. Phase behavior of gas mixtures in compression equipment, however, is a continued research need.

The UT studies on CO_2 injection simulation used to arrive at field abandonment criteria are outlined above under "Integrity of Geologic Systems".

Identification of operational efficiencies and economic offsets will be crucial both to project development decisions and safe and effective operation of CO_2 storage facilities. An understanding of how depleted hydrocarbon fields will perform technically and economically is of particular importance as these are likely "early opportunities" for large scale CO_2 storage. Introduction of CO_2 impurities such as modest levels of SOx and NOx are of little concern for subsurface systems including CO_2 EOR, but their effect on surface infrastructure materials and operability may be substantial. It is evident that development of site specific parameters, tied to local tax and regulatory regimes, will be decisive factors in project approval.

Optimization of CO_2 Transportation

The Norwegian transportation studies reexamined CO_2 transportation in carbon steel pipelines for a Northern latitude offshore setting as opposed to the well-known US temperate onshore setting. At issue was the maximum hydration of CO_2 streams permissible before corrosion and hydrates effects become significant. Using thermodynamic models based on new high pressure CO_2 solubility in water and corrosion data from IFE (with and without inhibitors), Reinertsen Engineering found that proposed (50 ppm) specifications for water content could be relaxed to the existing (600ppm 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_2 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.

Monitoring CO_2 Flood Performance and Containment.

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 TNO study provided a systematically approach to identify monitoring needs based on site-specific features, events and processes (FEPs). The survey of atmospheric monitoring technologies (CalTech) documented the applicability and costs of instruments useful over various CO_2 leakage flux / mode and over various scales and sampling frequency. The remaining SMV monitoring studies addressed specific technologies applicable to selected potential and actual CO_2 storage venues.

"Hyperspectral geobotanical" surveys, processed by LLNL to detect CO_2 leakage indirectly (effects on ecosystems and soils), were applied to the Mammoth Lake, CA natural volcanogenic release area and to the Rangely Field, Colorado CO_2 EOR operation. 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_2 detection is thought to require long term evaluation of such changes. An independent soil gas survey shows that the majority of not all of the CO_2 flux over the field can be attributed to near-surface microbial activity rather than the EOR operations (although increased methane flux is attributed to the operation).

Stanford University examined the potential for interferometric synthetic aperture radar (InSAR), a remote satellite technique, to detect ground deformation due to CO_2 injection. Initial, calculations indicated that the resolution of the technique may not be adequate given topographic and atmospheric influences.

Near-surface and atmospheric monitoring techniques were investigated for their applicability to detect CO_2 leakage. Caltech examined the efficacy of open path detection (laser spectroscopy) on field geometric and leakage rate and mode parameters under various ambient CO_2 levels and atmospheric conditions. The eddy covariance laser spectroscopic technique used for CO_2 ecosystem flux determinations was evaluated by PSU for CO_2 leakage detection potential under various scenarios. Both studies showed that, given a point leakage source (e.g., fault or well), CO_2 flux from the deep subsurface is detectable over natural flux. Near ground techniques are established technologies whose installation will likely be required for early onshore CO_2 storage projects.

Geophysical techniques, particularly time lapse 3-D seismic, have proven useful in monitoring subsurface CO_2 movement in reservoirs and may be applicable in early detection of seal failure. Their expense, non-universal applicability and limitations on detecting CO_2 saturation above threshold levels, however, highlight the need for better interpretation techniques or alternative technologies. New seismic interpretation approaches and novel non-seismic techniques including gravity, electromagnetics (EM) and streaming potential (SP) were variously simulated by LBNL on a North Slope Alaskan EOR scheme, the Frio Brine Pilot and the In Salah injection project. The results show that given appropriate reservoir dimensions and properties, non-seismic approaches, particularly EM, comprise viable alternatives to conventional surface seismic. Numerical modeling studies were conducted by LBNL to determine whether gravity and electromagnetic techniques could be used to detect the existence and migration of re-injected CO_2 separated from gas from the In Salah gas field. Study results indicate both gravity and electromagnetic measurements could be used to monitor the movement of a CO_2 – brine interface within a 20 m thick reservoir at 1900 m depth. Reference to the LBNL studies on seismic detection of leakage from seals appears above under "Integrity of Geologic Systems".

Electo-optic converters designed and constructed by Sabeus Photonics were tested as an alternative to conventional geophone systems. The Sabeus system uses fiber optics to transmit electronic signals to a remote location. Fiber optic systems should be less expensive plus they would allow electronics to be shared by multiple permanent fiber optic sensor installations. Test results for the electro-optic converters were inconclusive. The equipment performed as designed, but the sensitivity was below current standards for seismic equipment.

A geochemical monitoring study by LLNL assessed the utility of noble gases for detecting CO_2 movement out of target reservoirs. A Xenon isotope (one of ten) was selected based on cost, availability and distinctiveness (relative to native and atmospheric noble gases) for the model Mabee CO_2 EOR oil field in West Texas. Because the subsurface transport properties of Xe were not addressed, however, it is not known how well it partitions with respect to CO_2. The development of tracer systems for CO_2 storage projects will become increasingly important for monitoring performance, leak detection and volume verification.

Schlumberger has designed a test chamber for use in testing the ability of conventional wireline tools to detect a CO_2 – oil – water contact. The chamber was designed to allow testing in the presence of multiple sands and multiple fluids and to allow dragging the tool through the chamber to simulate actual depth – logging conditions.

Remote, indirect atmosphere approaches to monitoring CO_2 leaks may be applicable to high flux leakage in well-vegetated areas with ground-based calibration. The applicability of direct monitoring approaches is needed for detection of low CO_2 flux, particularly in arid areas. Existing near-surface atmospheric approaches to CO_2 detection are commercially available and readily adaptable to CO_2 storage. Seismic *geophysical monitoring of CO_2 is available but a better understanding of rock response to CO_2 flooding and new processing and interpretation strategies require development. Much less expensive non-seismic geophysical approaches such as gravity, EM and SP may have the resolution to track CO_2 movement in the subsurface. Geochemical techniques such as tracer gas surveys are potentially cost effective but further development is needed. Well-based approaches to leakage detection are particularly promising given the vulnerability of wells to leakage.*

Risk Assessment Using Leakage Scenarios and Remediation Strategies

Development of leakage scenarios, early detection technologies and remediation strategies will prove essential in the siting and deployment of CO_2 storage facilities. A study by LBNL outlined possible leakage scenarios from CO_2 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, available from the natural gas storage, oil and gas production, groundwater / vadose zone treatment industries were outlined.

HSE consequences of leaks are important for large leaks but also for persistent small leaks that might cause CO_2 accumulation in low lying areas and into occupied structures. A coupled model developed by LBNL simulates CO_2 flow in the shallow subsurface (vadose zone), atmosphere and water bodies. When CO_2 concentrations in the near subsurface are high (either by primary seepage or CO_2 infiltration as a dissolved component of rainwater), surface layer winds act to rapidly disperse the CO_2 in the flux cases simulated. CO_2 seepage into surface waters is not likely to be significantly attenuated because bubble rise velocities are too high and lakes with deep, stagnant regions with CO_2 fluxes from below provide the conditions that favor build-up of potentially dangerous CO_2 concentrations at depth in surface water.

Near surface and atmosphere seepage simulations and contingency planning for remediation will play an important role in stakeholder acceptance of CO_2 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_2 storage but require further development. Additional remediation approaches should be sought or developed.

Comprehensive Risk Assessment Frameworks

Risk assessment models and methodologies were developed to specifically address the CO_2 storage case. These methodologies employed similar probabilistic techniques but varied in approaches to scenario development and hazard definition. Although the two methodologies were developed and tested using models of distinct geological storage venues, they are applicable to other venues.

The TNO SAMCARDS methodology involved extensive scenario and model development over multiple Earth compartments. A performance assessment (PA) module involving numerous simulations over these compartments is capable of statistical analysis that predicts CO_2 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_2 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. As the system tested did not leak, the consequence analysis was not run. The SAMCARDS risk assessment methodology is comprehensive yet 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 risk assessment methodology was applied to the Tiffany Field (Durango, CO), a coal bed methane development currently under N_2 flood and a candidate for CO_2 ECBM. The four major elements of the methodology (hazard identification, event and failure quantification, predictive modeling, risk characterization) were used through Monte Carlo simulations to test the Tiffany Field for CO_2 flood performance leakage risk. Predictive quantitative modeling shows that elevated pressure from N_2 injection caused coal fractures to extend from the injectors to producers. The risk of early gas (N_2 and CO_2) 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 highlights the importance of pressure effects on rock and fault stability over the entire field history (coal dewatering, methane production, N_2 injection, CO_2 injection).

The two independently developed risk assessment methodologies are based on the same principles but differ in details and initial application. The significance of the TNO clastic aquifer case is that leakage appears unlikely and vulnerable natural and engineered elements of the storage system that present a leakage hazard can be identified and thus mitigated. The INEL methodology provides the opportunity to test specific field development scenarios against possible consequences. The next step methodology development involves benchmarking and quantification of risk.

Risk Assessment and Regulator, NGO and Public Acceptance

An early SMV study by LBNL examined HSE issues relevant to CO_2 handling and put into perspective the experiences of potential industrial analogs to CO_2 storage (oil production by CO_2 EOR, acid gas disposal, nuclear waste repository development, deep well hazardous waste injection). The HSE lessons learned from an industrial analogs study concluded that: 1) there is an abundant base of experience to draw on that is relevant and suggests that CO_2 can be stored safely, 2) the health effects of exposure to elevated concentrations of CO_2 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_2 storage and 5) regulatory paradigms and approaches vary and none address all of the issues that are important for CO_2 storage.

A set of potentially relevant industrial analogs to CO_2 storage were examined in the SMV program. The CO_2 EOR experience survey by NMT showed that CO_2 leakage monitoring is not a perceived need because no fatalities attributed to CO_2 leakage have occurred in over 30 years of CO_2 EOR operations. The nuclear waste disposal analog study by MSCI addressed protocols for site characterization and public involvement. Although the public perception of CO_2 storage is likely to be much more benign than that of nuclear waste disposal, the general principles are relevant as are approaches to understanding gas migration. The excellent safety record of the natural gas storage industry is encouraging and instructive to CO_2 storage.

Environmental issues associated with CO_2 storage were not extensively studied in the SMV program as these are generally well understood. One study conducted by Princeton University, however, addressed the effect of CO_2 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_2-rich conditions. The results demonstrated that prevalence of various microbial classes might be impacted by CO_2 injection. Conceivably, operations might be impacted via gas generation (e.g., methanogenesis) or permeability reduction (e.g., biofilms).

State of Texas permitting and abandonment requirements for CO_2 EOR projects and wastewater disposal wells were reviewed by UT. Current regulatory requirements for EOR projects focus on the plugging of abandoned wells. Disposal well regulations deal mainly with ensuring that neighboring formations are not contaminated by the injected fluids. While these regulations are not directly applicable to a geological CO_2 storage operation, they may eventually serve as a baseline for future regulatory frameworks.

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_2.

Common Economic Model

The Common Economic Model Team's main objective was to develop and apply a common set of approaches and methods in cost estimation and economic screening of CO_2-capture technologies in the CCP-program.

The reported costs and performance data reflect the current "best estimates" of cost levels and operational performance of the technologies at a point in time when they are believed to reach their mature state of development, enabling implementation in commercial applications. More specifically, the estimates reflect the expected realization phase cost and emission performance under future operations of the capture technologies integrated with different types of existing or new CO_2-emitting combustion plants, reflected by the defined CCP-"scenarios" (Table 1) in UK, Alaska, Norway and Canada:

Table 1 CCP-scenarios

Scenario		Fuel source	Uncontrolled CO_2-emissions
UK refinery	Heaters and boilers in the existing UK Grangemouth refinery	Refinery fuel oil and gas	2.6 mill. ton/yr from target H&B's
Alaska turbines	Small, powergen gas turbines in the existing Prudhoe Bay complex	Natural gas	2.6 mill. ton/yr
Norway gas power	New, non-built gas powergen plant (CCGT) on the Norwegian W-coast	Natural gas	1.3 mill. ton/yr
Canada coke gasifier	New, non-built coke gasification plant (IGCC) in W-Canada	Petroleum coke	4.9 mill. ton/yr

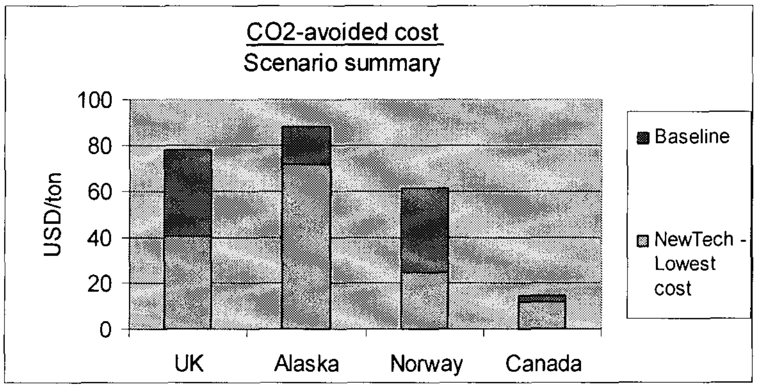
The future "commerciality point in time" is uncertain and will vary across technologies, depending first on the technical challenges in each case and on the strength of external pressures from national/ international government energy and climate policies, and other technology and market developments. Table 2 summarizes the evaluated economic performance of capture technologies scenario by scenario, measured in terms of cost per ton of CO_2 captured or avoided compared to original, uncontrolled CO_2-emissions. The "capture cost" reflects the total cost per tonne (the metric ton, 1000 kg) of reduced "target" emissions, while the "avoided cost" also include the indirect emissions inherent in the additional energy demand of the capture systems. The unit CO_2-costs are here established from the incremental capture system capex, opex and energy costs, but do not include any front-end R&D-costs, or back-end CO_2-transportation and storage costs.

The incorporated costs are estimated at "generic" and scenario site specific sets of unit costs and rates for utilities, energy and labor supplies. Generic prices are established from current market price level observations, but can be interpreted as long term (10-25 yrs horizon) expected price levels. The basic capital charge rate applied to CO_2-cost calculations was 11%, corresponding to a pre-tax discount factor of 10% over a 25 year lifetime. Main CO_2-cost results are provided at the generic cost and price level.

The final CO_2-cost results reflect the underlying physical scopes and cost estimates of integrated "Scenario-Capture Technology cases". A major challenge was to calibrate the physical scopes and contents across the "cases" enabling a fair and consistent cost and economic comparison of capture technologies. The Norwegian and Canadian scenario-cases are believed to be well aligned while varying physical contents of processing facilities/ utilities and shifting fuel/ feedstock assumptions in the UK scenario suggest that the comparisons include more than cost and performance of capture technologies.

Figure 2 provides a snapshot of the baseline and lowest cost option for each scenario. It shows that the higher cost of weatherization and personnel in Alaska raises the scenario costs substantially. The lowest costs seen in the Canada scenario are aided by the type of CO_2 stream being handled (higher concentration in a new-build.)

Figure 2 CO_2 avoided cost (generic) – Scenario summary



Common Economic Model Conclusions

1. **The CO_2-capture technologies studied in CCP have been improved dramatically the expected costs of CO_2 capture from the baseline.**

- For some technologies, CO_2-cost reductions of more than 50% were found compared to current baseline (BAT)-technologies.
- Most technologies are still in development phases and will need more R&D resources and testing to reach commercialization.
- New build gasification (IGCC) shows the lowest CO_2 avoided cost because it's inherently high CO_2 content in the exhaust gases.
- Pre-combustion (hydrogen fuel) and oxyfuel combustion show the greatest expected reduction in CO_2 capture costs from the baseline post-combustion capture.
- Best Integrated Technology (BIT) for post-combustion capture shows the greatest potential for cost reduction of any post-combustion technology.

2. **An economic model was developed and applied a common set of approaches and methods in cost estimation and economic screening of CO_2-capture technologies in the CCP-program. It is referred to as the Common Economic Model (CEM.)**

- The basic CO_2-cost results cover capture, separation, purification, and compression for transportation.
- Transportation and storage costs are addressed through sensitivity analyses.
- Reported costs and performance data reflect our "best estimates" of cost levels and operational performance of the technologies at a point in time when mature enough to be installed real plant operations.
- The estimates reflect the expected realization phase cost and emission performance under future operations of the capture technologies integrated with different types of existing or new CO_2-emitting combustion plants, reflected by the defined CCP-"scenarios" in UK, Alaska, Norway and Canada.

Table 2 Overall CO_2 Capture Project Economic Comparison – All Scenarios

		Output; MW	Cap Sys capex MUSD	CO_2 captured; MMT/yr	CO_2 avoided; MMT/yr	CO_2-capture cost		CO_2-avoided cost	
						USD/T CO_2	% change rel. to BL	USD/T CO_2	% change rel. to BL
UK scenario; 13 Heaters and boilers, Refinery fuel oil and gas, 2.6 million tonne(MMT) CO_2/yr									
Post Combustion	Baseline (BL) Amine MEA	1351	362	2.19	1.55	55.3	0 %	**78.1**	0 %
Pre Combustion	Membrane Water Gas Shift w/DOE-membrane (MWGS/DOE)	1351	520	2.19	1.54	59.8	8 %	**84.9**	9 %
	Membrane Water Gas Shift GRACE&DOE-membrane (MWGS/Grace/DOE)	1351	214	1.99	1.50	36.4	-34 %	**48.1**	-38 %
	Membrane Water Gas Shift GRACE & Pd-membrane (MWGS/Grace)	1351	251	1.99	1.50	39.6	-28 %	**52.4**	-33 %
Oxy Fuel	H&B's w/FlueGas Recycle & ASU (FG-Rec ASU)	1351	422	2.08	1.87	43.8	-21 %	**48.7**	-38 %
	H&B's w/FlueGas Recycle & ITM (FG-Rec ITM)	1351	639	2.09	1.95	38.2	-31 %	**41.0**	-48 %
Alaska scenario; 11 Gas Turbines, Natural Gas, 2.6 million.tonne (MMT) CO_2/yr									
Post Combustion	Baseline (BL) Amine MEA	358	1012	1.90	1.96	90.9	0 %	**88.2**	0 %
Pre Combustion	VeryLargeScale AutoThermal Reformer (VLS-ATR)	358	713	2.88	2.24	59.0	-35 %	**76.0**	-14 %
	Sorption Enchanced WaterGasShift (SEWGS)	358	771	2.50	2.10	60.5	-33 %	**71.8**	-19 %
Norway scenario: 400Mw gas turbine(CCGT), Natural Gas, 1.3 million.tonne (MMT) CO_2 /yr									
Post Combustion	Baseline (BL) Amine MEA	323	129	1.09	0.87	49.0	0 %	**61.6**	0 %
	Nexant BL design-basis	322	134	1.09	0.87	47.6	-3 %	**60.0**	-3 %
	Nexant BL design-"low"	332	82	1.09	0.90	36.8	-25 %	**44.7**	-27 %
	Nexant BL design-"integrated"	345	61	1.09	0.94	30.2	-38 %	**35.1**	-43 %
	MHI-Kværner; Membrane Contactor/ KS1	335	127	1.09	0.91	39.5	-19 %	**47.5**	-23 %
	BIT; Best Integrated Concept; Nexant Integr. & MHI-KS1	357	69	1.09	0.98	25.3	-48 %	**28.2**	-54 %
Pre Combustion	Hydrogen Membrane Reformer (HMR)	361	98	1.27	1.17	22.5	-54 %	**24.4**	-60 %
	Sorption Enhanced WGS ($SEWGS-O_2ATR$)	360	150	1.28	1.02	34.1	-30 %	**42.7**	-31 %
	Sorption Enchanced WGS (SEWGS-Air ATR)	424	178	1.47	1.21	28.2	-42 %	**34.4**	-44 %
Canada scenario: Coke gasification(IGCC), Petroleum Coke, 4.9 million.tonne (MMT)CO_2/yr									
Post Combustion	Baseline (BL) IGCC with capture	588	519	6.80	5.28	11.1	0 %	**14.5**	0 %
Pre Combustion	IGCC with CO_2LDSEP	699	516	6.44	5.22	9.9	-11 %	**12.2**	-16 %
	IGCC with CO_2LDSEP +100 % black box cost"	734	689	6.44	5.22	14.6	31 %	**18.0**	25 %

"Tonne or T" is used as the term for metric tonne (1000 kg).

"Uncontrolled CO_2 emissions" are emissions with no control - the usual case.

"Million tonnes CO_2 Captured" Gross amounts of CO_2 processed through the capture plant.

"Tonnes CO_2 Avoided or MMT CO_2 Avoided" Net amounts of CO_2 emissions avoided -Considers CO_2 emissions from the capture, purification, and compression processes.

Policies and Incentives

Members of the CO_2 Capture Project realized from the beginning the reality of interdependency between technology and policy developments. The **key vision of success** is gaining public and regulatory acceptance of CO_2 capture and storage technology and that the technology can be applied safely and cost effectively.

The Policies and Incentives Team provided information and advice to the CO_2 Capture Project on national and global policies, regulations and legislation, incentives and any other external developments that may impact or benefit the technology program. The team surveyed existing policies and incentives and their potential future development and initiated a preliminary "gap analysis" to understand what the current state is and what would be desirable in terms of policy development that would favorably impact the development and deployment of CO_2 capture and storage.

Interpretation of international treaties such as the London Convention and the OSPAR Convention already raise significant issues that need to be clarified in order to understand their applicability to the deployment of CO_2 storage in offshore geologic structures. The key issue of whether to treat CO_2 as a waste needs to be resolved, which would affect the applicability of the London, the OSPAR, and the EU Water Framework Directive. Currently, public awareness is low to non-existent, posing a significant challenge for eventual public acceptance if the technology is to be widely deployed. More work in these policy and public outreach efforts will have to be done by future collaborations and commercial projects aiming to develop and deploy CO_2 capture and technology. Further, future projects should develop and adopt monitoring and verification frameworks appropriate for public and regulatory acceptance.

The results of their work showed:

1. Clear momentum exists as projects are being deployed and technology continues to be researched and developed.
2. The London Dumping Convention and the OSPAR Convention ("Oslo Paris Convention) may apply to CO_2 capture and storage deployment offshore in geologic formations. Issues for clarification may require several years of intergovernmental negotiations in order to accommodate such deployment.
3. In general, there is little policy and regulatory development specifically addressing CO_2 capture and storage in individual countries.
4. Specific countries (Netherlands, Norway, Canada, United Kingdom (UK), and the United States (US)) are moving in the direction of policy development specific to CO_2 capture and storage.
5. Public awareness is low to non-existent. Some NGOs will likely play key role in the public acceptance of the technology.
6. Some non-government organizations (NGOs) and the public in the European Union are becoming slightly less skeptical of the technology. However, it is still too early to assess the level of public skepticism, which will become clearer when specific projects are reviewed for permitting or licensing.
7. Existing and emerging financial incentives in Australia, Canada, the European Union, Denmark, Germany, Italy, Netherlands, Norway, the United Kingdom, and the United States are focused

principally on research and development. Such incentives are needed to improve the cost-effectiveness for deploying CO_2 capture and storage technology.

8. CO_2 capture and storage technology is becoming recognized and credited in some regulatory regimes, though it is not yet widely recognized nor credited. A monitoring and verification framework is needed to achieve wide recognition and crediting.

Communication of Results

CCP was conceived as a public collaboration to address the society-wide issue of carbon dioxide emissions. **"Progress through Partnership"** was the watchword throughout the project design and development. Public critique and scrutiny were invited to ensure that the best feasible program was developed. Early on project leadership recognized that we could succeed technically but fail in implementation if we didn't ensure that stakeholders understood and agreed with project results. The Executive Board found that continuous engagement of the stakeholders would be needed through the life of the project. An on-going program of communications was developed.

BP, the U. S. DOE, and the International Energy Agency's Greenhouse Gas Program jointly sponsored the first planning meeting. Over 150 people attended to provide input into the program and its potential to reduce carbon dioxide emissions. Their input and interest was used to shape the program. Policy makers, the scientific community, non-governmental organizations, and the general public are stakeholders with different views and needs. CCP needed to address all stakeholders to be successful.

The assumptions behind the communication strategy are:

- CCP could succeed technically and yet fail socially if geologic sequestration is deemed environmentally unacceptable.
- NGOs will plan an important role in securing public acceptance of geologic sequestration as a safe and environmentally benign method for carbon dioxide storage.
- NGOs will regard sequestration options with suspicion.
- CCP activities must be viewed as open and transparent by the environmental community.
- CCP must seek positive engagement with governments, NGOs, and the public to ensure their understanding of the merits of geologic storage.

Through the program numerous opportunities for communication about CCP occurred. Location of CCP's center of activity in Washington, DC presented numerous opportunities for interaction with U. S. government agencies at the highest levels. The Executive Board Chairman testified to the U. S. Congress on industry interest and actions in greenhouse gas mitigation and the U. S. Energy Policy. The Bush administration chose to use CCP as a keystone in describing its actions on climate change. This led to accelerated approval of CCP's funding and work plan.

Outreach to the NGO Community

Non-governmental organizations will have substantial influence on CO_2 capture and storage projects through their ability to shape public opinion. CCP has opened a dialogue in a transparent way that attempts to engage stakeholders in constructive conversation rather than in an adversarial exchange.

During 2000-2001, two workshops were held to inform environmental activist groups (NGO's) about the CCP. A workshop was held in Washington, DC on 3-4 October 2000 and a second in Amsterdam, Netherlands on 12-13 June 2001. The consensus was that the sessions were informative, helpful, and "a good start" at understanding the issues. NGO representatives made it clear that they were not endorsing capture and storage as a method for greenhouse gas mitigation and that their agenda will remain reduction in CO_2 release to the atmosphere through conservation and renewable energy sources.

Subsequent workshops in 2002 and 2003, presented CCP results and plans to the NGO community with the intent of informing them about the project and soliciting their input and questions so that they could be addressed in an open atmosphere.

Each workshop used a similar format intended to inform the NGO participants about the project, its objectives, the state of the art, and the technical issues being faced. Each discussion was organized to inform, solicit questions, and to engage in dialogue about the issues. Breakout sessions were used to allow informal discussion and viewpoint exchange.

Stakeholder Community

The CO_2 Capture Project encouraged its team members and technology providers to publish their work in the open literature as much as feasible. Very few of the results were held confidential and then only in support of inventions made during the project. Below are listed a few of the technical conferences in which CCP results and plans were made public.

- First NETL Conference on Carbon Sequestration – May 2001 Pittsburgh PA
- November 2001 SMV Workshop – Potsdam
- Second Annual NETL Conference on Carbon Sequestration – May 2003 Pittsburgh, PA
- Third Annual NETL Conference on Carbon Sequestration – May 2004 Pittsburgh, PA
- GHGT-5 Greenhouse Gas Technology Conference – August 2000, Cairns, AU
- GHGT-6 Greenhouse Gas Technology Conference – September 2002, Tokyo, JP
- European Workshop – Brussels, BE June 2004
- GHGT-7 Greenhouse Gas Technology Conference – September 2004, Vancouver, BC

Outreach to the Scientific Community

CO_2 Capture Project Results Volumes

The CO_2 Capture Project worked with the technology providers to produce a two volume set of papers of the results of the CCP program. It was published in December 2004 by Elsevier Science Press of London. The two volume set includes seventy-two papers and is 1331 pages long. It is entitled:

"Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO_2 Capture Project:"
Volume One: Capture and Separation of Carbon Dioxide from Combustion Sources," Edited by David C. Thomas
Volume Two: Geologic Storage of Carbon Dioxide with Monitoring and Verification," Edited by Sally M. Benson.

A copy of the set is provided with this final project report.

Individual Scientific Papers

As noted above the technology providers were encouraged to prepare and present papers based on their work. While the CCP team made an effort to collect the references for these presentations we are uncertain exactly how many papers have been presented to date. The current bibliography lists 141 papers and presentations.

Outreach to the Public

The CO_2 Capture Project developed a publicly available website that includes general information about the project, selected technical reports and information about future plans. It is available on the Internet at:

http://www.co2captureproject.org/index.htm

Summary Report

In 2001, The U. S. DOE National Energy Technology Laboratory issued a comprehensive list of topics to address geologic sequestration technology development. The CCP was independently developing a program to address the same concerns. As a result, the CCP responded to the DOE's solicitation with a comprehensive proposal that addressed virtually all the DOE questions. Since the program as envisioned by the CCP was well beyond the DOE's budget capabilities, the CCP worked through its international partnership to obtain funding from other sources including the European Union and the Norwegian Research Council's Klimatek program. The resulting program included over 100 individual research contracts and projects managed and led by CCP member companies. Needs of the member companies, funding agencies, and technology providers were included in the planning.

Table 3 shows the correspondence of the CCP's research program as represented by the technology provider reports and CCP staff summaries to the comprehensive DOE solicitation table. Only one area was unstudied by the CCP team, development of oxygen transport membrane technology. The topic was being well studied by other DOE funded programs and the CCP did not wish to duplicate or dilute their effort. CCP maintained a close liaison with the oxygen transport teams and feel that development will be a key to future combustion systems.

Table 3 Correspondence between U.S. DOE Tasks and CCP Projects

Task	Description	Related Report Section
0.0	**Project Definition**	Background 0.1 Formation of the CCP 0.2 Review & Evaluation 0.3 Technology Selection
0.1	Identify Relevant Separation, Capture, and Sequestration Scenarios	Scenarios
0.2	Establish State-of-the-Art Separation and Capture	0.2. Review & Evaluation 0.3 Technology Screening 1.1.3.2 Post-Combustion Baseline Studies 4. Economic Modeling
0.3	Develop and Apply Common Economic Model	4. Economic Modeling
0.4	Define Work Plan	Background Technology Advisory Board
0.5	Select Technology Developers	Background Technology Advisory Board
1.0	**Develop Post-Combustion Separation and Capture**	1.0 Capture Studies 1.1 Post Combustion Studies
1.1	Advanced Solvents	1.1.1.4 Amine Scrubbing / Membrane Contactor
1.2	Advanced Absorbers/Desorber Designs	1.1.1.4 Amine Scrubbing / Membrane Contactor
1.3	Systems Integration and Optimization	1.1.3.1 Cost Efficient Design 1.1.3.2 Post Combustion Baseline Studies
1.4	New and Novel Concepts	1.1.1.1 Radical Post-combustion technologies. 1.1.1.2 Self-Assembled Nanoporous Materials 1.1.1.3 Radical Chemical Concepts 1.1.1.5 Electric Swing Adsorption Studies 1.1.1.6 Removal of CO_2 by CFCMS / Electric Swing Adsorption
2.0	**Develop Pre-Combustion De-carbonization Techniques**	1.2 Pre-combustion De-carbonization (PCDC) Program
2.1	Gas Turbine Fuels	1.2.1.2 Sorption Enhanced Water Gas Shift (SEWGS) 1.2.3.1 Gas Turbine Retrofit Study
2.2	Fuel-Grade Hydrogen Generation	1.2.1 Hydrogen Transport Membrane Studies 1.2.1.1 Sulfur-Tolerant Membrane Studies 1.2.1.1.1 Sulfur resistant Pd/Cu Alloy Membranes 1.2.1.1.2 Silica Membranes for H_2 fuel 1.2.1.1.3 Sulfur resistant Pd/Cu Composite Membranes 1.2.1.1.5 Sulfur resistant Zeolite Membranes

Task	Description	Related Report Section
		1.2.1.1.6 Design, Scale up, and Cost Estimation Membrane Shift Reactor 1.2.1.1.7 Membrane Water Gas Shift (MWGS) 1.2.1.1.8 Hydrogen Transport Membrane 1.2.1.5.1 Hydrogen Membrane Reactor Studies 1.2.1.5.2 Pd Alloy Membranes for H_2 Production 1.2.1.5.3 Pd Zeolite Composite Membranes 1.2.1.5.4 Silica Membranes 1.2.1.5.5 Experimental Evaluation of H_2 Membranes 1.2.1.5.6 Pd Zeolite Membranes 1.2.1.5.7 H_2 Membrane Reactor Design & Costs 1.2..1.7 Pd Alloy Hydrogen Transport Membranes 1.2..1.8 High Temperature Hydrogen Membrane Technology 1.2..1.9 Sorption Enhanced Water Gas Shift
2.3	Systems Integration and Optimization	1.2.1.1.6 Design, Scale up, and Cost Estimation Membrane Shift Reactor 1.2.1.1.7 Membrane Water Gas Shift (MWGS) 1.2.1.5.7 H_2 Membrane Reactor Design & Costs 1.2.3 Integration & Scale-up Studies
2.4	New and Novel Concepts	1.2.1.1 Sulfur Tolerant Membrane Studies (1.2.1.1.1-.7) 1.2.1.2 Sorbent Enhanced WGS Studies 1.2.1.5 Hydrogen Membrane Reactor Studies 1.2.3.2 Standardized PCDC 1.2.3.3 Very Large Scale ATR 1.2.3.4 Advanced Syngas Systems 1.2.3.5 Compact Reformer with APSA 1.2.5.1 Generation of H_2 Fuels
3.0	**Develop Oxyfuel Technologies**	**1.3 Oxyfuel Technology**
3.1	Advanced New/Retrofit Boiler Designs	1.3.1 Advanced Boiler Study 1.3.2 Advanced Gas Turbine System 1.3.3.1 Zero Recycle Oxyfuel Boiler 1.3.3.2 High Pressure Oxyfuel Boiler 1.3.3.3 Zero or Low Recycle Oxyfuel Boiler 1.3.3.4 Oxyfuel Power Generation Cycles
3.2	Membrane Air Separation Units	Not Studied to Avoid Duplication with other U.S. DOE funded work.
3.3	Systems Integration and Optimization	1.3.3.5 Oxyfuel Heaters & Boilers – Cryogenic Oxygen 1.3.3.6 Oxyfuel Heaters & Boilers – Ion Transport Membranes 1.3.4 Chemical Looping Combustion
3.4	New and Novel Concepts	1.3.4 Chemical Looping Combustion 1.3.4.1 Chemical Looping Combustion Economics & Scale Up 1.3.4.3 Particle Development, Screening & Testing 1.3.4.4 Chemical Looping Combustion 10kW Prototype Reactor 1.3.4.5 CLC Fluidization Studies 1.3.4.6 Carrier Optimization for CLC
4.0	**Establish Key Geologic Sequestration Controls and Requirements**	2. Storage, Monitoring and Verification (SMV) Studies
4.1	Understanding Geologic Storage	2.1 Risk Assessment and Analysis - studies under this heading 2.2 Optimization- studies under this heading 2.3 Integrity 2.3.1 Natural CO_2 Reservoir Analogues – Leaky Systems 2.3.2 Long-term Sealing Capacity of Cemented Wells 2.3.3 Geomechanical Effects on Seal Integrity 2.3.4 Natural CO_2 Reservoir Analogues – Competent Systems 2.3.5 Chemical Influence of CO_2 Injection on Reservoirs & Caprocks 2.4 Monitoring – studies under this heading
4.2	Flexibility in CO_2 Purity	2.2.4 CO_2 Impurities Tradeoff – surface 2.2.5 CO_2 Impurities Tradeoff - subsurface
4.3	Maximizing CO_2 Sequestration	2.2 Optimization 2.2.1 Depleted Gas Reservoirs for Geologic Storage 2.2.2 Screening Tool for CO_2 miscibility 2.2.3 Reservoir Simulation of CO_2 storage

Task	Description	Related Report Section
		2.2.4 CO_2 Impurities Tradeoff – surface 2.2.5 CO_2 Impurities Tradeoff – subsurface 2.2.6 Long-term CO_2 Storage 2.2.7 CO_2 Conditioning and Pipeline transportation 2.2.8 Materials Selection 2.2.9 Gas Storage Experience – Applicability to Geologic Sequestration 2.2.10 CO_2EOR Storage Optimization & Economics 2.2.12 Natural Gas Storage Anaulogues 2.2.13 Field Abandonment Studies 2.2.14 In Salah Field Test 2.3 Integrity - studies under this heading 2.3.6 Long-term sealing capacity of Cemented Wells
4.4	Measurement and Verification	2.4 Monitoring 2.4.1 Atmospheric CO_2 Measurement Systems Critical Review 2.4.9 Atmospheric CO_2 Measurement Systems – Prototype Design 2.4.2 Novel Geophysical Techniques to Monitor CO_2 Movement 2.4.3 Optimum Monitoring Technology 2.4.4 Hyperspectral Geobotanical Remote Sensing 2.4.5 Long-term Monitoring with Noble Gas Isotope Tracers 2.4.6 Monitoring Geologic Sequestration with Satellite Radar Interferometry 2.4.7 Measurement of Leaks from Underground CO_2 Reservoirs
4.5	Risk Assessment and Mitigation Options	2.1 Risk Assessment and Analysis 2.1.1 Safety Assessment Methodology 2.1.2 HSE Probabilistic Risk Assessment Methodology 2.1.3 HSE Risk Assessment of Deep Geologic Sites 2.1.4 Lessons Learned from Nuclear Disposal 2.1.5 Reactive Transport Modeling to Predict Long Term Caprock Stability 2.1.6 Early Detection & Remediation of Leaks 2.1.7 Impact on Subsurface Microbes 2.1.8 Literature Search HSE Risk Methodologies 2.1.10 EU-NGCAS Assessing Risk & Potential of CO_2 Storage in the UK (2.1.10.1 to 2.1.10.6)
5.0	**Project Management, Reporting, and Technology Transfer**	Background Technology Advisory Board Communications 4. Economic Modeling
5.1	Project Management	Background Technology Advisory Board
5.2	Routine Project Reporting	Communications
5.3	Technology Transfer	Communications

Background:

0.1 Formation of the CO_2 Capture Project

In 1999, BP, the U.S. DOE, and the International Energy Agency's Greenhouse Gas R&D Programme agreed to sponsor a workshop on CO_2 Capture and Geologic Sequestration. Out of this exploratory workshop grew the CO_2 Capture Project reported here.

The workshop, *CO_2 Capture and Geologic Sequestration: Progress through Partnership,* was a collaborative effort to open a dialogue on research needed to develop new solutions to the challenge of CO_2 capture and geologic sequestration. The workshop held in Houston, Texas on September 28-30, 1999 brought together representatives from the major stakeholders. It included:

- International, national, and industry perspectives.
- Panel discussions on CO_2 capture and geologic sequestration technologies.
- Status reports from on-going CO_2 sequestration projects.
- Working sessions to develop an industry work program leading to breakthroughs in costs and performance.

Over 140 participants attended the workshop with 75% of the participants representing industry and 30% coming from outside the United States.

This meeting gauged interest in industry and government in a joint-industry-government partnership for technology development with the final goal of commercially feasible technologies for geologic sequestration of CO_2. The workshop led to formation of the CO_2 Capture Project in early 2000.

- The workshop summary report is presented in Appendix A under the same report reference.

0.2 Review and Evaluation Phase

The CCP was unique in its complexity. Most of the participants had worked together before in joint ventures in oil and gas exploration but had never collaborated as closely as envisioned on technology development. The teams had to work together very closely while still protecting the proprietary interests of their home companies. Also, most of the companies had not worked with governmental funding agencies as diverse as the U.S. DOE, the European Union, and the Norwegian Research Council. For these reasons, transparent processes had to be developed to allow the companies assurance that their contributions were recognized, their needs were met, and the costs were fairly distributed among the partnership.

Even before the final agreements were signed, the participants commissioned a multi-company team to gather information about the present state of sequestration technology, to evaluate those technologies, to recommend technologies for further evaluation, and to define the work processes that the teams should use.

The results of the Review and Evaluation Phase are summarized here primarily for historical and archival purposes. The R&E Phase was successful and led to the full CCP program under the direction of the Executive Board.

- Their full report is in Appendix A under the same report reference as this summary.

Summary:

Key technical recommendations were that an Analysis Phase should be carried out by technology teams in these areas:

- Post-combustion capture of CO_2
- Oxyfuel capture
- Pre-combustion decarbonization
- CO_2 Sequestration.

The CO_2 capture teams are united in their belief that no one capture technology area can be shown to be inherently superior to the others and that therefore all three areas should be pursued.

Post-combustion capture of CO_2

State of the art: The post-combustion capture of CO_2 has been practiced on a commercial scale for at least twenty years, although the flow rates that are envisaged for the CCP would be unique. The successful processes are based upon chemically absorbing CO_2 into primary amines, with subsequent heating to release it.

Three developments to existing post combustion separation technologies are recommended for study: according to priority:

- Kværner membrane contactor technology, enhanced by sterically hindered amines, with a potential 50% cost reduction.
- Development of Mitsubishi Heavy Industries (MHI) technology, combined with extensive simplification of design standards, with a potential reduction cost of 45%.
- Development of Fluor Daniel (FD) technology, enhanced with MHI technology as appropriate and simpler design standards. Potential cost reduction - 40%.

Three new technologies for which the team has not yet estimated benefits or development costs are recommended:

- Oak Ridge National Laboratories (ORNL) electrical swing adsorption (ESA) technology.
- Solmec's vacuum swing adsorption technology.
- Norsk-Hydro's radical exhaust channel treatment technology

Oxyfuel

State of the art: No oxyfuel technology has been demonstrated on a commercial scale for the capture of CO_2 and so there is no state of the art against which to assess cost reductions for new approaches. Thus the reductions quoted below are against estimated costs from studies of flue gas recycle techniques in boilers.

Technologies to be developed:

The team identified the following seven technologies as having the potential to offer reduced CO_2 capture costs. They are listed in order of priority:

- Advanced gas turbine cycles with water injection - possible capture and compression cost reduction: 65%
- Boilers/heaters with flue gas recycle - reduction: 25%
- Ceramic membrane ASU integrated with combustion (advanced boiler concept and GT's) - reduction: 40-60%
- Chemical looping - reduction: 45%

- CCGT with flue gas recycle - reduction: 25%
- Zero or low recycle boiler - reduction: 35%
- High pressure boiler - reduction: 35%

Pre-combustion decarbonization

State of the art: Today no process or technology completely fulfils the requirements set for fuel-system PCDC with CO_2 capture and so SOA, as such, does not exist for this type of technology. However, many of the individual components do exist and, in formulating the list of technologies to be developed, the team has considered how these might be assembled into a complete system.

Technologies to be developed:

- Advanced syngas generation
- Very large scale POX/ATR
- Combined syngas generation and CO_2 separation
- Improved CO_2 separation techniques
- Hydrogen utilization

The team highlighted their belief that one technology - membrane reactor technology - is seen as having potential for significant cost reduction.

Sequestration, Monitoring & Verification of CO_2

State of the art: There is significant activity outside the CCP that can be leveraged. The Team is already actively leveraging several key efforts. The Team is not fully engaged with several of the opportunities, and new efforts are likely to be initiated. The Team found that SM&V efforts outside of the CCP were addressing roughly 80% of the technology gaps.

Technologies to be developed:

- Critical Health, Safety & Environmental (HSE) Risk Assessment R&D was woefully inadequate.
- Critical Long-Term Monitoring & Verification R&D strategies were not being addressed.
- Outside of HSE risk assessment, the Team identified several medium importance level gaps from the following areas:
    - Understanding Geological Storage
    - Maximizing Sequestration
    - Monitoring & Verification

Novel technologies:

Whilst the teams were able to do a good job finding and analyzing data on "what we know", they were all conscious that more was needed in the area of "**finding out what we don't know**". In other words, we need to find out more about novel technologies.

0.3 CCP Technology Selection Summary

The CO_2 Capture Project (CCP) brought together scientists and engineers from different technical disciplines, corporate cultures, and national cultures. A rigorous and fair, but readily understood, process for technology selection was needed to ensure that diverse technical and political stakeholder needs were considered. This document describes the technology selection process used to gather input, shape the technology development program and to ensure that appropriate technologies for further development were chosen. It also serves as an archive of information about the program and its processes.

The CCP technology selection process began with the September 1999 Informational Conference sponsored by BP, the IEA-Greenhouse Gas Programme, and the US Department of Energy. Attendees were encouraged to describe technologies that could be used to separate and capture carbon dioxide from combustion sources and to raise other issues and concerns. The conference highlighted the need for broad cooperation between stakeholders (industry, government researchers, technology developers, academics, and policy makers.) Policy and public acceptance issues were raised as major issues not adequately addressed. The proposed technology program was generally endorsed and significant improvements were made as a result of the conference.

Participants who joined the CCP sponsored a detailed review and evaluation of the public input, past industry work, government and academic research, and their proprietary research studies. The Review and Evaluation (R&E) Phase focused the program on capture techniques, combustion processes, geologic storage, and public acceptance issues. The evaluation teams recommended that industrial application designs (scenarios) be used as the basis for technology development. Scenarios include the unit operations and integration common to industrial plant design and ensure that technology is not developed in isolation. Public acceptance potential was gauged through two CCP sponsored conferences with environmentally-focused non-governmental organizations (NGO.) The results of those conferences make the CCP cautiously optimistic that its work will meet with NGO acceptance.

While the R&E Phase focused the program, specific research activities and government funding discussions led the CCP to carry out a detailed Analysis Phase that included scoping studies to further sharpen the direction of the program. The teams agreed to use four scenarios as the framework for further technology development. These scenarios are based on common industrial operations that represent a substantial fraction of business applications. They included:

- **Refinery** – gas and oil fired heaters commonly found in refinery and chemical plant service for direct heating of process units, process steam, and electricity generation service with both steam and direct fired gas turbines.
- **Very Large Gas Turbines** – Natural gas fired turbines with electricity generation capacities greater than 300 MW intended to provide electricity to public power grids.
- **Distributed Gas Turbines** – Natural gas-fired turbines with electricity generation capacities less than 100 MW intended for direct shaft power or smaller electricity generation service. The scenario includes multiple installations distributed around a major site.
- **Gasification** - Steam, electricity cogeneration, and hydrogen production fueled by gasified solid fuel (petroleum coke). The main applications would be in chemical plants and refineries to service those plant needs. Electricity might be sold into the public power grid.

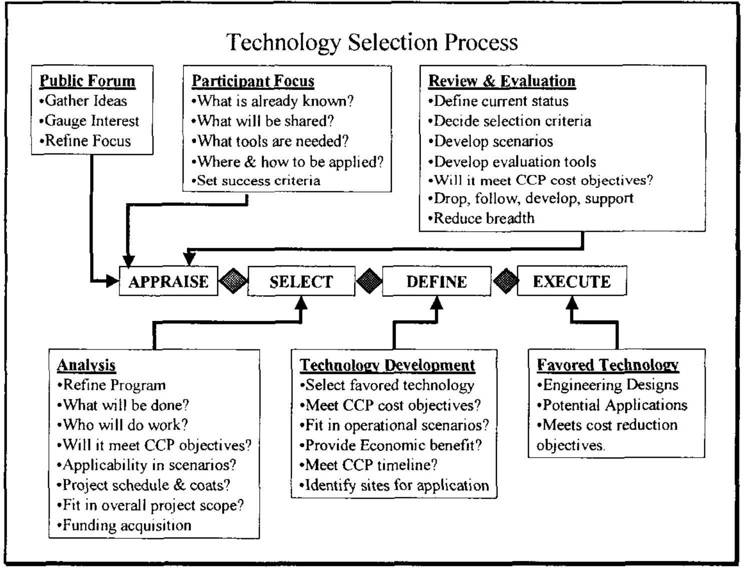
Compression and transportation of carbon dioxide to storage sites was reviewed and found to be commercially available technology and not in significant need of enhancement.

Each technology development team has chosen areas on which to concentrate their activities in support of CCP goals.

- **Oxyfuel** activities are centering on gas turbines with flue gas recycle, boilers and heaters with flue gas recycle, and on chemical looping for oxygen separation.
- **Post-combustion** will concentrate on combining membrane contactor technology with improved sterically hindered amines, cost reduction through simpler design standards for conventional amine processes, electrical swing adsorption of CO_2, and a novel in-pipe separation technology.
- **Pre-combustion decarbonization** will concentrate on water gas shift membrane reactors, membrane reformers, the compact reformer with carbon dioxide membrane contactors, very large scale auto thermal reactors, sorption enhanced water gas shift, and novel approaches in solid fuel gasifiers to separate carbon dioxide from the hydrogen rich stream. Several other technologies needing long-term development that will be encouraged are ion transport membranes, electrical swing adsorption, ElectroPOX, and IFE's MeO power process.
- **Storage, Monitoring, and Verification** concentrated on addressing monitoring, verification, and public acceptance issues. Public acceptance issues, monitoring, and verification of safe storage were deemed to be the dominant geologic storage issues and were studied thoroughly. Technologies to carry out geologic storage are either already in commercial service or readily derivable from current oil field technologies and were not heavily studied in the CCP. Geologic storage will be dominated by enhanced oil recovery opportunities where an economic incentive to use the carbon dioxide exists. Aquifer storage was viewed as a viable option that uses similar technologies to commercially available enhanced oil recovery technologies. Coal-bed storage with associated methane production is of interest but is not a central theme of the CCP.

After the CCP began operations, the selection process intensified and was managed by a **stage-gate decision-making process and technology assurance process (Figure 3**.) Each technology team used similar processes to ensure that a valid comparison could be made. The teams developed a technology selection process that is used by all. The decision-making process uses tools developed by the Common Economic Model Team. This report describes the technology selection work done and processes used by the teams.

Figure 3 Stage Gate Process for Technology Selection



This document is organized to discuss the processes, actions, and results of each step in the Technology Selection Process up to September 2001. As shown in Figure 1, it follows the Technology Assurance Process and adheres to stage-gate decision-making. It provides the assurance that prudent technology development choices are being made.

- The report is presented in Appendix A under Report Reference 0.3.

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 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 4:

Table 4 Industrial Scenarios Used in CCP as Basis for Technology Comparison

Scenario	**Fuel Source**	**CO_2 Source**	**Geologic Sink**	**Location**
Refinery	Hydrocarbon Gas & Liquids	Heaters & Boilers	Storage	European Refinery
Very Large Gas Turbines	Natural Gas	Large Electric Power Generation (CCGT)	Storage	Western Europe
Distributed Gas Turbines	Natural Gas	Small Distributed turbines	Storage	Alaska North Slope
Gasification	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_2 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

Activity began in mid-2001 with an intense period of program development and technology provider selection, and in early 2002 with the technology development program. All of the R&D activities and economic evaluations planned in 2001 were concluded by January, 2004. The results from the 2001-2003 programs are reported here.

Based on positive technical and economical results, the CCP decided to continue several projects in 2004 to provide necessary information for Phase 2. This report includes the results of those selected projects along with the earlier studies.

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

- **Post Combustion (PC)** capture technology, where CO_2 is captured from the exhaust of a combustion process.
- **Pre-combustion De-Carbonization (PCDC),** where a hydrogen-rich fuel is produced and CO_2 is captured from the produced syngas.
- **Oxyfuel,** where a pure oxygen stream is produced and used for combustion resulting in a combustion effluent containing only CO_2 and water.

In the early part of the Program, three technical teams were formed to monitor separately the progress in each category. In 2004, a single Capture Team was formed to monitor capture projects because of the narrower focus and close inter-relationship of the projects. This final report includes all reports received up to 1 April 2005. 2004 activity concentrated on PCDC technologies, reflecting its potential found in earlier studies. Plans for Phase 2 in 2005-2007 CCP will include both Post-Combustion and Oxyfuel technology efforts.

1.1 Post-Combustion

The current post-combustion capture practice is to install a physical or chemical (amine) absorption/stripping unit downstream the combustion chamber. Capital and operating costs for this type of operation are directly proportional to the dilution of CO_2 in the flue gas and inversely proportional to the total pressure of flue gas. Moreover the presence of oxygen or impurities (SO_x, NO_x, and ash) in the flue gas is problematic for conventional amine plants because it may lead to degradation of the amine. Collectively these factors result in enormous amine circulation rates, large equipment, and large energy requirements. In the case of CO_2 capture from power plants, the heat duty of the amine stripper places a substantial burden on the low-pressure steam supply.

Despite the maturity of this approach, the CCP was able to identify, in the "Cost Efficient Design" study performed by Nexant with co-funding by NORCAP, ample opportunities for substantial improvements. Nexant studied a generalized "low-cost" design for amine plants to be integrated into a power generation plant. This activity led to the definition of the Best Integrated Technology (BIT), with potential saving in capture costs >50% compared to state-of-the-art technologies. The main features of BIT are:

- Partial recycle of flue gas to the combustion chamber to increase CO_2 concentration reducing the size of the amine plant.
- Integration of stripping reboiler in the HRSG system of the power plant.

- Use of novel solvents requiring less heat for regeneration.
- Use of structured rather than random packing in the absorber.
- Relax of metallurgy and standards compared to chemical plant applications.
- Use of plate and frame heat exchangers rather than tube and sheet.

Extensive studies and tests are still needed to assess the technical feasibility of BIT. The CCP has formed a Consortium, co-ordinated by Nexant, with the participation of selected technology providers, including major producers of gas turbine components, developers of liquid absorbents and engineering firms with the target to perform all the necessary activity to assess the feasibility of the concept, reaching a "ready for pilot" stage by 2007. A proposal for a 2.5 years Project along these guidelines was submitted to the Norwegian RENERGI Program on climate change in October, 2004.

The other studies performed in the Post-Combustion program did not identify technologies with potential to achieve the CCP targets in terms of cost reduction opportunities. The CCP will however continue monitoring novel radical ideas that may be generated in this field, with special attention to novel solvents that may also contribute to further improvement of BIT.

1.2 Pre-Combustion

The CCP contributed to significant progress 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 potential of significant advancement in efficiency and cost compared to best available capture technology.
- Three of the new advanced technologies were engineered for three different CCP case studies 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.
- Significant advancement achieved in membrane materials for selective hydrogen permeation, covering a wide temperature range.
- Pre-Combustion technology can be developed to meet stringent requirements on NOx and SOx formation. The lowest NOx formation was predicted to be 5 ppm vol. from a combined cycle gas turbine. For open-cycle gas turbines NOx formation may be reduced by 50%. SOx formation is virtually zero.
- Pre-combustion technology can be designed as a stand-alone facility for both retrofit and new built application giving a wide application range and benefits with respect to integration in existing complex facilities, e.g. refineries.
- Novel pre-combustion technology has potential for use in other applications, e.g. GTL, ammonia synthesis, hydrogen and syngas production, thus increasing the economic potential of the technology and return on investment.
- Significant improvement in energy and CO_2 capture efficiency was envisaged for several technologies, resulting in efficiency penalty for combined cycle gas turbines of less than 5 percentage points and close to 100% CO_2 capture.
- 15% improvement of gas turbine heat rate can be obtained when switching from natural gas to a hydrogen-rich fuel, making pre-combustion technology a strong candidate for the large numbers of open-cycle gas turbines in the US.
- Existing Pre-combustion technology can be considered proven for a wide range of CO_2 capture applications including the CCP scenarios.

The CCP Pre-combustion Technology program was the largest capture program in the 2001-2003 CCP completing 13 individual projects including about 20 different technology suppliers.

The 2004 pre-combustion technology was based on the outcome of 2001-2003 R&D activities and on the economic evaluations that the CCP executed in the second half of 2003. The CCP decided that further research activity was needed in 2004 for four pre-combustion technologies to achieve the Proof-of-Feasibility stage. These technologies are:

1. Pd-alloy hydrogen separation membranes (Technology Provider: SINTEF – Co-funder: NORCAP).
2. Dense ceramic hydrogen transport membranes (Technology Provider: Eltron – Co-funder: DOE).
3. Sorption Enhanced Water Gas Shift (Technology Provider: Air Products – Co-funder: DOE).
4. Hydrogen Membrane Reforming (Technology Provider: Norsk Hydro – Co-funder: NORCAP).

Results of the 2004 activity have enabled the CCP to make the most appropriate choices in the definition of the 2005-2007 programs. A brief summary of the 2001-2003 achievements, description of the results of the 2004 program and a brief outline of the 2005-2007 proposed program are reported here below for each technology.

1.2.1 Palladium alloy hydrogen separation membranes (Report Reference 1.2.1.7)

In the CCP / EU project GRACE, SINTEF developed tubular Pd-alloy hydrogen separation membranes building on their patented technology. Four generations of membranes were designed, manufactured and tested, an evolution that ended with a prototype for 15 bar differential pressure. The performance of the membranes, especially related to H_2-separation and selectivity improved during the project period and became very good for the lower pressure range. An economical study showed that this method has the potential for up-scaling and integration into large H_2/C_2 separation plants.

The membranes developed by SINTEF consist of a very thin (1-5 μm) dense Pd/Ag film supported by a porous stainless steel tube. 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.

- Testing of the hydrogen flux through the membrane at 300 °C suggests a permeance of 0.3 mol/ ($m^2 \cdot s \cdot bar$) at perfect selectivity.
- The SINTEF membrane potentially represents a significant improvement over the "state of the art" assumptions made in the report for CCP prepared by Haldor Topsoe A/S.
- Testing the membranes in a WGS membrane reactor resulted in CO conversion significant above equilibrium.
- The manipulation and especially the mechanical sealing of such fragile films requires great care and often resulted in small leaks which needed manual treatment before dense layer was achieved.
- The latest generation of tubular membranes using reinforced porous stainless steel tubes is designed to withstand a transmembrane pressure of 15 bars.
- The reactor simulation model describes a water gas shift reactor with a medium temperature catalyst and a membrane model based on experimental results obtained with the SINTEF membrane. After some programming bugs had been fixed and a number of minor modifications made, BP was able to use the model to predict membrane reactor performance for process design calculations.

Due to delays in the Contract Signature phase between the CCP and SINTEF, work started only in December 2004, with conclusion expected in May, 2005.

The Klimatek / CCP project on Pd-alloy separation membranes builds on the EU-GRACE project results and by further development increase their length and durability. In order to achieve these goals a new basis of knowledge is of great importance, which needs to be achieved by carrying out experiments and developments on existing membranes. The objective of the project is to manufacture and test a 7 cm long membrane. This is a major step and requires substantial development. In addition, the work of improving the durability of the membrane will be continued.

A longer membrane requires modification and in some cases entirely new tools, equipments and procedures. Experience from the previous project showed that the success and efficiency of work did very much depend on the availability of appropriate tool and equipment.

The project is divided into two phases. The first phase will produce input data for the development of a longer membrane and in the second phase the development, manufacturing and testing of the 7 cm long membrane will be pursued.

The CCP Program for this Project will be focused on assessment of resistance of these membranes to pressure differential in the 2nd half of 2005, in the frame of the Norwegian RENERGI program. Later on, in case of positive results from the activity carried out in the 2nd half of 2005, the development of these membranes will be included in the large Integrated Project (EU co-funded) CACHET, targeting hydrogen production with CO_2 capture from gaseous fuels. All of the technologies included in CACHET will reach the "ready-for-pilot" stage by the end of 2007.

1.2.2 Dense ceramic hydrogen transport membranes (Report Reference 1.2.1.1.8)

This project has completed the research work conducted by Eltron Research, Inc. in 2002-2003. The final target is the development of a technology combining water gas shift reaction and CO_2 separation by hydrogen selective permeation through dense membranes. Hydrogen flux through the vanadium-based membranes greatly exceeded best expectations. Record hydrogen fluxes were set at 346 mL min-1 cm-2 (2.1 mol s^{-1} m^{-2}) at 440°C and 100% selectivity for 31 bar differential pressure under ideal hydrogen-helium conditions. It was concluded that at these flux rates, the membrane materials would provide a cost effective means for separation of hydrogen from many gas mixtures.

Key highlights from the test program were as follows:

- Very high hydrogen flux and permeance values were achieved (see following section).
- As expected with a dense membrane, essentially infinite H_2:CO_2 selectivity was demonstrated.
- Gas diffusion limitations initially limited hydrogen flux. Modifications to the test rigs reduced the gas diffusion limitation effect.
- Guard beds were required to capture 1) wall contaminants and 2) sulfur evolving from the upstream water gas shift catalyst beds.
- High pressure tests with wet, syngas feed were completed with full structural integrity intact.
- A proof-of-concept test rig consisting of a series of shift reactors and hydrogen membranes was constructed. The results from this rig showed that the membrane does, in fact, increase the equilibrium limited shift reaction toward the production of hydrogen.

The 2004 project was kicked off in July and consisted of three primary work tasks:

- Test membranes under higher steam and gas flow rates in high pressure apparatus.
- Long term tests in Water Gas Shift mixture
- Development of low-cost catalyst deposition techniques.

High pressure testing verified that CO adsorption will negatively affect performance. Higher temperatures will however minimize this effect. In addition, the water gas shift reaction will reduce the concentration of CO in the reactor.

Long term testing (~ 3000 hours) with H_2/He and wet syngas mixtures. Surprisingly, the membrane subjected to wet syngas demonstrated a lower rate of decline compared to the H_2/He testing and permeability appeared to be leveling off after 2500 hours.

Electroless deposition was examined as an alternative method for applying the dissociation catalyst. Flux performance was quite poor compared to vacuum deposition. Further activity is needed.

The CCP has planned continuation of the development of Eltron membranes targeting the development of sulfur resistant membranes based on the same principle in a 2-years research Project in the frame of DOE solicitation DE-PS26-04NT42249-0 "Development of Technologies and Capabilities for Coal Energy Resources" , Sub-Topic 3D "Advanced Water Gas Shift Membrane Reactor".

1.2.3 Sorption enhanced Water Gas Shift

The technology comprises a high temperature cyclic pressure swing adsorption (PSA) process for removal of CO_2 from a reactor in which the water-gas shift conversion (1) of CO is simultaneously occurring.

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad (1)$$

The technology built upon earlier work by Air Products and Chemicals (APCI) on small scale hydrogen production by 'sorbent-enhanced reforming' SER. Some of the technical hurdles in that process are overcome when the approach is used with the water gas shift reaction, though this necessitates inclusion of a syngas generation stage in the process.

The SEWGS system is primarily targeted at gas turbine combustion systems where it has particular efficiency and emissions benefits, therefore the technology was evaluated in the NorCap 400 MW CCGT case study and the Alaska distributed gas turbine gas study.

The development work in the CCP/DOE funded project comprised adsorption development and characterization, design and evaluation of CO_2 Capture processes incorporating the SEWGS, and experimental proof of concept. The work was undertaken in four phases:

- Phase 1 – Preliminary characterization of the leading candidate adsorbents, Mathematical modeling of the SEWGS system and initial evaluation of the process concept by comparison with conventional pre-combustion concepts.
- Phase 2 – Main experimental program including construction of a single bed adsorption process test unit (PTU) for cyclic experimental work, testing of a range of materials in the rig and by thermogravimetric analysis (TGA) and proof of concept runs in which combined reaction and adsorption tests were undertaken in the PTU.
- Phase 3 – Incorporating the experimental results into a capture process design for the two CCP case studies.
- Phase 4 – Additional evaluation of an alternate adsorbent material.

The key findings were that in the rapid cyclic service of a SEWGS system, the hydrotalcites have the highest CO_2 capacity of the materials tested.

This project has completed the research work conducted by Air Products and Chemical, Inc. in 2002-2003. The schedule called for the following four work tasks to be completed in the July 1, 2004 through December 31, 2004 time frame. Each task addresses areas of technical concern that arose during the previous development work at APCI. The test rig had to be moved from its Iron Run location to APCI's main campus. After that, the unit needed re-commissioning.

- CO_2 rinse step testing – This task had to verify that the CO_2 concentration reaches steady state values after multiple rinsing. Modifications to the CO_2 rinse cycle, namely adding a pressure equalization step, were not capable of eliminating this issue. Further investigation of alternative cycles is needed.
- High purge gas flow testing – This task had to determine if increasing the regeneration gas flow is feasible. Regeneration efficiency is not affected by purge gas flow rate over a wide range. This is an important finding because an inefficient regeneration at higher purge rates would require excessive amounts of steam in the industrial case.
- Methane production – During the CCP1 work, it was observed that methane was being produced in the bed. This task attempted to identify the cause of this production. The formation of methane was confirmed, but it may be eliminated by increasing the water content of the syngas.
- Alternative adsorbents – High temperature adsorbents by Toshiba (Li_4SiO_4 modified with K_2CO_3) showed exceptional CO_2 adsorption properties (e.g. 30-34% wt of CO_2 at 650°C and 1 atm CO_2). May be operated in PSA at 650-700°C using N_2 as purge gas, or in TSA mode.

The CCP has planned continuation of the development of APCI adsorbent materials targeting the development of sulfur resistant adsorbents based on the same principle in a 2-years research Project in the frame of DOE solicitation DE-PS26-04NT42249-0 "Development of Technologies and Capabilities for Coal Energy Resources" , Sub-Topic 3E "Advanced Solvents and Solid Sorbents based separation systems."

The continuation of development activity targeting clean natural gas feedstock will be carried out in the frame of the EU co-funded CACHET Project.

1.2.4 Hydrogen Membrane Reforming

From July-2001 until end 2003 Norsk Hydro conducted a research program (with SINTEF and the University of Oslo) with CCP/NORCAP funding to develop dense ceramic high temperature hydrogen mixed conducting membranes for the application of a natural gas membrane reformer integrated in a power plant with CO_2 capture. This membrane reformer is designed such that both the rather pure CO_2 product stream and the H_2-rich GT fuel gas streams are released from the membrane reformer at elevated pressures. Milestones were:

- Candidate membrane materials were identified that can meet the 5 Nml/min/cm^2 criteria necessary to obtain 50% CO_2 cost reduction;
- Supported membrane tubes, consisting of a porous tubular support and a thin (50μ) membrane coating, were fabricated. This as a first step towards envisaged monolith structures in the design concept;
- Proof of concept flux measurement: a prototype tube measured at 1000° and 20 bar good (higher than expected) hydrogen flux. The target flux considered reached, although after the experiment corrections had to be made for the measured porosity of the membrane coating.

- Thermodynamic analysis revealed that temperature needs to exceed 750 °C in order to assure thermo-chemical stability.

- A process design for the three stage membrane reformers and power plant was made, including a conceptual design of the monolith-membrane reactors based on Hydro background information. Cost evaluation of the whole concept with Hydro's own cost assumptions on the membrane reactor systems confirmed the more than 50 % avoided CO_2 cost reduction, both caused by lower capex required and by lower energy consumption (higher net exported power) compared with the baseline case;

- The third stage of the reformer is used to convert combustible components to 'purify' the CO_2 stream and to recover the energy. The chosen "hot shift burner" may not be able to convert all CO. For the process design higher than proven extraction of air from gas turbine was required in order to cool this "hot shift burner".

- The catalytic activity of the membrane material proper was tested rather low, and will need to be increased by appropriate activation by nickel coating etc., this to avoid undesirable temperature profiles and thermal stresses.

It is realized that this process with its advanced membranes and reactor concept is still in an early stage of development.

Since June 2004 an extension program, always with CCP/NORCAP funding, was conducted by Hydro to focus specifically on the membrane material, with completion expected by February 2005:

- Improve the 'sinterability'. Influence of various conditions/aids will be tested and characterised on small disks first.
- Apply the found conditions/aids to the supported tubular membranes and test thin membrane coatings on porous supports to be fully gas impervious.
- Test hydrogen flux under similar to process conditions.

To improve the sinterability of the membranes, six main groups of sintering aids were first identified. Sample disks of different membranes using the six candidates were fabricated and tested by sintering at 1550-1650°C. The best candidate (SA5) was selected, giving >100°C reduction in sintering temperature at a level as low as 2% mol, ensuring homogeneity of slips and dense sintered layers.

Several membrane tubes have been prepared using the identified sintering aid, and tested to achieve a fully gas impervious coating. Optimization in the operating parameters for fabrication is ongoing with considerable improvement in the features of the fabricated tubes. Full success is expected by January 2005. The test rig ahs been prepared and commissioned, and testing on the most promising tubes under process conditions will take place by February 2005.

The CCP has planned continuation of the HMR development in a 3-years Project co-funded through the Norwegian RENERGI Program, addressing all the necessary issues to achieve a "ready-for-pilot" stage by the end of 2007.

1.2.6 Other planned Pre-Combustion activity

One of the CCP case studies is related to a coal gasification unit set in Western Canada. The application of pre-combustion techniques for CO_2 removal in this scenario was studied by Fluor under DOE co-funding. Fluor studied the application of state-of-the-art amine washing and of their CO_2LDSEP technology based on separation by refrigeration. The CCP is considering the option to study this application further, considering possible synergies and cost reductions by novel separation technologies, like, for instance, Sorption Enhanced Water Gas Shift or Membrane Water Gas Shift.

Other interesting novel Pre-Combustion technologies have been included in the above mentioned CACHET project for hydrogen production from gaseous fuels with CO_2 Capture. HyGenSys is a technology under development by Institut Francais du Petrole (IFP) whose focus is a novel heat exchange compact reformer with very high heat exchange coefficients, enabling complete capture of CO_2 generated during hydrogen production. Activity will be focused on a large "mock-up" to demonstrate the expected hydrodynamics of the heat exchange section.

Some variations of the Chemical Looping Technology described below and studied by the CCP Oxyfuel Team will also be included, namely the Chemical Looping Reforming (partial combustion rather than complete combustion in the reactor) by the Chalmers University of Technology and the "One Step H_2" concept by EniTecnologie employing a solid carrier able to capture oxygen from H_2O with direct production of hydrogen. For these technologies activity will be focused on the development of active and durable solid carriers.

1.3 Oxyfuel technologies

The mission of the CCP Oxyfuel Team was to investigate the potential savings that combustion using pure oxygen (oxyfiring) may give in CO_2 capture, compared to conventional combustion with air. This involved monitoring and sponsoring R&D, which may contribute to further reduction of CO_2 capture costs by the year 2010.

When CO_2 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_2 capture, however, oxyfiring has a unique advantage of generating an effluent stream composed almost exclusively of CO_2 and H_2O. It may be very cheap and easy to capture CO_2 of the necessary purity for sequestration from this stream, simply by water condensation, depending on the purity requirements for sequestration.

Another unique environmental advantage of oxyfiring is that NO_x emissions are dramatically reduced compared to conventional air combustion. Although no detailed assessment was done for CCP, in the experience of Oxyfuel Team members, the abatement cost for NOx is estimated to be about 2,500 $/ton using conventional technology. If this credit is accounted for, the CO_2 avoided cost is reduced by about $10/ton for the UK refinery scenario.

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, mainly with DOE funding, outside the CCP frame, to develop novel technologies able to reduce consistently the cost of air separation. While this development is not driven by CO_2 capture considerations, their application to oxyfiring may contribute to reduce the costs of CO_2 capture in oxyfiring systems.

The scope of work carried out by the Oxyfuel Team in the 2001-2003 timeframe included the following:

- Definition of an Oxyfuel baseline, potentially applicable "today": CO_2 capture with state-of-the-art cryogenic 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).

- Investigation of novel boiler and heater designs which take advantage of Oxyfuel firing to reduce equipment size (and hopefully, cost) and increase efficiency compared to conventional fired equipment, maintaining conventional air separation.
- Investigation of advanced thermodynamic cycles for power generation systems, most of which involve turbine modification.
- Investigation of novel air separation technologies (e.g. ionic transport membranes for oxygen) for application to conventional boilers/heaters.
- Investigation of novel technologies integrating steam or power generation system and novel techniques for oxygen supply (e.g. Chemical Looping).

For commercial application by 2008-2010, oxyfuel technologies under development show promising potential for a very broad range of applications. Current state-of-the-art technology allows retrofit of existing heaters and boilers with the lowest CO_2 capture costs among currently available technologies. Oxyfiring with flue gas recycle may be considered as a CCP Baseline Case, with possible application to revamping of boilers and heaters without any research activities. A demonstration of oxyfiring with flue gas recycle is the only pre-requisite to commercial implementation. In case a CO_2 avoided cost of 40-45 \$/ton, corresponding to a CO_2 capture cost of 35-40 \$/ton may be acceptable, this is a short-term feasible solution.

No improvement in boiler design, which directly tries to harness the advantages of Oxyfiring, was identified that would result in consistent savings over the Oxyfiring Baseline. Pure oxyfiring application to CCGT systems with conventional air separation would require consistent and very expensive development in the field of gas turbines 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 perspectives.

Novel membrane systems for pure oxygen production, currently under development and expected for commercialization by 2008-2009, will produce oxygen at substantially lower cost than conventional cryogenic separation. However, the specific process cycle to produce oxygen (e.g. low pressure versus use of sweep, extent of oxygen extraction from air, etc) needs to be assessed for each application. For example, it seems that a cycle that does not extract most of the oxygen from air must likely generate substantial excess power. In this case, it may not be a good fit for revamping of existing heaters and 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 because of its similarity to existing coal fired boilers (CFBs.) Furthermore it produces rather pure CO_2 compared to the Oxyfuel Baseline. A decision on the opportunity 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).

Based on the above conclusions, the CCP decided to include Chemical Looping among the technologies for continuation of funding in the 2005-2007 period. It was also decided that, since the previous EU-funded Project came to an end by December 2003, continuation of funding in 2004 was advisable to maintain the progress on a fast track. It was consequently decided to apply for DOE co-funding in a project aimed to optimize solid carrier materials, completing the Proof-of-Feasibility stage.

It is also the intention of the CCP to continue monitoring the development of ceramic transport membranes for oxygen transfer, checking the status of the related projects by mid-200

1.3.1 Chemical Looping

The major R&D Project (actually the only one directly funded) in the Oxyfuel field was the concept called Chemical Looping. The work was done by a Consortium formed by BP (Coordinator), Alstom Boilers, Chalmers University, CSIC and Vienna University in a 2-years EU-cofunded project coming to a conclusion by December 2003. Total budget of this Project was 1.5 MM€.

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

Fuel reactor: $MeO + CH_4 \Rightarrow Me + 2H_2O + CO_2$
Air reactor: $Me + 0.5O_2 \Rightarrow MeO$

This project focused on atmospheric pressure applications, typical of the CCP UK Scenario, but the concept is also applicable to higher than atmospheric pressure in gas turbine systems, as already studied in another project outside the CCP funded by the DOE. In the case of a turbine application, the trade-off is between thermodynamic efficiency and percentage of captured CO_2, since Chemical Looping Combustion takes place at relatively low temperatures (800-900°C). Also, the need for hot dust filtration or development of turbine materials that can accept "dust" are additional issues to address in this case.

The main risk in developing Chemical Looping is the availability of a suitable oxygen transport material capable of undergoing repeated oxidation/reduction cycles, while maintaining both chemical activity and mechanical resistance. The screening activity performed during the first year of the project identified a few materials for further development. In the meantime, with the support of fluidized bed testing in cold units, a pilot unit was designed and built to achieve "Proof-of-Feasibility" of the technology, i.e. the main target of this Project. The pilot unit at Chalmers has two integrated 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 a Ni-based oxygen carrier 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 loss of activity by the carrier.

The second-half 2004 DOE co-funded project activity by CSIC (Consejo Superior Investigaciones Cientificas) targeted optimization of oxygen carrier materials through modification of composition of Ni carriers to reduce CO and H_2 emissions.

The main results are summarized here below:

- The addition of Cu to the Ni-based carrier led to a relatively long time of complete combustion of methane (no CO and H_2) at the expense of lower reactivity compared to the carrier without Cu addition.
- The addition of Mn to the Ni-based carrier resulted in a similar behavior, but the time of complete combustion, before appearance of CO and H_2 was very short.
- The addition of Na to the Ni-based carrier had no significant effect.

- K and La salts were further added to Ni-Cu carriers. Both additions resulted in a small increase in reactivity. K also increased the time before CO and H_2 began to appear in the effluent gas from combustion.

Based on the above it is clear that Ni-Cu carriers, possibly added with promoters, are a very promising option for application to Chemical Looping Combustion to avoid presence of CO and H_2 in the CO_2 recovery stream, while maintaining the high reactivity of Ni carriers.

Based on the results of this Project, the CCP has decided to continue development of Chemical Looping Combustion submitting a proposal to the EU for a 2 –year Project targeting scale-up from 10kW to 200kW continuous circulating fluidized bed reactors.

1.1 Post Combustion Studies

Task - 1.0 - Develop Post Combustion Separation and Capture Scenarios

Background:

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

The current post-combustion capture practice is to install an amine separation unit at the flue-gas source. This is a very difficult separation, since the gases are hot, dilute in CO_2 content, near atmospheric pressure, high in volume, and often contaminated with other impurities (SO_x, NO_x, 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_2 capture from power plants, the heat duty of the amine stripper places a substantial burden on the low-pressure steam supply. Despite the maturity of amine technology, there appears to be ample opportunities for finding improvements with new technology.

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

- Step-change cost reduction through improving existing amine technology (e.g., better solvents, better solvent contactors, cost-effective plant design).
- High-risk, entirely novel approaches to post-combustion capture (e.g., DOE-funded work in Self-Assembled Nanoporous Adsorbents).
- The CCP funded several engineering studies and technology development programs in the post-combustion area.

From the work completed thus far, the CCP has learned that entirely new radical approaches would be required to reduce the cost of post-combustion CO_2 capture by the levels specified at the outset: by 50% for retrofit and 75% below conventional amine technology for new-build scenarios.

Post Combustion Separation Technology

1. Introduction

Flue gas separation at the scale envisioned by the CCP was a very new research area. Earlier carbon dioxide separation technologies were designed to work at much smaller scale to provide dry ice, food-grade carbon dioxide and for chemical processes. The largest plants in operation were too small by a hundred-fold (100 tonnes/day versus greater than 10,000 tonnes/day) for flue gas capture. There was not much research dedicated to flue gas carbon dioxide recovery going on around the world. Many approaches tested ended up in nothing.

The Group was charged with evaluation of technologies that might be useful at the large scale needed and with stimulating development of technologies of appropriate scale. Work began by challenging researchers worldwide to propose research and evaluations that would aid CCP in its search for appropriate technologies. The Group covered a considerable territory since its creation more than 3 years ago.

The choice of projects must be seen in the context of the CCP's goal of achieving a 50 % cost reduction in retrofit to existing plants and a 70 % cost reduction in new built plants. Technologies without the potential to meet these targets were not considered for CCP support.

2. Invitations to Contribute

At the outset the Group invited 20-30 researchers at universities and research institutes in Europe and USA to submit proposals. These were researchers engaged in relevant research for carbon dioxide separation from flue gas. Few projects materialized from these invitations. Presentations were also given at meetings where open invitations to participate were made without result. Later on additional attempts to stimulate research in radically new technologies were made with some success (two projects.)

It may be tempting to reflect on the limited response received. It could be attributed to people wanting to develop their ideas independently, or maybe ideas were not available due to lack of interest in the field. The answer to this would be of interest to policy makers in research.

3. Absorption Processes (Not Absorbents)

Absorption-desorption processes can be designed to handle large gas volumes and have been used in the past to treat flue gas. On this basis this is considered the default process to apply at this point in time. This section is equipment and process oriented. Discussion of new absorbents is left to the section on "New Capture Chemicals".

3.1 The Base Case

The Group has had the responsibility of overseeing the study work on the so-called Base Case. This is the absorption-desorption process of Fluor based on their Econamine process which is based on MEA (a 30 % aqueous solution). Studies were made on scenarios "Alaska Gas Injection Facility", "Norwegian Power Plant", and "European Refinery". The base case technology is commercially available today. It was originally developed to recover carbon dioxide from flue gas to produce carbon dioxide for the industrial gases market. The availability of this process for many years does not, however, mean that this processing segment is mature. Carbon dioxide sequestration requires processing of huge volumes, and represents a new challenge for cost reduction.

3.2 Nexant Work on "Simplified Standards"

It was decided by the Group that the base case process should be analyzed in detail to uncover all possibilities to reduce costs. The base case design was done according to the oil industry's API standards that go beyond the needs of simple flue gas treatment. There should hence be opportunities to re-optimize the process. Nexant was contracted to perform this analysis for the CCP. Since they could not have access to the Fluor work, they had to produce their own generic MEA process for comparison. Their work was done in two stages, first to reduce costs as much as possible for a stand-alone separation plant, secondly to exploit possible synergies in integrating the separation and power plants.

Their findings can be summarized as follows, where the last two points can be attributed to integration:

- Improved absorber design based on structured packing with lower pressure drop and resulting shorter column height.
- Elimination of the flue gas cooler by allowing warmer gas into the absorber.
- Smaller flue gas fan due to reduced pressure drop.
- Replacement of the S&T water wash cooler, lean amine cooler and economizer with plate and frame heat exchangers.
- Changing from API to ANSI classified pumps.
- Using live steam from the power plant directly into the desorber, thus reducing reboiler load.
- Going from two in parallel to one carbon dioxide compressor.
- Cheaper PSA based carbon dioxide gas dryer to replace the glycol based absorption.
- Integration of the carbon dioxide recovery plant with the power plant by allowing recirculation of the flue gas back to gas turbine to reduce the volume of flue gas to be treated.
- Integration of the carbon dioxide recovery plant with the power plant by relocating 75% of the amine reboiling duty directly into the HRSG (Heat Recovery Steam Generator).

Except the simple equipment swaps of pumps and heat exchangers, these proposals must be tested before acceptance. The Nexant estimates were analyzed by the CCP's cost estimator in cooperation with the Group. The equipment cost estimates/quotations from Nexant were consistently lower than others received. In addition, the points in the simplified design regarding carbon dioxide compressor and plate-frame heat exchangers were already included in the Fluor base case. Some alignment of costs was needed. The need for cost alignment does not reflect on the quality of Nexant's work, all estimates were adjusted to make sense when compared. It must be understood that the present accuracy of estimates was +/- 35 %. The adjustments were much less. The final conclusions regarding the improvements in carbon dioxide separation costs achieved by Nexant after alignment of content and cost data with the other post-combustion projects are given elsewhere.

Some of the proposed 'cost saving ideas' have a potential impact on unit availability (e.g., single train compression and lower cost pumps). At this point it is difficult to accurately assess the impact of these changes and evaluation of the overall impact requires further work. Clearly the availability will potentially also be reduced when the plants are integrated and thus made more interdependent.

3.3 Combination of Kvaerner-Gore and MHI

This process combines two established technologies for the capture of carbon dioxide from industrial flue gas streams. (Falk-Pedersen et al., 2000; Mimura et al., 1998)

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

The technology was evaluated in the context of the "Norwegian Power Plant" scenario. Also for this study an extra base case study was included for comparison. The Kvaerner-Gore membrane contactor was used to replace the absorber including the amine wash section.

Tests were performed to verify the compatibility and performance of the KS-1 solvent and the Kvaerner-Gore membranes. The solvent migrated across the membrane into the flue gas, implying that a water-wash section was needed. Further tests done with a membrane water wash section using MEA as the amine were successful. This extra section unfortunately added to the overall cost of the facility.

Analysis of the combined process showed that capital cost savings (versus conventional absorber/desorber equipment) are within the uncertainty of the estimates. The membrane contactors' biggest potential advantage is that of low weight and space. The main advantage of this combination lies in the lower energy consumption (and hence operating cost) required for the KS-1 solvent regeneration. In comparative studies against conventional MEA processes, a reduction in regeneration energy of over 25% is reported for KS-1.

The combined process has not been used commercially, but both the membrane and the solvent have been installed separately in one commercial facility.

3.4 TNO

The Dutch research institute TNO has a similar membrane absorber to that of Kværner-Gore. They use polypropylene membranes which are believed to be cheaper. (Feron et al., 1998). At least the starting polymer is cheaper. However, this cost advantage will be diluted by the time it is all assembled to a process. It was expected by the Group that the CAPEX of this concept would be similar to that of the Kværner-Gore concept. Since their development work had come shorter than that of Kværner-Gore, the Group found no merit for the CCP in pursuing this line of investigation

3.5 BIT (Best Integrated Technology)

The Group has observed that some technologies can be combined in such ways that the resulting improvements are better than the best of the individual technologies. Of the investigated technologies, it is clear that the MHI absorbent can be combined with the "Nexant low cost" and "Nexant integrated" designs. The lower energy needed to regenerate this absorbent compared with the conventional MEA will give further energy savings compared to the two Nexant processes. The circulation rate of absorbent is also lower leading to reduced pumping costs and smaller heat exchangers.

The BIT is then defined as the "Nexant low cost" and "Nexant integrated" designs combined with the MHI absorbent. The estimates presented are based on the investment of the Nexant designs and the operating cost is as the "Nexant integrated" reduced by the power savings allocated to the Kvaerner-MHI design.

Time and resources have not allowed a deeper analysis like accounting for marginal effects on individual equipment items which would include

- No reclaimer (needed for MEA operations)
- Reductions in auxiliary equipment to handle make-up, bleed and solution quality management
- Smaller circulation pumps
- Smaller coolers for lean amine and wash water
- Smaller economizer (lean/rich heat exchanger)
- Smaller reboiler for desorber, and thus smaller overhead condenser
- Smaller steam system since less is used

The BIT as a concept can be further improved as technologies become available. It should be pointed out that BIT as defined refers to those technologies included in the final CCP studies. Better absorbents could well be found as pointed out in the "Radical Chemistry" project, and the "RAD" project preliminary study indicated cheaper equipment. Hence, there are already ideas afoot that can further improve the BIT to achieve even lower capture costs for the post-combustion carbon dioxide removal.

4. Adsorption Processes

A number of proposals and existing adsorbents and/or processes have been looked at. Much work has been published in this area before and during the existence of the CCP. All alternatives studied have turned out to be too expensive to be of interest for flue gas carbon dioxide removal. It is the opinion of the

Group that further efforts in the area of adsorption are futile unless a break-through process is reported. Work on new process concepts could be considered, but work on new adsorbents is not recommended now. The Group tried to commission an adsorption process study to see what it would take to make such a process economically competitive, but this had to be abandoned. Such a study would be valuable and could contribute by setting research targets for adsorption projects.

4.1 Electrical Swing Adsorption

The Group worked with Oak Ridge National Laboratory (ORNL) to evaluate their 'Electrical Swing Adsorption' (ESA) process. Limited tests were undertaken to assess the loading capacity of a 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. It is clear from the simple cost analysis that there is no economic incentive to take this idea any further for post-combustion separation. The cost is likely to be higher than the base case and there are several technical obstacles still to overcome (e.g. low carbon dioxide loading and high pressure drop for CFCMS material) which can only result in an even higher cost for a facility based on this technology. Finally, the 'Electrical Swing Effect' was not clearly demonstrated during the CCP test program.

The Group cannot recommend this technology for further development at this time.

4.2 Rubicon / Solmec Process

There appeared to be a promising process based on adsorption developed in Israel. It was chased with some skepticism. This investigation ran into nothing because it turned out to be impractical to receive any solid information on it. The idea was thus abandoned.

4.3 SRI work on New Sorbents

This project was the result of an active search for radically new approaches to carbon dioxide separation using contacts in US academia. A partnership was entered into with SRI. This work involved the 'design' of self-assembled, nanoporous adsorbents for improved adsorption of carbon dioxide from low pressure flue gas streams. It comprised thermodynamic assessment of co-operative bonding in adsorption processes, modeling co-operative bonding effects with copper dicarboxylate materials, and laboratory performance testing of such materials. This work also included the development of a preliminary process design to adsorb carbon dioxide from low-pressure, dilute, flue gas streams.

The results were assessed based on a simple adsorption cycle (PSA/VSA) concept. Due to the large adsorbent beds and vacuum blowers/energy requirements, simple cost estimates clarified that this was not a way to go. Further work in this area is not recommended unless a break-through process design and adsorbent is found.

5. Membrane Processes

Membrane separation processes based on differences in permeation rates are dependent on partial pressure differences of the permeating species to drive the process. For flue gas carbon dioxide capture, the feed has a partial pressure of carbon dioxide in the order of 0.04 to 0.10 bars. The entire flue gas stream would have to be compressed to raise the carbon dioxide partial pressure. It is deemed by the Group that this makes membrane separation processes unsuitable for flue gas carbon dioxide removal. Hence, no action to pursue such processes was taken. At the end of the CCP program we still stand by this decision. A new approach would be needed to make permeation membrane technology interesting.

6. Cryogenics or Refrigeration-Oriented Processes

Cryogenics is considered a major workhorse for gas separations. However, a cryogenic process would need nearly complete water removal before chilling starts. Even carbon dioxide itself would pose a challenge with respect to freezing, but processes have been described in the past that master this. Due to the drying needs and extensive heat exchange needed, it was early on deemed by the Group that such technologies would not be worth pursuing.

One exception was discussed, however. That was freezing the carbon dioxide out as a hydrate. Data on temperature and partial pressure needs quickly ruled this out.

7. Novel Process Concepts

7.1 Recycling of exhaust gas

This was not pursued from the beginning for a variety of reasons. There was general consensus that the resulting increase in carbon dioxide partial pressure would not increase the rich amine loading when using MEA. The question was eventually raised again based on using the MHI absorbent KS-1. Approaches were made to gas turbine engineers without much response. The effect of recycling the exhaust gas was evaluated in the Nexant studies on the absorption process. (See above). The conclusion drawn was that the ensuing reduction in gas flow to the separation plant makes this very interesting irrespective of the solvent available. It is strongly recommended to pursue this.

7.2 RAD (Rotating Absorber and Desorber)

This idea was offered by Norsk Hydro for the consideration of the CCP. A preliminary study was made and it showed a potential investment saving of more than 50 % relative to the base case as it was then defined. There would be further saving if e.g. MHI's KS-1 were to be used, but this was never looked into. Further work on this line of research was recommended by the Group, but work was stopped for a variety of reasons.

7.3 Radical Chemistry / Klimatek Project

The radical chemistry project run under NorCap / Klimatek produced 3 novel process concepts as well as new ideas for chemistry that is discussed below. This project was operated by Norsk Hydro and involved co-operation with Norwegian universities and the SINTEF group. The assessments referred to below were based on documented assumptions of properties of the ideas. The values assumed could be lower or higher. These assumptions will become natural research targets if this work is pursued.

The Group found all three concepts interesting and worthy of further investigation.

7.3.1 FST ("Fast Shaking Truck")

This is based on going in a new direction with the chemistry. There are 3 ideas in this concept. The carbon dioxide carrying material ("truck") is expected to be based on transition metal complexes. If necessary, the mass transfer could be made faster by adding a biomimetic compound as a catalyst ("fast"). Finally, it was foreseen that sonic chemistry could be used to help the desorption ("shaking"). A rough flowsheet was made and assessed. Potential cost savings in the order of 50 % were identified.

7.3.2 pH swing

This process is based on finding a chemical system that allows pH control such that the solution is alkaline when it absorbs carbon dioxide while desorption is facilitated by lowering the pH such that carbon dioxide comes off. A process with absorption and desorption columns is foreseen, but there is a crystallizer added where the pH lowering chemical is precipitated before the solution is recycled to the absorber. The investment will not be reduced, but there is potential for lowering the operating costs. A similar process has already been made to recover SO2 from flue gas (Erga, 1986). Assessment of the process indicates an interesting potential for reducing energy consumption. Potential savings could be 50 % on NPV depending on the pricing of energy.

7.3.3 MPS. (Melting Point Swing)

This process is based on the use of salt hydrate melts to absorb carbon dioxide, and desorption being effected by solidifying the melt. Such chemicals have been identified with melting points allowing the use of waste heat to operate the cycle (Quinn, 1990). An elegant all-in-one apparatus was conceived. The assessment of this process indicates a cost saving potential in the order of 50 %, possibly more.

8. New Capture Chemicals

8.1 New Absorbents Reviewed

The MEA absorbent has a few undesirable properties. There is significant degradation of the amine. It is not quite clear how much of that is thermally induced and much is chemically caused by components in the gas such as NOx and oxygen, or possibly a combination of both. The vapor pressure of MEA is high enough to necessitate a water wash downstream of the absorber. Furthermore, it is very reactive with a high heat of absorption which contributes to a lot of energy being needed to regenerate it. Any new absorbent that alleviates one or more of these drawbacks would represent an improvement. Based on knowledge accumulated in this project it can be said that at least three alternative absorbents are available, or could be available after necessary testing. These are

- Mitsubishi's KS-1. (Mimura et al., 1999)
- University of Regina's PSR. (Chakma et al., 1999)
- Praxair's solvent. (Chakravarti et al., 2002)

All of these have energy consumptions lower than that of MEA by approximately 30 %, and the degradation is also lower by a factor of 3 to 10. Solvent costs will vary.

It is clear that the use of energy for regeneration and the degradation rates differ significantly between the various absorbents available. Clearly this should be an inspiration to widen the field when choosing an absorbent for this application. No work was started in this field early on because of the initial statement in the CCP sphere saying that efforts should be concentrated on reducing the investment needed. In retrospect, this was unfortunate since switching chemicals have later proved to lower the investment as well as reduce the need for energy. See e.g. the comments on Kværner-Gore-MHI above.

9. Summary

The Post-Combustion technology group has found a number of interesting ways in which the cost of carbon dioxide removal could be reduced from the base case defined and evaluated. A number of technologies have been investigated. This summary has not specified those invitations to participate that was extended without resulting in proposals. Suffice it to say that attempts were made to approach the most well-known workers in relevant research areas.

It is the feeling of the Group that there are many good research opportunities with respect to reducing the total cost of carbon dioxide removal. Extensive studies have been done with respect to

- Base case
- Nexant low cost design
- Nexant integrated low cost design

- Kvaerner-MHI to study a new contactor combined with a new absorbent

The Group has further looked into

- Better adsorbents
- The basis for dismissal of membranes and cryogenics for this application
- New chemical approaches, producing a few research proposals
- Alternative equipment technologies

Finally, the Group has defined what is referred to as BIT (Best Integrated Technology) based on the studied technologies. BIT is not ready to be built as some features need to be checked. The BIT concept must not be seen as the ultimate post-combustion solution as there are more research opportunities available, and more are foreseen for the future.

10. Abbreviations

ANSI	American National Standards Institute
API	American Petroleum Institute
ARI	Adsorption Research Inc
BIT	Best Integrated Technology
ESA	Electrical Swing Adsorption
HRSG	Heat Recovery Steam Generation
MEA	Monoethanolamine
MHI	Mitsubishi Heavy Industries
NTNU	Norwegian University of Science and Technology
ORNL	Oak Ridge National Laboratory
PSA	Pressure Swing Adsorption
QP	Quick Place (The CCP data base)
S&T	Shell and Tube
SINTEF	A Norwegian research organization
TNO	A Dutch research organization
UOP	Universal Oil Products
VSA	Vacuum Swing Adsorption

11. References

A. Chakma, P. Tontiwachwuthikul, (1998) “Designer solvents for energy efficient CO_2 separation from flue gas streams”, GHGT-4, Fourth International Conference on Greenhouse Gas Control Technologies, Interlaken, proceedings, page 35-42

S. Chakravarti, A. Gupta, B. Hunek, W.R. Williams, (2002), ”Novel Technology for CO_2 Capture”, IBC’s 2nd Annual Carbon Sequestration Conference, May 15 & 16, London

O. Erga, (1986), "SO2 recovery by means of adipic acid buffers". Ind. Eng. Chem. Fundam. 25, pp. 692-695.

O. Falk-Pedersen, H. Dannström, M.S. Grønvold, D.-B. Stuksrud, O. Rønning, (2000) “Gas Treating Using Membrane Gas/Liquid Contactors”, GHGT-5, Fifth International Conference on Greenhouse Gas Control Technologies, Cairns, proceedings, page 115-120.

P.H.M. Feron, A.E. Jansen, (1998), “Techno-economic assessment of membrane gas absorption for the production of carbon dioxide form flue gas”, GHGT-4, Fourth International Conference on Greenhouse Gas Control Technologies, Interlaken, Proceedings, page 53-58.

T. Mimura, S. Satsumi, M. Iijima, S. Mitsuoka, (1998) “Developments on energy saving technology for flue gas carbon dioxide recovery by the chemical absorption method and steam system in power plant”, GHGT-4, Fourth International Conference on Greenhouse Gas Control Technologies, Interlaken, Proceedings, page 71-76

Robert Quinn, Guido P. Pez, (1990), “Use of salt hydrates as reversible absorbents of acid gases”, US patent 4973456

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 attempted to stimulate new technology ideas for novel ways to capture CO_2 after combustion. The objective was to evaluate and select up to three promising candidates for further exploratory development. A related effort to stimulate new research concepts through a structured process is reported in **Section 1.1.1.3.**

At the outset the Group invited 20-30 researchers at universities and research institutes in Europe and USA to submit proposals. These were researchers engaged in relevant research for carbon dioxide separation from flue gas. Few projects materialized from these invitations. Presentations were also given at meetings where open invitations to participate were made without result. Later on additional attempts to stimulate research in radically new technologies were made with some success (two projects.)

It may be tempting to reflect on the limited response received. It could be attributed to people wanting to develop their ideas independently rather than share rights through participation in the CCP. A second reason may have been that researchers had not yet considered post-combustion separation as a viable area for innovative research because of low funding opportunities and little incentive to embark on what would become an expensive research program.

The answer to this would be of interest to policy makers in research. A similar request today (early 2005) might garner broader interest because of the heightened interest in CO_2's role in global warming.

1.1.1.2 Self-Assembled Nanoporous Materials for CO_2 Capture

Task - 1.4 - "New and Novel" Concepts
Principal Investigator: Ripudaman Malhotra
Technology provider: Stanford Research Institute (SRI)
Co-funder: U.S. DOE

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^2/g. Reproducibility and scale-up problems were encountered. A 450 m^2/g surface area sample showed over 90% of the area in pores less than 20 A°. Surface morphology analysis by SEM showed a multi-lamellar structure.

- The samples showed high capacity for CO_2 adsorption with a selectivity 8 times greater than for N_2 adsorption. High adsorption capacity was demonstrated by CO_2 isotherm measurements that did not level off at 1 atm CO_2, corresponding to 25 atm flue gas containing 4% CO_2. The copper terephthalate material performed best CO_2 pressure above 1atm or above 25 atm total pressure with a 4 % CO_2 flue gas. The highest CO_2 purity obtained in the experiments was 67.9% CO_2 with 34.1% recovery.

- A simulated 400MW gas-fired power plant with 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_2 and a parasitic power load of about 1 GW. Work was halted on this project because other processes were more attractive.

Summary

SRI International, Chemical Science and Technology Laboratory, proposed and executed the title study to produce sorbent materials for CO_2 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_2 from power plant flue gases. The study materials were based on work of Seki (Osaka Gas) who has shown that a range of nanoporous structures can be made from copper salts of dicarboxylic acids. The materials have a square cavity whose dimensions can be controlled by the choice of the dicarboxylic acid. Solids with cavities large enough to accommodate four to five methane molecules were shown to have the highest capacity for methane. SRI proposed to synthesize and test these materials that would physi-sorb CO_2 by relatively weak van der Waals forces and that would have a high adsorption capacity for CO_2.

Structures that could accommodate multiple CO_2 molecules at each site may exhibit cooperative binding of CO_2. Binding is considered cooperative when subsequent molecules of CO_2 adsorb onto the material with slightly greater heats of adsorption. In such a case, the PSA system would require less work to capture an equivalent amount of CO_2 than a non-cooperative system. The 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_2 sorbents under PSA conditions, and to perform a cost analysis of a process based on the new materials.

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

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^2/g and 1200 m^2/g. The pore size distribution of a 450 m^2/g surface area sample was found to have over 90% of its pores less than 20 A° in size. Earlier molecular structure calculations indicated that cavities should be about 10A° in size. The materials have been characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD) and thermogravimetric analysis. SEM studies included a comparison of a high surface area SRI material with Seki's material. Seki's sample showed a cubic morphology while the SRI sample exhibited a multi-lamellar structure. XRD analysis showed that the $2\theta = 9°$ peak intensity that is an indicator of nanoporosity was intermediate between Seki's published data and that measured in our laboratory for Seki's sample. These results give us confidence that our laboratory procedures are capable of producing nanoporous copper phthalate materials.

SRI prepared and reference samples from Osaka Gas were tested by a subcontractor, Adsorption Research Inc. CO_2 and N_2 adsorption isotherms for the SRI sample showed that the CO_2 isotherm did not level off at the highest pressures tested (1 atm. CO_2 which corresponds to 25 atm. flue gas containing 4% CO_2). The result is consistent with a high capacity of the material to adsorb CO_2. The selectivity of the material for CO_2 over N_2 was estimated to be about 8. The advantage of copper terephthalate manifests itself only at CO_2 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_2 from a 400 MW gas-fired power plant that would meet the specifications of 90% capture and 96% CO_2 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_2 product is recovered by pulling a vacuum on the adsorbent. The highest purity obtained in the experiments was 67.9% CO_2 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 kgmol/hr at a CO_2 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_2 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, electric power, labor, installation, and a modest profit margin. The resulting power requirements for CO_2 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_2 partial pressure, system.

Reports and Publications

- See Appendix A for the project final report under the same heading as this report.

1.1.1.3 Radical Chemical Concepts

Task - 1.4 - New and Novel Concepts
Principal Investigator: Dag Eimer
Technology Provider: Norsk Hydro
Co-funder: Klimatek

Summary

The project was a conscious effort to stimulate radically different approaches to CO_2 separation through a structured creativity enhancement process. The philosophy behind this effort was that something radical was needed to dramatically reduce CO_2 separation costs.

A diverse group of scientists from Norwegian universities and research institutions were invited to come together for two days to produce ideas for future research. Fifteen chemists accepted the challenge. The participants were given concentrated training in the use of Lateral Thinking techniques for creating new ideas and spent the second day creating those ideas. Getting fifteen chemists to work together and share their ideas was a challenge. They had to be convinced that their ideas would not be stolen. Mutual openness was needed to ensure the free flow of ideas in a non-threatening or judgmental environment.

The end result was a list of 120 ideas for evaluation. Eleven ideas were picked by an evaluation team using a set of challenging criteria and on her/his insight into the field and professional judgment. The ideas were subjected to further analysis to choose the ideas that appeared to have potential. The group produced flow sheets for the envisioned processes that emerged from the ideas. The refined ideas were finally evaluated by an experienced cost estimator working with the team. By the end, the number of ideas had been reduced to three because of perceived lack of economic potential or technical feasibility.

The surviving ideas were:

- An absorption process based on transition metal complexes with the possible use of a biomimetic compound as a mass transfer catalyst and desorption aided by sonification.
- An absorption process with the swing between absorption and desorption controlled by changing the pH of the solution.
- An absorption process in which CO_2 is absorbed in salt hydrate melts from which the CO_2 will desorb when the melt solidifies.

The cost estimates suggest that they have good potential for bringing the cost of carbon dioxide separation down significantly. There are potential synergies with conventional adsorption cycles.

Publications

- Eimer, Sjøvoll, Eldrup, Heyn, Juliussen, McLarney, Swang, (2003), Third Nordic Minisymposium on Carbon Dioxide Capture and Storage, Trondheim, Norway, Oct 2-3. "New thinking in CO_2 removal".
- See Appendix A for the project final report under the same heading.

1.1.1.4 Amine Scrubbing/Membrane Contactor

Task - 1.4 - New and Novel Concepts
Principal Investigator: Olav Falk Pedersen
Technology Provider: Kvaerner Process Systems / Mitsubishi Heavy Industries
Co-funder: Klimatek

Highlights

- Kvaerner Process Systems' novel membrane contactor was successfully tested with MHI's novel amine-based adsorbent.
- The cooperative research, fostered by the CCP team, led to a synergism of two excellent concepts to produce even greater value.
- The CCP economic analysis showed that there is potential for this technology alone to reduce CO_2 removal costs by 15-20 % in a large scale GTCC power plant. (Norwegian Power Plant Scenario).

Summary

Mitsubishi Heavy Industries and Kansai Electric Company have developed a new absorption process referred to as KS-1. This process is the product of a joint-research project between Kansai and MHI. A key point in this process is the utilization of a new amine-type solvent (KS-1) for the capture of CO_2 from flue gases. Pilot and laboratory research studies, as well as commercial experience have shown that the KS-1 process technology had advantages over other amine-type processes in both capture performance and energy consumption.

The Kvaerner G/L Membrane Contactor Technology: Kvaerner and W.L. Gore & Associates GmbH, Germany (Gore) have developed and tested process concepts and membranes to be used in CO_2 removal from flue gases.

This technology is based on the same principles as the baseline but differs in two respects:

1. The absorber column is replaced by porous membranes developed by Gore and Kvaerner.
2. The baseline's Econamine FGSM solvent is replaced by the new and improved solvent referred to as KS-1.

The Kvaerner Gas/Liquid (G/L) Membrane Contactor operates with liquid on one side and gas on the other (Figure 4.) Unlike gas separation membranes where differential pressures across the membrane provide the driving force for separation, the pressure is almost the same on both sides of the Kvaerner membrane. Absorption into the liquid provides the driving force. The Gore membrane material (ePTFE) is virtually non-destructible under the operating conditions encountered in typical natural gas or exhaust gas applications, employing most of the common treating solvents.

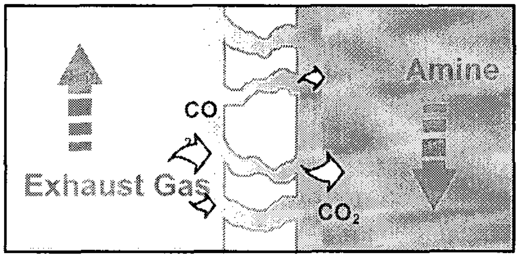


Figure 4. Principle of the membrane contactor

Study Results: Pilot tests were executed at the Nanko Pilot unit in Osaka. The membrane contactor was tailor-made for this project. A simulation program was used to compare the results with the theory. Upscale calculations were done for a 28.5 MW and a 350 MW unit. In both cases, the membrane contactor units were compared with a conventional MEA unit with a contactor column. The results of the upscale calculations showed that:

- The equipment cost is almost similar for the two processes, but size and weight is reduced for the combined process compared to the conventional process with MEA
- Operational cost is reduced, mainly because of the use of KS-1 solvent.

The savings are due to:

- Lower regeneration energy for KS-1 compared to MEA.
- Lower circulation rate of solvent (due to higher loading capacity)
- Lower corrosion rates of the KS-1 solvent compared to MEA.
- Lower degradation rates of the KS-1 solvent compared to MEA.
- Lower installation costs for this combined technology compared to conventional MEA technology, due to smaller and lighter equipment.
- Reduced pressure-drop in the absorber.

Reports:

This Klimatek funded report is held confidential to CCP participants and Klimatek and is not included in the courtesy submission to the U.S. DOE or EU. This non-confidential summary is for DOE use.

1.1.1.5 and 1.1.1.6 Removal of CO_2 Using CFCMS / Electric Swing Adsorption

Task - 1.4 - New and Novel Concepts
Principal Investigator: Olav Falk Pedersen / Tim Burchell
Technology Provider: Kvaerner Process Systems / Oak Ridge National Laboratory
Co-funder: CCP Participants / U. S. DOE

Background:

The CCP contracted with the Carbon Materials Technology Group of Oak Ridge National Laboratory to evaluate the performance of Carbon Fiber Composite Molecular Sieve (CFCMS) for the removal of CO_2 from industrial flue gas streams containing low quantities (3 mol% to 10 mol%) of CO_2 at low (0.7 Barg) pressure.

CFCMS is a monolithic adsorbent carbon material composed of petroleum pitch-derived carbon fiber and a phenolic resin-derived carbon binder. Because of its unique construction CFCMS is electrically conductive which facilitates rapid desorption of adsorbed species upon application of a low voltage, hence 'Electric Swing Adsorption'. This desorption mechanism is not fully understood. It is postulated that the application of a low voltage generates a current flow, which disrupts the weak 'Van der Waals' forces between the carbon adsorbent and the adsorbed species, releasing the latter.

The gas composition selected for the study was 3 mol% CO_2, 14.3 mol% O_2 and 82.7 mol% N_2. This is a typical exhaust gas composition from an industrial gas turbine fired on natural gas.

Highlights:

- The performance of the ESA process in the three CCP Post Combustion baseline scenarios is not expected to favor its use over current 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 in a Post Combustion CO_2 capture scenario;
    - The low CFCMS loading
    - The 'Electrical Swing Effect' – is it real?
    - The impact of other gas components (water, NO_x, SO_x etc.).
    - Cycle pressure drop and its influence on cycle time (particularly desorption).
    - Power requirements for desorption.

- The CCP do not expect ESA technology to achieve CCP goals for reduced cost of CO_2 capture in Post Combustion scenarios at its current stage of development.

- ESA technology is likely to be better suited to high-pressure applications where concentration in feed gas is high (high partial pressure). In such environments, CFCMS loadings will be higher, vacuum assisted desorption will be unnecessary and the impact of CFCMS pressure loss can be more readily managed within the cyclic operation.

Discussion:

Adsorption Cycle: The maximum CFCMS CO_2 capacity achieved during testing was 0.78wt%. This may be enhanced to about 1.0 wt% assuming equilibrium loading is achieved. The low loading capacity is a direct consequence of the low CO_2 partial pressure in the feed gas. CFCMS capacity for CO_2 is reduced by the presence of water in the feed gas because of competitive adsorption. A reduction of 7% (versus dry gas capacity) was noted during testing. Stabilization was achieved after only a couple of adsorption cycles. CFCMS capacity is a strong function of operating temperature. Adsorption temperatures less than 30°C for are likely to be required for industrial scale units. Cycle times between 8 and 11 minutes were observed for adsorption during the laboratory testing.

Desorption Cycle

The initial phase of the regeneration cycle could not be interpreted clearly because the gas analyzer used had an upper range limit of 20,000 ppmv CO_2. The 'Electric Swing effect' was not observed directly. Nonetheless, it was clear that average CO_2 production during the peak evolution period was 15% to 20% higher when the 'Electric Swing effect' was applied. The way that power was applied during desorption step lead to the a temperature spike within the CFCMS bed that made it unclear whether 'Electric Swing' or 'Resistive Heating' was primarily responsible for the increased CO_2 evolution rate.

The laboratory regeneration technique utilized purge gas to create low CO_2 partial pressures during the desorption step. This approach cannot be used commercially, since it reverses the separation achieved by the process. A vacuum desorption system will be required to create low CO_2 partial pressures of around 5 kPa abs. The process clearly relies to some extent upon 'Pressure Swing' effects to aid desorption.

Cycle times between 15 and 40 minutes were observed for desorption during the laboratory testing. Around 65% of the absorbed CO_2 was evolved during the peak period, which varied over the range 6 to 14 minutes across the test program, i.e. the first one-third of the full desorption cycle. When the 'Electric Swing effect' was applied this increased to about 70% of the adsorbed CO_2.

Because of the limitations of the analytical instrument it is not possible to say what the actual CO_2 evolution profile looked like during the peak period. Only the average figures can be deduced. Feed gas velocities and evolution rates are quite low across the range of tests conducted. The pressure drops are commensurately low. For industrial scale applications CFCMS open flow area and pressure drop are likely to be critical.

Industrial Scale-up

The CCP sponsored two brief studies to highlight scale-up issues and applications at industrial scale (Figure 5.) Kvaerner undertook a review of the engineering issues that would have to be addressed, while the CCP reviewed the likely costs of an ESA unit versus a more traditional Amine removal unit based around the Fluor Econamine® process.

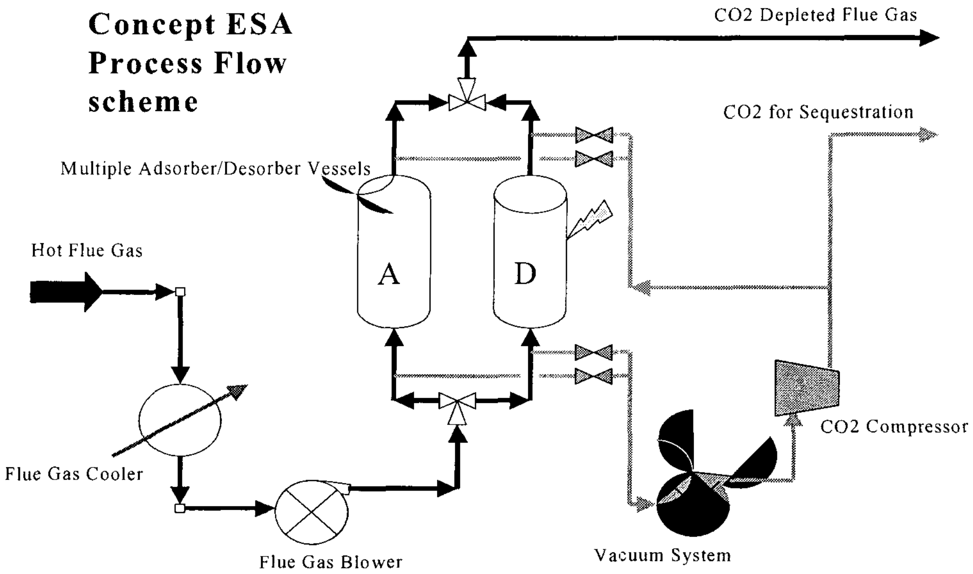
The Kvaerner study highlighted the following issues;

- Short cycle times could be employed because of CO_2's rapid adsorption onto carbon-based substances.
- Cycle times as low as 2 seconds are feasible. Rapid opening/closing valves are available but not at the scale of operation required. Engineering development is a likely requirement.
- Adsorber/Desorber vessel design will have to address both pressure drop limitations and good gas distribution requirements through the CFCMS bed.

CCP economic evaluation

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

Figure 5 The ESA process scheme



Key process assumptions and conditions for this evaluation were;

- 10 minute adsorption and 10 minute desorption/purge cycle times. This was based on observed times for the adsorption step, with desorption step time chosen to reflect that two-thirds of the CO_2 evolution occurs during the first one-third of the observed cycle time. This leads to an assumption of a delta loading of CO_2 on CFCMS of 0.65%wt (based on a maximum loading of 1.0%wt).
- Vacuum system capable of producing a pressure of 5kPa in the desorber vessels.
- Flue gas cooler reducing flue gas temperature to 25 °C
- Flue Gas blower to compensate for CFCMS pressure drop.
- Compression to 220 barg for sequestration.

Key conclusions from the evaluation were,

Unit Capital Cost:

- The number and size of adsorber vessels and the requirement to design for low (vacuum) pressures will result in high equipment cost. Furthermore, the number and size of switching valves combined with the complex arrangements required for power distribution are likely to add a further significant cost burden.
- The volumes of Carbon material are large (600 metric tonnes) and will add significant cost.
- Low gas velocities will be necessary if pressure loss is to be minimised. Based upon current observed pressure loss through CFCMS, a flue gas blower has been utilised for the economic evaluation. A pressure loss of 25 kPa has been assumed. Blower capital and operating cost is high because of the need to compress the entire flue gas stream.
- The Vacuum pumping system will be a significant cost item.

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 optimise, or even minimise the power required for regeneration. This conclusion may not be reasonable without further work to confirm minimum (optimised) power needs for ESA.

Publications:

- See Appendix A for the final reports under the same heading.

1.1.3.1 Cost Efficient Design Integration to improve Amine Separation Processes for CO_2 Separation

Task 2.3 Systems Integration and Optimization
Technical Provider: Nexant
Co-Funder: Klimatek

Highlights

- During Phase-I of the project, a comprehensive technology survey was developed to highlight the current, state-of-the-art in the design and practice of amine processes for CO_2. Numerous literature and patent references are included.
- Comprehensive trade-off studies were conducted on a number of cost-cutting ideas. Implementing the most promising ideas resulted in a "Low-Cost" standalone amine plant that had 40% lower capital cost and 12% lower operating cost than an amine plant based on API/refinery standards.
- Additional savings were found by integrating the "Low-Cost" plant with the power plant. These modifications lead to a design that had a 55% lower capital cost than an amine plant based on API/refinery standards.

Summary

Nexant, Inc., under contract from Statoil on behalf of the CO_2 Capture Project (CCP), has conducted a comprehensive study to evaluate new engineering design options to reduce the cost of amine-based CO_2 removal processes. About 2850 tonnes/day of CO_2 is to be recovered from the exhaust of a 400-MW natural gas-fired combined-cycle (NGCC) power plant located in Norway. The CO_2 is purified and compressed to 220 barg for enhanced oil recovery (EOR). Three engineering designs are prepared in this work:

1. A standalone plant using 30 wt. % monoethanolamine (MEA) with a proprietary oxygen inhibitor, designed in accordance to refinery/API practices and standards. This is known as the "Base Case Design."

2. A standalone plant using the same solvent as the "Base Case," but is designed with more cost-effective and innovative design and standards. Creative brainstorming and extensive review of practices from other industries are employed to generate the most promising, technically-feasible ideas. This "Low-Cost Design" has the following distinguishing features:

    - Use of Plate-and-Frame heat exchangers for liquid/liquid service, in place of conventional Shell-and-Tube heat exchangers.
    - The reduction of imported steam for the amine reboilers, achieved by flashing the lean amine and using the flashed water vapor as stripping media.
    - Reduction of a two-train CO_2 compression train to a single train.
    - Elimination of the direct-contact flue gas cooler and relying on evaporative cooling of the hot flue-gas as it enters the absorber.
    - High-efficiency structured packing, in place of random packing.
    - Use of ANSI-standard pumps instead of API-standard pumps.

3. An integrated plant that ties the "Low-Cost Design" with the NGCC as a single unit. Here, the use of process integration results in additional cost savings. In addition to the features of the "Low-Cost Design," the "Integrated Design" has:

- A single-train amine system, achieved by recycling half of the incoming flue gas back to the air-compressor of the NGCC. This causes the volumetric flow of flue-gas to be halved while doubling the CO_2 concentration.
- Reduced amine reboiler duties and equipment costs, due to using a portion of the NGCC's heat recovery system to regenerate the rich amine solvent.

With these three designs, CCP will be in a position to evaluate the potential in cost-savings with the existing, MEA-based technology, and specifically which areas to focus on for cost reduction. Although the cost-cutting ideas in the lower-cost designs are all technically feasible (based on process simulations and vendor-supplied quotes and know-how), it is highly recommended that pilot-plant testing be conducted to confirm performance.

Reports and Publications

During the course of this work, eight separate and standalone reports have been issued by Nexant, Inc. to the CCP. Details on studies, designs, and cost estimates are included in these reports.

- Process Design Specifications – Base Case Conventional Amine Plant (Issued January 2003)
- Base Case Amine Plant Cost Estimate (Issued May 2003)
- Phase I – Technology Survey Report (Issued May 2003)
- Phase I – Interim Report (Issued June 2003)
- Low-Cost Alternative Amine Plant Design and Cost Estimate (Issued June 2003)
- 400 MW Natural Gas Combined Cycle Power Plant Design, Cost Estimate and Modification for CO_2 Recovery (Issued July 2003)
- Assessment of Alternative Fuels on the Amine CO_2 Capture Design (Issued September 2003)
- Integrated Low Cost Power Plant/Amine System Design and Cost Estimate (Issued September 2003)
- See Appendix A for the final reports under the same heading.

1.1.3.2 Post Combustion Separation and Capture Baseline Studies for the CCP Industrial Scenarios

Task 0.3 Establish State-of-the-Art Separation and Capture
Technology Provider: Fluor
Co-funder: CCP

Background:

The aim of the CO_2 Capture Project is to develop new and novel technologies that significantly reduce the cost of capturing and storing CO_2. The project has three distinct elements; pre-combustion de-carbonization, the use of oxygen-rich combustion systems and post-combustion CO_2 capture. In order to evaluate any new or novel technology, baseline studies are required that quantify the current best available technology. This report summarizes two such studies for the post-combustion CO_2 capture element based on two BP owned or part-owned operating facilities:

- The Central Gas Facility, Prudhoe Bay, Alaska – representative of CO_2 recovery from the exhaust gas of multiple simple cycle gas turbines,
- BP's Grangemouth Complex, Scotland – representative of CO_2 recovery from multiple flue gas emissions from a refinery or petrochemical complex heaters and boilers.
-

The studies were conducted by Fluor. They detail process designs and cost estimates to capture approximately 1.8-2 million tonnes of CO_2 per year and deliver the captured CO_2 to the battery limits of the particular site at a pressure of 220barg and essentially water-free. The study assesses generic issues that will be common to any retro-fit post-combustion CO_2 capture project, and provides a suitable baseline against which developing technologies can be evaluated.

Conclusions

Both the Prudhoe Bay and Grangemouth studies have shown that, despite the unprecedented scale of the facilities, post-combustion capture of up to 2 million tonnes of CO_2 per year is technically feasible, using current best-in-class technology.

The cost, however, of recovering such amounts of CO_2 is extremely high, with the capital expenditure of the Prudhoe Bay facilities estimated at $1.659 billion and those at Grangemouth at $476 million. The two facilities have, more or less, the same design basis and the significantly higher cost for the Prudhoe Bay facilities is considered to be due to a combination of the following:

- The location of the Prudhoe Bay facilities on the North Slope of Alaska creates a considerable cost penalty. The modular construction strategy, equipment transportation costs and the cost of labour lead to higher inherent costs than an equivalent stick-build construction in Central Scotland.
- Prudhoe Bay facilities include four Heat Recovery Steam Generators to provide bulk removal of the heat energy upstream of the Econamine FG absorbers. These are expensive units and are not selected for the Grangemouth facilities where a simple water quench column performs the entire cooling duty. Whilst the water quench option proves economically optimum for the Grangemouth study, it does not do so for Prudhoe Bay as the flue gas temperature is considerably higher, thus leading to a significant increase in the cooling duty. Furthermore, it is not considered prudent to install a large-scale water quench column in the severely cold conditions at Prudhoe Bay.
- As a result of incorporating the HRSG units, the Prudhoe Bay facilities are considerably more energy efficient and virtually self-sufficient in terms of energy demand. Consequently, the overall CO_2 emissions to atmosphere are significantly lower than for the Grangemouth design where the

design has not been optimised from an energy perspective. The Prudhoe Bay facilities do, however, pay a capital cost premium for this energy efficiency. This will be offset by lower operating costs although this has yet to be evaluated in full.

It must also be noted that this study has not considered the cost of transporting the captured CO_2 to a suitable location for subsurface storage or re-use, nor for the cost of a re-injection well. Both will clearly increase the cost of any re-injection project with the former potentially proving very expensive depending on the distance between CO_2 capture and re-injection sites. However, should the CO_2 be used for EOR purposes, some benefits would accrue from increased hydrocarbon recovery.

For both Prudhoe Bay and Grangemouth, the size of the process equipment and the associated infrastructure required to support the capture plants will have a significant impact on the existing production complex. The Fluor studies highlight and assess a wide range of issues that will be common to any retrofit, post-combustion CO_2 capture project.

Finally, the results of the two studies provide a suitable baseline against which developing technologies can be assessed.

Introduction

The CO_2 Capture Project (CCP) is a joint project undertaken by eight major energy companies to develop new and novel technologies that significantly reduce the cost of capturing and storing CO_2. The project is split into three distinct elements:

- Pre-combustion de-carbonisation,
- The use of oxygen-rich combustion systems, and
- Post-combustion CO_2 recovery.

For each element, technologies will be developed in the context of certain scenarios that relate to combustion sources and fuels common to the operations of the CCP participants. Four scenarios are considered:

- Large gas-fired turbine combined cycle power generation,
- Small or medium sized simple cycle gas turbines,
- Petroleum coke gasification, and
- Refinery and petrochemical complex heaters and boilers.
-

In order for any new or novel technology to be evaluated, baseline studies are required that quantify the current best available technology. Within the Post-combustion element, the CCP concluded that amine scrubbing is the best available technology for CO_2 capture.

Fluor were subsequently contracted to produce process designs and cost estimates incorporating their proprietary Econamine FG amine technology for each of the above scenarios. It is based on the use of a 30wt% aqueous MEA (Mono-Ethanolamine) solvent and incorporates inhibitors to counter the corrosion effects caused by high levels of oxygen in the flue gas. The process is capable of delivering almost pure CO_2 and is widely used in small-scale plants to produce high purity CO_2 for industry. However no unit has been built to the scale envisaged by the CCP project.

To provide additional context to the Fluor study, each process design is based on an actual operating facility. Two of the baseline studies for the Post-Combustion element are based on BP owned or part-owned facilities. The Central Gas Facility at Prudhoe Bay, Alaska is the basis for the simple cycle gas turbine scenario and BP's Grangemouth complex in central Scotland for the refinery/petrochemical complex heaters and boilers.

Results and Discussion

Small or Medium-Sized Gas Turbine Scenario - Prudhoe Bay Study

This study is based on the Central Gas Facility at Prudhoe Bay, Alaska and is representative of the "small or medium sized simple cycle gas turbine" scenario.

The Central Gas Facility (CGF) at Prudhoe Bay, Alaska processes associated gas from a number of fields on or close to the North Slope in Alaska. Dehydrated gas is fed from the gathering centres to the CGF and then dew pointed using refrigeration units to recover NGL's. These are then either used as miscible injectants for improved oil recovery or spiked into the crude oil product. The remaining light gas fraction is then compressed and re-injected back into producing reservoirs to maintain reservoir pressure.

The gas throughput of the CGF is huge with approximately 8billion scfd of gas being processed. Eleven simple cycle gas turbines (GT) are used to provide mechanical shaft power to drive the gas reinjection and refrigeration compressors. Each gas turbine is fired with a portion of the processed gas. This produces a flue gas with only dilute levels of CO_2 (approximately 3.3mol %), virtually no SO_2 (< 20ppmv) and low levels of NO_x (average of approximately 90ppmv). Flue gas temperature is fairly high averaging about 480°C. Currently only a small proportion of the heat energy available in the gas turbine exhaust is recovered using a single waste heat recovery unit connected to one of the Frame 5 machines.

Design Basis for Post-Combustion CO_2 Capture in the Prudhoe Bay Scenario

The design criteria for the baseline study are to:

- Capture 1.78 million tonnes of CO_2 per year emitted by the gas turbines.
- Deliver the recovered CO_2 to the CGF battery limits:
    - at a pressure of 220barg,
    - with a moisture content of less than 50ppmv, and
    - With a minimum CO_2 content of 97mol%.

The above battery limits conditions are intended to reflect those necessary for either Enhanced Oil Recovery (EOR) or subsurface storage purposes. They are also common, more or less, to each baseline study and thereby allow each process design to be compared on the same basis.

Proposed CO_2 Capture Facility Configuration

The process selected by Fluor to meet the above design criteria is outlined here. The flue gas is collected from each of the eleven gas turbines and fed to one of four equally sized parallel trains. The size of each train, with consequential impact upon the number of trains needed, is limited by the size of the largest commercially available Heat Recovery Steam Generator (HRSG) and by the diameter of the largest Econamine FG absorber column that can be built with confidence.

Each train contains an HRSG, a Direct Contact Cooler, a blower and an Econamine FG absorber. Rich solvent from the four absorbers is collected and fed to a common solvent stripper tower to regenerate the solvent and liberate the captured CO_2. This CO_2 is then dehydrated and compressed to meet the required CGF battery limits specification.

Other than the supply of treated seawater to supply boiler feed water for the HRSG units and for make-up to the Econamine FG process, the CO_2 capture facility is essentially self-sufficient in terms of energy and utility supply. The heat recovery unit is used to raise steam, which, in turn, is used as the motive force for the CO_2 compressor, to generate power and as the heating medium for the Econamine FG solvent stripper reboiler and reclaimer. The electrical power raised by the CO_2 capture facility is not only sufficient to meet both its internal process and utility needs, but will also allow an export of approximately 18MW to the local grid, thus creating the opportunity to displace power generation elsewhere in the CGF facility.

Flue Gas Gathering

The eleven gas turbines considered in this study are located fairly close to one another, thus limiting the extent of the flue gas gathering system. The flue gas is collected and split evenly between the four separation trains. There is no flow control as such between the four trains, merely identical train design creating similar pressure drops for similar gas throughput. The ducting is sized to limit the pressure drop between the gas turbine exhaust and the HRSG to a maximum of 152mm H_2O and is designed to be flexible to allow each GT and absorption train to be individually isolated as required by operations or for maintenance purposes.

Flue Gas Cooling/Heat Recovery

The collected flue gas must be cooled to around 38°C before being fed to the blower and then the Econamine FG unit. Although amine-CO_2 reaction kinetics is promoted by high temperature, amine loadings are not and the optimum temperature is a compromise between amine loading and reaction kinetics. For a primary amine system such as the Econamine FG process, a temperature around 50°C is considered suitable. The flue gas temperature increases across the blower and hence some additional cooling duty is required upstream in mitigation.

The hot flue gas is initially fed to a Heat Recovery Steam Generator (HRSG). The heat load of the flue gas is very high due to the high mass throughput and temperature, and the selected design seeks to utilise this available energy by recovering as much heat energy as possible and raising steam. Approximately 140MW of heat energy is recovered per HRSG – i.e. a total of 560MW.

Three levels of steam are generated – high, intermediate and low pressure. High pressure steam is used to generate electricity via a steam turbine power generator and then used as motive steam to drive the CO_2 compression train. Intermediate pressure steam is used to provide heat to the Econamine FG solvent stripper reboilers and reclaiming operation. Low pressure steam is used to deaerate the boiler feed water. Finally, in addition to raising steam, a heating coil in the HRSG is used to recover more energy for space heating of the new and existing CGF modules.

The partly cooled flue gas is then fed to the DCC, where it is quenched by direct contact with a descending water spray. The DCC circulating water is cooled and filtered, thereby removing any particulates from the flue gas upstream of the amine absorber. As indicated above, the fully cooled flue gas is then re-pressured slightly by a blower to counter the pressure drop caused by both the Econamine FG absorber packing and the subsequent discharge stack.

Econamine FG Process

The process design for the CGF facility incorporates four absorbers feeding rich solvent to and receiving lean solvent from a single solvent system. This solvent system incorporates a single stripping column, solvent circulation pumps and solvent filtration. Although the solvent contains inhibitors to limit solvent degradation, a certain amount of solvent will degrade and form heat stable salts (HSS). The amine bound by these salts cannot be regenerated merely by the action of heat, and hence a reclaimer is required. A slipstream of amine is fed to the reclaimer where sodium carbonate is added and heat applied to recover most of the bound amine. A residual slurry waste is produced that must be removed and disposed of off-site.

CO_2 Dehydration and Compression

CO_2 liberated from the amine unit stripping column is compressed using a 5-stage centrifugal machine to the required battery limits pressure of 220barg. Dehydration using a proprietary glycerol process is undertaken between the 3rd and 4th stages in order to meet the water specification.

Utilities

The selected process configuration is almost self-sufficient in terms of utility demand with no additional requirement placed on existing CGF infrastructure other than the supply of treated seawater. Steam raised in the four HSRG units raises sufficient power to drive both the process and utility systems, and to export up to 18MW of electricity to the local grid.

Prudhoe Bay Scenario Study Results

Costs

Based on the costs developed by Fluor, the cost of CO_2 capture is estimated at around $137/tonne of CO_2 captured (or $130/tonne of CO_2 emissions avoided). It is believed that this is representative of the cost of retrofitting CO_2 capture technology at a location with a very harsh working environment. The cost of CO_2 capture in Alaska is clearly high and is attributable in part to the following reasons:

- An execution strategy on the North Slope with a limited construction window of only 2-3 months per year,
- A prolonged schedule due to limitations on the window within which sea-lifts can be undertaken,
- A very high labour field cost,
- A construction strategy based on super-modules weighing about 10,000 tonnes each,
- A very dilute feed gas containing only 3.3mol% CO_2,
- A need for large collection ducts to gather flue gas from multiple sources,
- A design for severely cold weather leading to the need for a costly glycol cooling system,
- A lack of fresh water leading to an expensive water supply system incorporating a reverse osmosis unit.

Locations that have less harsh climates will clearly be capable of delivering a similar process design at significantly lower costs.

Refinery Scenario – Grangemouth Study

The study is based on BP's Grangemouth facilities and is representative of the "refinery and petrochemical complex heaters and boilers" scenario. BP Grangemouth is fed, via the Forties Pipeline System, with oil and gas from a number of fields in the Central North Sea. It is an integrated site and consists of the following:

- **Kinneil** – to which the oil and gas from the Central North Sea is fed, and which stabilises the oil either for further processing in the Refinery or for export, and provides the gas feedstock to the Chemicals factory.
- **Refinery** – which refines crude oil from Kinneil to produce LPG, Alkylate, Petrol, Diesel, Jet Fuel, Kerosene and Fuel Oil?
- **Chemical Factory** – which produces a range of petrochemical products from the gas feed from Kinneil and light distillate from the Refinery?
- **Power Station** – This provides power and steam to the complex.
-

The Grangemouth site is split into two halves by a public road. Kinneil, the Refinery, the Power Station and part of the Chemicals Factory lie in the **North Site**, whereas the bulk of the Chemicals Factory is located in the **South Site**. The complex has a large number of point CO_2 flue gas emission sources, scattered throughout the complex. The sources are varied in terms of composition, flow rate and temperature. The variation in composition relates to differing fuels being used throughout the complex with those used on the Refinery typically containing sulphur and those in the Chemical Factory being sulphur-free.

Grangemouth currently emits 3½-4 million tonnes of CO_2 per year. There is also currently no recovery of CO_2 from flue gas at the Grangemouth complex.

Design Basis for Post-Combustion CO_2 Capture in the Grangemouth Scenario

The design basis for the Grangemouth study is to:

- Capture 2 million tonnes of CO_2 per year, and
- Deliver the recovered CO_2 to the complex battery limits:
  - at a pressure of 220barg,
  - with a moisture content of less than 50ppmv, and
  - with a minimum CO_2 content of 97mol%.

The above battery limits conditions have been chosen to provide a source of high purity, high pressure CO_2 suitable for North Sea Enhanced Oil Recovery or subsurface storage purposes. The study target of 2 million tonnes per annum of CO_2 is selected to match the requirements of a potential North Sea EOR project.

Proposed CO_2 Recovery Facility Configuration

Flue gas from the North and South Sites is collected in two separate gathering systems and processed separately. Each site separately treats the flue gas to, firstly, remove NO_x and, in the case of the North Site, SO_x components, and then to cool the flue gas prior to it being fed into the Econamine FG absorber (coolers not indicated on the above diagram). The rich Econamine FG solvent from the absorbers on both sites is collected and fed to a common solvent stripper, which, in turn, liberates the captured CO_2. This CO_2 is then dried and compressed to meet the required battery limits specification.

Flue Gas Gathering

The study target of 2 million tonnes/year of CO_2 capture represents around 55% of the annual CO_2 production from the complex's many heater and boiler stacks. Selection of the most appropriate sources was based largely on layout and proximity issues in an attempt to minimise the site cost of flue gas ducting. Final source selection grouped together seven sources from the North site and two sources from the South site from a total of 20 potential sources.

Detailed ducting layout and optimisation studies were conducted by Fluor that resulted in a flue gas collection network comprising about 2km of ducting and having a maximum cross-sectional area of 9m^2. Blowers are required to push flue gas through this ducting network and to overcome the pressure drop imposed by the structured packing of the Econamine FG absorbers and downstream emission stack. The total power demand for these two blower duties is 15MW and 10MW respectively. Although the ducting network and blower power demand is very large, the system is regarded as technically feasible.

The ducting studies conducted by Fluor provide an accurate basis for the cost estimate. However, if such a system were to be built, careful consideration must be given to the safety hazards related to low-level flue gas ducting and the inter-connection of heater fire boxes via the duct system.

SO_x/NO_x Removal

Pre-treatment of the flue gas upstream of the Econamine FG absorber is necessary to reduce NO_x and SO_2 levels and avoid excessive degradation of the Econamine FG solvent. NO_x is present in the flue gas

gathered from both North and South sites to levels of up to 300ppmv and is best reduced to less than 20ppmv. SO_2 removal is only required from the North site flue gas and is best reduced to less than 10ppmv.
Selective Catalytic Reduction (SCR) is selected for NO_x removal. This process reacts O_x with injected ammonia over a titanium catalyst bed to convert the NO_x to water and nitrogen. A wide range of SCR processes are available although the choice of catalyst is somewhat reduced by the relatively low flue gas temperature of 250-300°C. This is a lower temperature than the majority of current commercial installations, but there are suitable catalysts available that will meet the required performance criteria.
The Cansolv process is selected for SO_2 removal. This is an amine-based process and produces significantly less secondary waste than rival options. The process is commercially available although there is limited industrial experience of its operation. Fluor undertook a review of several processes capable of removing SO_2 at the prevailing process conditions and concluded that, at the time of the study, only Cansolv could readily achieve the preferred performance of <10ppmv SO_2 in the flue gas to the Econamine FG unit.

Econamine FG Process

Fluor's Econamine FG process was selected to capture the CO_2. The flue gas must be cooled to about 40-50°C upstream of the Econamine FG absorbers in order to achieve acceptable solvent loading. Water quench columns are included in the design to meet this cooling duty. As mentioned previously, two separate Econamine FG absorption units are required to absorb the CO_2 from the North and South site flue gas systems. The gas throughput and CO_2 absorption demand is huge and dictates that each absorption unit consists of two parallel absorption columns (on both the North and South sites), each with a diameter of approximately 10.3m. Rich amine from all four columns is collected and fed to a common stripping tower located on the South site. Again, the size of this column is very large with the diameter being approximately 10.4m. The Layout section gives further detail on equipment size and complexity.

In common with the Prudhoe Bay process design, a reclaimer will be required to recover bound amine from heat stable salts (HSS) and remove degraded material from the system. Although the Econamine FG process incorporates inhibitors to limit solvent degradation, a certain amount of solvent will degrade nonetheless. Bound amine in these salts needs to be recovered to reduce amine make-up demand and HSS must be removed to maintain performance. The concept of absorbing CO_2 from the North and South site flue gas separately avoids the need for excessive lengths of large cross-sectional ducting and associated blower power demand that would be required to move flue gases between the two sites. However, the amine system is extremely substantial requiring large diameter circulating pipe work, high pump power loads and a very large site-wide inventory of amine. Even though the scale of the amine unit is considerable, it is believed that there are no technical barriers to overcome in order to deliver the process design. Significant site fabrication would, however, be required due to the size of equipment required.

CO_2 Dehydration and Compression

The Econamine FG solvent stripper produces a water-saturated CO_2 stream at a pressure of approximately 1.5bara. A 6-stage, electrically driven compressor is then used to meet the required battery limits pressure of 220barg. Molecular sieves are used to dry the gas between the 3rd and 4th stages of compression.
The scope of the project does not account for the delivery of the CO_2 to a suitable subsurface storage zone or EOR project. Hence no account has been taken in the process design or cost estimate beyond the battery limits of the Grangemouth site.

Utilities

Installing a post-combustion CO_2 capture process of the scale considered by the Fluor study requires the provision of significant utility systems. To deliver the required steam and power demand, a Combined Heat and Power (CHP) plant has been included. This would be fired using natural gas with an energy content of approximately 396MW (assuming 18% power generation efficiency). The additional cooling demand to quench the flue gas upstream of the Econamine absorbers requires two additional cooling towers. One critical point to note relates to the additional CO_2 emissions that result from the firing of the CHP plant, which equates to about 0.6 million tonnes of CO_2 per year. This is not subsequently recovered by the Fluor process design and therefore, the NET capture of CO_2 is reduced from 2 million tonnes/year to 1.4 million tonnes/year.

Refinery – Grangemouth Scenario Study Results

A breakdown of the capital cost for the Grangemouth CO_2 capture project is given in the report. A full breakdown of the annual operating costs is not available. However, preliminary calculations indicate that the dominant factor is the cost of natural gas to raise steam and generate power in the CHP plant. Based on the above costs developed by Fluor, the cost of CO_2 capture from the Grangemouth facilities is in the range of $50-60 per tonne of CO_2 captured. This range relates to the likely variation in operating costs and will be sensitive to future swings in the price of natural gas.

Reports and Publications

- The Alaska baseline report is included in Appendix A under the same heading.
- The Grangemouth baseline study is summarized here but the report is held confidential because of proprietary BP information.

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_2 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 2010-2015 with costs in the range of $ 15-40 MM.
- Pre-combustion technology can be developed to meet stringent requirement on NOx, CO and SOx formation. The lowest NOx formation was predicted to 5 ppm vol. from a combined-cycle gas turbine. For open-cycle gas turbines, the NOx formation was reduced by 50%. The CO and SOx 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_2 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_2 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_2 avoided cost numbers for the Canadian scenario – CO_2 capture from pet coke fired IGCC – approximately 10-15 $/ton.
- Existing Pre-combustion technology can be considered proven for a wide range of CO_2 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_2 Fuels

1.2.6 Sorption Enhanced Technology

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 go directly into next phase, which was pilot testing.

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_2 and CO called syngas and separation of CO_2 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 use 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^3/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^3/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_2 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^3/h or 450-600 MW (LHV). Approximately 1,000,000 tonne/year of CO_2 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_2 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.

3. System optimization of well known technologies
4. 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_2 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_2 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 has and will create a platform for new developments of reforming technology.

Commercial Value - Present and Future

Pre-combustion Technology for CO_2 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_2 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 whether pre-combustion technology could be used for retrofitting gas turbines – in particular large combined-cycle gas turbines as for the Norwegian scenario. This issues 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_2 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_2 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_2-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.

A consortium of European membrane developers was created with a common task of developing 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_2 capture efficiency and low cost CO_2 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. - Hydrogen Membrane Reactor

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 NOx formation – 5 ppm vol and a potential CO_2 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_2 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_2 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_2 recovery above 85%, delivering hydrogen at gas turbine pressure, sulphur tolerance, sulphur content in CO_2 stream etc. Based on these criteria the CO2LDSEP was seen as the most suitable option. Due to confidentiality issues the capital cost was assessed by a sensitivity analysis – showing that the CO_2 avoided cost for the technology was in the range of 10-20 $/ton.

Results indicated that very low CO_2 avoided cost can be obtained in US DOE Canadian scenario by adopting pre-combustion technology – in the range 10-15 $/ton CO_2.

1.2.3.1 Study of Gas turbine retrofit requirements to burn decarbonized fule (hydrogen)

A critical success factors 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. NOx formation is another issue and by changing from natural gas to hydrogen-rich fuel, GE estimated that a 50% NOx reduction could be achieved and for some hydrogen fuel mixtures single-digit NOx 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_2 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_2 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.

1.2.3.5 - 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.

1.2.5.1 - Generation of H_2 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_2 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% HLV was estimated for the heaters and boilers option if an electricity credit was included. Finally, 90% CO_2 capture efficiency could be obtained for both applications. Since CaO is converted into $CaCO_3$ 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.

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

The leading adsorbent material ADS1-2 has a CO_2 removal capacity of up to 1.1% in PDU cyclic testing. However, a new material has been identified which the potential for significantly higher CO2 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 Hydrogen Transport Membrane Studies

Task - 2.2 Fuel-Grade Hydrogen Generation

Hydrogen Transport membrane studies dominated in the CCP Pre-combustion De-carbonization Technology Program with major programs co-funded by the DOE, EU and Klimatek. This concentration resulted from the very promising results achieved by the hydrogen membrane technologies in the analysis phase performed during 2000 and 2001. Hydrogen membrane technologies were identified to have the best potential to achieve the CCP cost reduction target.

CCP's Membrane Studies Program of CCP Pre-combustion De-carbonization Technology Program consisted of three main projects and one screening study with contributions from 15 different technology providers divided into four sub-projects as listed below:

1.2.1.1.1-.7 Sulfur Tolerant Membrane Study (DOE)
1.2.1.2 Sorption Enhanced Water Gas Shift (DOE)
1.2.1.4 Hydrogen Membrane Reformer (NorCap)
1.2.1.5.1-7 Hydrogen Membrane Reactor (EU GRACE)
1.2.1.6 Pre-combustion Membrane Reactor Study (Topsoe)

CCP membrane development work 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_2 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 followed by a membrane-based separation system in a Membrane Water Gas Shift (MWGS) Reactor. Conventional processes use a shift section downstream of the reformer followed by a physical and/or chemical CO_2 removal system. Our research tested membrane based systems to convert the remaining CO in the syngas and simultaneously separate the product gases (hydrogen and CO_2.)

The major advantages of hydrogen membrane technologies are:

- Smaller equipment by combining reaction and separation in a single unit
- Above equilibrium conversion through selective removal of hydrogen product from reactor
- Reduced compression costs because of production of CO_2 at elevated pressure

Major challenges related to membrane technologies are:

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

Key results and highlights for the hydrogen membrane projects are discussed below.

1.2.1.1 Sulfur Tolerant Membrane Study

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**
Co-funder: DOE	

Subprojects included in this discussion were:

1.2.1.1.1 Sulfur-resistant Palladium/Copper Alloy Composites (CSM)
1.2.1.1.2 Membrane WGS Reactor Development Study (ECN)
1.2.1.1.3 WGS Sulfur-resistant Palladium/Copper Alloy Composites (TDA)
1.2.1.1.4 Membrane WGS Reactor Metal Alloy Membranes (Eltron)
1.2.1.1.5 Zeolite Membranes Applied to Membrane Reactors (U Cinn)
1.2.1.1.6 WGS Reactor Design & Scale up (SOFCo.)
1.2.1.1.7 Membrane WGS Economics and Design (Fluor Federal)

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.)

Phase I conclusions were:

- Eltron developed metal alloy membranes demonstrated sufficient selectivity and potentially represent a significant improvement of the state-of-the art. Eltron was selected to continue their development work during phase II of the project. The rest were set aside.
- Process simulations showed that 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 so 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 membrane water gas shift reactor concept still has potential to reduce the CO_2 avoided capture costs.

Phase II Achievements were:

- **Eltron developed metal alloy membranes developed by Eltron have ten times the hydrogen permeability of state-of-the-art (25 μm) Pd membranes at a fraction of the cost.** The 127 μm thick membranes have been tested 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 $Nml \cdot min^{-1} \cdot cm^{-2}$ corresponding to a permeance of 0.6 $mol \cdot m^{-2} \cdot s^{-1} \cdot bar^{-0.5}$

- Extremely high hydrogen flux of 346 $Nml \cdot min^{-1} \cdot cm^{-2}$ was achieved using a 90% H_2/He mixture at elevated hydrogen partial pressure of 29 bar with a 127 μm 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_2S-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 sequestrating 2 million tonnes per year of CO_2. 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.

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

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

Task - 2.2 Fuel-Grade Hydrogen Generation

Technology Providers:	**Colorado School of Mines (CSM)** **TDA Inc,**
Co-funder:	**DOE**

Objectives/Background

The objective of this project was to develop dense palladium/copper alloy membranes for use in a water gas shift membrane reactor. The project work period was from March, 2002 to February, 2003 and represented Phase I of the Membrane Water Gas Shift study.

Highlights

CSM and TDA noted the following achievements:

- Through the course of the CCP work, our group prepared thin films on ceramic supports that can separate hydrogen with a flux of 0.36 mol/m^2.s while maintaining an ideal selectivity of 70,000.
- In this research, may be for the first time, Pd-Cu alloy membranes were tested under WGS reaction conditions with high sulfur concentrations.
- The binary gas experiments with H_2/CO, H_2/CO_2 and H_2/H_2O showed that hydrogen can be separated from these mixtures without 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.
- The membranes exposed to the H_2S-free WGS stream performed reasonably well, achieving H_2/CO, H_2/CO_2 and H_2/H_2O selectivity of 20, 12 and 18, respectively. We observed that the separation factor decreased with the addition of the mixture gases.
- The H_2/H_2S binary gas experiments showed that in the presence of H_2S, the hydrogen flux decreases due to inhibition by sulfur inhibition. Under dry gas streams, where no water vapor was present, a lower (up to 30 to 40% of the original flux) but stable hydrogen flux can be maintained at 20 ppm, 115 ppm and 600 ppm H_2S inlet concentrations. The membrane also maintained its integrity when exposed to H_2S.
- In two attempts, however, the membranes failed when exposed to WGS gases with 630 ppm H_2S (protocol conditions). In these experiments, overall gas flux increased and the separation effectiveness decreased to Knudsen diffusion level.

Summary

Prior to the start of the project, this initiative by CSM/TDA represented the most promising membrane in terms of both permeance and selectivity. Being a dense membrane, it was expected that the $H_2:CO_2$ selectivity would be infinite. The key question was whether the palladium alloy layer could be fabricated thin enough so that the permeance was satisfactory and the raw material costs were acceptable.

Unfortunately, defects in the film and/or in the seals reduced the performance considerably. The expected H_2:CO_2 permselectivity at the MWGS reactor feed conditions was only 5.5, which resulted in a carbon recovery of only 46% (the target was 90%). The target permselectivity was 50. The presence of H_2S reduced the permeance by 50-60 percent.

Overall evaluation

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

Reports and Publications

- The final project report is presented in Appendix A under the same heading

1.2.1.1.2 Development of Silica Membranes for Hydrogen Fuel Production by Membrane Reaction and Development of Mathematical Model of Membrane Reactor

Task - 2.2 Fuel-Grade Hydrogen Generation
Technology Providers: Energy Research Center of the Netherlands (ECN).
Co-funder: DOE

Objectives/Background

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

Highlights

ECN noted the following achievements:

- The maximum H_2/CO_2 permselectivity measured at 350°C for standard silica membranes calcined at 400°C is 39. At a H_2/CO_2 permselectivity of 50 the hydrogen permeance is expected to be between 1 and $0.5*10^{-7}$ mol/m^{2}sPa (= 0.01-0.02 cc (STP)/sec/cm^2 at dP= 1 bar). Selectivity improvement is focused on higher sintering temperatures. Increase of the H_2/CO_2 selectivity by increasing the sintering temperature of the silica membranes has not yet been experimentally proven at ECN. Heat treating the modified silica membranes (with built in inert groups) at 600°C instead of 400°C did not increase selectivity. Also the majority of these membranes cracked so 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 is well above 0.1 mol/s.m^{2}bar, which is the target permeance for the application.
- H_2/H_2S selectivity is 400. Three days testing with H_2S has no detrimental effect on a standard silica membrane. Exposition of standard silica membrane to steam at 350°C shows as expected a decline in permeance and selectivity. In 15 days the H_2/CO_2 selectivity decreased from 29.7 to 20.9 and the hydrogen permeance with a factor of 3. Thermodynamic calculations at ECN with FactSage^{TM} show that the hydrothermal stability of zirconia and titania is not expected to be significantly better than standard silica. ECN has focused on the modified silica membranes for improved hydrothermal stability. A modified silica membrane has been on stream in wet gas stability testing for 1000 hours and shows stable and reproducible performance.
- Gas separation with a dry gas mixture showed that from a feed stream containing 35% hydrogen a permeate stream containing 75% hydrogen could be derived. The presence of water in the feed mixtures reduces the hydrogen permeance and hydrogen purity in the permeate compared to the tests without water. Values for Q_o (permeance) and E_{act} (activation energy) to be used as input in the software model have been obtained for the different components in the feed mixture (H_2O, H_2, CO_2, CO and H_2S) through silica membranes.
- A CD-ROM with the installation and sample files and the installation and operation manual of the water gas shift membrane reactor model was provided to Fluor for use in modeling.

Summary

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

Stability concerns

ECN indicated that they would address the stability concerns by 1) replacing OH- groups with alkyl-groups to reduce viscous sintering and 2) examining alternative materials, such as zirconia or titania. Method 1) was largely successful in that modified membranes showed stable performance for periods over 1000 hours in steam atmosphere testing. The presence of H_2S did not 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 $H_2:CO_2$ permselectivity of 50. Permeance equations supplied by ECN showed that the expected $H_2:CO_2$ permselectivity was only 4.7 at feed conditions. This poor selectivity resulted in an unacceptable carbon recovery of 23%. The target carbon recovery was 90%.

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.

Overall evaluation

The failure of ECN's microporous silica membrane to achieve the target $H_2:CO_2$ permselectivity was not unexpected.

Reports and Publications

- The final project report is presented in Appendix A under the same heading

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

Task - 2.2 Fuel-Grade Hydrogen Generation
Technology Providers: Eltron Inc
Co-funder: DOE

Eltron was one of four membrane developers asked to produce 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_2 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 $mL\text{-}min^{-1}\text{-}cm^{-2}$ (STP) corresponding to permeabilities for hydrogen of up to 6.4×10^{-8} $mol\text{-}m\text{-}m^{-2}\text{-}s^{-1}\text{-}Pa^{-0.5}$ at 320°C, which is superior to that of palladium under similar conditions.
- Membranes of select elements were successfully operated in high-pressure reactors and remained leak-free to helium up to 15 bar differential pressure and 450°C in hydrogen-helium test mixtures.
- A membrane of a select element was run continuously for over three months at 400°C in a hydrogen-helium test mixture, demonstrating long-term stability of the membrane materials towards hydrogen diffusion.
- Various hydrogen dissociation catalysts were screened under the full water-gas shift mixture with steam. Supported platinum-based catalysts showed the best promise.

Eltron noted the following achievements in Phase II:

- 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_2S 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

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 bars) without the need of a porous support. This configuration was used for testing with the protocol MWGS reactor syngas feed composition.

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

Phase II

Eltron was chosen to continue membrane development in Phase II because they were the only membrane developer that could demonstrate adequate H_2:CO_2 permselectivity. Since this membrane is significantly impaired by H_2S, the flowsheet was modified to eliminate H_2S. Eltron has demonstrated significantly higher permeabilities than achievable with pure palladium. In addition, the metal alloy they 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 mL-min^{-1}-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.

Table 5 Gas Compositions observed in the WGS Mixture

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

	CO Content (Vol %)		**CO$_2$ Content (Vol %)**		**H$_2$ Content (Vol %)**	
Initial dry feed	5.22		28.15		66.31	
Type of Guard bed	Al_2O_3	Cu/ZnO	Al_2O_3	Cu/ZnO	Al_2O_3	Cu/ZnO
After 1st WGS, *(expected value)*	2.2 *(2.08)*	2.0	31.0 *(30.30)*	31.2	66.3 *(67.32)*	66.0
After 1st CMR *(expected value)*	2.4 *(2.29)*	2.1	34.3 *(33.50)*	38.4	62.9 *(63.87)*	58.9
After 2nd WGS *(expected value)*	1.8 *(2.00)*	1.6	34.8 *(33.69)*	38.4	63.4 *(63.97)*	59.2
After 2nd CMR *(expected value)*	2.0 *(2.17)*	1.1	38.0 *(36.41)*	43.5	59.9 *(61.05)*	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_2:CO_2 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

Task - 2.2 Fuel-Grade Hydrogen Generation
Technology Providers: University of Cincinnati
Co-funder: DOE

Objectives/Background

The objective of this project was to develop microporous silicalite (zeolite) membranes for use in a water gas shift membrane reactor. Improvements in H_2:CO_2 permselectivity was 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:

- 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 the silicalite-seeded α-Al_2O_3 supports.
- Characterization by SEM and pervaporation showed that good quality silicalite membranes were prepared. SEM showed a silicalite membrane thickness of about 5 μm. The membranes were further characterized by pervaporation experiments with 1,3,5-tri-isopropylbenzene and xylene and the results indicated good quality of the silicalite membranes prepared in this work. For the single gas mixture under dry conditions, the ideal separation factors of H_2/CO and H_2/CO_2 are as high as 6 at 500°C with hydrogen permeance of 1.2×10^{-6} mol/m^2.s.Pa. However, at low temperature the separation factors of H_2/CO and H_2/CO_2 are not so high. The ideal separation factors of H_2/CO and H_2/CO_2 for silicalite membranes under wet conditions are as high as 9.4 and 8.8, respectively, and the permeance of hydrogen is around 10^{-7}mol/m^2.s.Pa.
- With the protocol syngas as the feed in the separation experiments, separation factors for H_2/CO and H_2/CO_2 as high as 11.6 and 12, respectively, were obtained for the silicalite membrane. The separation factor decreases at the higher feed side pressure, especially for H_2/CO_2.
- The silicalite membranes are chemically very stable. Temperature dependency for the permeability for the linear flux equation was obtained for H_2, CO and CO_2 for the silicalite membrane prepared in this project.

Summary:

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

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

Publications:

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

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

Task - 2.2 Fuel-Grade Hydrogen Generation
Technology Providers: **McDermott Technology (SOFCo)**
Co-funder: **DOE**

Objectives/Background

The project objective was to design and to provide preliminary cost estimates for a commercial-scale water gas shift membrane reactor.

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 detailed 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 involved consideration of pressure, gravity, and differential expansion loading. Designs that satisfy stress and instability constraints for several permeate gap heights were found.

Table 6 summarizes an early analysis of several support and membrane configurations.

Table 6 Summary Analyses of Support and Membrane Configurations

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

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 Table 7, show the agreement is adequate for design purposes.

Table 7 Comparison of Aspen and SOFCo Simulations

	Baseline 315°C			400°C Case 1			400°C Case 2		
	Aspen	**SOFCo**	**% Diff**	**Aspen**	**SOFCo**	**% Diff**	**Aspen**	**SOFCo**	**% Diff**
Operating Conditions									
Membrane Area, m^2	17,325	17,325		11,410	11,410		11,780	11,780	
Catalyst Volume to Area, m^3/m^2	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	
Performance Comparisons									
Average H_2 Flux (mol/m^2-sec)	0.186	0.185	**-0.4%**	0.275	0.277	**0.7%**	0.272	0.274	**0.6%**
H_2 Recovery, %	95.3%	95.0%	**-0.3%**	93.3%	93.9%	**0.7%**	95.2%	95.7%	**0.5%**
CO_2 Purity (dry)	90.2%	88.90%	**-1.3%**	86.86%	86.84%	**0.0%**	90.04%	89.97%	**-0.1%**
CO Out, PPM	995	1,000	**-0.5%**	3,000	4,077	**-35.9%**	2,000	3,063	**-53.1%**
Permeate Outlet Temp, °C	347.5	346.5	**0.3%**	419.9	417.3	**0.6%**	421.9	420.4	**0.4%**
Retentate Outlet Temp, °C	327.7	329.0	**-0.4%**	421.8	422.7	**-0.2%**	418.0	418.9	**-0.2%**

Reactor configuration selection

The reactor model was used to estimate membrane area, catalyst volume, and total volume for four different flow-path configurations

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

Based on the perceived advantages and disadvantages of each configuration shown in Table 8, the multi-pass cross-flow configuration was chosen for further development.

Table 8 Reactor Configuration Selection

Option	Advantages	Disadvantages
Counter-Flow	- Minimum membrane required	- Large wafer plates difficult to braze - Catalyst packing between plates
Baffled Counter-Flow	- Minimum membrane required	- Large wafer plates difficult to braze - Baffle plates
Cross Flow	- Assembly of manifolds - Smallest wafer package	- 22% more membrane than counter-flow option
Multi-Pass Cross Flow	- Assembly of manifolds	- 8% more membrane than counter-flow option

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.

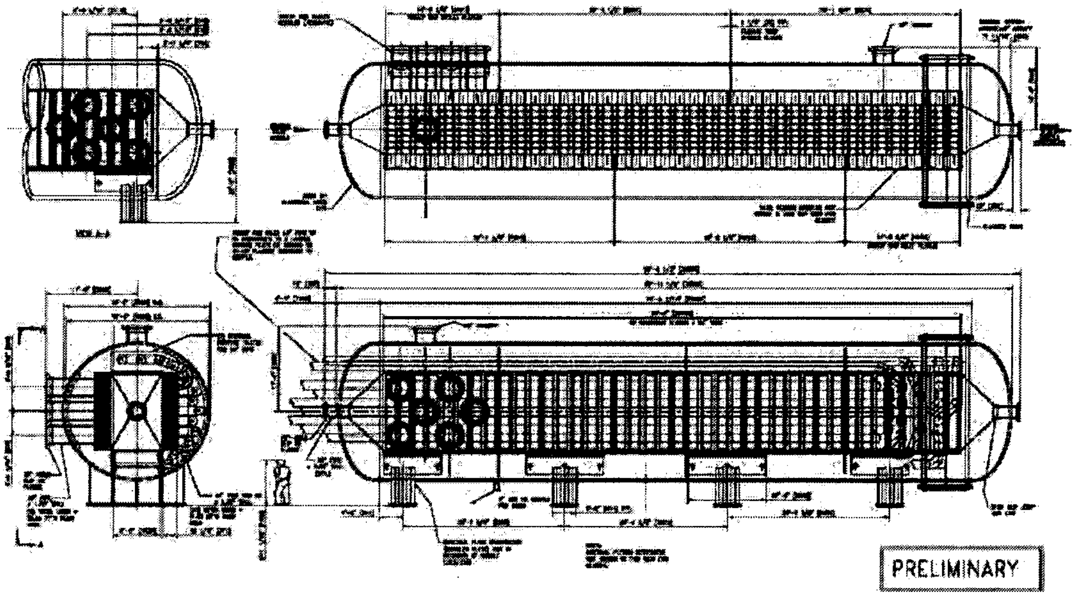
Overview

The reactor (Figure 6) 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.

Figure 6 Proposed Reactor Design



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 tube sheet 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_2 Capture

Task - 2.2 Fuel-Grade Hydrogen Generation
Technology Providers: Fluor Federal
Co-funder: DOE

Objectives/Background

The objective of this project was to develop a process flowsheet based on gasification incorporating a membrane water gas shift reactor. The Phase I project work period was from March, 2002 to February, 2003. The Phase II work period started in April, 2003 and extended to the end of September, 2003.

Highlights

Phase I

Fluor developed an AspenPlus process simulation model for a full capture plant that included these units.

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

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

Phase II

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

Summary

Phase I, 3/02 – 2/03

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

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

Phase II, 4/03 – 9/03
Flowsheet development and equipment sizing was completed on schedule. A final report was supplied to the CCP on 9/3/2003. The equipment specifications list was submitted to the common cost estimator (also Fluor).

A summary of the overall performance of the gasification plant is shown in Table 9.

Table 9 Gasification Plant Performance

Gasification Plant Performance **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.

1.2.1.1.8 Integrated Water-Gas Shift/Hydrogen Transport Membrane Technology for Simultaneous Carbon Dioxide Capture and Hydrogen Separation

Technology provider:	Eltron Research, Inc., Boulder, CO
Co-funder:	DOE

Highlights

- Long term testing (~3000 hours) was conducted with H_2/He and wet syngas mixtures. Results were mixed. There was a significant, steady decline in performance with the H_2/He mixture, while, surprisingly, the membrane subjected to the wet syngas demonstrated a lower rate of decline and appeared to be leveling off after 2500 hours. Post-test examinations of the membranes should determine the reasons for the differences in performance
- In high pressure testing, Eltron verified that CO adsorption on the disassociation catalyst will negatively affect performance. Higher temperatures, however, will minimize this effect. In addition, the water gas shift reaction will reduce the concentration of CO in the reactor.
- Electroless deposition was examined as an alternative method for applying the disassociation catalyst. The resultant inconsistent layers of catalyst were thought to be due to contaminents in the solvent. Flux performance was 40% of that achieved with vacuum deposition.

Summary

In 2002-2003, the CCP supported Eltron Research, Inc. in the development of a hydrogen transfer membrane for use in a membrane water gas shift reactor. Due to the success of this work, Eltron was asked to continue membrane development in 2004. This summary only covers work conducted by Eltron in 2004.

The 2004 work scope was kicked off in July and consisted of three primary work tasks.

Task 1 Test Membranes Under Higher Steam and Gas Flow Rates in High-Pressure Apparatus

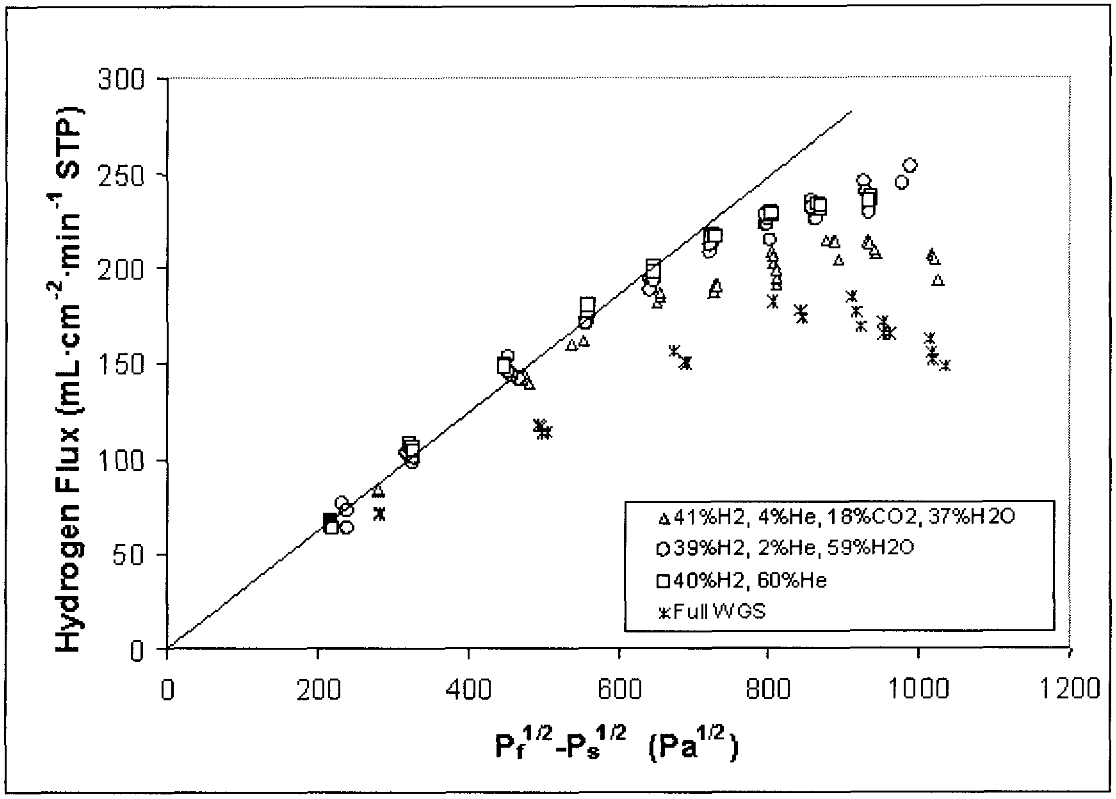
Task 2 Long-Term Tests in Water-Gas Shift Mixtures

Task 3 Development of Low-Cost Catalyst Deposition Techniques

High Pressure Testing

In Task 1, hydrogen fluxes were measured at 420C and at feed side pressures up to 32 bar. Four feed compositions were tested: H_2/H_2, wet H_2/He, wet syngas without CO and wet syngas with CO. Figure 7 shows the results.

Figure 7 High Pressure Testing



The results for the hydrogen/helium mixture shows that up to about 10 barg feed pressure, the hydrogen flux follows Sievert's law. Above 10 barg, the fluxes were less than expected, probably due to limitations from gas diffusion. Adding water to the feed did not affect the membrane performance.

Testing with a wet CO-free syngas mixture showed a slight falloff in performance. Eltron also attributed this to gas phase diffusion.

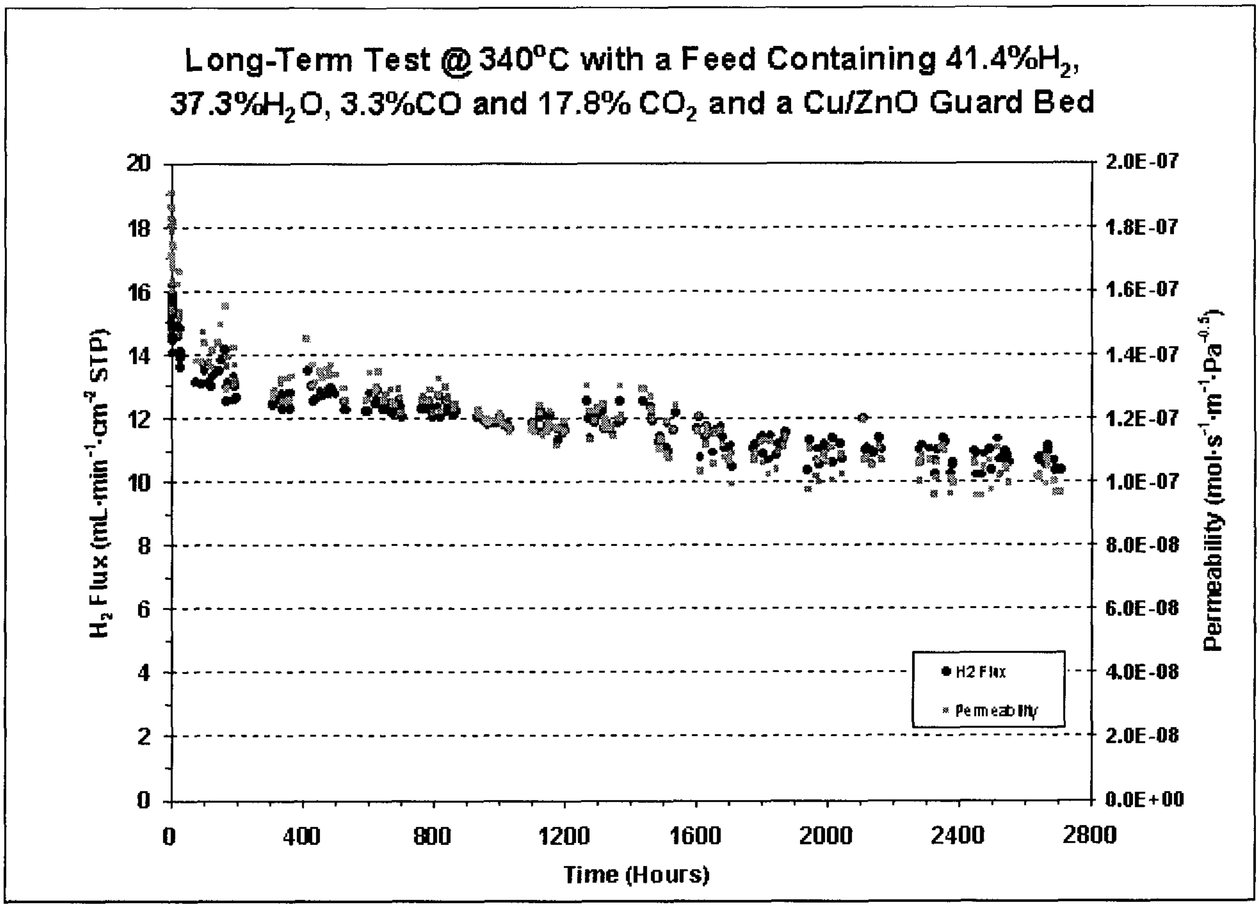
When the feed mixture was changed to the full syngas composition (3% CO), there was a significant dropoff in performance. This was attributed to CO adsorption on the disassociation catalyst surface. Tests conducted at 440°C showed no effect of CO, while tests run at 324°C showed a significant dropoff in performance. These results support a theoretical calculation of CO adsorption, which showed that CO adsorption increases exponentially with decreasing temperature. It should be noted that the CO concentration of 3% was estimated for the inlet to the reactor (and after a bulk water gas shift reactor) and should decrease as the shift reaction takes place. In other words, the detrimental effect of CO should diminish as the shift reaction takes place.

Long Term Testing

Two long term durability tests were conducted at atmospheric pressure.

In the first test, the membrane was subjected to a 60% H_2/40%He mixture at 340°C. There was a significant and steady decline in flux over a 3000 hour time period. The second test, however, showed more promising results with a syngas mixture. Figure 8 shows that the flux performance leveled off after about 2500 hours. Eltron surmised that the difference between the two test results was due to the use of a larger guard bed in the second test. The second test is continuing, but after its conclusion, the membrane will be inspected and compared to the membrane in the first durability test to determine the cause of the different performance decline results.

Figure 8 Long-term Testing Results



Alternative catalyst deposition techniques

Preliminary tests were conducted on using electroless plating techniques to apply the disassociation catalyst. Electroless plating may be required for membrane reactors with tubular geometry.

Systematic screening techniques were used to identify the parameters required to provide a 0.4 micron thick catalyst layer. However, there was difficulty in obtaining a consistent layer over the membrane with some areas exhibiting poor adhesion. Eltron attributed this problem to impurities in the coating solution. Flux tests with electroless coated membranes showed that the performance was about 40% of membranes coated via vacuum deposition.

Reports and Publications

- "Dense Membranes For Separation Of H_2 From CO_2 In High-pressure Water-gas Shift Reactors", Michael Mundschau, 7th International Conference Greenhouse Gas Control Technolgies, September 5-9, 2004, Vancouver, BC.
- The final project report is in Appendix A under the same heading as this summary.

1.2.1.2 CCP Summary Report Hydrogen Production by Sorbent Enhanced Water Gas Shift Reaction

Task - 2.1 Gas Turbine Fuels

Technology Providers: Air Products and Chemicals Inc (APCI)
Co-funder: DOE

Highlights

- A sorbent enhanced water gas shift (SEWGS) process has been developed to convert CO to CO_2 and H_2 and simultaneously remove the produced CO_2 by adsorption onto a solid as a means to decarbonize gaseous fuels.
- Adsorbents have been identified which are capable of removing CO_2 at high temperatures and experimental proof of concept test runs have been performed to confirm the feasibility of this approach
- Processes incorporating this system have been designed for decarbonization of gas fuels for gas turbines, with designs evaluated in the CCP NorCap case study (400 MW combined cycle gas turbine) and the Alaska case study (11 distributed gas turbines).
- The system exhibits high efficiency owing to the product fuel being at high temperature and containing the excess reaction steam which results in low NO_X emissions (below 25ppm is achievable).

Summary

The technology comprises a high temperature cyclic pressure swing adsorption (PSA) process for removal of CO_2 from a reactor in which the water-gas shift conversion (1) of CO is simultaneously occurring.

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \qquad (1)$$

The technology built upon earlier work by Air Products and Chemicals (APCI) on small scale hydrogen production by 'sorbent-enhanced reforming' SER. Some of the technical hurdles in that process are overcome when the approach is used with the water gas shift reaction, though this necessitates inclusion of a syngas generation stage in the process.

The development work comprised the following areas,

- Adsorption development and characterization,
- Design and evaluation of CO_2 Capture processes incorporating the SEWGS
- and
- Experimental proof of concept.

The work was undertaken in four phases:

Phase 1 – Preliminary characterization of the leading candidate adsorbents, Mathematical modeling of the SEWGS system and initial evaluation of the process concept by comparison with conventional pre-combustion concepts.

Phase 2 – Main experimental program including construction of a single bed adsorption process test unit (PTU) for cyclic experimental work, testing of a range of materials in the rig and by thermogravimetric analysis (TGA) and proof of concept runs in which combined reaction and adsorption tests were undertaken in the PTU.

Phase 3 – Incorporating the experimental results into a capture process design for the two CCP case studies.

Phase 4 – Additional evaluation of an alternate adsorbent material

The following adsorbent types were evaluated

Promoted hydrotalcites (HTC) with a range of promoters (7 types)
Double Salts- Combinations of metal oxides and carbonates (20 combinations)
Metal Oxides as pure materials or supported on alumina
Toshiba's Lithium Orthosilicate-based material

The key findings were that in the rapid cyclic service of a SEWGS system, the hydrotalcites have the highest CO_2 capacity of the materials tested. HTCs promoted with potassium carbonate showed higher CO_2 capacity in cyclic testing than those promoted by rare earth metals. The highest capacity was exhibited by a Sasol sample that differs in MgO /Al_2O_3 ratio from other vendor materials, this material designated HTC2 was used as preferred adsorbent in the equipment sizing and the proof of concept tests.

No other material was found to give superior performance in cyclic service to HTC2. Supported double salts had high potential capacity but needed to be supported on alumina or other carrier, which results in lower capacity overall. Metal oxides were found to interact with the support material rendering them inactive for CO_2 adsorption under SEWGS conditions.

The lithium orthosilicate material was found to have very high capacity in temperature swing adsorption (TSA) tests and in slow cyclic PSA operation at higher temperatures of around 600 °C, but did not give satisfactory performance under the selected conditions for the operation of the SEWGS system.

A large number of parametric test runs were conducted in the PTU in order to characterize the HTC2 adsorption and desorption characteristics, with the initial intention of verifying and tubing the mathematical models APCI had for modeling of such systems. APCI found that the existing models were unable to accurately represent the full cyclic process, particularly the desorption step and the response of the process to purge gas. A hypothesis which could explain this unusual adsorbent behavior is that there are multiple adsorption sites in the material which have different mass transfer rates, which cannot be represented adequately by the non-isothermal dual site Langmuir isotherm model normally used. As a result of this finding APCI used the experimental work to test the capacity of the adsorbent and response to operating parameters under conditions, which were the closest possible to those of the real plant. These results were used to determine the adsorbent volume and number of trains of SEWGS in the capture processes. These experiments indicated working capacities for the adsorbent phase as 0.25 for an air blown ATR case and 0.32 mmol/g for an O_2 blown ATR case.

The proof of concept testing was conducted in breakthrough and cyclic modes using mixtures of conventional shift reactor catalyst and HTC2. These confirmed that the CO conversion could be greatly enhanced, with the CO slip of 1.7% compared with an equilibrium conversion of 7.8%, confirming the conversion enhancement afforded by the CO_2 adsorption. A total carbon recovery of around 83% was achieved in cyclic system, which is lower than is anticipated in the real plant due to the shorter bed length and the inability of the single bed unit to run in identical cyclic conditions. The breakthrough tests conducted with the bed initially free of CO_2 exhibited total conversion of CO and removal of CO_2 until the bed became saturated at which point the reaction essentially stopped and both CO and CO_2 in the product is essentially equal to that in the feed.

The process comprises a seven bed unit, each bed containing a mixture of adsorbent and high temperature shift reactor catalyst (copper promoted iron oxide). The vessels are 12 feet in diameter and are interconnected by a series of valves and manifolds to enable them to be operated in a complex PSA cycle with a cycle time of 4.7 minutes.

The SEWGS system is primarily targeted at gas turbine combustion systems where it has particular efficiency and emissions benefits, therefore the technology was evaluated in the NorCap 400 MW CCGT case study and the Alaska distributed gas turbine gas study. In both cases, APCI developed process design to optimally deploy the system to decarbonize natural gas feed.

For the Alaska case study, the process was based on an oxygen blown autothermal reformer (ATR) as the primary syngas generator. The product is cooled and passed through a conventional first stage of shift reaction before it is fed to the SEWGS system where the CO is converted to hydrogen and CO_2 which is removed by adsorption process. The product leaving the SEWGS is combined with nitrogen from the air separation unit and cooled to 540 °F which is the maximum temperature for direct use in a gas turbine. This hot decarbonized fuel gas has a high mass flow and steam content resulting in approximately 14% lower heating rate requirement (LHV basis) on the gas turbine to maintain output, contributing to a high overall efficiency. The process was designed as a stand alone plant, generating all the electrical power required within the battery limits, hence a combined cycle gas turbine was included within the scope to balance the power. This unit was heat integrated with the CO_2 capture process to optimize capital cost and efficiency and is supplied with decarbonized fuel from the plant to minimize CO_2 emissions.

The NorCap scenario involves integration of a similar process to that used in Alaska into a 400 MW CCGT power plant. APCI prepared two alternate schemes, one based on air blown ATR and the other using an oxygen blown ATR. The overall efficiencies of these two options were 48.3% for the air blown and 47.3% for the oxygen blown plants, a significant increase over the baseline technology. In addition the air blown plant actually exports more power than the uncontrolled case, although this necessitates a higher gas usage. This arrangement gives extremely good utilization of the power plant capacity and although the capital cost of the scheme is somewhat higher than the oxygen blown case it results in an attractive cost of CO_2 capture.

Publication:

- The final project report is attached in Appendix A under the same heading.

1.2.1.4 Hydrogen Membrane Reformer - Hydrogen Membrane Technology Ceramic Material, Reactor and Process Design - Phase 1 & 2

Task - 2.2 Fuel-Grade Hydrogen Generation
Technology Provider: Norsk Hydro
Co-funder: Klimatek

The project objective was to develop dense Hydrogen Mixed Conducting Membranes (HMCM) with sufficient H_2 transport rates and stability under normal steam reforming conditions and to further develop a techno-economically viable pre-combustion de-carbonization process applying these materials. The objectives of this project were to develop and evaluate ceramic hydrogen mixed conducting membrane materials and membrane reactor system designs for use in decarbonization of natural gas fuels for refinery, distributed gas turbines and CCGT applications. Further to incorporate these designs into integrated flow schemes for efficient and cost effective pre-combustion power and/or heat generation processes.

- Forty candidate membrane materials were synthesized and characterized. More than 35 hydrogen permeability measurements were performed. Based on the measurements and theoretical evaluations, a main candidate materials system was selected.
- 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_2 flux in the test rig was 18 $\text{Nml}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$, which compares favorably with model predictions and exceeds the flux target set to 5 $\text{Nml}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$ H_2 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_2 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_2 capture efficiency close to 100% for the Norwegian scenario. The NOx formation was predicted to be approximately 5 ppm vol.

The sinterability of the membrane materials and the imperviousness of the resulting porous tube supported membranes were addressed in the project extension starting from July 2004, duration eight months. By adding small concentrations of sintering aid formulations, and by modifying the sintering conditions the desired dense structure of the thin membrane layer was targeted to be improved.

- From a theoretical study six main groups of sintering aid materials were selected and screened for their capability to form dense membrane (disks) at 1600-1650 °C. Of the six three displayed similar promising sintering in small concentrations, of which one was selected for fabricating supported membrane tubes. The addition level of 2 mol% was selected.
- With the sintering aid, a total of 20 porous tubes were fabricated by isostatic pressing and further coated and sintered at temperatures in the range of 1600-1700°C.
- Various parameters in the slip coating / sintering procedure were varied to optimise the quality of the membrane. For the selected material sintering aid combination these parameters were successfully determined and five of these supported thin layer membranes tubes were manufactured with negligible leakage rates.
- Two supported tubes were tested with at 1000°C to verify the hydrogen flux predicted by the hydrogen flux model. With the measurements the predicted high hydrogen flux was largely verified. No major effect of the sintering aid addition to the permeability of the membrane was observed.

Summary

Potential benefits of integrating a hydrogen membrane reformer into a power generation process with CO_2 capture will be to increase conversion of equilibrium limited reactions by removing H_2, combination of reforming reaction and separation, CO_2 separation at high pressure and that no traditional CO_2 removal system will be required.

Hydrogen membrane reformer technology is premature and no commercial units are available. Major challenges are found in membrane development (flux, stability and fabrication), reactor design (sealing, manifold, surface/volume ratio) and integration with combined cycle gas turbines (CCGT).

This project represents a major step forward for the Hydrogen membrane reformer technology and very promising results have been obtained, yet quiet some more development is needed before commercialization. A next step in the membrane development is the fabrication of a monolith supported membrane of the selected material.

Overall evaluation

The Hydrogen membrane reformer project has delivered results on time and budget. Promising flux measurements have been obtained and a reactor model has verified that the target flux calculated for 50% cost reduction can be achieved.

Reports and Publications

The final project reports of both phases of the project are attached in Appendix A under the same heading.

1.2.1.5 Hydrogen Membrane Reactor

Task - 2.2 Fuel-Grade Hydrogen Generation
Technology Provider: Norsk Hydro
SINTEF
Universidad de Zaragoza (UNIZAR)
University of Twente (TWENTE)
Institute for Membrane Technology (ITM)
KTH
BP
Co-funder: EU-GRACE

The main objective of the hydrogen membrane reactor project was to develop membranes for integration into a Pre-combustion De-carbonization process for H_2S-free fuel gas in a heater and boiler scenario.

Four membrane developer teams were selected to develop and test various types of hydrogen transport 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:

- SINTEF developed a membrane with a very thin (1-5 μm) dense Pd/Ag film supported by a porous stainless steel tube **that clearly exhibited the most promising results within this project** with virtually perfect selectivity and high hydrogen permeance: H_2 fluxes up to 30 $\mathrm{Nml \cdot min^{-1} \cdot cm^{-2}}$ have been achieved at a low differential hydrogen partial pressure of 0.34 bar, which corresponds to a permeance of 0.68 $\mathrm{mol \cdot s^{-1} \cdot m^{-2} \cdot bar^{-1}}$ assuming linear pressure dependence or 1.45 $\mathrm{mol \cdot s^{-1} \cdot m^{-2} \cdot bar^{-0.5}}$ 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 (H_2/CH_4 selectivity up to 1000 at a reasonable permeance of 0.2 $\mathrm{mol/sm^2bar}$ at 250°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 in both 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°C (up to 95% CO conversion at 280°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 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% CO_2 capture efficiency (79% if natural gas consumption for power generation is considered)
  - 91% purity in CO_2 capture stream (+ 9% N2)
- 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 m^2 for a plant sequestering 2 million tonnes per year of CO_2

1.2.1.5.1 GRACE Hydrogen Membrane Technology: Material, Reactor and Process Design

Task - 2.2 Fuel-Grade Hydrogen Generation
Technology Providers: Norsk Hydro
Co-funder: EU-GRACE

Background

The study "Hydrogen Membrane Reactor" is part of GRACE (Grangemouth Advanced CO_2 Capture Project), which is co-sponsored by the 5th Framework Programme of the European Commission. The project began on January 1st 2002 with a total duration of 2 years. Four teams were selected to work on developing hydrogen membranes for a membrane reactor fed with sweet fuel gas. The four membrane developer teams are:

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

All membrane developers were expected to carry out preliminary performance tests of their membranes for pre-selection and optimisation in their laboratories while standardised permeability and selectivity tests as well as performance tests in a laboratory-scale tubular membrane reactor were performed at the Institute for Membrane Technology (ITM-CNR).

The project included also the development of a mathematical computer model to predict the performance of a membrane with specific properties in a given membrane reactor system. This model was developed by SINTEF and submitted to ITM for experimental verification.

BP was responsible for the development of a PCDC process and a conceptual reactor design based on the membrane performance predicted by the mathematical model. The facilities were based on the Grangemouth refinery scenario with the feed streams consisting of fuel oil and fuel gas.

Summary of the membrane development activities

SINTEF

The SINTEF membrane consists of a very thin (1-5 μm) 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 permeability (0.3 mol/sm^2bar assuming linear pressure dependence). 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.

The production of tubular membranes of this type consists of four main process steps:

1. sputtering of a thin film on a flat surface
2. detaching the film from the flat surface
3. wrapping the film around a commercially available porous steel tube
4. mechanically sealing the ends

The manipulation and especially the mechanical sealing of such fragile films requires great care and often resulted in small leaks which needed manual treatment before dense layer was achieved. It is expected that significant technical development is required before this membrane type is ready for automated and cost efficient production.

Table 1 compares the performance of the SINTEF 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 SINTEF performance is based on tests conducted with a hydrogen/nitrogen 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 although the market price for palladium has decreased to roughly 15% of the price reported in 2001. Preliminary cost estimations indicate that for the thin Pd layers required by the SINTEF membrane the material costs are only a small fraction (<10%) of the total membrane manufacturing costs.

It is clearly apparent that the SINTEF membrane potentially represents a significant improvement over the "state of the art" assumptions made in the Haldor Topsoe report.

University of Twente

The focus of the Twente programme was to improve the hydrothermal stability of silica based membranes by modifying the γ-alumina support layer and doping the silica layer. H_2/CH_4 selectivity up to 350 at a reasonable permeance of 0.1 mol/sm^{2}bar has been achieved. A major issue has been the reproducibility of the membrane selectivity mainly due to variations in the quality of the commercial support tubes used. In most cases the surface roughness of the support tubes was the limiting factor. Another issue was the sealing of tube ends. Only recently necessary improvements of the sealing method have been achieved but these have not been tested in the ITM reactor.

A major challenge for Twente was the required tubular shape of the membranes. Despite focused development work over a period of more than 1.5 years, the state of the art performance of small planar silica membranes has not yet been achieved with tubular membranes.

The modified γ-alumina support was able to withstand simulated ambient steam reforming atmosphere (SASRA) for a period of 100 hours but so far is doubted that the silica layer will be similarly stable under these conditions.

University of Zaragoza (UNIZAR)

UNIZAR set out to utilise the fact that certain zeolite materials exhibit very narrow (0.35-0.41 nm) channels, which could act as a selective passage for hydrogen molecules. However, selectivity is so far very limited due the increasing probability of defects in thin zeolite layers of larger dimensions. During the first year of the project UNIZAR optimised the conditions for the production of thin, low defect zeolite films on Al_2O_3 support tubes. A variety of techniques to selectively block intercrystalline pores of the zeolite layer with Pd particles were studied experimentally. Unfortunately, none of the attempts succeeded to increase the hydrogen permselectivity significantly while maintaining sufficient permeance. This was most likely due to the formation of larger clusters of Pd particles that were unable to selectivity block the pores in the zeolite film.

The most successful Pd deposition method appeared to be impregnation followed by in-situ reduction of Pd resulting in acceptable H_2/CO_2 permselectivity of 146, however at insufficient permeance of 0.001 mol/sm^{2}bar.

KTH

The three main objectives of KTH have been

- development of a suitable technology for the preparation of nano-sized Pd particles,
- development of an efficient technique for the deposition of the Pd particles on membranes provided by Twente and UNIZAR,
- Single-gas flow tests for membrane evaluation regarding the selectivity.

Various methods to produce palladium nanoparticles in microemulsions have been studied. By in-situ reduction of palladium particles KTH succeeded in producing microemulsions with good control over the particle size distribution, which was in the range 2-7 nm. However, problems with the stability of these emulsions were encountered when the microemulsions were shipped to UNIZAR for deposition experiments. After a period of relatively unsuccessful trouble-shooting it was decided to ship the zeolite membranes prepared by UNIZAR to KTH instead and deposit the Pd particles there.

Several filtration techniques to selectively deposit Pd in non-selective intercrystalline pores formed of zeolite membranes were studied experimentally but none of them led to satisfying membrane performance in selectivity tests. The highest H_2/CO_2 permselectivity was 4.5, which too low for commercial applications. By modifying the calcinations procedure and working in a nitrogen atmosphere resulted in significantly improved H_2/CO_2 permselectivity of 3940 at a reasonable permeability of 0.15 mol/sm^{2}bar. However, these results have only been obtained very recently (September 2003), reproducibility has not been confirmed, and no reactor tests have been performed with this membrane. Consequently, it is too early to draw conclusions about the potential of this membrane.

Reactor experiments

Experiments with a laboratory-scale membrane reactor have been carried out by ITM. The test reactor consists of a small cylindrical pressure vessel in which the membrane module under investigation can be inserted. The reactor is connected to a number of gas bottles via a number of mass flow controllers. The product gas compositions (permeate and retentate) can be determined simultaneously by two separate gas chromatographs.

The reactor is preferably operated with the catalyst in the annulus formed between the tubular membrane and the cylindrical shell. Sweep gas (typically nitrogen) can be added on the permeate side of the membrane in order to increase the trans-membrane hydrogen partial pressure. The reactor allows both co-current and counter-current operation. Without catalyst the same reactor can be used for single or multiple gas permeation tests.

Initial reactor tests were performed at relatively low temperature and pressure (1.0-1.2 Bara, 210-265°C) with a CO, H_2O mixture in a stoichiometric ratio to study the water gas shift reaction. By increasing operating temperature and pressure above equilibrium, CO conversion was achieved. It has been observed that a significant fraction of the membrane was relatively inactive as the hydrogen concentration at the reactor inlet was zero and increased only slowly. By adding a conventional reactor upstream of the membrane reactor the inlet hydrogen concentration and hence the membrane utilisation was increased, leading to even higher conversion compared to equilibrium. Considering that a waster gas shift reactor is typically placed downstream of a reformer producing up to 30 mol% H_2, this configuration is actually closer to practical applications.

ITM has so far failed to operate the membrane reactor at a pressure realistic for industrial applications (typically >25 bar) due to limitations in the reactor design and limited strength of the support tubes used by the membrane developer teams.

Simulation model of catalytic membrane reactor

The mathematical model of a membrane reactor prepared by SINTEF allowed the computation of axial and radial concentration profiles on the feed side and axial concentration profiles of the permeate side of the membrane. This data could be used to predict the overall performance (conversion, separation) based on membrane parameters and operating conditions.

The reactor model was developed within the first 8 months of the project but first used by BP for process design calculations almost a year later. It was discovered that the model had a number of weaknesses and bugs most of which were fixed by SINTEF on request. Unfortunately the data input was not well suited for process optimisation calculations, which caused some delay in the process development work.

In its current version, the reactor model describes a water gas shift reactor with a medium temperature catalyst and a membrane model based on experimental results obtained with the SINTEF membrane.

Process development and conceptual reactor design

The objectives of this activity led by BP were to determine the feasibility and overall performance of a number of selected process options and to produce a design package for a plant capable of meeting pre-determined CO_2 capture targets and specification. Initially six different process options were specified and selected for further investigation. Each of these processes was simulated using HYSYS software. However the characteristics of the membrane reactor unit (and individual membrane and reactor units) were determined using a model provided by SINTEF. Much of the equipment has been sized using information held on BP's database. The exceptions to this are the membrane / reactor units and the heat exchangers. These were sized using the SINTEF model and TASC software respectively.

Based on the results from these process simulations a single process was selected which minimised the power deficit and maximised the H_2 purity while meeting the pre-selected CO_2 purity specifications. The selected process 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.

A tubular reactor design using the SINTEF membranes has been developed. The decision for a tubular reactor design was based on the following consideration:

- Membranes had been developed and tested in the tubular form and sealing solutions had been demonstrated for this arrangement.
- Pall (a commercial supplier of a variety of filter tubes), have experience of fabrication of large modules incorporating tubular sintered membrane supports for liquid applications the experience from which could be applied to large gas separation modules.

The process design selected requires a total of nine identical membrane units distributed over three discrete stages. The total surface area is 8000 m^2.

General Conclusions

- SINTEF was the only membrane developer to reproducibly produce tubular membranes with sufficient permeability and selectivity. Long term stability and cost efficiency has not been proven.
- The assumption that planar membranes are not suited for industrial applications and hence focus development solely towards tubular membranes was possibly premature. By allowing a more innovative reactor design, a number of membrane manufacturing issues could have potentially been avoided.

- No allowance was made to thoroughly test and improve the SINTEF reactor model during the course of the project. Difficulties arose when BP started process design calculations using the essentially untested beta-version of the model.
- The initial project proposal generally mentioned membrane reactors as a potential application for the membranes to be developed during the project and referred to water gas shift (WGS) and gas reforming as relevant examples. However, shortly after the start of the project it was realised that extending the reactor tests beyond WGS to membrane reforming was unlikely to be achievable within the given time. It was decided to focus solely on WGS, which was assumed to have a higher chance of success, even if the potential savings for a membrane reformer compared to baseline technology may be greater.

Table 10 Comparison of SINTEF Membrane to Haldor Topsoe's "State of the Art" Membrane

	Haldor Topsoe study	SINTEF
Thickness, μm	25	1
Temperature, °C	?	300
Permeance, mol/sm^{2}Pa$^{0.5}$		3.35E-04
Permeance, Nm^3/hm^2bar$^{0.5}$	20	100
Driving force, bar$^{0.5}$	0.7	0.7
Hydrogen flow, Nm^3/h	351,000	351,000
Area, m^2	25,071	5,014
Cost, $/oz	1,100	1,100
Palladium density, g/cm^3	11.97	11.97
Palladium volume req., m^3	0.63	0.01
Palladium weight req., g	7,502,000	120
Palladium weight req., oz	264,642	4,234
Palladium cost, MM$	191	9
Membrane cost, $/m^2	11610	929

Reports and Publications

- This summary is an analysis of following reports 1.2.1.5.2 to 1.2.1.5.7. No separate report exists.

1.2.1.5.2 Development of Palladium Alloy Membranes for Hydrogen Fuel Production by Membrane Reaction

Task - 2.2 Fuel-Grade Hydrogen Generation
Technology Providers: SINTEF
Co-funder: EU-GRACE

Objectives/Background

The objectives of this project were the development of tubular dense palladium alloy membranes for use in a water gas shift (WGS) membrane reactor and the generation of a simulation model of a catalytic membrane reactor.

Highlights

The membranes developed by SINTEF consist of a very thin (1-5 µm) dense Pd/Ag film that is supported by a porous stainless steel tube. 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.

- Testing of the hydrogen flux through the membrane at 300 °C suggests a permeance of 0.3 mol/ ($m^2 \cdot s \cdot bar$) at perfect selectivity.
- The SINTEF membrane potentially represents a significant improvement over the "state of the art" assumptions made in the Haldor Topsoe report.
- Testing the membranes in a WGS membrane reactor resulted in CO conversion significant above equilibrium.
- The manipulation and especially the mechanical sealing of such fragile films requires great care and often resulted in small leaks which needed manual treatment before dense layer was achieved.
- The latest generation of tubular membranes using reinforced porous stainless steel tubes is designed to withstand a trans-membrane pressure of 15 bar.
- The reactor simulation model describes a water gas shift reactor with a medium temperature catalyst and a membrane model based on experimental results obtained with the SINTEF membrane. After some programming bugs had been fixed and a number of minor modifications made, BP was able to use the model to predict membrane reactor performance for process design calculations.

Summary

Prior to the start of the project, SINTEF had developed prototypes of thin planar Pd alloy membranes with high hydrogen permeance at virtually perfect selectivity. The challenge during this project was to apply this technology to tubular modules for use in a membrane reactor. During the project a suitable tubular membrane design was developed and several generations of prototype membranes for reactor testing produced. Sealing issues were eventually solved but some manual after-treatment was necessary to seal small leaks, which occurred during membrane assembly.

SINTEF provided a simulation model, which delivered useful results for process design calculation performed by BP despite some weaknesses related to data input and result reporting. In addition, SINTEF tested a number of alumina tubes with different coatings, prepared by Twente University under simulated ambient steam reforming atmosphere (SASRA) conditions in order to investigate the stability of the membrane supporting layers.

Overall evaluation

SINTEF was the only membrane developer in EU GRACE to reproducibly provide tubular membranes with sufficient permeability and selectivity. Long term stability and cost efficiency of the membranes has not been proven.

Reports and Publications

- The final project report is attached in Appendix A under the same heading.
- T. Mejdell, J. Morud and T. Strøm: Membrane Reactor Model, SINTEF Report no. STF66F02104, 2002-10-16.

1.2.1.5.3 Development of Palladium Zeolite Composite Membranes for Hydrogen Fuel Production by Membrane Reaction

Task - 2.2 Fuel-Grade Hydrogen Generation
Technology Providers: **University of Zaragoza (UNIZAR) & KTH**
Co-funder: **EU-GRACE**

Objectives/Background

The objective of this study was the development of tubular palladium impregnated zeolite membranes for use in a water gas shift (WGS) membrane reactor. The main objectives of KTH have been

1) development of a suitable technology for the preparation of nano-sized Pd particles,
2) development of an efficient technique for the deposition of the Pd particles on membranes provided by Twente and UNIZAR,
3) Single-gas flow tests for membrane evaluation regarding the selectivity.

UNIZAR set out to utilise the fact that certain zeolite materials exhibit very narrow (0.35-0.41 nm) channels, which could act as a selective passage for hydrogen molecules. However, selectivity is so far very limited due the increasing probability of defects in thin zeolite layers of larger dimensions. The objective of this study was to develop a method to selectively block the intercrystalline pores of the zeolite layer in order to increase the hydrogen permselectivity.

Highlights

- During the first year of the project KTH focused on the preparation of Pd nanoparticles using the microemulsion technique. The effect of the metal precursor has been studied by using two different sets of Pd salts. Additionally, the effect of the different oil phases and surfactants has been also investigated. The result was the preparation of Pd nanoparticles with size range 5-9 nm and with rather good stability in the microemulsion solution.
- During the second year of the project, different Pd impregnation methods have been investigated experimentally to compare and investigate the Pd deposition mechanism and the effect of the impregnation (filtration) method on membrane permeance and selectivity:
  - Non-continuous vacuum filtration is Steel Module.
  - Continuous vacuum filtration in Glass Reactors.
  - High Pressure / vacuum filtration in Steel Module
- Promising H_2/CO_2 permselectivity of 3940 at a reasonable permeability of 0.15 mol/sm^{2}bar was achieved by KTH using an optimised calcinations procedure and operating in a nitrogen atmosphere. However, these results have only been obtained very recently (September 2003), reproducibility has not been confirmed, and no reactor tests have been performed with this membrane. Consequently, it is too early to draw conclusions about the potential of this membrane.
- During the first year of the project UNIZAR optimised the conditions for the production of thin, low defect zeolite films on Al_2O_3 support tubes. A-type Zeolite Membranes have been prepared according to the state of the art. Several issues related to the thermal treatments necessary for drying and testing have been solved in order to avoid thermal cracks due to uncontrolled loss of water.
- The most successful Pd deposition method developed by UNIZAR appeared to be impregnation followed by in-situ reduction of Pd, which resulted in acceptable H_2/CO_2 permselectivity of 145, however, at insufficient permeance of 0.001 mol/sm^{2}bar.

- Attempts to produce dense palladium layers by chemical vapour deposition and electroless plating on alumina support tubes were rather unsuccessful.

Summary

This study was done in cooperation with that reported under Report Reference 1.2.1.5.6 The team chose to report their work together in this summary. Separate reports appear in Appendix A.

KTH studied various methods to produce palladium nanoparticles in microemulsions. By in-situ reduction of palladium particles KTH succeeded in producing microemulsions with good control over the particle size distribution, which was in the range 2-7 nm. However, problems with the stability of these emulsions were encountered when the microemulsions were shipped to UNIZAR for deposition experiments. After a period of relatively unsuccessful trouble-shooting it was decided to ship the zeolite membranes prepared by UNIZAR to KTH instead and deposit the Pd particles there.

UNIZAR experimentally studied a variety of techniques to selectively block intercrystalline pores of the zeolite layer with Pd particles. Unfortunately, none of the attempts succeeded to increase the hydrogen permselectivity significantly while maintaining sufficient permeance. This was most likely due to the formation of larger clusters of Pd particles that were unable to selectivity block the pores in the zeolite film.

Pd impregnated zeolite membranes did not exhibit sufficient hydrogen permselectivity in early experiments. Only recently have some promising results been obtained by KTH using optimised calcination conditions in a nitrogen atmosphere. These results must be reproduced before any assessment of the potential of these membranes can be made.

Reports and Publications

- C. Dueso, M.P. Pina, E.Urriolabeitia, R. Navarro, A. Larrea, M. Menéndez, J. Santamaría. "Preparation of Palladium Nanoparticles for the Synthesis of New Materials". 9th Mediterranean Congress of Chemistry Engineering; Books of Abstracts, pp 258. Barcelona (España). 2002.
- L. Casado M.A. Urbiztondo, M.P. Pina, M. Menéndez, J. Santamaría. “New Strategies to improve hydrogen selectivity with type A zeolite membranes” SECAT'03. 4th Congress of the Spanish Catalysis Society. Books of abstracts, pp., Torremolinos (España). 2003.
- L. Casado M.A. Urbiztondo, M.P. Pina, M. Menéndez, J. Santamaría. "Pd-zeolite Composite Membranes for Hydrogen Separation". 4th European Congress of Chemical Engineering. Granada (España). 2003.
- The final project report is attached in Appendix A under the same heading.

1.2.1.5.4 Development of Silica Membranes for Hydrogen Fuel Production by Membrane Reaction

Task - 2.2 Fuel-Grade Hydrogen Generation
Technology Providers: **University of Twente**
Co-funder: **EU-GRACE**

Objectives/Background

The objective of this study was the development of micro-porous tubular silica membranes for use in a water gas shift (WGS) membrane reactor.

At the start of the GRACE project, the state of the art for silica membranes was small planar multi-layered membranes with a thick macroporous layer, a thin intermediate gamma-alumina layer and a micro-porous silica membrane. With silica top layer sintered at 600°C the following performance was achieved: hydrogen permeance: 0.04 mol/sm^{2}bar at a H_2/CO_2 permselectivity of 40 and a CH_4/H_2 permselectivity > 400.

The challenge of this study was to produce tubular membranes with similar performance parameters and improve the hydrothermal stability of the membranes under high moisture conditions.

Highlights

- H_2/CH_4 selectivity up to 1000 at a reasonable permeance of up to 0.06 mol/sm^{2}bar at 250°C and up to 0.2 mol/sm^{2}bar at 350°C has been obtained for tubular membranes. A major issue has been the reproducibility of the membrane selectivity mainly due to variations in the quality of the commercial support tubes used. In most cases the surface roughness of the support tubes was the limiting factor. Another issue was the sealing of tube ends. Only recently necessary improvements of the sealing method have been achieved but these have not been tested in the ITM reactor.
- The modified γ-alumina support was able to withstand simulated ambient steam reforming atmosphere (SASRA) for a period of 100 hours but so far is doubted that the silica layer will be similarly stable under these conditions.
- Short term tests have shown that the silica membranes are likely be stable under WGS conditions.
- Different sealing methods have been investigated, the former giving better results
    - Sealing the support tube first, followed by γ-alumina coating.
    - Sealing the tube after the γ-alumina coating.

Summary

A number of silica membrane prototypes were prepared and submitted to ITM for reactor testing. Difficulties were experienced with insufficient selectivity caused by small imperfections of the alumina support tubes and sealing issues for most of the samples. Towards the end of the project very promising results were obtained using higher quality support tubes and improved sealing methods. Due to the relatively late breakthrough in silica membrane performance it was not possible to test these high-performance membranes in the ITM test reactor but is expected that CO conversion will increase significantly beyond the already promising results of the low-performance silica membranes tested earlier on. The late breakthrough was also the reason why silica membranes were not considered in the current reactor design which had to be fixed 6 months before the end of the project.

Overall evaluation

A major challenge for Twente was the required tubular shape of the membranes. Only just before the end of the 2 year project period was the state of the art performance of small planar silica membranes has been achieved with tubular membranes. Verification of hydrothermal stability under WGS conditions needs further long-term testing.

Reports and Publications

- The final project report is attached in Appendix A under the same heading

1.2.1.5.5 Experimental Evaluation of Hydrogen Production by Membrane Reaction

Task - 2.2 Fuel-Grade Hydrogen Generation
Technology Providers: **KTH**
Co-funder: **EU-GRACE**

Objectives/Background

The objective of this project was the development of a laboratory-scale test reactor for tubular membrane modules supplied by the project partners (SINTEF, KTH, University of Twente, and University of Zaragoza) and performs standardized membrane performance tests.

Highlights

The experimental results obtained from the test reactor confirmed the suitability of the membranes developed by the project partners and verified the membrane WGS reactor concept. The most important results obtained are:

- Pd-alloy membranes developed by SINTEF and silica based membrane developed by Twente achieved higher than equilibrium CO conversion at temperatures above 250°C (up to 95% CO conversion at 280°C).
- The positive influence of increased temperature and sweep flow rate on the H_2 permeance of Pd-alloy membranes has been shown experimentally
- Increasing the temperature increased the H2 permeance and selectivity for the silica-based membranes developed by Twente.
- Surprisingly, an increase in temperature (288 vs. 256.5°C) has been found to reduce the H_2 permeance and selectivity by up to 40%.
- The H_2 permeance of silica-based membranes decreased significantly after exposure to steam.

Summary

The test reactor designed, installed, and operated by ITM allowed the investigation of various membranes under various operating conditions. The effect of a number of important operating parameters on membrane reactor performance has been investigated experimentally. During the course of the project the following operating parameters have been studied:

- **Temperature:** Increased reactor temperature moves the reaction regime from kinetically controlled to equilibrium controlled. Consequently, the difference of the CO conversion between a traditional and a membrane reactor increases with temperature. The critical value above which higher than equilibrium conversion has been achieved was approx. 250°C.
- **Reactor pressure:** Increasing the reactor pressure improves the transmembrane driving force for H_2 transport and has shown to improve overall CO conversion. The WGS reaction itself is not affected by an increase in pressure.
- **Sweep factor**: Increasing the amount of sweep gas reduces the permeate side H_2 pressure and improves the transmembrane driving force for H_2 transport and increases the overall CO conversion.
- **Space velocity**: High space velocities shift the reactor regime from equilibrium-controlled towards kinetically-controlled. At space velocities below 1000 h^{-1} higher than equilibrium conversion has been achieved. In addition, depending on temperature and reaction pressure, certain membranes improved conversion above the thermodynamic equilibrium conversion of a traditional reactor also at higher space velocities.

In addition to the reactor tests described above, a number of permeation tests (without reaction) were performed. The permeances and permselectivities measured are in general in agreement with the results provided by the membrane developers. However, the perfect selectivity measured by SINTEF could only reproduced by ITM for the second generation Pd-alloy membrane provided by SINTEF. The values for the other generations of Pd-alloy membranes were as low as 9 (H_2/N_2) possibly indicating defect seals during the ITM tests.

ITM performed reaction tests in a traditional reactor to calibrate the kinetic model incorporated in the reactor simulation model developed by SINTEF.

Overall evaluation

The experimental work performed by ITM provided valuable information about the different membrane types developed during the project and helped verifying the membrane WGS reactor concept experimentally. Initial tests were performed with a pure CO and H_2O mixture which is not a realistic feed to a WGS reactor and might lead to hot spots on the catalyst surface. Successive experiments involved either a traditional WGS reactor upstream of the membrane reactor or a synthesized gas mixture similar to the product gas from an oxygen-blown ATR, which probably gave a more realistic indication of the membrane reactor performance in an industrial application. Unfortunately, the experimental results obtained were never directly compared to the results predicted by the mathematic reactor model developed by SINTEF.

Due to the limitations regarding the mechanical strength of the membrane modules provided and the experimental reactor setup, reactor tests were performed at relatively low transmembrane pressure (< 2 bar) compared the pressure required for economical operation in a commercial process (> 30 bar).

Reports and Publications

- The final project report is attached in Appendix A under the same heading

1.2.1.5.6 Pd Zeolite Composite Membrane Studies

Task - 2.2 Fuel-Grade Hydrogen Generation
Technology Providers: **University of Zaragoza (UNIZAR) & KTH**
Co-funder: **EU-GRACE**

Objectives/Background

The objective of this study was the development of tubular palladium impregnated zeolite membranes for use in a water gas shift (WGS) membrane reactor. The main objectives of KTH have been

4) development of a suitable technology for the preparation of nano-sized Pd particles,
5) development of an efficient technique for the deposition of the Pd particles on membranes provided by Twente and UNIZAR,
6) Single-gas flow tests for membrane evaluation regarding the selectivity.

UNIZAR set out to utilise the fact that certain zeolite materials exhibit very narrow (0.35-0.41 nm) channels, which could act as a selective passage for hydrogen molecules. However, selectivity is so far very limited due the increasing probability of defects in thin zeolite layers of larger dimensions. The objective of this study was to develop a method to selectively block the intercrystalline pores of the zeolite layer in order to increase the hydrogen permselectivity.

Highlights

- During the first year of the project KTH focused on the preparation of Pd nanoparticles using the microemulsion technique. The effect of the metal precursor has been studied by using two different sets of Pd salts. Additionally, the effect of the different oil phases and surfactants has been also investigated. The result was the preparation of Pd nanoparticles with size range 5-9 nm and with rather good stability in the microemulsion solution.
- During the second year of the project, different Pd impregnation methods have been investigated experimentally to compare and investigate the Pd deposition mechanism and the effect of the impregnation (filtration) method on membrane permeance and selectivity:
  - Non-continuous vacuum filtration is Steel Module.
  - Continuous vacuum filtration in Glass Reactors.
  - High Pressure / vacuum filtration in Steel Module
- Promising H_2/CO_2 permselectivity of 3940 at a reasonable permeability of 0.15 mol/sm^{2}bar was achieved by KTH using an optimised calcinations procedure and operating in a nitrogen atmosphere. However, these results have only been obtained very recently (September 2003), reproducibility has not been confirmed, and no reactor tests have been performed with this membrane. Consequently, it is too early to draw conclusions about the potential of this membrane.
- During the first year of the project UNIZAR optimised the conditions for the production of thin, low defect zeolite films on Al_2O_3 support tubes. A-type Zeolite Membranes have been prepared according to the state of the art. Several issues related to the thermal treatments necessary for drying and testing have been solved in order to avoid thermal cracks due to uncontrolled loss of water.
- The most successful Pd deposition method developed by UNIZAR appeared to be impregnation followed by in-situ reduction of Pd, which resulted in acceptable H_2/CO_2 permselectivity of 145, however, at insufficient permeance of 0.001 mol/sm^{2}bar.
- Attempts to produce dense palladium layers by chemical vapour deposition and electroless plating on alumina support tubes were rather unsuccessful.

Summary

This study was done in cooperation with that reported under Report Reference 1.2.1.5.3. The team chose to report their work together in this summary. Separate reports appear in Appendix A.

KTH studied various methods to produce palladium nanoparticles in microemulsions. By in-situ reduction of palladium particles KTH succeeded in producing microemulsions with good control over the particle size distribution, which was in the range 2-7 nm. However, problems with the stability of these emulsions were encountered when the microemulsions were shipped to UNIZAR for deposition experiments. After a period of relatively unsuccessful trouble-shooting it was decided to ship the zeolite membranes prepared by UNIZAR to KTH instead and deposit the Pd particles there.

UNIZAR experimentally studied a variety of techniques to selectively block intercrystalline pores of the zeolite layer with Pd particles. Unfortunately, none of the attempts succeeded to increase the hydrogen permselectivity significantly while maintaining sufficient permeance. This was most likely due to the formation of larger clusters of Pd particles that were unable to selectivity block the pores in the zeolite film.

Pd impregnated zeolite membranes did not exhibit sufficient hydrogen permselectivity in early experiments. Only recently have some promising results been obtained by KTH using optimised calcination conditions in a nitrogen atmosphere. These results must be reproduced before any assessment of the potential of these membranes can be made.

Reports and Publications

- C. Dueso, M.P. Pina, E.Urriolabeitia, R. Navarro, A. Larrea, M. Menéndez, J. Santamaría. "Preparation of Palladium Nanoparticles for the Synthesis of New Materials". 9th Mediterranean Congress of Chemistry Engineering; Books of Abstracts, pp 258. Barcelona (España). 2002.
- L. Casado M.A. Urbiztondo, M.P. Pina, M. Menéndez, J. Santamaría. "New Strategies to improve hydrogen selectivity with type A zeolite membranes" SECAT'03. 4th Congress of the Spanish Catalysis Society. Books of abstracts, pp., Torremolinos (España). 2003.
- L. Casado M.A. Urbiztondo, M.P. Pina, M. Menéndez, J. Santamaría. "Pd-zeolite Composite Membranes for Hydrogen Separation". 4th European Congress of Chemical Engineering. Granada (España). 2003.
- The final project report is attached in Appendix A under the same heading.

1.2.1.5.7 Reactor and Process Design Incorporating Membrane Water Gas Shift Reactor

Task - 2.2 Fuel-Grade Hydrogen Generation
Technology Providers: **BP**
Co-funder: **EU-GRACE**

Objectives/Background

The objective of this project was the development and optimisation of a process for fuel gas decarbonisation incorporating a membrane WGS reactor based on the results from membrane development and testing. In addition, a conceptual reactor design was developed in cooperation with the most successful membrane developer of the GRACE project (SINTEF).

Highlights

- Based on the mathematical membrane reactor model provided by SINTEF and experimental data measured by SINTEF and ITM a process scheme was developed and optimised using HYSYS software.
- From initially six different process options one option has been identified as most suited and selected for further optimisation.
- 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% CO_2 capture efficiency (79% if natural gas consumption for power generation is considered)
    - 91% purity in CO_2 capture stream (+ 9% 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 m^2.

Summary

BP successfully developed a suitable process for decarbonisation of fuel gas for heater and boiler applications. The main components of the process include an air blown auto-thermal reformer and a staged membrane water gas shift reactor, which has been designed to incorporate the Pd alloy membranes developed by SINTEF.

The conceptual reactor design uses separate stages for CO conversion and H_2 separation and is based on commercially available tubular reactor design. Further development work will be necessary to

Overall evaluation

The process design package produced, provided an excellent basis for cost estimation. The accuracy of the data provided in the design package is assumed to be relatively high as much of the equipment was sized using information held on BP's database. The process scheme chosen limits the risk of failure as all components apart from the membrane shift reactor represent proven technology. Further cost reductions could be achieved by combination with oxyfuel technologies.

Reports and Publications

- P. Middleton, T. Hawkins, "Hydrogen Fuel Gas Production Using Palladium Membranes," BP Exploration Operating Co. Ltd, Exploration & Production Technology Group REPORT Number: S/EPTG/008/03.
- The final project report is attached in Appendix A under the same heading

1.2.1.6 Pre-combustion Decarbonization Membrane Reactor Literature Study

Task - 2.2 Fuel-Grade Hydrogen Generation
Technology Providers: **Haldor Topsoe**
Co-funder: **CCP**

Objectives:

The aim of this study is to identify the performance and cost requirements for membrane reforming and membrane water gas shift reactors, which are needed in order for the membrane technology to be cost effective and fulfill the CCP target.

Summary:

This scoping study was used as the basis for selection of starting points and directions for the hydrogen membrane studies funded by the EU-GRACE program. It is a good reference for the state of the art in 2001.

The study comprised two parts:

1. **The Membrane Study** A techno-economical analysis of membrane reactors adopted for hydrogen production.
2. **The Material Study** A survey of hydrogen conductive materials.

The Membrane Study

The main objective of this study is to establish two pre-combustion decarbonization schemes based on membrane reforming and membrane water gas shift reaction. The schemes are compared to relevant base cases. The following six cases were considered:

With **natural gas feed**:
1. Base case reforming (primary reformer)
2. Base case reforming (primary + secondary reformer)
3. Membrane reforming

With **synthesis gas from coal gasification as feed**:
4. Base case shift
5. Membrane shift (S-tolerant membrane)
6. Membrane shift (S removal up-stream shift)

Case 2 and Case 6 have been studied with a limited scope (i.e. PFD and operating performance).

The CO_2 avoidance costs are summarized in the following tables (Table 11 and 12). The membrane cost is based on state of the art performance of Pd based membranes.

Table 11 Reforming of Natural Gas

US\$/ton CO_2 avoided	Primary Reformer	Primary + Secondary Reformer	Membrane Reformer
Operating cost	12.9	14.8	18.8
Plant capital based	33.1	-	12.4
Membrane based	Na	Na	40.8
Total cost	46.1	-	72.0

Table 12 Shift of Gasifier Gas

US\$/Ton CO_2 avoided	Base Case Shift	Membrane Shift Sulphur Resistant	Membrane Shift Sulphur Removal Up-stream
Operating cost	1.9	2.6	16.5
Plant capital based	8.0	3.1	-
Membrane based	Na	11.8	-
Total cost	9.9	17.5	-

Tables 11 and 12 show that the cost of the CO_2 avoidance cost contribution from the plant investment (without the membrane) is, as expected, significantly lower for the membrane cases as compared to the base cases. However, the cost of the state of the art Pd membranes is extremely high resulting in a net increase in CO_2 avoidance cost for the membrane cases.

In order to assist in determining the performance and cost requirements necessary for membrane based plants to become competitive a set of curves was developed. These curves are shown below.

The Material Study

The objective of the hydrogen transporting material study was to produce a document that contains information on hydrogen transporting materials suitable for application in membrane reformer or water gas shift reactors. Priority has been given to references, which are new or particularly relevant for this objective.

The majority of the work covered in the study is based on Pd and Pd alloy membranes which appear to have the greatest potential. Also membranes based on group 5 metals, composite membranes, proton conductor and ceramic membranes are described.

Reports and Publications

- The final project report is attached in Appendix A under the same heading

1.2.1.9 Production of Hydrogen Fuel by Sorbent Enhanced Water Gas Shift (SEWGS) Reaction

Task - 2.2 Fuel-Grade Hydrogen Generation
Technology provider: Air Products and Chemicals

Highlights

- The hydrotalcite adsorbent slowly accumulated CO_2 under normal cyclic operating conditions, thus preventing long-term operation. Extended feed cycles can be operated successfully and do not show this increase in product CO_2 content at up to ~150 cycles.
- Regeneration efficiency does not appear to be affected by purge gas flow rate over a range of G-rates from 3-18 lb-mole/hr/ft^2. This is an important finding, for an inefficient regeneration process at higher purge rates would require excessive amounts of steam for purge in the industrial SEWGS process.
- Laboratory-scale catalytic activity testing has shown that the methane is formed with the HTC2/WGS catalyst mixture suggesting that methanation is occurring on the catalyst. Increasing the water content of the syngas can eliminate the methane production.
- The Toshiba adsorbent (Li_4SiO_4 modified with K_2CO_3) has exceptional CO_2 adsorption properties at high temperatures (e.g., 30-34 wt% CO_2 at 650°C and 1 atm CO_2). Adsorption and desorption are relatively fast at this temperature.
- An equilibrium model (infinite heat, mass, reaction rates) was developed to investigate the interplay of thermodynamics and heat profiles in lithium orthosilicate SEWGS fixed bed reactors.

Summary

This project is focused on the development of the Sorption Enhanced Water Gas Shift (SEWGS) process for decarbonizing syngas from an O_2 or air-based auto thermal reformer (ATR) to produce high temperature H_2 fuel for CO_2-free power generation. The SEWGS process combines the water gas shift reaction with high temperature CO_2 removal via a solid adsorbent to simultaneously react CO to low levels and remove CO_2. A high-pressure, high-temperature H_2 product stream is produced which is used to generate power in a gas turbine. Waste heat can be converted to power via steam turbines.

This report describes work carried out during October – December 2004 focused on evaluation of the stability of hydrotalcite (HTC) adsorbent to high pressure CO_2, the impact of high purge gas velocity on regeneration efficiency, determination of the source of CH_4 byproduct formation from the SEWGS system, and investigation of alternative high temperature adsorbents (e.g., Toshiba lithium orthosilicate) in power generation systems

Hydrotalcite Stability

The HTC adsorbent was found to slowly accumulate CO_2 beyond the expected amounts determined from breakthrough curves when the exposure was to relatively high partial pressure CO_2 for extended periods of time. The problem with this tendency is that it prohibits long-term operation of the cyclic SEWGS process, since the accumulation of CO_2 in the adsorbent apparently reduces the working capacity, and yields a continually increasing CO_2 content in the product gas with increasing cycles. A practical system must be able to achieve stable (and obviously relatively low) CO_2 concentrations in the product gas, achieving a so-called cyclic steady state condition.

Modifications to the CO_2 rinse cycle, namely adding a pressure equalization step, were not capable of eliminating this issue. Extended feed cycles, which do not generate high CO_2 partial pressure environments, can be operated successfully and do not show this increase in product CO_2 content at up to ~150 cycles. An alternative SEWGS cycle incorporating feed / high-pressure steam rinse / PE steps was proposed as a possible practical approach to minimize CO_2 partial pressures for an acceptable process cycle. Further investigation of this cycle is needed.

Impact of High Purge Gas Velocity on Regeneration Efficiency

The impact of purge gas flow rate on CO_2 desorption characteristics was investigated. Experiments with a recently modified test unit show that regeneration efficiency does not appear to be affected by purge gas flow rate over a range of G-rates from 3-18 lb-mole/hr/ft^2. This is an important finding, for an inefficient regeneration process at higher purge rates would require excessive amounts of steam for purge in the industrial SEWGS process. Additional experiments at 30-40 lbmole/hr/ft^2 are possible with the current experimental system, and these runs should be conducted to confirm this finding at conditions even closer to the industrially relevant flow rates.

Methane Formation

The third topic of experimental work was associated with the formation of methane in our SEWGS system from syngas feed. Laboratory-scale catalytic activity testing has shown that the methane is formed with the HTC2/WGS catalyst mixture, and increasing the water content of the syngas can eliminate the methane production. Additional experiments are planned to confirm these preliminary results, and to verify the expectation that the methanation activity comes from the catalyst.

Experimental and Simulation Work with Toshiba-Like Adsorbents

The final focus area for this report involves characterization of unique high temperature CO_2 adsorbents (e.g., lithium orthosilicate from Toshiba) and development of CO_2 separation processes based on these materials. The Toshiba adsorbent has exceptional CO_2 adsorption properties at high temperatures (e.g., 30-34 wt% CO_2 at 650°C and 1 atm CO_2). Adsorption and desorption are relatively fast at this temperature. Cycling experiments in the TGA showed that the adsorbent can be operated in a pressure swing mode at 650°C when a N_2 purge gas is used for desorption. Working capacities were 22-26 wt% CO_2. A modest increase in operating temperature to 700°C resulted in larger working capacities and improved desorption kinetics. Adsorption at 450°C was surprisingly slow.

The adsorbent can also be operated in a temperature swing mode. Regeneration can be carried out at a lower temperature when the purge gas contains lower levels of CO_2; i.e., purging with N_2 can more efficiently remove CO_2 at lower temperatures than purging with CO_2. Under a N_2 purge, CO_2 desorption begins at 470°C with a maximum rate at 590°C. Effective desorption could not be achieved even at 800°C when a 100% CO_2 purge was used. Heats of adsorption were measured by DSC to gain some insight into the thermodynamics of the relativley complex CO_2 adsorption mechanism of these materials.

Pure Li_4SiO_4 adsorbed CO_2 more slowly and less of it when compared to the Toshiba adsorbent. The enhanced properties of the Toshiba adsorbent are likely due to added K_2CO_3. Physical mixtures of Li_4SiO_4 and K_2CO_3 exhibited improved adsorption properties. When blended with an alkali carbonate eutectic mixture, still faster adsorption was observed. The composition and concentration of added carbonate clearly have a dramatic effect on adsorption capacities and rates.

An equilibrium model (infinite heat, mass, reaction rates) was developed to investigate the interplay of thermodynamics and heat profiles in lithium orthosilicate SEWGS fixed bed reactors. Heat management was found to be a key issue in developing successful process cycles, ideally constructing the cycle to utilize the energy produced during the reaction step to desorb CO_2 during the regeneration steps. Two-, three-,and four-bed PSA systems were investigated with the equilibrium model for the Norcap air-ATR system. The two-bed system was infeasible due to lack of adequate purge gas, and the four-bed system was steam-intensive. The best process design to date is a three-bed PSA utilizing a combination of the lithium orthosilicate adsorbent and WGS catalyst. Evaluation of the performance of this approach in the Norcap power generation scheme are in progress, along with process development for the O_2-ATR case.

Reports and Publications

- Hufton, J.R., R.J. Allam, R. Chiang, P. Middleton, E. Weist, V. White, "Development of a Process for CO_2 Capture from Gas Turbines using a Sorbent Enhanced Water Gas Shift Reactor System", paper prepared for the 7th International Conference on Greenhouse Gas Control Technologies, to be published.

- Allam, R.J., R. Chiang, J.R. Hufton, P. Middleton, E. Weist, V. White, "Development of the Sorption Enhanced Water Gas Shift Process", CCP Technical Volume I, to be published.

- Allam, R., R. Chiang, J.Hufton, R. Quinn, E. Weist, V. White, "CO_2 Capture Project – An Integrated, Collaborative Technology Development Project for Next Generation CO_2 Separation, Capture and Geologic Sequestration. Production of Hydrogen Fuel by Sorbent Enhanced Water Gas Shift Reaction", DOE Final Report, DE-FC26-01NT41145, December (2003).

- 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 Technology for Separation and Capture of CO_2 from Gasifier Process Producing Electrical Power, Steam and Hydrogen

Task - 2.2 Hydrogen Fuel Generation
Task - 2.3 Systems Integration and Optimization
Technical Provider: Fluor

Highlights

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

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

- Total Installed Costs for a Fort McMurray, Alberta plant are:
  - No CO_2 capture, uncontrolled release, case: $870 million USD
  - 90% CO_2 capture case: $1,360 million 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_2 with less than 30 ppmv of H2S
  - Ability to produce CO_2 at greater than 97 mol %
  - H_2 produced at pressure to minimize compression costs
  - Sulfur tolerant process

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

Summary

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

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

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

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

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

Advanced Technologies:

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

(i) learn how best to integrate these new technologies into a practical IGCC design,
(ii) Determine the reduction in CO_2 capture costs that can be obtained by using advanced technologies, and
(iii) Elucidate process performance and cost goals the advanced technologies must meet in order to deliver on the CCP cost reduction targets (75% for new facilities and 50% for retrofits)

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

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

In addition to the above technologies, Fluor Daniel has identified their proprietary autorefrigeration CO_2LDSEP 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 2nd Annual DOE NETL Conference on Carbon Sequestration, May 5-8, 2003.
- The final project report is attached in Appendix A under the same heading.

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 included five 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
1.2.3.5 Compact Reformer with Advanced Pressure Swing Adsorption System for Hydrogen Fuel

The objective in the integration and scale-up studies is to apply commercial, or close to, commercially available pre-combustion technology to 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.

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_X 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_2 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 in 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_2 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 emphasis 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_2 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_2 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_2 capture directly affects the efficiency of the scheme. This is mainly due to the energy intensive nature of CO_2 removal processes.

Of the schemes which comply to the base case definition of CO_2 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.

1.2.3.5 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 Study

Task 2.3 Systems Integration and Optimization
Technical Provider: General Electric
Co-Funder: DOE

Highlights

- Specifications of the gas turbines in the Alaska case study were reviewed and evaluations made of the changes required and performance expected for them firing three alternate decarbonized fuels representing different PCDC technologies
- 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_X 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_2 capture by fuel decarbonization.

Summary

The CCP elected to study the feasibility and cost of CO_2 capture using a range of technologies from four different case studies, one of which was BP Prudhoe Bay Central gas compression facility in Alaska. This study centered on the capture of CO_2 from 11 gas turbines driving gas compressors on the Alaskan North Slope, which together emit 2.2 million tonnes of CO_2 per year.

Pre-combustion decarbonization (PCDC) was identified as an attractive option to capture CO_2 from the gas turbines, benefiting from the possibility of using a central decarbonization 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 decarbonization 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 decarbonization processes. Three fuels were selected as representing the range of decarbonized fuel types likely to be considered for gas turbine firing, listed in Table 13. 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_2 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 13 Fuel Compositions

		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 14 for the three fuels at the ambient temperature of 32 °F.

Table 14 Key Results for Test Fuels in Alaska Scenario

	Model 6B			Model 5-2C		
Parameter	***Fuel A***	Fuel B	Fuel C	***Fuel A***	Fuel B	Fuel C
Change in Maximum Output % relative to current	**+15.7**	+17.5	+15.8	**+17.3**	+13.5	+25.3
Change in Fuel Rate per KW (LHV)	**-13.8**	-9.1	-13.8	**-12.7**	-8.6	-18.2
NO_X Emission without steam injection	**44**	79	7	**45**	79	<10
NO_X Emission with steam blend	**24**	22	NA	**23**	25	NA
Injected Steam/Gas mass ratio	**0.1**	0.5	NA	**0.1**	0.5	NA
Cost for first unit retrofit	**$3.32 million**			**$3.39 million**		
Cost for subsequent units	**$3.02 million**			**$2.49 million**		

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_X 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_X emission of 42ppm falling to 25ppm with steam addition of 10% by weight.
- Fuel C can give exceptionally low NO_X emissions of <10 ppm with no additions
- Costs for retrofitting these machines are $3.3 million for the first of each model falling to $2.5-3 million for subsequent units.

No additional technical of development work is considered necessary in this field. The next logical step will be to demonstrate CO_2 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
- The final project report is attached in Appendix A under the same heading.

1.2.3.2 Standardized PCDC

Task 2.3 Systems Integration and Optimization
Technical Provider: Jacobs Engineering
Co-Funder: Klimatek

Highlights

- Screening in 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 recommendation for a standardized PCDC is to comprise the following step:
  - Air blown ATR
  - High pressure steam production from waste heat recovery
  - High temperature and low temperature shift reaction
  - Two-step aMDEA CO_2 absorber with stripper and HP/LP-flash
  - Either steam injection or saturation
  - Fuel mix containing 50/50 Hydrogen/Nitrogen and steam for NOx control
- 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_2 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.

Summary

The study was carried out in collaboration with IEA GHG program under the Annex 16 subtask A. The focus was pre-combustion technology for a large natural gas fed 400 MW combined cycle power plants, i.e. the Norwegian CCP scenario. It should be mentioned that the CCP studies only covers the initial phase of the IEA program. The IEA program aims at demonstrating the technology at a later stage.

The project was divided into two phases wherein the aim of phase 1 was to assess previous studies covering PCDC technology for 400 MW combined cycle plants in order to identify starting points for efficiency, cost and concept. The study was carried by Norsk Hydro as an in-kind contribution. The key sources were:

- CCP Advanced Syngas Study
- Hydrokraft Project (Norsk Hydro)
- Naturkraft Retrofit (Norsk Hydro)
- Different IEA studies

The assessment showed great deviation in investment cost for the PCDC technology part between the different studies. Even after aligning the scope the difference in cost amounted to almost 100% between lowest cost and highest cost study. For efficiency there was a consensus at around 43-44% (LHV). The recommendation for the basis configuration was:

- Desulphurisation unit
- Preheating of feed streams in fired heater
- Air blown ATR
- High pressure steam production downstream of ATR

- HT and LT shift configuration
- Two-step aMDEA system with HP/LP-flash and stripper
- Either steam addition or saturation
- Fuel composition – approx. 50/50 H_2/N_2 (dry basis) with 15-20% water
    - Nitrogen content to be determined by maximum air extraction
- Minimum heat integration with gas turbine HRSG

The phase 2 of the study was contracted to Jacobs Consulting and contained the following focus areas:

- Fit for purpose selection and application of codes and standards
- Standardization of major equipment items
- Prefabrication of modules
- Modularization of components
- Integration and reduction of general facilities and utility systems
- Value engineering
- Capacity specifications
- Repeat manufacturing and construction

A base plant was developed based on a retrofit design. Based on brainstorming session several options were investigated with the result given in Table 15.

Table 15 Electricity production costs

		Electricity production cost	**Spec. Investment**	**Overall Efficiency**
		USD/MWh	**USD/kWe**	**-**
NGCC	**Standard power plant**	**33.69**	**461**	**55.9%**
PCDC CC	**Reference fuel plant**	**57.08**	**1076**	**41.3%**
Case A	Pressure drop	56.84	1092	42.1%
Case B1	SC 1.4	56.32	1063	42.1%
Case B2	SC 1.0	55.54	1050	42.9%
Case C1	NG Bypass 10%	55.03	1024	42.5%
Case C2	NG Bypass 20%	53.04	973	43.6%
Case C3	NG Bypass 30%	51.05	921	44.8%
Case C4	NG Bypass 40%	49.09	869	46.0%
Case C5	NG Bypass 50%	47.11	816	47.2%
Case D	HT shift only	55.60	1041	42.1%
Case E	Single stage CO_2 removal	59.56	1034	37.2%
Case F	Fired heater	56.81	1063	41.1%
Case G	Fuel gas preheat	55.38	1036	42.4%
Case H	Fuel gas saturation	56.82	1071	41.5%
Case I	CO_2 quality	56.51	1049	41.3%
Case J	Integration/air extraction	56.17	1034	41.3%
Case K	Combination ST/Air Comp.	56.04	1036	41.6%

An optimized concept was established and compared with results from the base case option. CO_2 avoided cost for the different options was estimated using the IEA GHG model.

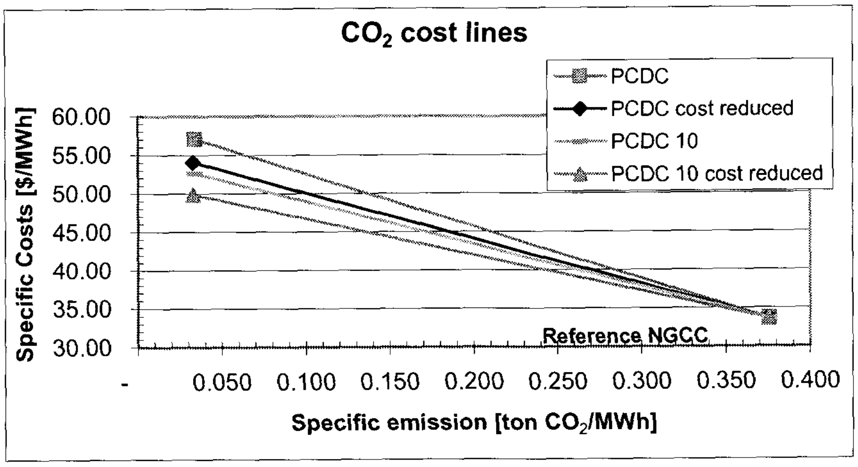


Figure 9 Cost lines reference and reduced cost PCDC plants

From the cost reduction part the cost reduction curves (Figure 9 and 10) were developed:

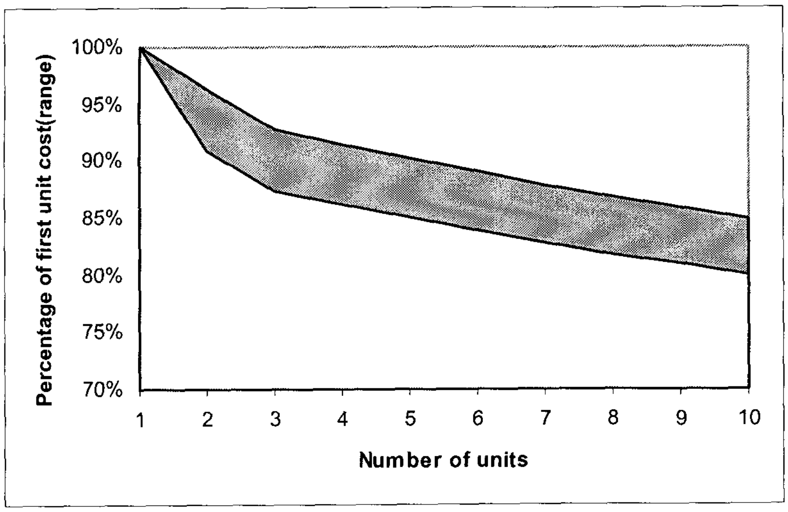


Figure 10 Cost Reductions for Multiple Units.

Conclusions

Overall benefits showed that approximately 20% reduction in CO_2 avoided cost could be achieved by cost reduction measures and 15% reduction could be obtained from value engineering and optimization. Thus leading to an overall reduction of 30% from base case to optimized case based on standard design

Recommendations for Further Work

For future work emphasis 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.

Reports and Publications

- The final project report is attached in Appendix A under the same heading.

1.2.3.3 Very Large Scale ATR

Task 2.3 Systems Integration and Optimization
Technical Provider: Jacobs Engineering
Co-Funder: CCP

Highlights

- Study established that the capture of CO_2 from the Alaska case study using VLS ATR can be implemented with all major equipment as a single train design, including compressors, CO_2 removal system and reforming section.
- The power balance suggests that there is no clear advantage of the AGHR system in this application over simple ATR.

Summary

The CCP elected to compare the feasibility and cost of CO_2 capture from combustion processes using four case studies to evaluate the technical performance and costs of the alternative capture systems. One case study was based on distributed gas turbines based at BP's Prudhoe-Bay central gas facility in Alaska. The CO_2 sources were 11 gas turbines driving gas compressors, firing the associated gas from oil producing fields in the area.

This study 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_2 removal. 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.

Key design decisions in this evaluation were use of air blown or oxygen blown ATR. Air blown was selected by the pre-combustion team, as it produces a fuel gas mixture which could be burned without the generation of high NO_X emissions. Further options included the use of conventional ATR or ATR heat exchange reformer combinations, the latter case being selected for this study, based on the Synetix advanced gas heated reformer, the design information for which was supplied to Jacobs by Synetix. An intended study of the simple ATR design case with a second vendor could not be completed due to issues of the background IP.

The basis for the design was the production of 1200 MW (thermal LHV basis) of Decarbonized fuel gas from the locally produced natural gas in a single train plant, recovering a minimum of 90% of the carbon in the feed as CO_2 at minimum 97% purity. The product fuel mix was required at 25 barg to facilitate firing on the gas turbines.

Parametric studies were undertaken to establish an optimal arrangement. The steam: carbon ratio was selected at 1.25 which represents the highest efficiency not requiring special catalyst provision in the autothermal reformer.

A proportion (20%) of the fresh feed to the ATR is by-passed around the AGHR stage, which as Synetix have confirmed, will permit the unit to be designed as a single train item.

A two-stage MDEA CO_2 removal system (with lean and semi-lean solution circuits) was selected, requiring 130MW lower re-boiler duty and a 40% reduction in stripper column diameter compared to a single stage design. This offsets the 60% higher pumping cost and taller columns of the two-stage design.

The fuel-mixture contains 35 mol% nitrogen and 63 mol% hydrogen on a dry basis with traces of other components- this mixture is saturated with 17 mol% water to reduce the peak adiabatic flame temperature in the gas turbine combustors which reduces the formation of NO_X. This saturation is achieved in a saturator tower by contacting with water at 148 °C. Jacobs estimates of the NO_X emission from the gas turbines at 42 ppm. for the fuel as generated was confirmed by the subsequent GE study which further demonstrated that NO_X levels of less than 25 ppm could be met with the addition of 10 wt% (or 6.7 mol%) steam. The saturation is achieved by contacting the gas with water at moderate temperature rather than by steam injection, this maximizes the thermal efficiency of the process.

The design can be constructed as a single train plant; the largest equipment is the CO_2 removal section with the LP flash vessel at 11 M diameter. Equipment vendors and fabricators have confirmed capability to supply the vessels and internals for such a system. Vendor evaluations of the large process air compressor and CO_2 product compressor have confirmed that single machines could be used for each of these duties. Some pumps (specifically the semi-lean solution pump) will require two units, but this is not expected to have a significant impact on the total system cost.

The overall system thermal efficiency was 74.9% thermal on LHV basis in terms of Decarbonized fuel heating value. Data from a study of retrofitting the GE gas turbines in the case study indicates that the substitution of this fuel for the natural gas will result in a reduction in fuel requirement of approximately 13% on LHV basis, the VLS ATR product fuel is very close in composition to that used as the basis for design of the retrofit study. This suggests that the overall efficiency of Decarbonizing gas turbines by use of Decarbonized fuel produced by VLS ATR technology will be 84.6%, ie.18% additional natural gas use.

The high power requirement for process air and CO_2 compression necessitates power generation by an additional gas turbine, fired on the Decarbonized fuel product, which increases the size of the decarbonization plant and adds to the cost. Preliminary studies of conventional ATR concepts not using gas heated reforming showed that the additional steam generation of these systems allowed the power balance to be maintained by steam turbines alone which would eliminate the need for the gas turbine. This suggests that although the more sophisticated AGHR has higher process efficiency, it is unlikely to give overall benefit over simple ATR in this application. The simple air blown ATR will have a fuel mix containing higher nitrogen concentration which is likely to give improved turbine performance and lower NO_X emission. There may be capacity limits on some sections of the simple ATR plant due to the higher air-flow and system throughputs, which would require study before a definitive selection could be made between conventional ATR and use of the AGHR for this service.

Equipment size and air compressor power requirement would be reduced by using oxygen rather than air; this option would require study to determine whether these advantages justified the additional cost of the air separation unit.

Conclusions

- 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.

Recommendations for Further Work

The requirement for further work on this area is dependant upon the economic evaluation of this and other PCDC capture routes. 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.

Reports and Publications

- Scott, S., 'Large Scale Facility for Hydrogen/Nitrogen Fuel mix' Final report to the CCP, Dec 2002.
- The final project report is in Appendix A under the same heading as this summary.

1.2.3.4 Process Design Evaluation of Advanced Syngas Systems for Decarbonization of Natural Gas

Task 2.3 Systems Integration and Optimization
Technology Provider: Foster-Wheeler
Co-Funder: CCP

Introduction

This report covers the evaluation of 7 different process schemes for pre-combustion de-carbonization of natural gas. The schemes consist of variations of a basic process using partial oxidation and shift reactions, followed by CO_2 removal to produce a hydrogen rich gas that is then combusted in a gas turbine to generate power.

The seven cases evaluated were:

- Base Case:- Standard scheme against which other cases were evaluated
- Case One:- Addition of a Gas Heated Reformer to the process scheme
- Case Two:- Use of Gas / Gas Exchangers to recover heat form the CPO Outlet
- Case Three: - Reduced Specification CO_2 Recovery
- Case Four:- High pressure operation
- Case Five:- Partial high pressure operation
- Case Six: - Reduced Specification CO_2 Capture.

A more detailed explanation of the cases is given below.

Results

A +/- 40% cost estimate was developed for each case to allow a comparative assessment of the cases. The results are summarized below.

Table 16 Comparative Assessment of Proposed Cases

Case	*Capital Cost MM$*	*Delta From Base Case MM$*	*Net MW power*
Base Case	267.9	0	367.7
Case One	273.2	+5.3	296.1
Case Two	258.4	-9.5	326.1
Case Three	265.8	-2.1	367.7
Case Four	345.2	+77.3	360.0
Case Five	292.7	+24.8	367.7
Case Six	262.7	-5.2	356.6

Conclusions

- None of the alternatives offers a significant advantage over the Base Case in terms of capital cost or net power production. Taking into consideration the accuracy of the estimate, Cases 1, 2, 3 and 6 require similar capital investment as the Base Case. However, only Case 3 matches the net power of the Base Case. Higher pressure operation, Cases 4 and 5, is unattractive in terms of capital cost.
- The Power Block constitutes around 60% of the total project cost. Therefore, even significant changes to the Reformer/CO_2 Removal Blocks have relatively little impact on the total installed cost.

- Case Three shows that a reduced product specification for the CO_2 appears beneficial and seems a good option to pursue.
- Cases Four and Five indicate that high pressure operation is not favorable and can probably be ruled out.
- Case Six shows that reducing the carbon capture reduces the installed cost of the project. However, even allowing for the fact that this case is not fully optimized, it does not appear particularly attractive when compared to the Base Case.
- This leaves Case Two and allowing for the effect of higher methane conversion Case One. These cases both appear comparable with the Base Case, but neither appears to offer a significant advantage.
- None of the cases offers a major benefit in reducing installed cost or increasing power production when compared to the Base Case to offset the additional technical risks involved.
- If further study work is undertaken then most benefit would be gained from concentrating on the Base Case, Case One and Case Two configurations.

Publications:

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

1.2.3.5 Compact Reformer with Advanced Pressure Swing Adsorption System for Hydrogen Production

Task 2.3 Systems Integration and Optimization
Technology Provider: **Air Products, Ltd.**
Co-Funder: **DOE**

Highlights

- The work scope was reduced to 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_2, 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 $C0_2$ 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_2 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_2 by utilizing refinery fuel gas streams as feed to the combined Reformer/PSA unit and subsequently utilizing the produced hydrogen as a substitute fuel in the refinery heaters and boilers. The CO_2, captured as a pressurized product from the Gemini PSA unit, 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:

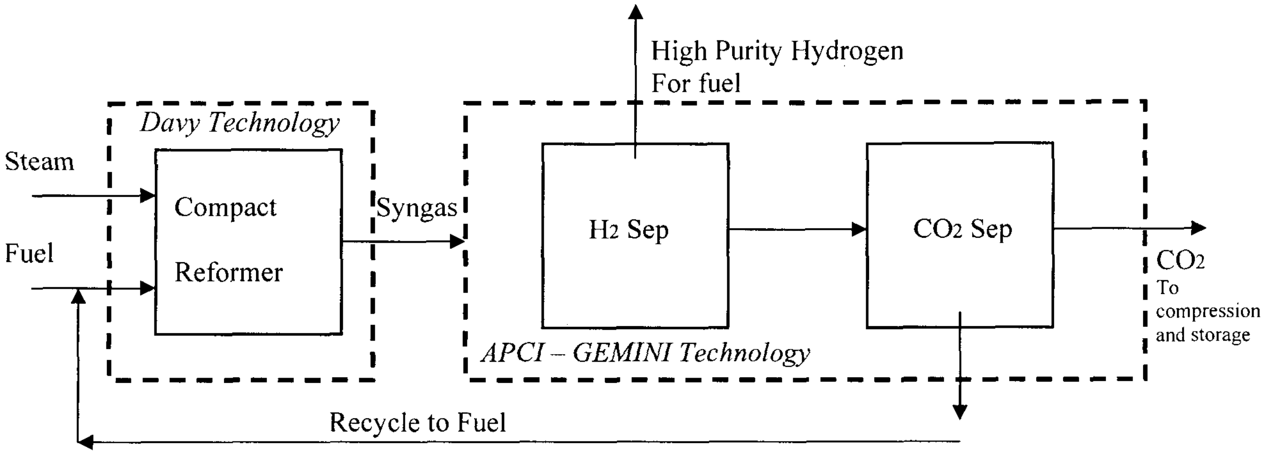
- Compact Reforming – Davy Process Technology
- Gemini Pressure Swing Adsorption (PSA) – Air Products Limited

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_2 product.

The overall schematic for the combination (Figure 11) is as follows;

Figure 11 Overall Schematic for Combined Davy and Gemini Technology



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_2 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.

1.2.5.1 Generation of H_2 Fuels

Task - 2.2 Fuel-Grade Hydrogen Generation
Technology Providers: Institute for Fuels Technology (IFE)
Co-funder: Klimatek

Highlights

- 90% CO_2 capture possible with Cao/$CaCO_3$ recycle concept
- The concept was developed for heaters and boilers as well as combined cycle gas turbines
- High conversion of methane at lower temperature than classical steam methane reforming is possible
- From an efficiency perspective the challenge of the CaO/$CaCO_3$ is the heat-integration.

Summary

In a research project recently started by IFE, a new integrated reforming reaction for hydrogen production is being developed. Hydrogen gas is produced from natural gas and water in a modified reforming reaction where CO_2 reacts with a metal oxide (MeO, e.g. CaO) to form a metal carbonate ($MeCO_3$, e.g. $CaCO_3$). The carbonate is decomposed thermally in a separate reaction and the metal oxide is recycled back to the reformer.

CCP engaged IFE to conduct at study describe how such a CO_2 removal process can be integrated in a hydrogen Combined Cycle Power Plant (CCPP) and a hydrogen steam boiler, the NorCap and EU refinery scenario respectively. The main difference is the fuel conditions:

- Generation of a N_2-diluted, H_2 fuel gas stream for gas turbines (H_2/N_2-ratio: 50/50) at high pressure
- Generation of a hydrogen-rich fuel (+ 95%) for steam boilers at low pressure.

.

The main reaction steps in the process are given below:

$$\text{Reforming: } CH_4(g)+H_2O(g)\longleftrightarrow CO(g)+3H_2(g) \qquad (1)$$

$$\text{Shift: } CO(g)+H_2O(g)\longleftrightarrow CO_2(g)+H_2(g) \qquad (2)$$

$$\text{Carbonation: } CaO(s)+CO_2(g)\longleftrightarrow CaCO_3(s) \qquad (3)$$

$$\text{Overall: } CH_4(g)+2H_2O(g)+CaO(s)\longleftrightarrow CaCO_3(s)+4H_2(g) \qquad (4)$$

The advantage of the CaO/$CaCO_3$ cycle is the equilibrium conditions. In the standard reforming process (without CaO), the hydrogen content increases with increasing temperature and reaches a maximum of about 76% at 950°C for CH_4:H_2O=1:2 and about 77% at 850°C for CH_4:H_2O=1:4. This increase is governed by the endothermic reforming reaction. On the other hand, with CaO, the hydrogen content reaches a maximum of about 90% at 685°C for CH_4:H_2O=1:2, and about 97% at 650°C for CH_4:H_2O=1:4 (in both cases the formation of $Ca(OH)_2$ has been taken into account). At lower temperatures, essentially all of the carbon oxides are removed by the sorbent and the major impurity in the hydrogen gas is CH_4. At higher temperatures, more CH_4 is converted and the main impurities are CO and CO_2. Without the CO_2-acceptor, a reformer temperature of about 825°C would be required to achieve the maximum H_2-content (followed by shift reaction and CO_2-separation) comparable to what can be achieved with the CO_2-

acceptor system at about 650°C. Figure 12 shows conversion curves by methane reforming and CaO-reforming.

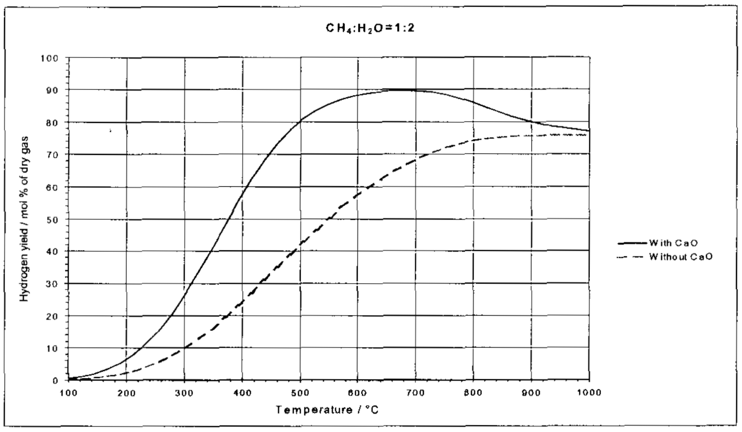


Figure 12 Equilibrium hydrogen content as a function of temperature with and without the CO_2-sorbent. P=5 atm and $CH_4:H_2O=1:2$

The process evaluation gave the following overall result (Figure 13) for the NorCap scenario.

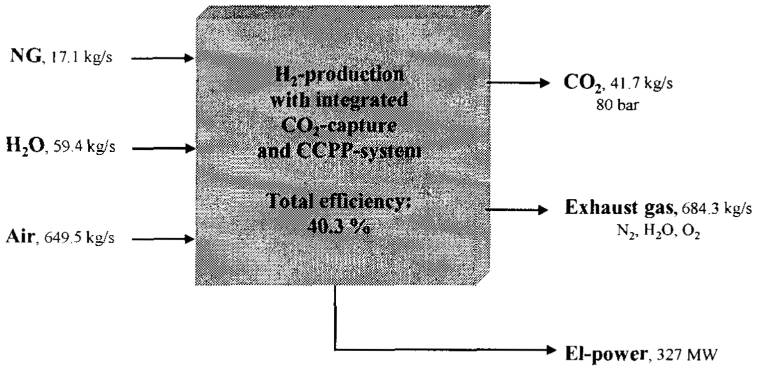


Figure 13 H_2 Production with Integrated CO_2 Capture – NorCap (Norwegian) Scenario.

And for the EU refinery (Figure 14):

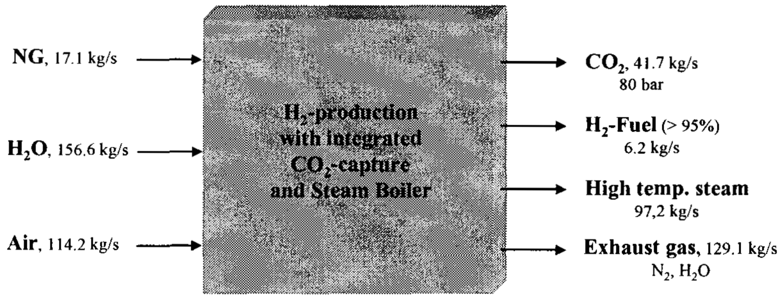


Figure 14 H_2 Production with Integrated CO_2 Capture in the UK Scenario.

From an efficiency perspective the challenge of the $CaO/CaCO_3$ is the heat-integration. Due to the high temperature required for carbonization a significant amount of excess heat is generated. For the refinery case the excess heat is used for steam generation thus the process generates about 360 t/h of high pressure steam. This is enough to produce about 120 MW of electrical power via steam turbines, which should be compared with the 554 MW of hydrogen produced. The total efficiency excluding steam credit and electricity is 71.4% (LHV). Including steam credit and power requirement the efficiency increases to 83.3% (LHV)

Conclusions

The HYSYS simulations show that 90 % CO_2 removal is possible using the IFE concept. Although reactor design is not a part of this pre-study, it should be pointed out that the assumptions are quite demanding on the reactor efficiency, especially because fluidized beds are one stage reactors.

The efficiency of the CCPP is significantly lower than comparable CO_2 removal processes. Bolland et al (1999) reported that the best known concepts yield LHV efficiencies in the range of 49 - 51 %. The main reason for the low efficiency in the present concept is the low pressure in the reforming process. If a continuous process in which the reforming reaction is kept at a high pressure (15bar) while the regeneration process is at low pressure (1 to 5 bars), we could avoid a fuel compressor. This would increase the efficiency to 44.3 %.

However, due to the high temperatures and circulation of large amounts of solid material, it seems difficult to reach the same efficiency figures as comparable concepts. Heat losses and auxiliary power demand will inherently be higher in the present concept.

For hydrogen fuel production for heaters and boilers it seems the efficiency penalty is less if surplus heat can be used efficiently.

Reports and Publications

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

1.3 Oxyfuel Technology

Introduction

The CCP investigated the potential savings that combustion using pure oxygen (oxyfiring) may give in CO_2 capture, compared to conventional combustion with air, is the mission of the Oxyfuel Team. This involved monitoring and sponsoring R&D activities whose results may contribute to further reduction of CO_2 capture costs by the year 2010.

When CO_2 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_2 capture, however, oxyfiring has the unique advantage of generating an effluent stream composed almost exclusively of CO_2 and H_2O. It is very cheap and easy to capture CO_2 of the necessary purity for sequestration from this stream by water condensation.

Another unique environmental advantage of oxyfiring is the complete avoidance of NOx emissions that are usually generated by high temperature reaction between nitrogen and oxygen in conventional air combustion. The potential additional benefit deriving from eliminating NOx capture systems has not been quantified in this phase of the CCP, but should be taken into consideration for future work.

Combustion of fuel in pure oxygen produces a much higher temperature than combustion in 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_2 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 component of 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_2 capture considerations, their application to oxyfiring may contribute to reduce the costs of CO_2 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, however, modifications to current commercial machines are necessary, at least in the combustion zone, to maintain high thermodynamic efficiency..

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

1. Definition of an Oxyfuel baseline, potentially applicable "today": CO_2 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_2 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_2 avoided cost" (47 \$/ton CEM vs. 43 \$/ton AP). Additional AP cases reduced the CO_2 avoided cost by a further 10%. The CO_2 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_2 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, and minor technical risk. A commercial-scale demonstration of oxyfiring is needed to provide a truth case for the process. In addition, the air separation unit needed for the Grangemouth scenario is about 20% larger than the largest existing unit. This level of cost could make it attractive in countries applying high value 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_2 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 avoid or minimize 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_2 in the case of oxyfiring. However, between the power required for air separation and for CO_2 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_2 capture, there has 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_2 capture, the studies have generally looked at CO_2, water, and combinations of those two.

The Norwegian R&D Company 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 be reached in operating conditions that cannot be realized in current commercial equipment. (E.g. 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_2 capture and sequestration – often requiring additional CO_2 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 is estimated that the cost to develop a novel turbine is in the range of the tens of millions of US Dollars. This type of development cannot be carried out in the CCP frame.

Novel technologies for air separation

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

Three consortia are developing these membranes:

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

All of these consortia are targeting the years 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, in the course of the study it became clear that since the membranes may extract only about 40% of the oxygen from the air stream and 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.

In Grangemouth this could result in the substitution of 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 (Combines Cycle Gas Turbine) systems. Different cases were considered by AP (all of them with considerable power export). The CO_2 avoided cost for the base case was evaluated by the CEM Team at 35.5 $/ton (vs. 37 $/ton by AP) with about 20% saving compared to the Oxyfuel Baseline. The other cases studied by AP allowed reduction of CO_2 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_2 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 because of the large associated export of power. In the new-built perspective, some technology providers are studying direct integration of ionic transport membranes into 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 in an EU-funded project 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 from 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_2 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 capability, whose development is among the targets of the project. Alstom calculated a CO_2 avoided cost in the 25-35 $/ton 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 effort is carried out by Praxair in developing 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 C1 – C2 fraction of natural gas, since C3-C4 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_2 capture in the 15-20 $/ton range.

These integrated systems are promising developments but are still at an early stage with considerable uncertainty. Commercialization expected not before 2010.

Chemical Looping

The only major R&D Project directly funded through the CCP Oxyfuel team was on chemical looping combustion in a consortium formed by BP (Coordinator), Alstom Boilers, Chalmers University, CSIC and Vienna University in a 2-year EU-cofunded project concluding in December 2003. Total budget of this project was 1.5 MM€.

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

Fuel reactor: $MeO + CH_4 \rightarrow Me + 2H_2O + CO_2$
Air reactor: $Me + 0.5O_2 \rightarrow MeO$

This project focused on atmospheric pressure applications typical of the CCP UK Scenario. The concept is also applicable to higher than atmospheric pressure in gas turbine systems as already proven in another project outside the CCP funded by the DOE. In this case the trade-off is between thermodynamic efficiency and percentage of captured CO_2 since chemical looping combustion takes place at relatively low temperatures (800-900°C). The ability of gas turbines to withstand "dust" from the chemical looping process is an added uncertainty in this case.

The main risk in developing the technology is the availability of a suitable material able to withstand repeated oxidation/reduction cycles while maintaining both chemical activity and mechanical resistance. The screening activity performed during the first year of the project identified a limited number of materials for further development.

One of the main objectives of the program was to show "Proof-of-Feasibility" of the technology. A pilot unit was designed and built to show feasibility. 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/Al2O3 for a total of about 300 hrs. 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.
A 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.

CCP should consider co-funding a subsequent phase of the project, which could achieve demonstration of the technology by the end of 2006 with the goal of 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 show the way to drastically reduce, or even eliminate, NOx emissions. This additional advantage has not been quantified in the 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_2 avoided cost of 40-45 \$/ton, corresponding to a CO_2 capture cost of 35-40 \$/ton, is 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 development in the field of gas turbines 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 perspectives.

- Novel membrane systems for oxygen production, currently under development and expected for commercialization by 2008-2009, do not look suited for revamping of existing boiler systems, since incomplete extraction of oxygen from air mandates export of power. 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 CFBs. Furthermore it produces rather pure CO_2 compared to the Oxyfuel Baseline. A decision on the opportunity 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

- Based on the economic analysis results of the Oxyfuel Baseline evaluation, the CCP should evaluate the option of funding a demonstration test of retrofitting and operating a small boiler in oxyfiring service to remove the remaining obstacles for commercial application.

- In case of a positive economic evaluation of Chemical Looping., the team recommends that the CCP fund a second phase of the R&D Project. The Partnership should be completed by a commercial catalyst manufacturer to bring in expertise on the scale-up of the production methodology of the material to commercial scale. Two options are recommended:

    1. **Aggressive development**: A 3-year project targeting a demo-unit operating by the beginning of 2006 (revamping an existing demo-CFB unit, as suggested by Alstom), with the first half of the project devoted to optimization of the solid material and definition of the scale-up procedure. Total budget for this project may be estimated in the 4-5 MM\$ range.

    2. **Staged development**: A 2-year project focused on the solid material issues and exploration of the whole range of possible applications, leaving the demonstration to a third phase starting in 2006. Budget for this approach estimated in the 2-2.5 MM\$ range.

- Low-cost oxygen production is a powerful driver independently from "greenhouse effect" issues. Oxyfuel capture may benefit in the future from advances in the various technologies under study. The Team recommends monitoring these projects with periodic updated evaluations.

- The Team recommends that CCP fund an activity to quantify the advantages deriving by reduction of NOx emissions through oxyfiring compared to combustion in air.

- The Team recommends that the overlap and synergism between oxyfuel and PCDC technologies be investigated. For instance, integration of oxyfiring and steam reforming may be an interesting (and possibly patentable) option.

1.3.1 Cost and Feasibility Study on the Praxair Advanced Boiler for the CO_2 Capture Project's Refinery Scenario

Task 3.1 Advanced New/Retrofit Boiler Designs
Technology Providers: Praxair
Co-funder: DOE

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_2 capture energy cost savings are approximately 80% when compared to the baseline case.

Summary

Praxair, Inc, is leading a consortium supported by the U.S. 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_2 and water from which the CO_2 can easily be separated. The technology promises to reduce the cost of capturing CO_2 from new boilers and potentially also 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:

- match the performance of a specified boiler within the CCP's Refinery Scenario (Grangemouth, Scotland)
- and
- to capture the CO_2 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_2 capture. This is required so that a net capture cost per ton of CO_2 can be derived.

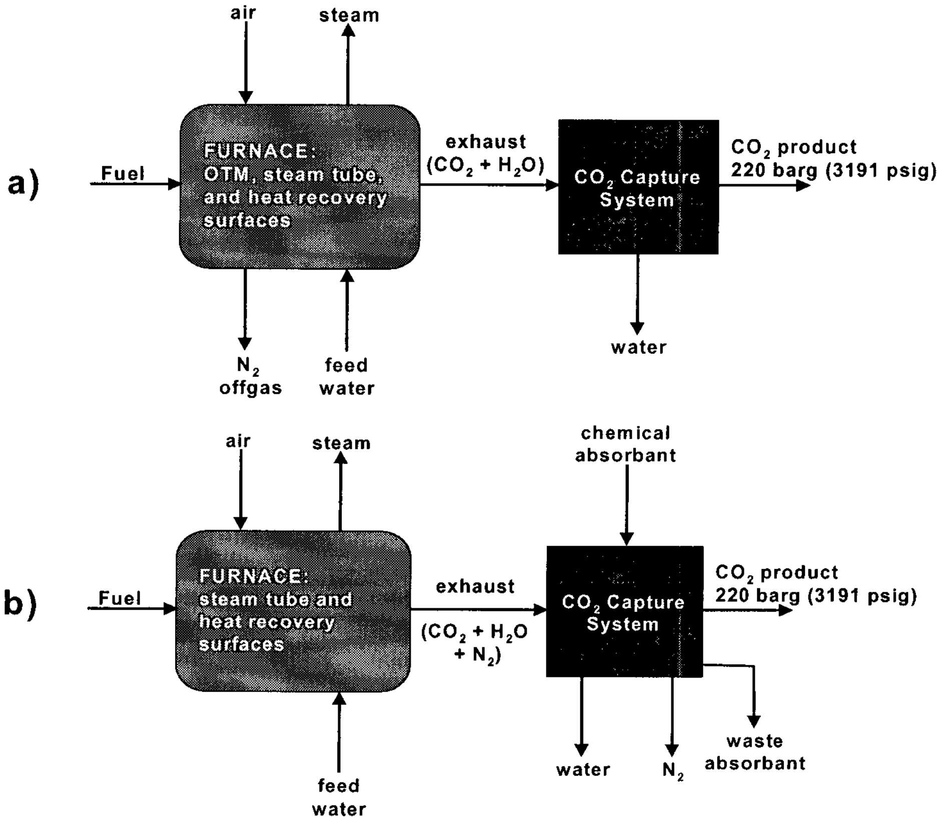
Results

One effective approach to produce a CO_2 rich flue gas from a combustion process is to use pure oxygen rather than air as the oxidant stream. Oxygen fired combustion systems offer a number of advantages over air fired systems. Over the last 2-3 decades Praxair has demonstrated that oxyfuel fired processes offer (i) increased fuel efficiency, (ii) reduced pollutant emissions (e.g., NO_x), and (iii) improved productivity/throughput. These advantages coupled with the fact that the exhaust products contain high concentrations of CO_2 make oxyfuel fired systems ideal candidates for high efficiency boilers with CO_2 sequestration.

As with any innovation, the performance advantages must justify the associated costs of adopting the new technology. To date, the primary issue limiting the application of oxy-fuel fired systems to a greater market is the cost of producing oxygen (i.e., separating O_2 from other gases present in air). Systems with high thermal efficiencies have typically not been candidates for oxy-fuel conversion as the incremental improvement in thermal efficiency is 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_2 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 by 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. The integration of the OTM materials into the firebox of a boiler offers several inherent advantages. First, as mentioned above, the flux of O_2 through the OTM material is driven by the gradient of the O_2 partial pressure across the

Figure 15 Oxyfuel Combustion Options with CO_2 Capture.



Supporting the combustion process on the surface of the OTM tube effectively creates a sink for O_2 on the process side of the tube, thereby allowing significant O_2 fluxes to be achieved. Additionally, heat generated by the combustion process can be utilized to maintain the OTM materials at their desired operating temperature. Steam tubes placed among the OTM materials capture the balance of the heat generated by the combustion process.

Thus, the implementation 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_2 sequestration in a technically compelling and economically competitive manner. Figure 15 (a) and (b) illustrate the basic configuration of an OTM boiler system with CO_2 capture and a conventional air-fired system with CO_2 capture. Because of the low concentration of CO_2 in the exhaust of the air-fired system, a chemical absorption process is required to remove the CO_2, 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 such that each tube is fed from a common air source. Steam tubes run parallel to the OTM tubes and are placed such 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 spent exhaust is purified and compressed through a series of compressors and coolers to produce a purified CO_2 product.

Based on the current design, approximately 13 MW (43 MMBTU/hr) less fuel is required in the Advanced Boiler relative to the conventional air-fired boiler sized for this case. However, because of the pressure drop across the OTM manifold, a large blower is required 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_2 capture system requires another 4.2 MW (14 MMBTU/hr) of energy and 0.3 m^3/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_2 capture system to the Advanced Boiler also shows an energy efficiency gain over the conventional boiler.

The analysis showed that based on the economic information gathered to date, a boiler with integrated ceramic membranes has the potential for substantial capital and operating cost savings when CO_2 capture is required. The capital cost savings are estimated to be greater than 60%, and the CO_2 capture energy cost savings are approximately 80%. In the case of a more conventional boiler without CO_2 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.

1.3.2 - Study of Advanced Gas Turbine System

Technology Providers:	Alstom
Co-funder:	Klimatek

Highlights

- Economic evaluation revealed very promising figures, estimating costs of CO_2 avoided of 22.1 US$/ton to as low as 8.3US$/ton, if a value of 20 US$ per ton produced CO_2 (as suggested by the CCP) is considered.

Summary

This study evaluates the techno-economic performance of gas turbine power plants with zero or low CO_2 emission. The plant concepts make use of "Mixed Conducting Membranes" (MCM) to extract oxygen from the inlet air and thus enable combustion of gaseous hydrocarbon fuels in a nitrogen-free environment. This technology is being developed in the ongoing EU FP5 Integrated Research Project "AZEP" (see www.azep.org). Unlike the combined cycle processes investigated in the AZEP project, the concepts considered here are simple cycle configurations. The scenario is based on the CCP Scenario D, a BP gas gathering and processing installation in Prudhoe Bay, Alaska.

Results

Three different base configurations were identified, each run in two different modes (with and without supplementary firing). These six cases were compared to a conventional non-capture gas turbine plant. The thermodynamic process simulations showed penalties in terms of the net electrical efficiency between 2.4 and 6.8 %-points for the different configurations. These penalties include the capture, purification and compression of the carbon dioxide. The economic evaluation revealed very promising figures, estimating costs of CO_2 avoided of 22.1 US$/ton to as low as 8.3US$/ton, if a value of 20 US$ per ton produced CO_2 (as suggested by the CCP) is considered.

Reports and Publications

- The final project report is in Appendix A under the same heading as this summary.
- Presentation at the "NorCap Seminar", Trondheim, October 2003, "Techno-economic evaluation of a power plant using MCM", by D. Buecker, D. Holmberg.

1.3.3.1 - Zero Recycle Oxyfuel Boiler Pre-Study

Technology Providers:	Alstom
Co-funder:	CCP

Highlights

- A scoping study for main parameters necessary for successful zero-recycle oxyfuel boiler development was completed.

Summary

Alstom Power Inc and Praxair Inc were engaged by the CCP to conduct a pre-study which provides a cost comparison between zero recycle and flue gas recycle oxyfuel boiler systems. Both systems include oxygen plants and CO_2 removal subsystems. Captured CO_2 will be compressed and injected into an oil field to promote additional crude oil recovery and/or sequestered into some other suitable reservoir. The aim of this pre-study is to determine whether the zero recycle case offers significant reduction in the overall capital and/or operating cost.

Results

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. Potential savings were offset by increased capital cost.

- Concept: Boiler designed for Oxyfuel combustion without external flue gas recycle, to establish benefits such as boiler compactness, efficiency improvements to assess continued concept development
- Scope: Back to back comparison of recycle versus non-recycle systems (boiler/steam turbine, air sep., CO_2 separation & compression)
- CCP contract with Praxair and Alstom Power in 2001

The main conclusions may be summarized as follows:

- Higher grade materials required to fabricate boiler are needed than are readily available.
- Cost comparison showed 'somewhat' lower Capex, electricity and CO_2 capture costs without recycle but…
- Cost savings attainable would be offset by these increased material costs
- Continuation of study not recommended.
-

Reports and Publications

- The final project report is in Appendix A under the same heading as this summary.
- "A Study on CO_2 Capture from a Gas-fired Boiler by Oxyfuel Combustion without Flue Gas Recycle", presented at the 2001 Joint AFRC/JFRC/IEA International Combustion Symposium: Towards Efficient Zero Emission Combustion - Advances in Air-fuel and Oxy-fuel Technologies, September 9-12, 2001.

1.3.3.2 - High Pressure Oxyfuel Boiler Study

Technology Provider: Mitsui Babcock
Co-Funder: CCP

Highlights

- Cost estimates for a high pressure oxyfuel boiler system was completed.

Summary

The concept addressed within this project is based upon a novel process whereby the fuel gas is burnt in a mixture of oxygen and recycled flue gas within a furnace. As a consequence of the removal of the inert nitrogen ballast from the combustion process, the system results in a flue gas of high carbon dioxide content. The flue gas exiting the boiler is cooled to condense and remove the water, then via compression of the remaining gas a high pressure carbon dioxide end product is produced.

The aim of this High Pressure Oxyfuel Boiler Pre-Study is to establish whether, by operating at gas side pressures greater than atmospheric pressure significant cost savings for CO_2 capture are achievable. It was expected that a pressurized Oxyfuel boiler would impact advantageously on both capital and operating costs. With considerable capital cost directly attributed to the air separation unit and the back-end clean up and CO_2 compression plant, it was necessary to determine whether designing for a pressurized furnace / boiler would result in a reduced physical size and operating cost of these system elements.

Results

The main conclusions arising from this study are: -

- ***Cost Per Tonne of CO_2 Removed –***
  The operation of a high pressure Oxyfuel boiler with appropriate ASU and CO_2 compression plant at the optimum flue gas pressure of 5 bara, resulted in a higher CO_2 removal cost in comparison to a new build atmospheric flue gas pressure boiler and supporting plant.
  - The total plant capital cost was estimated at £37.7m (11.2% increase compared to a new build atmospheric boiler with appropriate CO_2 plant and ASU cost of £33.9m).
  - The capital cost per tonne per year of CO_2 capture was estimated at £110.75 (14.8% increase compared to a new build atmospheric boiler with appropriate CO_2 plant and ASU cost of £96.50).
  - The Additional Operational and Annualized Capital cost per tonne per year CO_2 removal was estimated at £18.74(12% increase compared to a new build atmospheric boiler with appropriate CO_2 plant and ASU cost of £16.72).

  These figures should be quoted with a +/- 10% tolerance

- ***High Pressure Flue Gas Boiler Price –***

  From the boiler viewpoint a considerable contribution to the cost increase can be attributed to the price of the boiler pressure containment vessel. This shell was required to encapsulate the boiler radiant furnace and convective sections to allow for the 5 bara pressurized operation.

The high pressure flue gas boiler design resulted in an estimated 50% reduction in heating surface area in both the convective and radiative section of the furnace in comparison to a conventional atmospheric pressurized boiler with flue gas recycle.

- ***Comparison of HP Oxyfuel Plant Size with the Reference Atmospheric Oxyfuel Case***

  There is no envisaged reduction in the overall size of the plant as a result of designing for high pressure flue gas operation. From a boiler perspective, despite the reduction in heating surface area from the high pressure (HP) operation, the requirement to encapsulate the HP boiler in an appropriate pressure vessel with suitable internal maintenance access, results in no obvious space saving. In terms of the other main components of the plant, namely the ASU and CO_2 compression system, these are envisaged as having no significant change in overall size for HP operation compared with their atmospheric pressure counterpart.

Reports and Publications

- The confidential final project report is summarized here.

1.3.3.3 - Zero or Low Recycle Oxyfuel Boiler Study

Technology Provider: Mitsui Babcock
Co-funder: CCP

Highlights

- The proposed in-duct burner arrangement with zero or low flue gas recirculation as a means of restricting the adiabatic flame temperature to suitable value for the internal steel duct casing is not considered to be feasible.

Summary

The pre-study presented in this report covers the activities required to develop a basic boiler/steam generator design for a 'Zero or Low Recycle Oxyfuel Boiler' option. The previous studies were based on the Oxyfuel technology (oxygen and recycled flue gas firing) retrofitted to a conventional gas-fired refinery steam boiler. As an alternative to this, it is proposed to base the design of a new-build Oxyfuel boiler on a steam generator comprising horizontal flue gas path and vertical heating surfaces similar in style to a natural circulating Gas Turbine Heat Recovery Steam Generator (GT-HRSG). An in-duct burner arrangement is proposed with a number of fuel stages and inter-burner stage flue gas cooling through evaporative surface so as to limit the flame temperature and reduce the flue gas temperature to a maximum temperature of some 750°C - 850°C suitable for the internal stainless steel duct casing and entry to the superheater heating surfaces.

Results

1. From the results presented in the report it is concluded that for the new-build Oxyfuel steam generator concept, the proposed in-duct burner arrangement with zero or low flue gas recirculation as a means of restricting the adiabatic flame temperature to suitable value for the internal steel duct casing is not considered to be feasible. Depending on the oxygen stream mass flow rate, either the resulting balance between evaporation and superheat steam is incorrect or the oxygen content of the final flue gas is extremely high. The use of superheat surface between the later in-duct burner fuel stages is possible to achieve the required evaporation/superheat balance, but this option is considered to be uneconomic due the large number of fuel stages required (>14).

2. For both an economic and technically satisfactory design, the Oxyfuel steam generator concept is feasible with three in-duct burner stages and if flue gas recirculation is utilized. To achieve the correct boiler performance at the rated steam conditions and maintain sensible levels of oxygen in the final flue gas, some 75% flue gas recirculation is required.

3. For the reference new-build boiler (evaporation rate of 500,000 lb/hr) designed for oxygen and recycled flue gas firing, the basic total installed price is £33.5million or £101.39 per tonne of CO_2 captured per year. With the Oxyfuel steam generator design of the same steaming capacity, the total installed price is estimated to be some £30.0million or £90.80 per tonne of CO_2 captured per year. As a result, the comparison shows that the proposed steam generator design concept offers a reduction in installed price of some 10% when compared to the reference boiler design.

4. The approximate overall size of the proposed steam generating plant was compared against the conventional boiler reference design. The steam generator design is seen to offer a reduction in the height of the boiler plant, although the required footprint area approximately doubles.

Reports and Publications

The confidential project report is summarized here.

1.3.3.4 - Oxyfuel Power Generator Cycles Study

Technology Provider: SINTEF
Co-funder: CCP

Highlights

- Advanced thermodynamic power cycles for gas turbines were compared and evaluated. None were considered of sufficient interest to continue beyond these studies.

Summary

The purpose of this study is to assess and compare different so-called oxy-fuel power generation cycles. Of highest importance is to make an update on a previous IEA GHG initiated study on the "Water-cycle" in light of a concept put forward by Clean Energy Systems, Inc. Further, evaluations and comparisons of the so-called Graz-cycle and Matiant-cycle were done.

Several studies on oxy-fuel power generation concepts have been published. In many cases it is difficult to compare results and to judge the potential for "new" and "advanced" concepts. The computational assumptions are in many publications insufficiently described, intentionally or not. In this study, emphasis was made in order to obtain results on a technically realistic basis, as well as be able to compare different concepts on a common basis with respect to thermodynamic performance.

The overall intention of the report is to help establish a basis for deciding which concepts is worthwhile pursuing in the future.

Results

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_2 in the case of oxyfiring. However, between the power required for air separation and for CO_2 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_2 capture, numerous power cycles have been proposed in the literature. With the requirement that the working fluid used to moderate temperature in the combustion turbine must enable simple CO_2 capture, these studies have generally looked at CO_2, water, and combinations of those two.

The Norwegian R&D Company 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 be reached in operating conditions that cannot be realized in current commercial equipment. (E.g. 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_2

capture and sequestration – often requiring additional CO_2 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 is estimated that the cost to develop a novel turbine is in the range of the tenths millions of US Dollars.

Reports and Publications

- The project final report is included in Appendix A under the same heading as this summary.
- "A Thermodynamic Comparison of the Oxy-fuel Power Cycles Water-cycle, Graz-cycle and Matiant-cycle", International Conference on Power Generation and Sustainable Development, Liege, Belgium, 8-9 October 2001.

1.3.3.5 Oxyfuel Heaters and Boilers with Flue Gas Recycle - Cryogenic Oxygen Supply

Technology Provider: Air Products
Co-funder: CCP

Highlights

This work shows that it is feasible to apply Oxyfuel technology to a complete refinery system with multiple CO_2 emissions points spread out over a large area through a centralized oxygen supply system and a CO_2 recovery, purification, and compression facility

Summary

This feasibility study involved the potential application of Oxyfuel technology on a refinery-wide basis at the BP Grangemouth unit in Scotland. Previous studies in Oxyfuel technology have considered application for retrofit on a power station boiler and refinery process heaters.

A total of seven boilers and 13 process heaters of various types burning a mixture of refinery fuel gas and fuel oil form the basis of this study which results in the production of approximately 2.0 million tonnes per annum of CO_2.

The current study, primarily performed by Air Products (but involving specialist input from Mitsui Babcock and Foster Wheeler as subcontractors) considers the issues involved in modifying the process heaters and boilers for oxyfuel combustion and locating two world scale air separation plants totaling up to 7400 tonne/day of oxygen plus a CO_2 compression and purification system on a congested site.
In addition, a scheme is presented for distributing the oxygen around the site and collecting the CO_2-rich effluent from the combustion processes for purification, final compression, and delivery into a pipeline for enhanced oil recovery.

This work has shown is that it is feasible to apply Oxyfuel technology to a complete refinery system with multiple CO_2 emissions points spread out over a large area. This involves a centralized oxygen supply system and a CO_2 recovery, purification and compression facility.

It has been found that primary effluent gas cooling, compression and drying is best decentralized to be close to the emission points and an intermediate pressure CO_2 stream can then be routed to a centralized collection point for final purification and compression to pipeline pressure. The CO_2 purification system can be designed to handle practical levels of air infiltration into boilers and process heaters to produce a purity of CO_2 suitable for geological sequestration.

The level of air infiltration into boilers and heaters that are retrofitted for Oxyfuel means that it is more economic to design the air separation units for only 95% purity and reject the associated argon and nitrogen in the CO_2 inert gas removal system.

It is possible to integrate the air separation system and the refinery steam system by using an adiabatic air compressor with boiler feed-water preheating in the compressor after cooler. This minimizes requirements for cooling water and also reduces overall power consumption.

All additional power consumption has been provided by a new gas turbine combined cycle system. The combined cycle system can be specified with its own power producing steam system which will include a steam turbine and condenser etc. or the gas turbine exhaust can discharge through a waste heat boiler producing steam at refinery conditions with resulting lower levels of steam production in the existing boilers and lower oxygen requirement for oxyfuel combustion.

It is possible to take this one step further and generate hydrogen for gas turbine fuel from natural gas in an autothermal reformer fired with pure oxygen and using an MDEA system for CO_2 removal. Costing these processes to show net CO_2 flows and costs leads to the choice of lowest cost system being the hydrogen fired gas turbine with heat recovery steam generator integrated into a refinery steam system and having adiabatic main air compressors with boiler feed water heating supplying air to the two cryogenic air separation plants.

Possible further work in this area could include:

- Carrying out necessary burner tests to verify the design of the oxyfuel burners and their likely performance in both air and oxyfuel firing;
- Further studies are required to properly integrate the gas turbine waste heat boiler and refinery steam system and the condensate heating in the adiabatic compressor aftercoolers.

Reports and Publications

- The project final report is included in Appendix A under the same heading as this summary.
- Simmonds, M., Wilkinson, M.B., Allam, R., White V., 'Oxyfuel Conversion of Heaters & Boilers for CO_2 Capture', 2nd Annual Conference on Carbon Sequestration, May 2003.

1.3.3.6 Oxyfuel Heaters and Boilers with Flue Gas Recycle - Ion Transport Membrane Technology Oxygen Supply

Technology Provider: Air Products
Co-funder: CCP

Summary

This feasibility study involves the potential application of Oxyfuel technology on a refinery-wide basis at the BP Grangemouth unit in Scotland. Previous studies in Oxyfuel technology have considered application for retrofit on a power station boiler and refinery process heaters. A total of seven boilers and 13 process heaters of various types burning a mixture of refinery fuel gas and fuel oil form the basis of this study which results in the production of approximately 2.0 million tonnes per annum of CO_2.

The work in Phase 1 of the study considered the issues involved in modifying the process heaters and boilers for oxyfuel combustion and locating two world scale air separation plants totaling up to 7400 tonne/day of oxygen plus a CO_2 compression and purification system on a congested site. In addition, a scheme has been presented for distributing the oxygen around the site and collecting the CO_2-rich effluent from the combustion processes for purification, final compression, and delivery into a pipeline for enhanced oil recovery.

Phase 2 of this study looked at alternative oxygen generation technology that would replace the two cryogenic air separation units. This technology utilizes ion transport membranes (ITMs) to produce the oxygen.

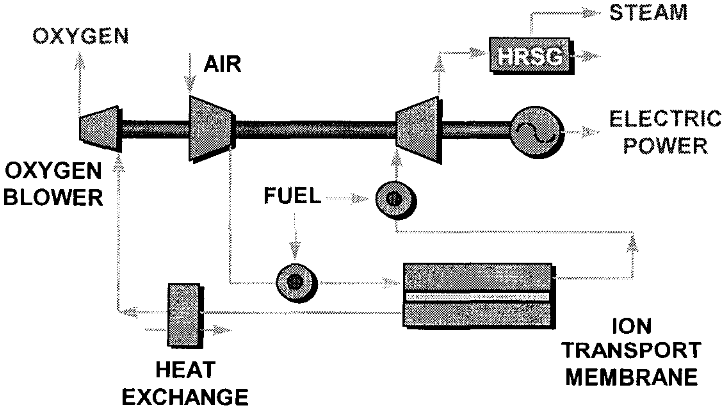


Figure 16 Oxyfuel Gas Turbine Schematic Design

The ITM Oxygen process is based on ceramic membranes that selectively transport oxygen ions when operated at high temperatures. Under the influence of an oxygen partial pressure driving force, the ITM achieves a high flux, high purity (99+mol%) separation of oxygen from a compressed-air stream. By integrating the non-permeate stream with a gas turbine system, the overall process co-produces high purity oxygen, power, and steam if desired (Figure 16.).

Three cases were evaluated as part of this phase 2 study. The base case, Case 1, involves the supply of the complete oxyfuel system with installation and startup and includes all required utilities. In order to provide the hot air for the ITM Oxygen process, two Siemens V94.2 combined cycle gas turbines are used and excess power is exported to the local electricity grid.

Two further cases are also presented. Case 2 also uses two Siemens V94.2 gas turbines plus a heat recovery steam generator producing steam primarily at the refinery condition of 127 barg 518°C together with some additional supplies at 13.7 barg and some boiler feed water. The steam production from the existing boilers is reduced by a corresponding amount. The turndown of the steam boilers results in a reduction in the oxygen requirement from 6626 tonne/day to 3828 tonne/day.

Case 3 uses one Siemens V94.3 gas turbine plus a heat recovery steam generator, but in this case the fuel is hydrogen produced from an oxygen autothermal reformer with product steam generation and CO_2 removed using an MDEA system. The gas turbine waste heat boiler produces steam at the refinery conditions as in case 2. In this case the use of hydrogen fuel gas allows operation of the gas turbine combustor at a much lower oxygen inlet concentration compared to cases 1 and 2 which use natural gas fuel. This feature allows for greater oxygen recovery, which allows the entire oxygen requirement to be met with a single gas turbine, thereby minimizing export power and decreasing capital cost. In each of these three cases the total quantity of CO_2 emission avoided and the quantity of CO_2 available for pipeline delivery is calculated, costed and presented in the final report.

The study has shown that the oxyfuel process, using advanced low-cost oxygen production technologies still under development, is capable of application to this difficult multi-source refinery system giving still lower costs for CO_2 capture compared to cryogenic oxygen production. A key factor in the selection of the optimum configuration is the cost of the natural gas fuel for the gas turbine system and the price achieved for excess power production as is shown in the plots below. It would appear that the most economic case is the single gas turbine with hydrogen fuel which maximizes the potential oxygen production even when accounting for the oxygen required by the autothermal reformer producing the hydrogen fuel.

Possible further work suggested includes:

- Continuing to develop the ITM Oxygen production technology ;
- Progress to a demonstration phase in which a prototype ITM module producing 50-100 tonne/day oxygen is integrated with a gas turbine and properly demonstrated.

Reports and Publications

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

1.3.4 Chemical Looping Combustion

Co-funder: EU-GRACE

The only major R&D project directly funded by the CCP oxyfuel area was the chemical looping project carried out by a consortium formed by BP (Coordinator), Alstom Boilers, Chalmers University, CSIC and Vienna University in a 2-year EU-cofunded project that concluded in December 2003. Total budget of this Project was 1.5 MM€.

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

Fuel reactor: $MeO + CH_4 \rightarrow Me + 2H_2O + CO_2$
Air reactor: $Me + 0.5O_2 \rightarrow MeO$

This project focused on atmospheric pressure application, typical of the CCP UK Scenario, but the concept is also applicable to higher than atmospheric pressure in gas turbine systems as already proven in another project outside the CCP and funded by the DOE. In this case the trade-off is between thermodynamic efficiency and percentage of captured CO_2, since Chemical Looping Combustion takes place at relatively low temperatures (800-900°C). "Dust" coming from degraded metal oxides entering the gas turbine is an additional issue and technical risk for this approach.

The main risk in developing the technology is the availability of suitable oxygen transfer materials able to undergo repeated oxidation/reduction cycles while maintaining both chemical activity and mechanical resistance. Screening activities performed during the first year of the project identified a few materials for further development. In the meantime, with the support of hydrodynamic testing on cold units, a pilot unit was designed and built to demonstrate "Proof-of-Feasibility" of the technology which was the main project objective. The pilot unit at Chalmers University 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_2O_3 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.

A preliminary economic evaluation performed by the CEM Team in 2002 for a system to replace a boiler in the Grangemouth refinery resulted in 43% saving compared to the Post-combustion Baseline.

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.

Team Recommendations

- If the economic evaluation of chemical looping combustion is positive, the Team recommends that a second phase of the R&D project be funded. The team should include a commercial catalyst manufacturer to take care of the scale-up of the production methodology of the material to commercial scale. Two options may be considered:

1. **Aggressive development:** A 3-year project targeting a demo-unit operating by the beginning of 2006 (revamping an existing Demo-CFB unit, as suggested by Alstom), with the first half of the project devoted to optimization of the solid material and definition of the scale-up procedure. Total budget for this project may be in the 4-5 MM$ range.

2. **Staged Development:** A 2-year project focused on the solid material issues, and exploration of the whole range of possible applications, leaving the demonstration to a third phase starting in 2006. Budget for this approach estimated in the 2-2.5 MM$ range.

1.3.4.1 - Chemical Looping Combustion Economics and Scale-up

Technology Provider:	Alstom Power Boilers
Co-Funder:	EU-GRACE

Summary

This EU/CCP funded Project is based on the transfer of oxygen for the combustion from air to fuel by means of an oxygen carrier in the form of a metal oxide. The heart of the system is an interconnected air reactor and fuel reactor using fluid bed technology close to conventional circulating fluid bed technology for which Alstom is a recognized expert.

Alstom Power Boilers is responsible for the concept development of the industrial application to a 200MWth refinery gas boiler – Grangemouth refinery.

Results

Alstom started by developing a design concept for large scale chemical looping combustion boiler using existing CFB technology with fluid bed heat exchangers.

After confirmation of the reference industrial case data (Grangemouth refinery) and terminal points conditions, a general heat and mass balance of the CLC boiler has been conducted, based on a preliminary process flow diagram.

After final selection of the oxygen carrier based on Chalmers University hot prototype testing (mid-2003), specific solids loop heat and mass balance have been carried out to allow a preliminary sizing of the main equipment and to define a preliminary CLC boiler arrangement.

A preliminary costing has been performed from which a CO_2 abatement cost has been deducted.
The Alstom design concept for the large scale Chemical Looping Combustion boiler has been used for cold pilot plant geometry and process definition (TUW-CFM2). These particular cold model results have been reviewed in great detail for their applicability to large scale unit.

Support (fluidization nozzles design) was brought for hot prototype (Chalmers University) operation and results review for scale-up to industrial scale.

Reports and Publications

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

1.3.4.3 - Particle Development, Screening & Comprehensive Testing

Technology Provider: Consejo Superior de Investigaciones Cientificas (ICB-CSIC)
Co-Funder: EU-GRACE

Summary and results

This project aims to reduce barriers to the widespread use of technologies allowing the capture and separation of carbon dioxide generated during the combustion of fossil fuels as a viable option to assist in meeting Kyoto obligations for the reduction of Greenhouse Gas emissions within the European Union. The main obstacle to widespread utilization of this technology is the cost of capture and separation of CO_2. The specific objective of GRACE is to develop technologies to enable the capture of CO_2 from the fired heaters and steam boilers of a power station, refinery and petrochemical complex in the UK with an important reduced cost of applying current technology.

From the different technologies analyzed in GRACE Chemical-looping Combustion (CLC) offers tremendous potential to reduce the cost associated with CO_2 separation because the only by-product of combustion with air is wet carbon dioxide that can be easily collected for subsequent sequestration.

The CLC concept is based on the transfer of oxygen from the combustion air to the fuel by means of an oxygen carrier in the form of a metal oxide. The system is composed of two reactors, an air and a fuel reactor. The fuel, e.g. natural gas, is introduced to the fuel reactor, where it is oxidized by the oxygen carrier, i.e. the metal oxide, MeO. At full conversion of the fuel gas, the exit gas stream from the fuel reactor contains CO_2 and H_2O, and almost pure CO_2 is obtained when H_2O is condensed. The particles of the oxygen carrier are circulated to the air reactor where they are regenerated by taking up oxygen from the air. The flue gas from the air reactor will contain N_2 and any unreacted O_2. The extent of the reactions above may vary depending on the metal oxide and the reaction conditions. The total amount of heat evolved from reactions of reduction of oxidation of the oxygen carrier is the same as for normal combustion, where the oxygen is in direct contact with the fuel. The significant advantage compared to normal combustion is that the CO_2 is not diluted with N_2, and therefore no energy is expended for this separation.

The capture and separation of CO_2 by CLC has been divided in the following tasks:

1 - Oxygen carrier particles
2 - Comprehensive particle testing
3 - Fluidization testing
4 - Bench-scale chemical looping combustor
5 - Engineering and cost studies

Within GRACE, the Consejo Superior de Investigaciones Científicas (CSIC) has been involved in tasks 1 and 2. The objective of this work was to develop an oxygen carrier with enough reduction and oxidation rates, resistant to the attrition and with high durability, maintaining the chemical, structural and mechanical properties in a high number of reduction-oxidation cycles. In task 1 of the project, a preliminary screening of the most feasible particles to be used in a CLC system was carried out.

After the selection of the materials, CSIC prepared 240 samples corresponding to all the possible combinations between metal oxides (CuO, Fe_2O_3, MnO_2, NiO), and inerts (Al_2O_3, sepiolite, SiO_2, TiO_2, ZrO_2) in three different MeO/inert ratios and calcined at four different temperatures from 950 to 1300 °C. The inert is used to supply a convenient mechanical strength to the samples and to improve the reactivity of the carriers. The manufacturing method of the carriers consisted in the mechanical mixing of the materials, the extrusion and the calcination at the desired temperature. Other preparation methods as the impregnation of the metal oxide in a resistant porous inert, and other possible oxygen carriers as a perovskite or several mixed oxides without inert were also tested.

The preliminary screening of the carriers was carried out based on several key points. The first criterion for carrier rejection was an unacceptable low melting point of some one of the compounds either in their reduced or oxidized forms. The second one was the crushing strength of the fresh carriers and the third the reactivity obtained in TGA tests during both the reduction and the oxidation reactions.

> - The crushing strength was determined by the standard ASTM D-4179 test. In general, a higher calcination temperature produced an increase in the mechanical strength of the oxygen carriers. However, there was not a clear relation between crushing strength and metal oxide content.
>
> - Oxygen carrier reactivity characterization was carried out through thermogravimetric analysis (TGA). The experiment consisted of exposing the oxygen carrier to alternating oxidizing and reducing conditions. The oxygen carrier reactivity corresponding to the cycle 5 was used for comparison purposes.

Based on the experience obtained during the screening some particles of the carriers previously selected were manufactured by other methods as impregnation (CSIC) or freeze-granulation (Chalmers) to avoid the attrition and agglomeration trends of some carriers. These carriers were subjected to multi-cycle testing of reduction-oxidation in TGA to analyze the effect of the cyclic structural changes inside the oxygen carrier during the reactions. In this way, it was possible to select particles which survive at least 100 reduction/ oxidation cycles without any other effect. The best behavior was found with the following carriers:

> Extrudated: Fe40Al, Fe40Zr;
> Impregnated: Cu33Ti;
> Freeze granulated: Mn40Zr, Ni40Ti.

However, to finally improve the screening it was necessary to know the behavior of the carriers during successive reduction/oxidation cycles in a fluidized bed, which considers both the structural changes as a consequence of the chemical reaction, and the attrition phenomena existing in a fluidized bed, as well as the possible agglomeration of the particles. Based on the results obtained by CSIC together with the data obtained by Chalmers University, three kinds of particles were finally selected to be produced and tested in the pilot plant located at Chalmers: **Cu/TiO_2 (impregnation), NiO/Al_2O_3, and Fe2O3/Al_2O_3.** In the fluidized bed were also tested some other carriers prepared by an industrial supplier although these carriers were finally rejected due to the bad results herein obtained.

Reports and Publications

Adánez, J.; de Diego, L. F.; García-Labiano, F.; Gayán, P.; Abad, A.; Palacios, J. M. Selection of Oxygen Carriers for Chemical-Looping Combustion. Energy&Fuels (accepted for publication).

de Diego, L. F.; Adánez, J.; García-Labiano, F.; Gayán, P.; Abad, A.; Palacios, J. M. Development of Cu-based oxygen carriers for Chemical-Looping Combustion. (submitted for publication).

García-Labiano, F.; de Diego, L. F.; Adánez, J.; Gayán, P.; Abad, A. Kinetic of the reduction-oxidation reactions of Fe-based oxygen carriers to be used in chemical-looping combustion. (in preparation).

Adánez, J.; de Diego, L. F.; García-Labiano, F.; Gayán, P.; Abad, A. Kinetic of the reduction-oxidation reactions of Cu-based oxygen carriers to be used in chemical-looping combustion. (in preparation).

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

1.3.4.4 - Chemical Looping Combustion 10kW Prototype Reactor

Technology Provider:	Chalmers University
Co-Funder:	EU-GRACE

Highlights

A 10 kW prototype for chemical-looping combustion was designed, built and run with nickel-based oxygen carrier particles.

Summary and results

A 10 kW prototype for chemical-looping combustion has been designed, built and run with nickel-based oxygen carrier particles. As far is known this is the first unit where this process was run continuously. A total operation time of more than 100 h was reached with the same batch of particles, i.e. without adding fresh, unused material. The operation involves twelve days of operation, with typically eight hours per day. During night-time and during start-up of operation the system was kept at high-temperature and circulation with electrical preheating. Thus, the actual time that the particles have been circulating in the system is close to 300 h.

A high conversion of added methane was accomplished, with approximately 0.5% CO, 1% H_2 and 0.1% methane in the exit stream. The presence of CO and H_2 is a thermodynamic effect of related with the NiO/Ni system, and means that the process is very close to equilibrium. The presence of these compounds corresponds to a fuel conversion efficiency of 99.5% based on fuel value.

The best way to treat the unconverted fuel is not clear, possible options are i) storage with CO_2, ii) separation and recycling, iii) burning by addition of oxygen, iv) a subsequent step with another oxygen carrier. A study of suitable methods and costs for recovering CO, H_2 and CH_4 from liquid CO_2 should be made.

There was no detectable leakage between the two reactor systems. Firstly, no CO_2 escapes from the system via the air reactor. Thus, 100% of the CO_2 is captured in the process. Secondly, the leakage of gas from the air reactor to the fuel reactor was tested during initial testing with sand particles, and no leakage was found. Thus, the CO_2 leaving the fuel reactor should be pure, with the possible exception of unconverted fuel, or inert compounds associated with the fuel, e.g. N_2.

No decrease in reactivity was seen during the test period. This was also verified by laboratory analyses of particles elutriated from the system at the end of the testing period. Furthermore analysis of crushing strength of these particles indicated that the particles were equally hard, or even harder, after 100 h of operation than the original particles.

The loss of fines was small and decreased continuously during the test period. In the end of the period the loss of fines, i.e. particles smaller than 45 µm was 0.0023% per hour. If this assumed to be a relevant measure of the steady-state attrition, it corresponds to a lifetime of the particles of 40 000 h.

Assuming a lifetime of the particles of 4000 h, the cost of particles in the process is estimated to be below 1 €/ton of CO_2 captured.

A shorter test series with an iron-based oxygen-carrier was made just before the end of the project.
The lowest concentrations obtained for CO and CH_4 were slightly below 2%. This result is consistent with the lower reactivity of iron-based materials. The test period, 17 h, was too short for any conclusions on the lifetime of the particles.

Reports and Publications

Mattisson, T., Johansson, M., and Lyngfelt, A., 2003 "Multi-cycle reduction and oxidation of different types of iron oxide particles - application to chemical-looping combustion" *submitted for publication*

Mattisson, T., Johansson, M., and Lyngfelt, A., 2004, "The use of NiO as an oxygen carrier in chemical-looping combustion." *minor adjustments to paper remain before submission*

Johansson, M., Lager, C., Mattisson, T., and Lyngfelt, A., 2004, "Investigation of Fe_2O_3 on $MgAl_2O_4$ support for chemical-looping combustion." *minor adjustments to paper remain before submission.*

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

1.3.4.5 Chemical Looping Combustion Fluidization Studies

Technology Provider:	Vienna University of Technology
Co-Funder:	EU-GRACE

Highlights

Summary and results

This paper is aimed to report the results of the work package of Vienna University of Technology in the Grangemouth Advanced CO_2 Capture Project (GRACE). The GRACE project has the objective to analyze the Chemical-looping Combustion (CLC) system.

CLC is a combustion technology with the main benefit of inherent separation of CO_2. The process is based on oxygen transport from air to gaseous fuel by means of an oxygen carrier in form of metal oxides. The reactor system consists of two reactors, namely an air and fuel reactor, one for fuel oxidation and one for oxygen carrier regeneration. The work package of Vienna University of Technology was concerned with the design and scale-up of a CLC reactor concept. To this end detailed modeling was carried out experimentally in cold flow models and mathematically by simulating several process aspects.

The experimental part of this work is grouped into three tasks: The testing and optimization of the design of the CLC prototype, the testing of a large-scale concept and the analysis of an alternative concept. For each design a cold flow model of Perspex glass was designed and manufactured whereby special focus was given to the observance of scaling criteria in order to allow the transfer of the results to 'hot' units including the reactions and, more importantly, offering the possibility to use the data as basis for the scale-up procedure towards large CLC units.

The design of the cold flow model 1 (CFM1) was developed for the CLC prototype. For this reason a very flexible unit with large safety margins in terms of residence time and solid flux was worked out. The experimental tests show that these requirements could be fulfilled and results of the prototype by Chalmers University confirm this. The flexibility of the unit is demonstrated by a design chart that shows the solids circulation flux for the lab-scale (hot) unit at different total solid inventories (TSI) and superficial gas velocity in the air reactor. Limits for stable operation (Gscrit) and for satisfying the mass and energy balances (Gs, min) are indicated and a range up to over $100 kg.m^{-2}.s^{-1}$ can be realized.
Gas leakage values are found to be low and effective countermeasures are identified. The design of the fuel reactor was optimized and the performance in the prototype is found satisfactory.

The second cold flow model was designed for analysis of an alternative option of particle circulation flux. It is of major importance for an optimized CLC system to accurately adjust the solid circulation flow rate to the requirements of the heat transfer between the two reactors and the oxygen transport for full fuel gas conversion and high efficiency. An improved design was developed and realized. Together with the CFM1 a modular concept was chosen, which allows testing of different combinations of particle separator, particle flow control and riser geometry. The results show that the solid flux can be controlled precisely by the fluidization of a loop seal independently of the air flow. This independency allows alteration of the flow without changing the load of the unit. Also residence time and gas leakage are found being appropriate for the CLC process.

The third cold flow model is based on a reactor concept of a large scale unit. Due to space limitations and restricted scale-down factor a 0.5MW unit was modeled instead of the 200MW plant, which is used as design basis for the Grangemouth scenario. The concept is based on a conventional CFB riser concept including an external fluidized bed heat exchanger in the return line and loop seals between the oxidation (split into the riser and an extra air reactor) and the reduction section. All operating parameters were satisfied and it is concluded that the concept forms a consistent design of large scale CLC units working at atmospheric pressure and with methane or similar gaseous fuel such as refinery gas.

The experimental findings are integrated into mathematical models as well as the kinetics and residence time distribution of the fuel reactor and the mass and energy balances. A mathematical model considering chemical equilibrium was adapted for the Grangemouth requirements and detailed calculations on the demands on the solid flux and the gas, as well as solids, conversion are available. An important aspect in this context is the fact that for some oxygen carriers such as Nickel incomplete gas conversion results because of thermodynamic limitations, which causes a slight reduction of the overall system efficiency.

A model of the fuel reactor incorporates the fluid dynamics of the fluidized bed by a modified two-phase model, mass transfer between bubble and emulsion phase, reaction kinetics of gas-solid reaction, and residence time distribution of the solid material. In order to simulate batch tests as well as continuous operating modes the model is developed dynamically. The results show, that inter-phase mass transfer as well as reaction kinetics are rate limiting. However, for sufficient bed height high conversion of the gas can be achieved.

The derivation of scale-up guidelines for the CLC is grouped into three distinct areas, the hydrodynamics, reaction engineering and the heat transfer. The scale-up of the CLC process must because of the nature of the process, focus on the fuel reactor. Clearly, the twin reactor concept coupled by the solid flow gives a rather large degree of freedom. On the other hand, it is clear that the driving force of the unit is the riser. This makes it obvious that the scale-up must particularly focus on the hydrodynamics of the riser and the reaction engineering of the fuel reactor.

The decrease of the solid circulation rates by increasing the riser height is to be compensated by either an increase of the total solid inventory or the riser velocity. However, large scale units in general are being operated such that the riser length is larger than the TDH (transport disengaging height) and in this case the solid flux is considered independent on the reactor height. High and similar fuel gas conversion in the fuel reactor can only be obtained when the gas solid contacting is similar in the different scales and, again, gas bubbles are dominating this mass transfer issue. As a basic scale-up factor constant gas residence time is recommended.

For the air reactor/riser a constant mean solid residence time is required. Due to the design with a separate air reactor this can be achieved by variation of the air reactor bed mass. The decoupling allows an independent adjustment in the design process and a constant ratio of the fuel mass flow rate to the riser/air reactor bed mass is recommended as scale-up factor. The gas residence time is not crucial for the air reactor because the excess air compensates for the potentially larger riser gas velocities.

Reports and Publications

- TAGWERKER C. 2002, Aufbau und Betrieb eines Labormodells zur Untersuchung der Fluiddynamik eines Chemical Looping Combustion Wirbelschichtsystems, Diploma thesis, Vienna University of Technology.

- LUENGO A.M., (2003), Process simulation of a Chemical-Looping Combustion Power Plant; Master thesis carried out at Vienna University of Technology.

- VALENCIANO R. (2003), Effect of solids residence time distribution on fuel reactor performance of a Chemical Looping Combustor. Master thesis carried out at Vienna University of Technology.

- KRONBERGER B. (2003), Scale-up of Circulating Fluidized Bed Reactor Systems for Chemical-Looping Combustion. PhD thesis in progress, Vienna University of Technology.

- KRONBERGER B. G. Löffler, H. Hofbauer. Residence Time Distribution of Solids in a Fluidized Bed Fuel Reactor of a Chemical-Looping Combustion Prototype (in preparation)

- KRONBERGER B. A. Lyngfelt, G. Löffler, H. Hofbauer. Design and hydrodynamic testing of a 10kWth prototype for continuous Chemical-Looping Combustion. (in preparation).

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

1.3.4.6 Carrier Optimization for Chemical Looping Combustion

Technology Provider: Consejo Superior de Investigaciones Cientificas (CSIC)
Co-Funder: EU-GRACE

Highlights

This project has completed the development work conducted by a Consortium including BP, Alstom Boilers, Chalmers University, CSIC and Vienna University of Technology, in the frame of a CCP/EU co-funded Project (GRACE) in 2002-2003.

The GRACE Project identified Ni-based materials as the preferred oxygen carriers among the hundreds of materials tested in lab reactors. Positive results were confirmed in the bench scale experiments performed by Chalmers University of Technology.

Ni-based carriers allow working at high temperature and a complete CH_4 conversion can be reached. Thermodynamic restrictions however result in the presence of small amounts of CO and H_2 in the effluent gas. These amounts increase with pressure and may make it necessary to include expensive process modifications to reduce the amount of non.-condensable gases in the CO_2 compression and condensation stages.

The modification of Ni carriers by addition of other elements to reduce the co-production of CO and H_2 was the objective of this Project. Reactivity of the various carriers prepared were tested at the lab level in a thermogravimetric analyzer (TGA) and in a batch fluidized bed reactor.

The main results are summarized here below:

- The addition of Cu to the Ni-based carrier led to a relatively long time of complete combustion of methane (no CO and H_2) at the expense of lower reactivity compared to the carrier without Cu addition.
- The addition of Mn to the Ni-based carrier resulted in a similar behavior, but the time of complete combustion, before appearance of CO and H_2 was very short.
- The addition of Na to the Ni-based carrier had no significant effect.
- K and La salts were further added to Ni-Cu carriers. Both additions resulted in a small increase in reactivity. K also increased the time before CO and H_2 began to appear in the effluent gas from combustion.

Based on the above it is clear that Ni-Cu carriers, possibly added with promoters, are a very promising option for application to Chemical Looping Combustion to avoid presence of CO and H_2 in the CO_2 recovery stream, while maintaining the high reactivity of Ni carriers.

Project Summary

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

Fuel reactor: $MeO + CH_4 \Rightarrow Me + 2H_2O + CO_2$
Air reactor: $Me + 0.5O_2 \Rightarrow MeO$

This Project has been focused on atmospheric pressure application, typical of the CCP UK Scenario, but the concept is also applicable to higher than atmospheric pressure in gas turbine systems, as already studied in another Project outside the CCP frame and funded by the DOE. In the case of a turbine application, the trade-off is between thermodynamic efficiency and percentage of captured CO_2, since Chemical Looping Combustion takes place at relatively low temperatures (800-900°C). Also, the need for hot dust filtration or development of turbine materials that can accept "dust" are additional issues to address in this case.

The main risk in developing Chemical Looping is the availability of a suitable material able to undergo repeated oxidation/reduction cycles, while maintaining both chemical activity and mechanical resistance. The screening activity performed during the first year of the Project identified a few materials for further development. In the meantime, with the support of fluidized bed testing in cold units, a pilot unit was designed and built to achieve "Proof-of-Feasibility" of the technology, i.e. the main target of this Project. The pilot unit at Chalmers has two integrated 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 a Ni-based oxygen carrier 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 loss of activity by the carrier.

Based on the results of this Project, the CCP has decided to continue development of Chemical Looping Combustion submitting a proposal to the EU for a 2 –year Project targeting scale-up from 10kW to 200kW continuous circulating fluidized bed reactors.

Reports and Publications

- Adanez, J; de Diego, L.F.; Barcia-Labiano, F. CSIV Final Report of the gRACE Project (ENK5-CT-2001-00571), 2003.

- Adánez, J.; de Diego, L. F.; García-Labiano, F.; Gayán, P.; Abad, A.; Palacios, J. M. Selection of Oxygen Carriers for Chemical-Looping Combustion. Energy & Fuels 2004a, 18, 371-377.

- Adanez, J: Garcia-Labiano, F; de Diego, L.F.; Gayan, P.; Abad, A.; Celaya, J; Development of oxygen carriers for Chemical Looping Combustion. In the CO_2 Capture and storage Project (CCP) for carbon dioxide storage in deep geologic formations for climate change mitigation. Volume 1 – Capture and separation of carbon dioxide from combustion sources. Ed. Thomas, D., Elsevier Science, London, 2004c.

- de Diego, L. F.; García-Labiano, F.; Adánez, J.; Gayán, P.; Abad, A.; Corbella, B. M.; Palacios, J. M. Development of Cu-based oxygen carriers for chemical-looping combustion. Fuel 2004, 83, 1749-1757.

- de Diego, L. F.; Gayán, P.; García-Labiano, F.; Adánez, J.; Celaya, J.; Abad, A. Impregnated $CuO/\gamma\text{-}Al_2O_3$ oxygen carries for chemical-looping combustion: suppressing fluidized bed agglomeration. 2005. Submitted.

- García-Labiano, F.; de Diego, L. F.; Adánez, J.; Abad, A.; Gayán, P. Reduction and oxidation kinetics of a copper-based oxygen carrier prepared by impregnation for chemical-looping combustion. Industrial&Engineering Chemistry Research 2004, 43, 8168-8177.

- The project final report is included in Appendix A.

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_2 Capture Project (CCP) includes transportation and geological storage of CO_2 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_2 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_2
- **Optimization** – processes that improve the efficiency and economics of CO_2 transportation and storage
- **Monitoring** – techniques to track CO_2 movement within and outside of the target storage reservoir
- **Risk Assessment** – methods to identify and minimize the probability and impact of CO_2 leakage from storage sites

Summaries of the objectives, results and CCP assessment of some 30 projects distributed over the four technical themes appear later 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_2 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_2 storage. Basic requirements include depth (pressure and temperature) sufficient to inject and maintain CO_2 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_2. Additional studies addressed the need for characterization of prospective CO_2 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_2 also show that CO_2 is amenable to retention in natural systems by multiple mechanisms.

There are numerous instances worldwide both of large natural CO_2 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_2 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_2 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_2-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_2 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_2 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_2 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_2 injection. The study by GFZ-Potsdam (Schuett) showed experimentally that injection of CO_2- 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_2 injection. Geochemical processes driven by CO_2 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_2 influx (rate, focality and duration) parameters. In contrast, increase of cap rock permeability due to geomechanical effects is controlled by reservoir and CO_2 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_2 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_2 flooding in clastic aquifers and the CO_2 EOR water-alternating-gas (WAG) process. Other possible mechanisms of CO_2 immobilization include buoyant flow, brine density convection and mineralization. The fate of CO_2 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_2 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_2 dissolution as the principal trapping mechanism, showed similar results over the 1000 year timeframe. Our understanding of CO_2 behavior in the subsurface, backed by independent simulations, show that CO_2 immobilization can be highly effective given an appropriate reservoir. The solubility of CO_2 makes it likely; furthermore, that CO_2 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_2 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_2 storage facilities. It is of considerable importance that independently-run simulations using distinct software and favoring different CO_2 trapping mechanisms predict immobilization of most of injected CO_2 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_2 retention. Foremost among the vulnerabilities of CO_2 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_2 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_2-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_2 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_2 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_2-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_2 storage. Site selection criteria relevant to CO_2 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_2 storage sites. The GTI study has identified siting and technology issues in natural gas storage that will be useful in developing and maintaining CO_2 storage facilities.

The integrity of engineered systems used in CO_2 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_2 storage. Successful development of natural gas storage as an engineered system analog for CO_2 storage will progress its future application and safety.

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

Injection of CO_2 into depleted oil fields is considered an early opportunity for CO_2 storage given that the cost of CO_2 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_2 EOR experience in the World over the last 30 years. Storage of CO_2 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_2. Deep unmineable coals also present an opportunity as increased methane production is possible. The ability of the CO_2 storage reservoir to accommodate impurities (e.g., SOx, NOx) might reduce CO_2 capture costs and avoid their emission into the atmosphere.

The survey of CO_2 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_2 EOR is that by Tie-Line Technology (Stenby). Models and software are available for screening CO_2 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_2 EOR studies identify the major reservoir and fluid character issues that need to be addressed before large scale CO_2 EOR with storage can be effectively applied.

The tools necessary to make CO_2 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_2 storage in such reservoirs. The highly compressible nature of CO_2 indicates that up to five times the volume of CO_2, relative to original gas, may be stored under appropriate conditions. Hydrocarbon and CO_2 gas PVT experiments predict the phase behavior of gas mixtures in reservoirs. A "CO_2 Sequestration Parameter" was developed for quickly assessing the suitability for and capacity of reservoirs for CO_2 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_2 impurities (e.g., SOx, NOx) 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_2 raises the potential for lowering CO_2 capture costs. The modeling framework established should be useful for testing the effects of other gases such as N_2, hydrocarbons and O_2.

Identification of operational efficiencies and economic offsets will be crucial both to project development decisions and safe and effective operation of CO_2 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_2 Transportation (Reinertsen/SINTEF, IFE, BML)

The Norwegian transportation studies coordinated by Reinertsen Engineering (Heggum) and supported SINTEF and IFE (Seiersten) aimed to reexamine CO_2 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_2 streams permissible before corrosion and hydrates effects become significant.

Using thermodynamic models based on new high pressure CO_2 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_2 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_2 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_2 storage venues. TNO (Arts) conducted a broad survey of geophysical and geochemical monitoring techniques aimed at recommending "optimal" techniques for various CO_2 storage venues and potential failure modes (e.g., FEPs, or features, events and processes). In addition, the importance of characterizing the effects of CO_2 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_2 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 CO2 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_2 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_2 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_2 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_2 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_2 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_2 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_2 ecosystems flux determinations, is theoretically tested for CO_2 leakage detection under various scenarios. The near ground techniques are established technologies whose installation will likely be required for early onshore CO_2 storage projects. Optimization of instruments and configuration will allow field scale CO_2 leakage monitoring considerable cost savings.

Geophysical techniques, particularly time lapse 3-D seismic, have proven useful in monitoring subsurface CO_2 movement. Their expense and limitations on detecting CO_2 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_2 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_2 / 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_2 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_2 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_2 EOR oil field of W. Texas. Given the volume of CO_2 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_2 movement would perform. The development of tracer systems for CO_2 storage projects will be important for monitoring performance, leak detection and volume verification.

The SMV assessment of technologies and techniques to monitor CO_2 reservoir performance and leakage / seepage is unique in its variety and scope. Remote atmosphere approaches to monitoring CO_2 leaks are shown to require further development. Existing near-surface atmospheric approaches to CO_2 detection are commercially available and adaptable to CO_2 storage. Seismic geophysical monitoring of CO_2 is available but a better understanding of rock response to CO_2 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_2 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_2 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_2 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_2 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_2 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_2 leakage were identified. Predictive quantitative modeling shows that elevated pressure form N_2 injection caused coal fractures to extend from the injectors to producers. The risk of early gas (N_2 and CO_2) 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_2 injection, CO_2 injection).

Further testing of the model on other CO_2 storage venues and benchmarking will demonstrate the broader applicability of the methodology.

The two independent developed risk assessment methodologies are based on the same principles 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 those 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_2 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_2 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_2 accumulation in low lying areas and into occupied structures. The coupled model developed by LBNL (Oldenburg) simulates CO_2 flow in the shallow subsurface and atmosphere. When CO_2 concentrations in the near subsurface are high (either by primary seepage or CO_2 infiltration as a dissolved component of rainwater), surface layer winds act to rapidly disperse the CO_2 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_2 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_2 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_2 handling and put into perspective the experiences of potential industrial analogs to CO_2 storage (oil production by CO_2 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_2 can be stored safely, 2) the health effects of exposure to elevated concentrations of CO_2 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_2 storage and 5) regulatory paradigms and approaches vary and none address all of the issues that are important for CO_2 storage. These findings are elaborated upon with examples and needs for further research.

A set of potentially relevant industrial analogs to CO_2 storage were examined in the SMV program. In the CO_2 EOR experience survey by NMT (Grigg), it is evident that CO_2 leakage monitoring is not a perceived need. Anecdotally, this may result from the absence of fatalities attributed to CO_2 leakage over the 30+ years of CO_2 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_2 storage is likely to be much more benign than that of nuclear waste disposal, the general principles are clearly relevant. The natural gas storage experience should reflect well on CO_2 storage as its safety record is excellent. CO_2 storage may in several respects be considered a mild analog to natural gas storage as CO_2 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_2 storage are also likely to be more rigorous.

Environmental issues associated with CO_2 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_2 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_2-rich conditions. The results demonstrated that growth of various microbial species (many of which have yet to be identified) will be impacted by CO_2 injection. More importantly for CO_2 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_2 storage.

2.1 Risk Assessment and Analysis

Task - 4.5 Risk Assessment and Mitigation Options

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_2 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_2 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_2 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, Colorado which is presently under N_2 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^{TM}. The geomechanical study revealed processes that lead to risks of developing leakage paths at each step of CO_2 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_2 injection caused the coal fractures on the preferred permeability trends to expand and extend from injectors to producers. The risk of early gas (N_2 plus CO_2) breakthrough and high non hydrocarbon gas cut during gas injections are increased if CO_2 injection is placed within three miles of an outcrop. The importance of evaluating the effects of processes employed prior to CO_2 injection (e.g., coal bed depressurization and dewatering, N2 injection) on CO_2 movement is highlighted. Further testing of the methodology on additional, candidate CO_2 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_2 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_2 flux and concentration. The coupled model framework is built on integral finite difference multiphase and multi-component reservoir simulator (TOUGH2) and models CO_2 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_2 can reflux into the subsurface as a dissolved component in infiltrating rainwater. Whereas CO_2 concentrations in the subsurface might be high, surface layer winds act to reduce CO_2 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_2 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_2 storage projects as the behavior of CO_2 at the surface is of the most immediate concern.

Mitigation and Remediation (LBNL)

Early detection and remediation of CO_2 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_2 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_2 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_2 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_2 in structures. The study establishes a framework from which CO_2 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_2 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_2 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_2, which are the most immediate concerns associated with CO_2 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_2 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_2 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_2 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_2 storage (leakage between geologic units, performance versus practice based requirements, state versus federal regulatory oversight, and 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_2 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_2 storage. Although the potential hazard levels associated with CO_2 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_2 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_2 injection on microbes in different environments (reservoir lithologies, ground water types) over three reservoir temperatures and constrained pCO_2 and pH/Eh. Fe (III) reducers and fermentative anaerobes are not favored by the presence of CO_2 but there is an increase in methanogenesis and acetogenesis. Considering chemical changes induced by CO_2 presence and microorganism response, several implications to CO_2 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_2 storage performance issues such as porosity changes, methane gas production and bacterial growth near gas water contacts.

2.1.1 Safety Assessment Methodology Assessment for CO_2 Sequestration (SAMCARDS)

Task - 4.5 - Risk Assessment and Mitigation Options
Technology Provider: TNO-NITG
Co-Funder: DOE

Highlights

- An *overall* methodology for long-term safety assessment of underground CO_2 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_2 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_2 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_2 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_2 sequestration in various geological media of the North Sea region. The main deliverable, consisting of risk assessment methods and computational tools, are 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 one onshore depleted gas field in the Netherlands and one 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_2 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_2. 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_2 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_2 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_2 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_2 concentrations and fluxes in the biosphere, and is therefore able to predict probabilities of CO_2 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_2 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_2CRC), 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_2 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.

Reports and 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 summary.

2.1.2 HSE Probabilistic Risk Assessment Methodology

Task - 4.5 - Risk Assessment And Mitigation Options
Technology Provider: INEL
Co-funder: DOE

Highlights

- A mathematical model for probabilistic risk assessment of CO_2 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_2 at each step in the process of CO_2 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_2 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_2 plus CO_2) breakthrough and high inert gas cut during gas injections are increased if CO_2 injection is placed within a three miles of an outcrop.

Summary

To evaluate the geomechanical issues in CO_2 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_2 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_2 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_2 or N_2 injection because of the response of coal structure to gas injection.
- The simulated early inert gas (N_2 plus CO_2) breakthrough and high inert gas cut during future gas injections suggests that the future gas injection and CO_2 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_2 or N_2 injection may not be accurate.
- Any CO_2 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_2 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_2CRC), 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_2 storage.

Publications

- S. Wo and J.-T. Liang, (2004) "Simulation Assessment of N_2/CO_2 – Coal Contact Volume and Its Impact on Outcrop Seepage in N_2/CO_2 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_2 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_2 Storage in Coal Beds.

- Risk Assessment Workshop in Nottingham, May 29, 2002: Methodology for Conducting Probabilistic Risk Assessment of CO_2 Storage in Coal Beds.

- CCP workshop in Santa Cruz, CA, October 22, 2002: Methodology for Conducting Probabilistic Risk Assessment of CO_2 Storage in Coal Beds.

- CCP workshop in Dublin, Ireland, September 22-24, 2003: Methodology for Conducting Probabilistic Risk Assessment of CO_2 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
Co-funder: DOE

Highlights

- The injection of carbon dioxide (CO_2) into deep geologic carbon sequestration sites entails the risk that CO_2 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_2 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_2 seepage flux and near-surface CO_2 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_2 flux and concentration.

- The coupled modeling framework is built on the integral finite difference multiphase and multicomponent reservoir simulator TOUGH2 and models CO_2 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_2 can reflux into the subsurface as a dissolved component in infiltrating rainwater. Whereas CO_2 concentrations in the subsurface are high, surface-layer winds reduce CO_2 concentrations to low levels for the fluxes investigated.

Summary

A coupled modeling framework for modeling CO_2 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_2 flow and transport from the deep CO_2 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_2 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_2 concentrations possible in the shallow subsurface. These results show that if leakage leads to CO_2 migrating as far as the vadose zone, high CO_2 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_2 to the subsurface that occurs when CO_2 dissolves in infiltrating rainwater. Although no leakage of stored CO_2 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_2 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 LBNL-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_2 Sequestered in the Subsurface: Requirements and Design of a Coupled Model for Risk Assessment, Task 2 Report, Lawrence Berkeley National Laboratory Report LBNL-51131, July 2002b.

- Oldenburg, C.M., A.J.A. Unger, and R.P. Hepple, On Atmospheric Dispersion of CO_2 Seepage from Geologic Carbon Sequestration Sites, Task 3 Report, Lawrence Berkeley National Laboratory Report LBNL-51734, November 2002c.

- Oldenburg, C.M., and A.J.A. Unger, Coupled Modeling Framework for CO_2 Leakage and Seepage Risk Assessment, Task 4 Report, Lawrence Berkeley National Laboratory Report LBNL-53009, June 2003b.

- Oldenburg, C.M., Y. Zhang, J.L. Lewicki, and P.D. Jordan, Preliminary application of a coupled modeling framework for leakage and seepage at the Rio Vista Gas Field, Task 5 Report, Lawrence Berkeley National Laboratory Report LBNL-54051, 2003a.

- 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 LBNL-52477, May 2003a.
- http://esd.lbl.gov/TOUGHsymposium/pdfs/OldenburgUnger.pdf

- Oldenburg, C.M., and A.J.A. Unger, On leakage and seepage from geologic carbon sequestration sites: unsaturated zone attenuation, Vadose Zone Journal, 2, 287–296, 2003c.

- 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.

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

2.1.4 Lessons Learned from Nuclear Waste Disposal

Task - 4.1 Understanding Geologic Storage
Task - 4.5 Risk Assessment and Mitigation Options
Principal Investigator: Mike Stenhouse
Technology Provider: Monitor Scientific
Co-funder: DOE

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_2 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_2 storage. The key technical issue that needs to be addressed in planning for CO_2 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 cites. Elements of these efforts parallel the situation likely to be encountered in future geological CO_2 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_2 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_2 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_2 sequestration.

Reports and Publications

- CCP-SMV 2002 Workshop, Santa Cruz
- The final project report for this project is in Appendix A under the same heading as this summary.

2.1.5 Reactive Transport Modeling to Predict Long-Term Cap-Rock Integrity

Technical Provider: Livermore National Lab

Task - 4.1 - Understanding Geologic Storage
Principal Investigator: Jim Johnson
Technology Provider: LLNL
Co-funder: DOE

Highlights

Reactive transport modeling was used to predict long-term cap rock integrity during natural and engineered CO_2 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_2-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_2 leakage. It further suggests that the secure cap rock of a given natural CO_2 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_2 reservoirs: are they natural analogs to engineered geologic storage sites?" 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_2 storage sites.

CO_2 influx that forms natural accumulations and CO_2 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_2 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_2 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_2 injection for EOR or saline-aquifer storage, in CO_2 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_2 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_2 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_2 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_2 reservoirs: are they natural analogs to engineered geologic storage sites?: Special Session on Geological Sequestration of CO_2, 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_2 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_2 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_2 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_2 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_2 Capture Project Workshop: "Building the SMV Family of Technology Providers", Potsdam, Germany, Oct 31-Nov 2, 2001 (oral presentation).

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

2.1.6 Early Detection and Remediation of Leakage from CO_2 Storage Projects

Task - 4.1 - Understanding Geologic Storage
Principal Investigator: Sally M. Benson
Technology Provider: Lawrence Berkeley National Laboratory
Co-funder: DOE

Highlights

- Scenarios for CO_2 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_2 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_2 into structures. Remediation plans for a range of eventualities are necessary for public assurance of CO_2 capture and storage efforts.

Summary

The need for methods of early detection and remediation of leakage from CO_2 storage projects is a recurrent theme in discussions with environmental NGO's about the acceptability of geologic storage of CO_2 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_2 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
- The final project report for this project is in Appendix A under the same heading as this summary.

2.1.7 Impact of CO_2 Injection on Subsurface Microbes and Surface Ecosystems

Technology Provider: Geolas (Princeton)
Co-Funder: DOE

Highlights

Laboratory tests and calculations were made to evaluate the potential effects of injected CO_2 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_2 injection was a reduction of pH in ground water by one unit in siliciclastic reservoirs. CO_2 injection should cause a short term stimulation of Fe(III) reducing communities.
- Dolomitic or carbonate aquifers may be more severely impacted by the CO_2 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_2 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_2 injection should be less pronounced.
- For long term sequestration of CO_2 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

The objective of this project was to identify organisms that might be present in the deep subsurface and to evaluate the potential effects on these organisms of CO_2 injection.

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_2 injection – dissolution of aquifer minerals fails to restore pH. Injection of H2 would stimulate CO_2 reduction in methanogens, raising the pH. During long term CO_2 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_2 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_2 injection, the study is useful for anticipating untoward reservoir engineering problems,

Reports and Publications

- Tullis C. Onstott, Impact of CO_2 injections on Deep Subsurface Microbial ecosystems, CCP SMV International Meeting, Dublin, Ireland, September 21, 2003.
- The final project report for this project is in Appendix A under the same heading as this summary.

2.1.8 Literature Search and Synthesis of HSE Risk Methodologies

Technology Provider: Lawrence Berkeley National Lab (Berkeley)
Co-Funder: CCP

Highlights

- A comprehensive compendium of information relevant to CO_2 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 is the product of this study.
- Human health and ecosystem responses to various levels of CO_2, which are the most immediate concerns associated with CO_2 capture, transportation, injection and leakage, is also addressed.

Summary

Large-scale injection of anthropogenic CO_2 into reservoirs for the purpose of CO_2 sequestration is not commonly applied to date. A study on the human health and ecosystems impacts of CO_2 is relevant to putting the probability and impact of unintentional release into perspective. Documenting experiences from the industrial disposal or storage of hazardous materials provides useful analog data. Lessons learned from three industrial activities, deep well injection of industrial wastes, natural gas storage and storage of nuclear waste in geologic repositories, were examined as follows:

- History, status and scope of the activity,
- Risk assessment framework and methods, including key issues, performance specifications and performance assessment methods,
- Risk management approaches, including regulatory oversight and permitting, site characterization methods, monitoring and performance confirmation,
- Risk mitigation and remediation methods employed or planned in the event that performance specifications are not met or other unintended consequences arise, and
- Case studies documenting responses to historical accidents.

Carbon dioxide is generally regarded as a safe, non-toxic, and inert gas that is essential to biological processes. Prolonged exposure to CO_2 levels $< 1\%$ is tolerated by humans (and air breathing vertebrates) with no physiological effects; 1-3%, physiological responses occur with no permanent adverse consequences; respiratory effects are noted in the 3-5% range; physical and mental impairment at the 5-10% range; death at $> 10\%$. The severity of adverse effects from CO_2 exposure is a function of the nature of the release incident rather than the source or initial size. Incidents occurring in settings where CO_2 is not allowed to disperse (e.g., low-lying areas with calm wind conditions) are of most concern. The CO_2 tolerance of living organisms varies widely. At the 20-30% level, nearly all forms of life except some microbes, invertebrates, fungi and insects are killed. The effects of elevated CO_2 levels on ecological systems are more complex. Plants are more tolerant to high CO_2 levels than animals but prolonged exposure has resulted in plant kills due to disruption of root respiration. Information on aquatic species of plants and animals is not known.

Carbon dioxide is regulated by federal and state authorities in the US for uses in numerous industries. Hazards associated with CO_2 handling are therefore well known and easily managed using standard engineering controls and procedures. Deaths and injuries from accidental leaks have been shown to have been preventable.

Natural analogs for CO_2 storage do exist but engineered solutions to geologic CO_2 sequestration requires understanding of containment properties and limits. The experience of operators of those facilities where

CO_2 is produced is essential. Risk assessment programs would include identification of leakage conduits, rates and local features such as topography to predict plume dispersion.

Deep well injection of industrial wastes has occurred in the US for decades with numerous leaks into drinking water. Most of these failures were the result of inappropriate well materials or operating procedures. Since strict new EPA regulations were enacted in 1988, leakage problems have not been encountered and improved monitoring post well closure has been added to identify leakage early. The US EPA has a five well regulatory classification, two of which might be applicable to CO_2 injection. The more stringent Class I includes injection of hazardous, industrial or municipal wastes below potable aquifers whereas Class II includes fluid injection in conjunction with oil and gas production. Arguments for the less stringent Class II well classification for CO_2 storage need to be made early to avoid regulatory complications and unnecessary expense.

Underground storage of natural gas in depleted oil / gas fields and brine aquifers has been used effectively and safely at hundreds of sites in the US and Europe. The few accidents that have occurred involved defective wells. More stringent regulation and better geological characterization of natural gas storage sites promise to improve safety with time. The CO_2 storage analog appears to involve less risk as CO_2 is not flammable.

A number of lessons learned come from the experience of nuclear disposal permitting efforts. There is a need for openness, transparency and sensitivity to public opinion. Robust simulation and risk assessment needs to be presented. Ensuring that containers are not prone to leak must be demonstrated. Post storage procedures involve emplacement of carefully designed monitoring programs. Although nuclear waste disposal presents much greater hazards than CO_2 storage, much can be learned from the processes that led to successful versus unsuccessful permitting.

The lessons learned report provides valuable perspective on how to assess risks associated with CO_2 storage and how regulatory and public perception problems can be address openly and honestly. This study led to the contracting of several of the later CCP-SMV studies.

Reports and Publications

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

2.1.10 The EU-NGCAS Project - Assessing the Potential for EOR and CO_2 Storage at the Forties Oilfield, Offshore UK

2.1.10.1 Basin Model Development

2.1.10.2 Geochemistry and Basin Modeling

2.1.10.3 Final Report

2.1.10.4 Optimization of Storage and Risk Assessment Methodology

2.1.10.5 Storage Option Assessment Methodology

Technology Providers:	BP Exploration Ltd British Geological Survey ECL Technology Ltd Institut Francais du Petrole (IFP) Geological Survey of Denmark and Greenland (GEUS) Universidade Federal do Rio Grande do Sul, Brazil
Co-Funder:	EU-NGCAS

Highlights:

- The Next Generation Capture and Storage Project **(EU-NGCAS)** was a comprehensive evaluation of a CO_2 sequestration opportunity that evaluated all the issues involved in developing a grass-roots sequestration project in an existing major oil refinery and petrochemical complex.
- The study coordinates with evaluations of CO_2 capture from the same complex by several methods and is closely linked to the CCP Grangemouth Scenario. It studied the potential to store underground 2 million tonnes of CO_2, approximately half the annual CO_2 emissions from the Grangemouth refinery and petrochemicals complex near Edinburgh, Scotland.
- The study concluded that the best potential storage site for these emissions was the Forties oil field in the UK sector of the North Sea. Numerical simulation indicated that EOR using a WAG process and CO_2 as the injection gas would yield significant incremental oil.
- A Features-Events-Processes (FEP) identification process was used to narrow down the risks to storage at the Forties field. Numerical modeling was then used to assess the risks of CO_2 escape.
- It was concluded that the geological risks of CO_2 escape were negligible, but it was not possible to analyze the chances of CO_2 escape via pre-existing wells. The wells are perceived as the main uncertainty in the analysis and it is recommended that a comprehensive risk assessment methodology for wells is developed.

Summary

The Next Generation Capture and Storage Project (NGCAS) was conceived in 2000 as a case study to test the potential for geological storage of large volumes of anthropogenic CO_2 captured from industrial plants. By the time the project was conceived, there was already an indication that an attractive option for CO_2 storage on this scale might be to use CO_2 for Enhanced Oil Recovery (EOR) in Europe's major oil province, the North Sea. The additional oil recovered would partly offset the costs of storage and there would be a more rational use of resources as a greater proportion of the oil resources in place would be produced. The Forties field stood out amongst BP's North Sea assets in terms of its storage volume: at least 75 million tonnes (Mt) of CO_2 could be stored underground as a result of EOR, with further potential if storage was continued for its own sake after EOR. Looking to the future, if a case could be made to build a CO_2 pipeline to the North Sea oilfields, there would be every opportunity for further CO_2-EOR projects because many North Sea oilfields appear technically suitable. This would accrue further benefits to the EU in terms of import reduction and security of supply. This option clearly merited further investigation, but it was decided that the choice of a storage site should not be completely pre-judged as it was uncertain whether Forties really was the most cost-effective storage option, given the long transport distances from even the most northerly major industrial point sources of CO_2 in the UK and the high costs of offshore operations. Therefore onshore and nearshore areas which might have CO_2 storage potential were also considered.

Given the above it was considered that the source(s) of CO_2 selected for the study should be chosen from amongst the largest industrial point sources in the northern UK because these are relatively close to the oilfields, which lie in the Northern and Central North Sea. An obvious possibility was BP's Grangemouth refinery and petrochemicals complex, some 30 km west of Edinburgh in Scotland, where a study was taking place to determine CO_2 capture costs. The Grangemouth site emits about 4 million tonnes of CO_2 annually. The Longannet and Cockenzie coal-fired power plants, which emitted 8.76 Mt and 2.47 Mt CO_2 respectively in 2000, are nearby. It was clear that these could be supplementary sources if required: they also added a "Cleaner Coal Technology" dimension to the project. Thus the Grangemouth site was selected as the nominal source for the project. It was arbitrarily assumed to have an additional 25 years of production, and thus that it would emit roughly 100 million tones of CO_2 in the future. If half of this were to be made available to be stored rather than emitted to the atmosphere, the operation of the capture plant would emit an additional 600,000 tonnes/year of CO_2 [3]. The net CO_2 avoided would be 1.4 million tonnes/year and the net emission reduction would be 35%. It has been estimated that this might cost about \$50-60/tonne CO_2, representing a total cost of about \$100 - 120 million/year [3]. However, the cost is sensitive to the price of natural gas, which is used as fuel in the capture plant.

Conclusions

The workflow necessary to select and characterize a site for storage of captured CO_2 emissions from a major industrial site has been illustrated by a case study based on the emissions from the Grangemouth refinery and petrochemicals complex.

Having selected the Forties oilfield as the most suitable storage site, a multi-scale, integrated approach was used to evaluate possible long term leakage of geologically stored CO_2 in this mature oil field. This approach was based on the use of commercial software. The workflow moved from the regional (basin) scale to the site specific (field) scale, allowing a reliable reconstruction on the fluid flow pattern around the gas storage target.

The approach comprised several stages:

- simulation of the fluid flow at basin scale using a 2D model
- simulation of the fluid flow in the aquifers around the field by 3D modeling
- evaluation of CO_2 and water interactions (diffusion) using a reservoir simulator
- Risk evaluation using sensitivity tests taking into account the uncertainties of the data.

Using this novel approach the most significant risks of CO_2 escape from the Forties field can be bounded numerically using a combination of numerical simulation and scoping calculations. The potential for escape of CO_2 via geological pathways (diffusion and advective flow through the cap rock, dissolution of CO_2 into the aquifer below the oil field and transport of CO_2-charged waters along the aquifer) is regarded as low. This is mainly due to:

- the quality and thickness of the cap rock and the overburden
- The very slow natural fluid flow velocity in the Forties reservoir and surrounding strata, controlled here by the sediment compaction rate.

Given that the risk of CO_2 escape by geological pathways appears to be very low, the potential for escape of CO_2 from the Forties field via active or abandoned wells, which could not be assessed meaningfully within the scope of the project, is perceived to be the most important unknown in the risk analysis.

Providing the risk from wells can be demonstrated to be acceptable, the Forties field appears to provide an excellent potential location for CO_2 storage.

Conclusions from Forties Risk Assessment

We have identified potential pathways for escape of CO_2 from the Forties reservoir, and made an assessment of risks associated with those pathways. The risk assessments that have been made are based on a combination of analytical models and numerical simulation, and the results of these assessments are specific to the particular reservoir and the particular assumptions that have been made. It should be noted that a similar approach might be used to assess the risks associated with CO_2 injection in a different reservoir; however the results of the risk assessment and the relative importance of the different risk factors depend on the particular circumstances that applied.

The main conclusions from the risk assessment of CO_2 storage in the Forties reservoir are:

(i) There are remaining uncertainties about well integrity and potential pathways to sea-bed through abandoned well bores. These need to be addressed through an audit of the well abandonment strategies that have been adopted to date and a review of well abandonment strategies to be applied in the future.

(ii) The risks associated with the escape of CO_2 through the cap rock and into the overburden (relating in particular to levels of overpressure and sealing of cap rock) have been shown to be negligible. A particular requirement for further work would be to address the long-term integrity of the seal in the presence of CO_2. This is an area where there is little historical experience to date.

(iii) Transport pathways through the underlying aquifer have been shown to have no significant areas of concern in the longer term. There are some possible short-term issues relating to the levels of overpressure around the injection wells and the detailed injection strategy that would need to be addressed as part of the design of the particular gas injection strategy that is adopted.

Recommendations

- It is recommended that a comprehensive methodology for assessing the risks of leakage of stored CO_2 via wells is developed.

Reports and Publication:

- The final project reports for this study are included in Appendix A under the same heading.

2.2 Optimization

Task - 4.1 - Understanding Geologic Storage

Optimization studies aimed to realize operational efficiencies or cost savings that might make CO_2 storage a technical and economic success.

Cost reduction in CO_2 capture, transportation and injection (BMI, UT, Reinertsen, IFE)

The Battelle (Gupta) study on CO_2 impurities tradeoffs serves as a link between storage studies proper and those examining transportation and capture issues. The substantial cost savings potential in CO_2 capture of delivering CO_2 contaminated with impurities such as SOx, NOx and others (e.g., N_2 , O_2, 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_2 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_2 under various conditions (e.g., offshore vs. onshore, distance, presence of cooling water, CO_2 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_2 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_2 indicate that the specification might be further relaxed to 1300 ppm. The effect of CO_2 impurities such as N_2 and CH_4 will have significant effects on water solubility in CO_2.

The IFE (Seiersten) study provided experimental results that were used in the Reinertsen Engineering study. Existing models and mechanisms for CO_2 corrosivity to carbon steel were found to be inadequate at pressures above 20 bars. Experimental data obtained at higher pressure (up to 50 bars) showed that CO_2 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_2 transport in inexpensive carbon steel pipelines which may improve the economics of CO_2 storage offshore.

Leveraging natural resources to offset CO_2 storage costs (NMT, TTU, and Tie-Line Tech)

The New Mexico Tech (Grigg) study surveys the performance of Permian Basin (West Texas, Southeast New Mexico) CO_2 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_2 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_2S 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_2 EOR survey is a valuable 'lessons learned' exercise for CO_2 storage efforts given the extensive and unique collective experience of such operations.

The feasibility of CO_2 storage in depleted gas and gas condensate reservoirs and possible enhanced gas condensate recovery was 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_2 Sequestration Parameter" tool for optimal CO_2 storage is ready for testing. It was determined that CO_2 compressibility is much higher (lower Z factor) than that of hydrocarbon gases, indicating that CO_2 storage capacity might be up to five times higher that that of the original hydrocarbons. Dry gas with high %CO_2 exhibits wet gas phase behavior whereas retrograde gases become dryer in behavior (retrograde liquid is vaporized). The "CO_2 Sequestration Parameter" tool will assess for a given reservoir the UCSV (ultimate CO_2 sequestered volume) and a material balance approach will assist project design and surveillance. The study has added much needed data on CO_2 and hydrocarbon phase behavior and the tools for rapid screening of candidate gas and gas condensate reservoirs for safe, effective and economic CO_2 storage.

Tie-Line Technology (Stenby) developed models and software for screening CO_2 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_2 EOR as CO_2 storage miscibility delays breakthrough and maximizes storage. Prediction of post breakthrough gas composition is essential for surface facility design.

Improving CO_2 injection and reservoir performance (UT-Pope)

The aquifer CO_2 injection simulation study by the University of Texas (Pope) was aimed at improving understanding of physico-chemical behavior of CO_2 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_2. The time required for CO_2 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_2 migration to the top of the formation. Immobilization of about half of the CO_2 injected occurs by the cessation of the 50 year injection period and >95% is immobilized in the 10^3 year timeframe. CO_2 mineralization rates depend on reservoir mineralogy and are expected to be significant on the 10^5 timeframe. The assumptions about various CO_2 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_2 is largely immobilized over the 10^2-10^3 year timeframe.

The University of Texas (Bryant) study examined the possible subsurface implications of injecting CO_2 with impurities (e.g., SOx, NOx) into aquifer (dissolution / precipitation affecting injectivity) and CO_2 EOR (MMP and fluid displacement) reservoirs. It was found that injecting CO_2 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_2 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_2 impurities (particularly soluble species such as SOx and NOx) are not of particular concern in aquifer injectivity or EOR performance. Other gases such as N_2, however, would present operational difficulties and degrade performance.

2.2.1 Depleted Gas and Gas Condensate Reservoirs for the Geologic Storage of CO_2

Task - 4.1 - Understanding Geologic Storage
Principal Investigator: Scott Frailey; Akanni S. Lawal
Technology Provider: Texas Tech University
Co-funder: DOE

Highlights

- The analyses of results show that irrespective of the CO_2/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_2 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_2 sequestered CO_2 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_2 storage; and the use of material balance reservoir model and volumetric equation to develop guidelines for selecting depleted gas reservoirs for CO_2 storage.

To quantify the volume of sequestered CO_2, enhanced gas recovery (EGR) and enhanced condensate recovery (ECR), a material balance model and volumetric equations are developed to determine how much CO_2 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_2. 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_2 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_2 in depleted or abandoned gas reservoirs.
- Determine EGR and EOR benefits of geologic CO_2 storage in dry gas, wet gas, and retrograde reservoirs.
- Develop guidelines for selecting candidate reservoirs for CO_2 storage.

The methodology used towards proving a reliable and resourceful means of validating the use of depleted gas reservoirs for CO_2 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_2 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, ϕ, and S_w) and PVT data (Z-factors, gas-type, liquid drop-out) are required. Material balance does not require petrophysical data, but PvT, 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 UCSV. 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 focused 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 Sequestrating 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_2 Miscibility Determination

Task - 4.1 - Understanding Geologic Storage
Principal Investigator: Erling Stenby
Technology Provider: Tie-Line Technology
Co-funder: DOE

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_2. in 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 produced during the gas injection process. The simulation tool will be of significant importance in evaluation of CO_2 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 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 is in Appendix A under the same heading as this summary.

2.2.3 Reservoir Simulation of CO_2 Storage

Task - 4.5 - Risk Assessment and Mitigation Options
Technology Provider: University of Texas
Principal Investigator: Gary Pope
Cofunder: DOE

Highlights

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

- The bulk of the CO_2 injected is stored in CO_2-saturated brine and CO_2-rich residual gas phases.
- Although temperature, salinity, aquifer dip, and residual gas saturation significantly affect the distribution of CO_2 in the aquifer, residual gas saturation has the greatest effect on the distribution and immobilization of CO_2 in the aquifer.
- Injecting CO_2 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_2 is rendered immobile and >95% is immobile after a few centuries. Mineralization resulted in 2 – 3% of the CO_2 stored after 10^3 years this figure may be more significant on the 10^5 year time frame.

Summary:

This project involved modeling and simulation of a CO_2 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_2 in deep saline aquifers and to quantify these phenomena. Specifically, the effects of dissolving CO_2 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_2. Storing CO_2 in a denser, CO_2-rich aqueous phase should reduce the risk of CO_2 escaping from the aquifer by reducing the potential for upward migration. Mineralization is another possible sink for CO_2. The CO_2 -rich aqueous phase is acidic and can react with the minerals present in the aquifer. The injected CO_2 is consumed in the production of secondary minerals. By this mechanism, CO_2 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_2 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_2 in brine at different temperatures, pressures, salinities, and CO_2 concentrations were obtained from the literature.

The second task was to quantify the effect of CO_2 on the brine density. The impact of some of the most important aquifer parameters on the storage of CO_2 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_2 trapped in the residual gas phase and in the brine. To determine the impact of well completion strategy on CO_2 storage, additional simulations were run using alternative CO_2 injection schemes.

The third task was to estimate the capacity for CO_2 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_2.

Simulations were run injecting pure supercritical CO_2 through a single, centrally located injection well. CO_2 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_2 was only injected into the lower half of the aquifer and CO_2 injection was increased to 50 years to see how injecting greater amounts of CO_2 affected storage. Total simulation time for these runs was 100,000 years.

Residual gas saturation may be the most significant aquifer parameter affecting CO_2 storage. Simulation results showed that the bulk of the CO_2 was stored in a CO_2-saturated brine and in a residual CO_2-rich gas phase with the largest percentage of CO_2 being stored as an immobile, residual gas. In most cases, only a few percent of the CO_2 remained as a free, mobile gas. Gravity-driven flow after CO_2 injection is stopped is the primary mechanism that leads to the conversion of free CO_2 to trapped forms. Movement of mobile CO_2 leads to contact with unsaturated water. More CO_2 dissolves in the unsaturated brine and some of the CO_2 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_2 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_2 storage mechanisms, magnitudes and time scales.

Well completion strategy can play an important role in increasing the amount of CO_2 stored in immobile forms. Results from simulations injecting CO_2 into only the lower half of the aquifer indicated that with time all the gas will be trapped in various forms and free CO_2 will never reach the top of the aquifer. The simulation results showed that, for the reservoir properties studied, reduction of CO_2 to trapped forms required on the order of a few centuries.

The amount of CO_2 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_2 injection. The simulation results showed that the amount of CO_2 trapped by mineralization is highly dependent on the amount and type of minerals present in the aquifer and that trapping of CO_2 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_2 Impurities Tradeoff – Surface (SOx/NOx) Impurities Study)

Task - 4.5 - Risk Assessment and Mitigation Options
Principal Investigator: Neeraj Gupta
Technology Provider: Battelle Memorial Institute
Co-funder: DOE

Highlights:

This work provides a review of existing technologies used for CO_2 gas separations. It addresses 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_2 streams on the aboveground processing equipment. The study, which focuses on SOx and NOx 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_2, SOx, and NOx species with moisture present.

Flue gas impurities such as SOx and NOx, as well as arsenic and mercury present in solid fuels, have the potential of interacting unfavorably with capture, compression, and pipeline transmission of CO_2. Absorption and regeneration characteristics of amines and other solvents used to separate CO_2 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_2 streams and the influence of NOx and SOx 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_2 and NO_2 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 SOx and NOx with CO_2 under pressurized wet conditions. A fundamental approach is suggested to qualitatively evaluate the effect of small amounts of SOx and NOx in CO_2 on corrosion properties of pipeline material.

This study provides a general overview of the state of knowledge of technical issues associated with CO_2 impurities tradeoffs. Once a range of CO_2 stream concentration possibilities is specified by those working on CO_2 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_2 Impurities Tradeoff – Subsurface

Task - 4.5 - Risk Assessment and Mitigation Options
Technology Provider: University of Texas
Principal Investigator: Steven Bryant
Co-funder: DOE

Highlights

- Presence of CO_2 impurities (e.g., SOx/NOx) in injected CO_2 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_2 capture cost and CO_2 EOR performance indicate that a reasonable SOx/NOx 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_2 on well injectivity and the EOR recovery process is deemed small to negligible at the likely levels of impurity occurring in CO_2 streams.

Summary

This project had two goals. The first one was to examine the potential effect of highly reactive impurities (SOx, NOx) on well injectivity into clastic aquifers during large-scale CO_2 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_2 (as opposed to, say, alternating water and CO_2), 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_2. 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_2 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_2 will extract intermediate components from the crude into the CO_2 - rich phase. The extraction depends strongly on the purity of the solvent. CO_2-N_2 mixtures are poorer extractors than CO_2 alone, whereas CO_2-H_2S mixtures are better extractors. MMP generally decreases as the solvent becomes more "oil-like". Thus, impurities in a CO_2 stream which behave more like the oil than CO_2 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_2 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 SOx/NOx 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_2 stream contaminants is unlikely to adversely affect injection rates into clastic aquifers or the performance of CO_2 EOR operations (e.g., WAG). Larger concentrations of some components (e.g., 5% SO_2) may have only a slight adverse effect on the EOR process. Thus capture processes that yield less than pure CO_2 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_2 Impurities Tradeoffs (Subsurface) – 2003 CCP-SMV Workshop Presentation, Dublin
- The final project report is presented in Appendix A under the same heading.

2.2.6 Long-Term CO_2 Storage - Using Petroleum Industry Experience

Task - 4.5 - Risk Assessment and Mitigation Options
Technology Provider: New Mexico Institute of Mining Technology
Co-funder: CCP

Highlights

- Around 160 projects have been studied for CO_2 IOR (Improved Oil Recovery) with 140 of them actually injecting CO_2. This research reviewed the 65% of these projects that are in the Permian Basin of West Texas/SE New Mexico.
- There is significant experience and knowledge in the industry to separate, compress, transport, inject, and process the quantities of CO_2 that are envisioned for CO_2 sequestration/storage.
- An area that is in its infancy is the monitoring and verification of CO_2 flow in geological formations.
- Experience has shown that CO_2 goes where expected unless the reservoir characteristics are not well understood and/or not honored if known.
- In the short geological time frame that CO_2 has been actively injected into geological formations, seals are retaining the CO_2 in place. Proven seals, to date, perform as expected.
- Since CO_2 is not flammable and is much less toxic than many other fluids that are transported in great quantities and at high pressure, it is well within the capability of the industry to separate, compress, transport, inject, and process enormous quantities of CO_2 at acceptable safety levels for the public.

Summary

This project comprised a survey of Permian Basin reservoirs that were either injected with CO_2 or were seriously considered for CO_2 injection. The focus was an assessment of successes and problems in these projects and their long-term CO_2 storage potential. Data includes information from the biannual Oil & Gas Journal EOR Survey, Society of Petroleum Engineers publications, and CO_2 field project engineers representing all but two of the CO_2 injection project operating companies.

There is significant experience and knowledge in the industry to separate, compress, transport, inject, and process the quantities of CO_2 that are envisioned for CO_2 sequestration/storage. Improvements will occur as incentives, time and fluid volumes increase. The most important requirement is the provision of incentives to sequester CO_2.

In some cases certain phenomena that had been noted during waterflood were not included in simulating CO_2 processes—an omission that can prove, and has proven, disastrous. When reservoir characteristics are well understood, CO_2 has performed as expected. Also, the phase properties of CO_2 must be honored in predictive models. High-pressure CO_2 performs as expected: it mobilizes oil, dissolves into brine, and promotes dissolution of carbonates. Brine can become supersaturated with dissolved solids and when pressure drops as it advances through the reservoir precipitants can form. However, the kinetics of dissolution and precipitation under many reservoir conditions require further study.

In the short geological time frame that CO_2 has been actively injected into geological formations, seals are maintaining their integrity and retaining CO_2 in place. Proven seals perform as expected in retaining CO_2. Monitoring and verification of CO_2 flow in geological formations is critical to verification of sequestration, but technical development is in its infancy.

Surface safety was not specifically covered in this discussion, but warrants review. In working for over twenty-two years in the area of CO_2 production, transportation, and injection into geological formations of significant quantities of CO_2, the author had not heard of one fatality. Safe transportation of CO_2 and other high-pressure gases warrants great optimism that global transport of CO_2 on an enormous scale would be accomplished at very low risk.

Reports and Publications

- CCP-SMV 2002 Workshop, Santa Cruz
- CCP-SMV 2003 Workshop, Dublin
- The final project report is presented in Appendix A under the same heading.

2.2.7 CO_2 Conditioning and Pipeline Transportation

Task - 4.5 - Risk Assessment and Mitigation Options
Technology Provider: Reinertsen Engineering
Co-funder: Klimatek

Highlights

- The extent to which carbon steel, as opposed to more expensive alloys, can be used in pipeline transportation of CO_2 is examined. Avoidance of free water is essential to prevent corrosion and hydrates formation.
- Pipeline transportation in carbon steel of relatively dry (~600 ppm) CO_2 has encountered few operational problems over the past 25 years. To date, the Sleipner Vest project (short export line / injection system from CO_2 separation facility on platform) is the only offshore CO_2 piping project.
- Planned offshore CO_2 piping operations will likely involve greater distances with minimal opportunity for gas conditioning. Experimental data suggest that the most stringent specifications (e.g., Hammerfest LNG; 50 ppm) might be relaxed under expected PT conditions to ~600 ppm and, based on theoretical calculations of free water precipitation from supercritical CO_2, possibly to ~1300 ppm.
- The ability to relax dehydration specifications as indicated by this study will have an important impact on project economics, particularly where long distance transmission is required.

Summary

This project has been concerned with recommending and documenting safe and cost effective methods for design, construction and operation of compression and pipeline transportation of CO_2-rich mixtures under different conditions, such as:

- Offshore versus onshore
- Distance long or short.
- Cooling water at 10 oC available or not
- CO_2 impurities like CH_4 ,N_2 , H_2S , water....

Pipeline transportation of CO_2 onshore has been going on for more than 25 years, with an excellent operational record. Liquid or dense phase CO_2 gives the optimal throughput and careful drying to avoid free water allows the use of ordinary carbon steel pipelines. Offshore injection has also been going on for 7 years at one field in the North Sea, using stainless steel for direct injection through one well.

The CO_2 pipeline transportation system can be split in three main parts:

- compression,
- drying,
- Pipeline transportation.

One major reason for CO_2 capture or concentration is, in addition to reducing the overall gas volumes to be handled, to get the efficiency benefits from being able to handle and transport CO_2 in the liquid or dense phase. This increases the capacity of the pipeline, but also allows the use of pumping, thus reducing the footprint and increasing the efficiency in relation to compressors.

In particular, common impurities such as nitrogen (N_2) or methane (CH_4) have a significant impact on the phase behavior of CO_2-rich mixtures, and thus the pressure/temperature needed to enter the recommended liquid or dense phase.

In order to obtain an optimized design for the compression process and pipeline system, accurate and reliable predictions of fluid properties, particularly phase envelope, density and water solubility, of CO_2-rich mixtures are of vital importance. In this project several thermodynamic models and tools for calculating properties for CO_2-rich mixtures have been tested against available experimental data, e.g. from the NIST database. For CO_2 phase behavior with impurities the Lee Kessler-model is recommended, as it is in satisfactory agreement with existing experimental data both in gas, liquid and dense phase.

To avoid the risk of corrosion and hydrate formation the CO_2 is usually dried, before entering the pipeline, so that no free water can precipitate. Drying of CO_2 with use of triethylene glycol (TEG) is most commonly used, and it is operating satisfactory at many locations today, just as molecular sieves is another option.

For solubility of water in pure CO_2, the SRK-model with the binary coefficient adjusted to 0.193 in Van der Waals mixing rule gives the best approximation to experimental data. Adding impurities such as CH_4, N_2, H_2S and amines to the CO_2-mixture will affect the phase curve, as well as the solubility of water. For example the addition of 5% methane lowers the calculated water solubility in the liquid phase considerably. However, more experiments are necessary to verify the models.

The modeling and experiments done by IFE in another CCP project clearly indicate that the drying requirements can be relaxed from existing practice. If 10°C cooling water is available, the water removal can be done in a scrubber at conditions where the water solubility in CO_2 is low (e.g. 600ppm at 50-60barg pressure). As the solubility in the dense phase is more than the double of this, no separate water removal unit should be necessary. If 10°C cooling water is not available a separate drying unit still is cost effective, but drying requirements should be adjusted to the level really needed.

The CO_2 conditioning and transportation study has reexamined existing operation practices by incorporating theoretical and new experimental (from IFE) into new models for more cost effective designs. Accurately predicting the behavior of water (free versus dissolved) in supercritical CO_2-rich fluids is essential for predicting the concentrations and conditions at which free water occurs and corrosion and hydrates formation become significant. Relaxation of specifications can extend the use of economical carbon steel such that project economics are acceptable.

Reports and Publications

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

2.2.8. Materials Selection for CO_2 Capture and Storage)

Task - 4.5 - Risk Assessment and Mitigation Options
Technology Provider: Institute for Energy Technology (IFE)
Co-funder: Klimatek

Highlights

- The literature survey and experiments performed in this project show that dry CO_2 and CO_2 that is not saturated with water is non-corrosive to carbon steel at transportation pipeline operation conditions.

- When using ordinary carbon steel for pipelines, the solubility of water in the relevant CO_2 -rich mixture in liquid/dense phase should be verified before determining the drying level necessary to avoid the free water precipitation.

- Existing corrosion prediction models generally are not valid for CO_2 pressures above 50 barg. Experiments indicate that corrosion rates are lower than earlier anticipated, and can be reduced to acceptable levels by the use of corrosion inhibitors.

- More experimental work is needed to develop valid corrosion prediction models for different steel alloys subject wet CO_2 -rich mixtures at high pressures.

Summary

The objective of this project is to establish an improved basis for materials selection for CO_2 capture, compression, transportation, and injection. The project has been closely coordinated with those of CO_2 Transportation project run by Reinertsen Engineering and SINTEF. The key deliverables are:

1. Quantification of the amount of water that can be dissolved in relevant CO_2-rich mixtures at 50-500 Bara and temperatures up to 30°C. The effect of trace elements from the CO_2 separation process is also addressed.
2. Deliver data needed by the Reinertsen/SINTEF project in the development of a cost effective design of CO_2 transportation systems.
3. To determine the corrosion rate of carbon steels in liquid/supercritical CO_2 as function of water content, temperature and pressure and to assess if it is possible to extend the use of carbon steels with corrosion inhibitors.

Choice of materials for transportation and storage of CO_2 is a critical issue although the oil industry has used re-injection of CO_2 for decades with little or no such problems related to corrosion. Low alloy carbon steel pipelines have been used for transportation of liquid CO_2 at high pressure, but in all these cases, drying the CO_2 and removing free water in the pipeline have eliminated the corrosion risk. Drying the CO_2 increases the handling costs especially at offshore installations. Based on the experimental results from this project, a corrected model for the calculation of water solubility in CO_2-rich mixtures has been proposed in the Reinertsen/SINTEF project.

If the transportation distance is more than a few km, carbon steel will be the most cost effective material for CO_2 pipeline transmission. Reliable design and operation of such pipelines will depend on trustworthy corrosion data. Such data will also have to be included in corrosion prediction models.

It is common knowledge that CO_2 is corrosive in aqueous environments as found in oil and gas pipelines. The seriousness of CO_2 corrosion has been thoroughly studied at partial pressures relevant for oil and gas transport; i.e. at $pCO_2 < 20$ bar, and there exist a number of corrosion prediction models that can be used to assess CO_2 corrosion rates. However, a thorough review of the literature in this field has revealed only a couple of earlier works on corrosion at CO_2 pressures above 50 bars. There is a need therefore for more experimental data for CO_2 partial pressures above 20-50 bars to make reliable corrosion assessments for future pipelines carrying wet fluids with high CO_2 content. If such data does not exist, a corrosion engineer reviewing a case will have no choice but to recommend an expensive, corrosion resistant alloy or specify extensive drying of the CO_2. Drying adds additional cost particularly in offshore installations. Corrosion resistant alloys will in many cases be a project "show stopper" if the transportation distance is long.

The long-term objective for the work on CO_2 corrosion at high pressures is to develop a corrosion prediction model. Whether this will be an extension of an existing model or a new development will depend on the corrosion mechanisms. If the mechanism(s) is the same as at low pressure it will probably be possible to make adjustments to existing models so that they can be used at higher CO_2 pressures. If the corrosion mechanism turns out to be different, new developments will be needed for high-pressure models. Understanding the corrosion mechanism(s) will not prevent corrosion, but it will be fundamental to define the operation window for models that can predict corrosion. Reliable corrosion models contributes to cost savings by making it possible to use the most cost effective materials and processes that are adequate to extend the use of low alloy carbon steel and limit the need for extensive drying of CO_2.

CO_2 with water levels above saturation is corrosive when water precipitates. The limited number of experiments done in this project show that the corrosion rates at high CO_2 pressures in systems containing only water and those containing water/MEG mixtures are considerably lower than predicted by existing corrosion models, particularly at the low temperatures typical for sub-sea pipelines in northern waters. More work is needed in order to understand the possible mechanistic reasons for these inconsistencies.

The materials selection / corrosion study provides much needed experimental data for documenting the behavior of hydrated CO_2 at elevated pressures expected in CO_2 transportation. The data provided to Reinertsen / SINTEF became an integral part of their study seeking approaches to lower the costs of pipeline transmission through use of carbon steel.

Reports and Publications

- CCP-SMV 2003 Workshop, Dublin
- Kongshaug, K.O. and Seiersten, M. (2004) Baseline experiments for modeling of corrosion at high CO_2 pressure, NACE / 2004, New Orleans (March 28-April 1).
- The final project report is presented in Appendix A under the same heading.

2.2.9 Gas Storage Technology Applicability to CO_2 Sequestration

Task - 4.5 - Risk Assessment and Mitigation Options
Technology Provider: Gas Technology Institute
Co-funder Klimatek

Highlights

- During the past 90 years of operation of approximately 600 natural gas storage fields in North America and Europe, only **nine** gas migration incidents have been identified. Three were due to caprock issues, five due to well-bore integrity and one due to reservoir selection (too shallow).

- Most gas migration incidents in underground gas storage operations have occurred due to well-bore integrity problems. In all these cases the leakages were stopped with remedial action procedures and technologies that are well established in the oil and gas industry.

- The gas migration incidents through cap-rock are facilitated by fracturing or faulting associated with development of the anticlinal structures of gas storage reservoirs. It is advisable, therefore, that selection of CO_2 aquifer storage sites favor those with more gently sloping caprock formations.

- The five most relevant technologies/techniques from underground gas storage applicable for CO_2 storage are:

    - "Watching the Barn Doors" (keeping track of gas in and gas out)
    - Gas Storage Observation Wells
    - Pump Testing Techniques to verify Caprock Sealing
    - Caprock Sealing
    - Surface Monitoring.

Summary

The underground storage of natural gas in depleted oil/gas fields, aquifers and salt caverns is currently a well-established industrial operation at nearly 600 locations around the world. Operators of CO_2 storage facilities will face many issues similar to those that gas storage operators and regulators have experienced. The principal concerns are:

- The Migration of Injected Gas over Time.
- Technologies for Monitoring the Location of the Gas.
- Integrity of Caprocks.
- Monitoring of Zones above Caprocks for Leakage.

The purpose of this study has been to review the portfolio of technologies available within the underground natural gas storage industry to assess its applicability to CO_2 sequestration.

This review of gas storage technologies has focused on three major areas:

1) Gas Storage Field Integrity Determination,
2) Gas Storage Field Monitoring and Leak Detection Techniques
And
3) Gas Storage Field Operator Response to Leaks and Leak Mitigation.

Emphasis has been placed on the technology developed in particular by the aquifer gas storage industry. The technologies developed and utilized by the operators of depleted oil and gas fields, however, have also been included. Where appropriate, gas storage technology issues specifically relevant to CO_2 storage are highlighted.

The study procedure entailed conducting a worldwide literature search with a focus on vertical gas migration issues and interviewing natural gas storage facility operators in Europe and the United States. Gas storage operators have accumulated a significant knowledge base for the safe and effective storage of natural gas. Whereas occasional unwelcome gas migration has occurred due both to mechanical problems with wells and geologic factors, overall gas storage has been remarkably safe and effective. Most gas leakage incidents in gas storage operations have occurred due to well-bore integrity problems. In all of these cases leakage has been arrested with remedial action procedures and technologies that are well established in the oil and gas industry.

All of the geologically-controlled gas migration problems have occurred in the cap-rock of aquifers being converted to gas storage. In each of these cases the most likely reason is due to some type of fracturing or faulting associated with the structural development of these anticlinal features. Site selection specialists for CO_2 storage operations should therefore avoid aquifer/trap systems that are intensely structured. Gently sloping structure and caprock formations may be preferable for long term CO_2 sequestration.

It is specially-noted that unwanted migration of gas has occurred despite application of practically all-available integrity determination techniques. Accordingly, the caution directed to the gas storage industry by Dr. Donald Katz, a pioneer in natural gas engineering and gas storage, in the 1960's is likely to be appropriate also for the developing CO_2 industry: "Caution must be exercised in claiming that no gas will ever be found outside the intended reservoir system. If any gas is found outside the intended system, it is possible that it can be handled so as to cause little or no harm, and should be no cause for calling a halt to the operations. Therefore, it is necessary in any full description of a fifty-year life for a storage operation to admit that, on occasions, some gas will enter the waters and even the soil, but that mechanical repairs are available so that the leak can be halted".

The "science of observation wells" as major early detection monitoring tool for CO_2 storage should be recognized and is recommended for additional research.

The natural gas storage analogs study has important implications for CO_2 storage. Natural gas storage has an exceptional safety record despite involving a flammable, highly mobile gas stored in shallow settings sometimes near urban areas. By analogy, the projected safety record CO_2 storage is more secure given that CO_2 will be placed deeper in the subsurface, it is soluble in water and because of public scrutiny sites will be relatively remote from populated areas. The principal adverse comparison is that CO_2 is heavier than air thus can act as an asphyxiant in closed structures or topographical depressions. Tools and protocols used to remediate natural gas leaks may apply in some cases to CO^2 leaks but further development is required.

Reports and Presentations

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

2.2.10 EOR/CO_2 Storage Optimization and Economics – Consolidated Summary

Technical Provider: Merchant Consulting

Highlights

The purpose of this project was to provide a summary of current knowledge of CO_2 flooding, reviewing the history of its development, explaining of how CO_2 flooding works, and discussing the technical and economic issues that are important to making a CO_2 EOR project profitable.

- CO_2 EOR projects have been in operation for over 30 years and many of the technical questions surrounding the theory and successful design and application of CO_2 floods have been answered.
- This report summarizes many of these technical and economic issues and provides a guide for the successful design and implementation of a CO_2 EOR project.
- Many of the issues highlighted as key for CO_2 EOR floods are also important for CO_2 sequestration projects in non-hydrocarbon bearing formations.
- The costs of CO_2 floods are well understood as well as how to best manage those costs.
- Future incentives associated with sequestering CO_2 may be sufficient to improve the marginal economics of many old and abandoned oil fields that are good technical candidates for CO_2 flooding.
- Transportation costs and issues, such as corrosion, for CO_2 sequestration projects have been defined and, in many cases, resolved through the experiences obtained from CO_2 EOR projects.
- Two projects, the Slaughter Estate Unit and the Yates field, are discussed in detail.

Summary

The objective of this project was to provide the CO_2 Sequestration Community with a report that summarizes the current understanding of the CO_2 EOR process and provides a review of key elements in the design, operation, and reservoir management of CO_2 floods. This knowledge base is the result of over 30 years of industry experience. The report includes (1) an overview of CO_2 EOR oil recovery methods including a history of its development, the types of reservoirs that are amenable to CO_2 flooding, and a discussion of CO_2 EOR project economics and tax treatments, (2) a discussion of key steps in CO_2 EOR flood design and implementation including a list of rules of thumb for successful EOR projects, the importance of reservoir characterization and modeling studies, pipeline transportation issues, and permitting and safety requirements, (3) a detailed discussion of two CO_2 EOR projects using different recovery methods, and (4) the impact of impurities in the CO_2 stream on CO_2 EOR project performance.

The historical review of CO_2 EOR projects focused mainly on experience gained in the Permian Basin in West Texas since this is the site of most CO_2 floods worldwide. Learnings from these floods were condensed into a list of technical and business issues that affect the profitability of CO_2 EOR projects. Technical issues include reservoir and rock properties, crude oil composition and properties, and the residual oil saturation following primary or secondary production.

The discussion of CO_2 flood design and implementation covered the importance of reservoir homogeneity, the benefits of achieving miscibility, the state of field infrastructure development and the condition and suitability of existing infrastructure for CO_2 flooding. In addition, pipeline and safety regulations were briefly discussed. The importance of reservoir management was covered in detail in the discussions of two CO_2 EOR projects.

The benefits and drawbacks of impurities in the CO_2 stream were also discussed. Some impurities, such as N_2 and CH_4, can raise the minimum miscibility pressure and consequently reduce the effectiveness of the EOR process. Other impurities, such as ethane and propane, can actually reduce the minimum miscibility pressure making it easier to achieve miscibility. In some cases, these C2 or C3 impurities have actually been added to a CO_2 stream to make it easier to achieve miscibility. Other impurities such as SO_x and NO_x can interact with formation minerals potentially impacting injectivity. Other studies, however, have concluded that these types of impurities are unlikely to affect injectivity. The fact that the CO_2 EOR process is robust enough to tolerate impurities in the CO_2 stream is evidenced by the fact that successful projects have been run using flue gas.

Key messages from this study include:

- Many of the technical questions surrounding the theory and successful design and application of CO_2 floods have been answered during the 30 years of industry experience gained from applying this technology.
- Reservoir properties and geometry dictate which of four CO_2 EOR methods are best suited for a particular reservoir. The choice of method has significant implications for CO_2 sequestration projects since the amount of CO_2 that can be sequestered ranges from minimal for huff-and-puff projects to up to 80% of the total pore volume for gravity stabilized floods.
- Projects do not need to operate above the minimum miscibility pressure to be successful, however, lower recoveries are typically obtained when miscibility is not achieved.
- Reservoir management programs are key to project success.
- Impurities in the CO_2 stream can either raise or lower the minimum miscibility pressure. However, successful projects have used CO_2 with contaminants. If fact, flue gas has been used in some applications.
- Many of the issues highlighted as key for CO_2 EOR floods are also important for CO_2 sequestration projects in non-hydrocarbon bearing formations.
- Future incentives associated with sequestering CO_2 may be sufficient to improve the marginal economics of many old and abandoned oil fields that are good technical candidates for CO_2 flooding.
- Transportation costs and issues, such as corrosion, for CO_2 sequestration projects have been defined and, in many cases, resolved through the experiences obtained from CO_2 EOR projects.

This report represents the key deliverables for this project, (1) a better understanding of the history of CO_2 flooding, (2) the types of reservoirs that CO_2 can be injected into, and (3) the economic hurdles that must be crossed in order to implement a new CO_2 flood. No additional work is planned on this project.

Reports and Presentations

- The final project reports are included in Appendix A. Three reports are included in Appendix A under heading 2.1.10, 2.1.11, and 2.1.15. The work was carried out under three contracts but the summary is consolidated here.

2.2.12 Quantification of Geologically Controlled Gas Leakage from Gas Storage Fields

Technical Provider: Gas Technology Institute (GTI)

Highlights

The purpose of this study was to screen and select leaking and non-leaking gas storage fields for use in further research designed to increase understanding of geologic leak mechanisms.

- Sets of selection criteria were established for the candidate leaking and non-leaking gas storage fields.
- One non-leaking and five leaking gas storage fields were identified as potential candidates for use in future studies.
- The Ancona-Garfield gas storage field, located in Livingston County, Illinois and operated by Nicor Gas, was identified as the best candidate of the five leaking gas storage fields evaluated.
- The Herscher gas storage field, operated by Kinder Morgan and located in Kankakee County, Illinois, was identified as the preferred backup field in the event Nicor Gas was unwilling to participate in the study.
- The Manlove gas storage field, operated by Peoples Energy Corporation and located in Champagne County, Illinois, was identified as a suitable non-leaking analog for use in future studies. Gas storage is in the Mt. Simon formation in all three of the preferred candidate leaking and non-leaking fields.
- A subcontract was executed with Utah State University in November in anticipation of modeling studies to be conducted on the leaking and non-leaking gas storage fields.
- All project goals were met except for securing participation of the operator of a leaking gas storage field. Operators of the two top-ranked leaking fields, Nicor and Kinder Morgan, were contacted for project participation. A proposal for participation was presented to Nicor management and is currently under review with a decision expected soon. The holdup is Nicor's concern over information and data on the gas leak going into the public domain. An agreement with the operator of the non-leaking gas storage field is not necessary since information and data on this field is already in the public domain.

Summary

This project was an extension of work reviewing natural gas storage fields and seepage of CO_2 from natural accumulations that was conducted for the CO2 Capture Project by Gas Technology Institute and Utah State University. This study constitutes the first phase of a larger project with the following specific goals:

- Geologically describe leakage pathways.
- Identify and characterize leak points, faults and other structures.
- Quantify relative volumes of the leakage into shallow formations and identify zones of accumulation and cause for accumulation.
- Establish criteria for determination of potential leaky fields.
- Form recommendations for mitigation of leakage, control of leakage and sealing of leakage where possible.

The objective is to achieve these goals through a comparison of data from two existing aquifer gas storage fields with similar geologic settings, one leaking and the other non-leaking. The goals for this first phase of the project are;

- Review, screen and select a leaking and non-leaking gas storage field
- Secure operator agreement to participate in further studies.
- Define the scope of modeling work to be conducted in subsequent studies.

The first step in the process for selecting the leaking and non-leaking fields was to develop a list of criteria to use in the selection process. The criteria selected are identified in the table. Detailed descriptions of these criteria are presented in the report.

CRITERIA	LEAKING FIELDS	NON-LEAKING FIELDS
Active field	X	X
Existing gas leak	X	
Leak to surface	X	
Leak controlled by operator actions	X	
Gas accumulation in secondary formations	X	
Monitoring wells available	X	X
Minimum ten years data	X	X
Adequate number of wells for geologic control	X	X
Operator agreement to participate	X	X

Using these criteria, five candidate leaking gas storage fields were identified. The Ancona-Garfield gas storage field, located in Livingston County, Illinois, and the Herscher gas storage field, located in Kankakee County, Illinois, were identified as the two best candidate fields. This assessment was based on the fact that both of these fields met all of the criteria with the exception of having an operator agreement in place. The Ancona-Garfield storage field is considered a better candidate than the Herscher field because it has newer well logs and more data in the public domain than the Herscher field. However, as yet, the operator of the Anocona-Garfield storage field, Nicor Gas, has not agreed to participate in any future studies. If Nicor Gas does not agree to participate, then Kinder Morgan, the operator of the Herscher field, will be contacted.

The Manlove gas storage field, operated by Peoples Energy Corporation in Champaign County, Illinois, was identified as the preferred non-leaking analog. The Manlove and Ancona-Garfield fields both inject gas into the Mt. Simon formation and the two fields have the same caprock. These two similarities are important and help make these fields an excellent choice for a study trying to understand and quantify a geologic gas leak.

The modeling work for subsequent studies will focus on development of a 3D model of the leak mechanism in the selected leaking gas storage field. The modeling effort will integrate the effects of faults on caprock integrity, mapping of leak points and description of flow through the caprock. The model will be tested against the non-leaking gas storage reservoir to determine its ability to discriminate between leaking and non-leaking fields. The anticipated modeling deliverable is a developed and tested model with the capability to:

- Geologically describe leakage pathways within a geologically leaking field.
- Assist with identifying and characterizing leak points, faults and other structures.
- Quantify relative volumes of the leakage into shallow formations and identify zones of accumulation and cause for accumulation.
- Assist with establishing criteria for determination of potential leaky fields.
- Assist with formation of recommendations for mitigation of leakage, control of leakage and sealing of leakage where possible.

Conclusions for this study are:

- A list of high potential leaking gas storage fields was developed using a set of selection criteria developed for this project. Two of these fields, the Ancona-Garfield and the Herscher gas storage fields, were identified as top candidates. The Manlove gas storage field was selected as the non-leaking analog control field.
- A review of existing data from these fields and an analysis of the type of leaks have led to the conclusion that the proposed subsequent studies would yield important findings for sequestration field selection and operations.
- The Ancona-Garfield gas storage field applied a robust portfolio of field integrity determination techniques during initial field evaluation and, in spite of this comprehensive testing, a geologic leak went undetected. The existence of this type of geologic leak and further understanding of its geologic and engineering "nature" could be very valuable to future CO_2 sequestration projects.
- Agreement with Nicor Gas for project participation has not been concluded. This is a critical milestone and ongoing negotiations should be continued. The critical issue is the sensitive nature of a public domain study investigating an active leak in an active field.

Reports and Presentations

The final report for this study is presented in Appendix A

2.2.13 Field Abandonment Strategies

Technical Provider: University of Texas (UTX)

Highlights

The purpose of this study was to lay the groundwork for future studies aimed at identifying technologies and methods that can be used to verify that a geological CO_2 storage project has meet its design criteria. The ultimate goal of this work is to provide a framework for the development of strategies for abandoning geological CO_2 storage projects.

- A matrix of operational and geological parameters was developed that indicates the sensitivity of certain characteristics of long term storage to specific aquifer properties. The matrix can serve as a screening tool to help an operator qualitatively assess the impact of aquifer properties on CO_2 storage project objectives.
- A preliminary analysis to assess the sensitivity of CO_2 storage project operating costs to aquifer properties was performed. The aquifer properties highlighted in the matrix were used for the economic analysis with the intent that the results from the sensitivity analysis would enhance the utility of the matrix. The results from this analysis indicate that operating costs are fairly insensitive to aquifer properties.
- Current requirements for CO_2 enhanced oil recovery (EOR) projects and wastewater disposal wells were reviewed. The Texas Railroad Commission staff was consulted and State of Texas regulations governing EOR procedures and disposal of fluids in non-hydrocarbon producing formations were reviewed. While these types of regulations are likely to provide the framework from which CO_2 storage project regulations evolve, they currently contain almost no language specific to CO_2 operations. In addition, input was solicited from CO_2 EOR project operators.

Summary

This project builds on work from the CCP study "Simulation of CO_2 Sequestration in Saline Aquifers" as well as subsequent research. The overall objectives of the project include:

- Providing a technical basis for risk-of-leakage assessments for geological CO_2 storage schemes
- Developing methods for verifying that CO_2 has been stored as planned

The research program consists of three phases:

1. A synthesis of current understanding of how operational and geological parameters affect the likelihood of leakage
2. A synthesis of current field abandonment requirements for analogous operations (CO_2 EOR operations)
3. The testing and development of methods and techniques for determining the location and disposition of CO_2 injected into a deep saline aquifer.

The objectives of this first phase of the work include:

- Developing a matrix that outlines the relationships between operational and geological parameters and CO_2 distribution in a reservoir
- Providing a summary of current field abandonment and permitting requirements for CO_2 EOR projects.

The matrix of guidelines provides a summary of the relationships between aquifer properties and certain characteristics of long term storage of CO_2 in the aquifer. The aquifer properties evaluated in this study include temperature, salinity, permeability, dip, nonwetting phase residual saturation, anisotropy and thickness. The long term storage characteristics include the extents of vertical migration and of lateral spread, and the relative amounts of CO_2 dissolved in brine, trapped as a residual phase saturation, and still mobile.

The relationships summarized in the matrix of guidelines were based on results from simulations conducted with the Computer Modeling Group's GEM simulator. Simulations were conducted on a model aquifer 53,000 ft long x 53,000 ft wide x 1,000 ft thick with an injector in the center of the aquifer. One million tons of CO_2 per year were injected for 50 years followed by shut-in. Simulations were continued for 950 years following shut-in.

To begin the process of establishing a framework for what form abandonment regulations for CO_2 storage projects might ultimately take, regulations pertaining to CO_2 EOR projects were reviewed. The Texas Railroad Commission's (TRC) Office of the General Council was consulted. The relevant parts of the "Texas Administrative Code" which contains all Texas Code regulations concerning oil and gas operations were reviewed. In addition, discussions were held with operators of CO_2 EOR projects.

Conclusions for this study are:

- A matrix of guidelines was developed to offer operators of CO_2 storage projects a first-look screening tool to identify preferred aquifer properties. The matrix shows the sensitivity of long-term storage to specific aquifer properties.
- The matrix was augmented with a preliminary analysis of the sensitivity of operating costs to the same aquifer properties. More work on the economic analysis remains to be done. However, this preliminary study showed that the only previously available information on this topic may have overestimated CO_2 injectivity and the sensitivity of operating costs to aquifer properties is smaller than previously thought.
- The information gathered on EOR project permitting and abandonment requirements showed that these regulations are not directly applicable to a geological CO_2 storage operation. For CO_2 EOR projects, current regulatory requirements focus on the plugging of abandoned wells. Disposal well regulations deal mainly with ensuring that neighboring formations are not contaminated by the injected fluids. These regulations may eventually serve as a baseline for future regulatory frameworks. One key finding from discussions held with CO_2 project operators was that operators performing the injection often remain liable even after abandoning or selling the field.

Reports and Presentations

The final report for this study is presented in Appendix A

2.2.14 Non-seismic Monitoring of CO_2 Injection into the In Salah Gas Field

Technical Provider: Lawrence Berkeley National Laboratory

Highlights

The purpose of this study was to use numerical modeling to determine if gravity or electromagnetic techniques can be used to detect CO_2 injected into the In Salah gas field.

- Numerical modeling studies were conducted to determine whether gravity and electromagnetic techniques could detect the existence and migration of CO_2 injected into a geologic formation.
- The model created for the study resembles conditions in the BP operated In Salah gas field.
- Modeling studies indicate gravity measurements can detect CO_2 injected into a geologic formation.
- Study results indicate electromagnetic data can be used to detect injected CO_2 and to detect a CO_2 – water contact that has migrated up to 500 m.
- Based on study results and the relative ease of deployment, the gravity method is recommended as the first option to test in the In Salah field.

Summary

This project involved modeling studies to determine whether gravity and electromagnetic techniques can be used to detect CO_2 injected into a geologic formation. The objectives of the study were to (1) determine whether gravity and electromagnetic methods have the capability to detect and monitor CO_2 injection, (2) determine if measurable signals will be produced by introduction of CO_2, (3) determine the order of magnitude of spatial resolution that can be expected from gravity and electromagnetic techniques as a CO_2 – brine front moves within the reservoir, and (4) determine if gravity and electromagnetic techniques are a feasible alternative to seismic for monitoring CO_2 injection into the Insalah gas field.

A lot of work has been done to demonstrate that seismic techniques can be used to monitor the movement of CO_2 injected into geologic formations. Seismic methods are highly developed because of the extensive experience gained from using them in the petroleum industry. However, seismic methods are expensive to apply. Gravity and electromagnetic methods are substantially less expensive alternatives to traditional seismic methods. The relevant physical properties for CO_2, water, oil, and their mixtures are known so the expected changes in the gravity and electrical properties of a reservoir resulting from the injection of CO_2 can be assessed. This report assesses the potential of surface gravity and electromagnetic methods as means for monitoring the movement of CO_2 within the BP operated In Salah gas reservoir.

The gravity and electromagnetic methods were tested on a model that, in general, resembles the conditions of the BP In Salah field. The model created is 20 m thick at a depth of 1900 m with a 20% porosity and variable CO_2 and water saturations. The model indicates that the signal resulting from the change in the bulk density of the reservoir due to CO_2 injection is measurable. A 10% change in CO_2 saturation is detectable. The gravity method is not, however, able to distinguish the shape of a laterally displaced CO_2 – brine contact for a thin reservoir.

The same model is used to evaluate the potential of electromagnetic measurements. To simulate the electromagnetic system, the electric field in the surface to the model is calculated using 100 m electric dipoles operating at a range of separations in-line with the transmitting dipole. The results obtained from this analysis indicate that the anomalies produced by the CO_2 – brine contact should be measurable. In addition, using electromagnetic measurements, a 500 m lateral movement of the contact should be detectable.

Conclusions for this study are:

- Both gravity and electromagnetic measurements could be used to monitor the movement of a CO_2 – brine interface within a 20 m thick reservoir at 1900 m depth.
- Changes of the CO_2 saturation of 10% produce changes in the vertical component of gravity.
- The electromagnetic response from an easily deployable field system should be measurable.

Future work on this project should include evaluation of a full field model. This would provide the most realistic simulation of the In Salah gas field and allow a more detailed assessment of gravity and electromagnetic signal strengths.

Reports and Presentations

The final report for this study is presented in Appendix A

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_2.

Defining geological features responsible for competent vs. ineffectual CO_2 storage (ARI, USU)

The ARI (Stevens) study on "competent" systems examined features of three large US CO_2 reservoirs: 1) McElmo Dome, CO (30 Tcf OCO_2IP at 2300 m; 800 MMscfd production; carbonate reservoir with thick halite cap rock), 2) Jackson Dome, MS (2 Tcf at 4700 m; 185 MMscfd production; sandstone with some carbonate reservoir with carbonate cap rock) and 3) St. Johns, AZ (14 Tcf at 500 m; 1 MMscf production; sandstone reservoir and anhydrite cap rock). These natural CO_2 accumulations vary in CO_2 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_2 storage is a natural process.
- Reliable reservoir seals require evaporites or shales as the cap rock.
- Natural analog CO_2 production practices provide insights for CO_2 storage.
- Efficient CO_2 storage operations will require specialized practices and technologies.

Recommendations include further analogs studies including general site suitability classification, specific elements characterization, modeling of injection processes, and monitoring. Future work will benefit from comparison of US fields with other natural CO_2 analogs (e.g., Australia).

The Utah State University (Evans) study on ineffectual natural CO_2 storage systems focuses on CO_2-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_2 to the surface. The CO_2 originates in the 1-1.5 km depth range from clay carbonate reactions. The Little Grand Wash and Salt Wash faults deliver supercritical CO_2 from depth to a shallow, temporary reservoir at 300-500 m where a phase change to CO_2 vapor provides the pressure necessary for CO_2 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_2 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_2 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_2 charged eruptions in the area. No untoward ecological or human health effects attributed to CO_2 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_2 storage. The fluid sampling techniques and the modeling of water and CO_2 origin are an important contribution of this study.

Assessment of reservoir and cap rock response to CO_2 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_2 injection and outlines techniques used to monitor rock stress / strength and CO_2 leakage. Increases in formation fluid pressure due to CO_2 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^{TM} or TrapTester^{TM}). Fault stability is also predicted by mapping fault geometry and constructing fault failure plots. In assessing the suitability of a CO_2 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_2 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_2 injection on cap rocks. It was shown that CO_2 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_2 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_2 accumulations and engineered CO_2 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_2 dissolves in water, particularly in large, unconfined reservoirs.

Changes in geophysical attributes and mineral stability with CO_2 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_2 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_2 injection. The *in situ* geophysical measurements (Vp, Vs, 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_2 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_2 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_2 storage site will assist in developing seismic monitoring protocols and assessing environmental impact.

Engineered systems competence to contain CO_2 (SINTEF, GTI)

SINTEF (Lindeberg and Akervoll) has addressed the well integrity issue, perhaps the most critical issue relevant to successful CO_2 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_2 from storage reservoirs were conducted. Experimental data on corrosion / erosion of cements and inference of chemical mechanisms involved show that initial CO_2 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_2-rich regime. A reservoir simulation of CO_2 leakage from an abandoned leaky cemented well showed that even in a worse case scenario (unremediated open borehole), not all CO_2 will leak from the reservoir (e.g., 60% over 100-200 years). More typically, dissolution of CO_2 in water can be expected to immobilize the vast majority of CO_2 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_2 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_2 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_2 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_2 storage. A modified pump test may be feasible for CO_2 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_2 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_2 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_2 storage. Regulation and public scrutiny will dictate CO_2 storage operations further from populated areas. To take advantage of the increased storage capacity of supercritical CO_2, storage depths will be deeper and thus remote from near surface conduits and potable water resources. Although CO_2 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_2 Charged Systems for CO_2 Sequestration

Task - 4.1 - Understanding Geologic Storage
Principal Investigator: James Evans
Technology Provider: Utah State University
Co-funder: DOE

Highlights

- A 3D structural / stratigraphic and fluid hydrology/geochemistry study was conducted on natural CO_2 seeps and geysers in East-Central Utah (Colorado Plateau) to infer features of geologic system that are prone to CO_2 leakage.
- The geologic and geochemical data constrains the origin of CO_2 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_2 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 is evidence for long-term CO_2 leakage to the surface (~10% of leaked CO_2 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_2 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_2 reservoir system analogs provide useful information on geologic features that govern the integrity of prospective engineered CO_2 storage venues. This "leaky" analogues study, focusing on CO_2-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_2.

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_2-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_2 into the free phase and not from pressure exerted by superheated water as is the case in better known geyser systems. Although the CO_2 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_2 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_2 flux versus carbonate precipitation suggests that about 10% of the CO_2 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_2 seepage, possibly by relieving reservoir pressure and evening out leakage point distribution. Although the CO_2 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_2 seepage.

Implications of the study for CO_2 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_2 storage sites. Recommendations for future research relate to determining CO_2 flux in space and time. The duration of CO_2 leakage might be inferred from travertine dating. The present day absolute CO_2 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_2 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_2 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_2 inferred from geochemical modelling). The study would have benefited form 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
Co-funder; DOE

Highlights

- Abandoned wells have been identified as potential leakage pathways from underground CO_2 storage reservoirs. A completely open well, however, will never leak more than a fraction of the CO_2 stored in the reservoir.
- When the CO_2 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_2 rich pore water is also corrosive to steel casings in the short term 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_2 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_2 demonstrates that this material is suitable for dry CO_2. However, if water is present the corrosion rates are high. The report summarizes relevant chemical reactions among CO_2 and steel and CO_2 and cement and cement in contact with steel.

When the carbon dioxide from a CO_2 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_2 and brine in the near well bore region are presented. Special CO_2 resistant cements have been developed that have better resistance against CO_2 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_2 rich environment. Other alternatives such as epoxy also exist, however, but there is no information about the long-term durability and CO_2/brine resistance for this product.

A reservoir simulation model has been run to estimate the amount of CO_2 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_2 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_2 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_2 storage. The development of new cement formulations and sealants will markedly increase the useful life and thereby longevity of CO_2 storage.

Reports and Publications

- Mid-term report June 2002: The Long Term Sealing Capacity of Cemented Petroleum Wells in a CO_2 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_2 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_2 Storage - Effects of Stress on Seal Integrity

Task - 4.1 - Understanding Geologic Storage
Technology Provider: **APCRC**
Principal Investigator: **Andy Rigg, Juergen Streit, Milovan Urosevic, D. Sherlock**
Co-funder: **DOE**

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_2 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_2 storage on rock stresses and seal integrity in deep saline formations and depleted hydrocarbon fields. Geological storage of CO_2 is optimized when CO_2 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_2 delivered to the reservoir maximizes the storage volume and the CO_2 column height that can be retained by top seals.

Increases in formation fluid pressure due to CO_2 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_2 migration. Assessments of the geomechanical stability of faults, reservoir rock, and top seal in potential CO_2 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_2 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_2 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_2 infiltration. The minimum change in fracture width resulting from CO_2 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_2 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_2 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 mud undergoing compaction for permeability, porosity, Vp, Vs, 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 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 CO_2 are small? The best documented use of microseismic measurements in the past was for monitoring hydro-fracturing, where the pressures input were large.
6. Will 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 CO_2?

The importance of geomechanical considerations for 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 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 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 CO_2 injection, submitted for presentation at the 7th International Conference on Greenhouse Gas Control Technologies (GHGT-7); Vancouver, Sept. 5-9, 2004.
- The final project report is in Appendix A under the same heading as this summary

2.3.4 Natural CO_2 Field Analogues for Geologic Sequestration

Task - 4.1 - Understanding Geologic Storage
Technology Provider: Advanced Resources, International
Principal Investigator: Scott Stevens
Co-Funder: CCP

Highlights:

- **CO_2 storage is a natural process.** Our study has documented in detail that CO_2 storage in geologic formations occurs on a large scale due to natural processes.

- **Reliable reservoir seals require evaporites or shales as the cap rock.** Complementing parallel modeling and laboratory studies, the Natural Analog study demonstrates empirically that, in favorable settings, CO_2 has been stored essentially "forever" (on human timescales; possibly 70 million years at McElmo and Jackson Domes) with no major adverse impacts on reservoir and cap rock

- **Natural CO_2 production practices provide valuable "lessons learned" for CO_2 storage.** During the past two decades, the commercial CO_2 production industry has developed safe and cost-effective CO_2 production, processing, monitoring, and safety techniques and equipment that can be adapted for long-term storage of CO_2.

- **Efficient operation of CO_2 storage will require its own set of practices and technologies.** Despite the encouraging evidence and lessons learned of long-term secure CO_2 storage at the three study fields, future geologic sequestration sites will differ is several important respects.

- **Future Natural Analog Work Needed.** The three CO_2 fields assessed in this study have yielded much useful information. But they cannot alone prove the case for safe, long-term storage in every geologic province. Additional work identified by this study, and estimated cost ranges, that could help advance CCP's goals in this area include:

Summary:

Naturally occurring geologic CO_2 fields are good analogs for geologic CO_2 storage sites. Natural CO_2 fields are common in sedimentary basins worldwide, offer extensive geologic and operational data sets providing unique insights on the long-term impacts of CO_2 on reservoirs and cap rock integrity, as well as field-tested technologies for safely and economically drilling and operating CO_2 sequestration sites. In the USA, several large CO_2 fields have been commercially developed to supply CO_2 for the food, pharmaceutical and, particularly, enhanced oil recovery industries, thus there is a large data set.

We performed a systematic compilation and analysis of existing data from three major natural CO_2 fields in the USA. The three CO_2 fields provide contrasting geologic settings (carbonate vs. sandstone reservoir; supercritical vs. free gas state; normally pressured vs. overpressured), as well as stages of commercial development (undeveloped to mature). The key findings are:

CO_2 storage is a natural process. Our study has documented in detail that CO_2 storage in geologic formations occurs on a large scale due to natural processes. Prior to being developed, the three study sites stored 2.4 billion t (46 Tcf) of CO_2, equivalent to over one year of power plant emissions in the USA. They are comparable in size to the largest proposed individual sequestration sites. By demonstrating that CO_2 storage is a natural process, this helps counter the notion that injecting it underground amounts to unprecedented "waste disposal." This evidence provides justification for industrial-scale geologic sequestration as an environmentally compatible GHG mitigation option.

Reliable reservoir seals require evaporites or shales as the cap rock. The study demonstrated empirically that, in favorable settings, CO_2 has been stored essentially "forever" (on human timescales; possibly 70 million years at McElmo and Jackson Domes) with no major adverse impacts on reservoir and cap rock. Thick salt cap rocks (such as the 400 m of halite at McElmo Dome) appear nearly impermeable and self-sealing to faults over geologic time in tectonically stable locations. Anhydrite (St. Johns Dome) and shale (Jackson Dome) also can be highly effective cap rocks. Remarkably, Jackson Dome's cap rock has contained excess pressures 50% above normal hydrostatic, probably for millions of years. We recognize that every geologic setting is unique and it is not realistic to formulate universal criteria for cap rock integrity based on our limited study. Nevertheless, this information can provide guidelines useful for screening candidate CO_2 storage sites, particularly in similar geologic settings. To build confidence, we recommend that early sequestration site selection follow existing CO_2 field analog criteria, including comparably thick and secure evaporite or shale cap rocks.

Natural CO_2 production practices provide valuable "lessons learned" for CO_2 storage. During the past two decades, the commercial CO_2 production industry has developed safe and cost-effective CO_2 production, processing, monitoring, and safety techniques and equipment that can be adapted for long-term storage of CO_2. The fields are collectively producing 18.5 million t/year (986 MMscfd) of CO_2 for commercial EOR use. Corrosion control is achievable with chromium steel, carbon steel with amine carbon gauze coatings, batch corrosion inhibitors (e.g., $NaHCO_3$), or cathodic protection of flowlines; corrosion surveillance using boroscope, ultrasound, weight-loss coupons, and other methods. Wireline-set plugs downhole can automatically shut in the well in case of accidental damage to the wellhead. However, certain components (e.g., well casing, cements, etc.) would need to be upgraded to withstand the much longer time scale required for geologic sequestration projects. For example, CO_2-resistant cements may be adequate for short-term application (decades), but require advancements to withstand the longer lifespan of geologic storage.

Efficient operation of CO_2 storage will require its own set of practices and technologies. Despite the encouraging evidence and lessons learned of long-term secure CO_2 storage at the three study fields, future geologic sequestration sites will differ is several important respects. A depleted oil and gas field will have significant remaining hydrocarbons, whereas the studied natural analogs are essentially pure CO_2 with minimal contaminants. Also, the natural accumulation took many thousands of years to fill, yet sequestration sites may inject CO_2 for a few decades or less.

Future Natural Analog Work Needed. The three CO_2 fields assessed in this study have yielded much useful information. But they cannot alone prove the case for safe, long-term storage in every geologic province. Additional work identified by this study that could help advance CCP's goals in this area include: development of a worldwide data base of natural CO_2 deposits; profiles of other natural analogs in high-priority sequestration basins located near major anthropogenic CO_2 sources, which more closely resemble local sequestration projects and thus could help strengthen scientific and public confidence; modeling of rapid CO_2 fill rates at natural analog sites, in contrast to the very slow natural fill rate; coring of natural CO_2 field cap rocks; soil gas analysis at natural CO_2 fields to confirm or disprove cap rock integrity; and development of new CO_2-resistant cements designed to withstand exposure for >10,000 years, rather than the current decades.

Reports and Publications

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

2.3.5 Influence of CO_2 Injection on Reservoir and Caprocks

Task - 4.1 - Understanding Geologic Storage
Technology Provider: GFZ Potsdam
Co-Funder: CCP

Highlights

- Geophysical and chemical effects of CO_2 sequestration on deep saline aquifers were assessed experimentally using a triaxial cell and autoclaves to reproduce reservoir conditions at 2000 m (supercritical CO_2). Multiple saturation cycles (e.g., WAG) could be tested on the same rock sample and fluid samples could be withdrawn for analysis.

- Geophysical measurements in-situ (Vp, Vs, electrical resistivity, stress-strain, flow rates) and geochemical analyses (ions) of withdrawn fluids enable characterization of likely effect of CO_2 flow on reservoir rocks.

- The geophysical data show that some effects are predicted quantitatively by standard models (e.g., Gassmann and Voight). Discrepancies noted can be attributed to laboratory measurement artifacts or fluid front instabilities. These findings may have implications for imaging of CO_2 flood performance and migration in reservoirs.

- Geochemical results suggest that major and minor ions, including some that may have a deleterious effect on groundwater quality (e.g., Pb, Cd, Co), are mobilized by dissolution of rock forming minerals which may be important for the structural integrity of the rock.

Summary

Seismic waves have proved to be the single most valuable tool for high-resolution 4D subsurface monitoring in the hydrocarbon industry. In order to achieve a complete 4D interpretation of CO_2 -related phenomena in porous rocks, time-lapse seismic signatures must be interpreted by honoring rock physics, fluid physics, seismic wave propagation, mineralogy, geochemistry, and reservoir engineering principles. Here the GFZ project breaks new ground by being the first experimental project that systematically evaluates the effect of CO_2 on a variety of geophysical parameters.

The workhorse for the experiments has been a triaxial cell that allows ultrasonic p- and s-wave measurements and resistivity logging under in-situ pressure and temperature conditions. Different fluids (e.g., brine and CO_2) can be passed through the pores, collected and analyzed using a variety of geochemical methods. Some of the main findings of this work are:

Bulk and shear modulus

The standard Gassmann equation cannot be used to infer the bulk modulus of CO_2-saturated rock. Although it reproduced the trends seen in the saturation-depending moduli the measured data differ by 10 % or more from the theoretical data including fluid substitution. This may in part be due to the dispersion, i.e. the frequency dependence of the velocities. Even more interestingly, the value of the shear modulus depends on the saturand: it is approx. 3.3 % smaller for CO_2 saturation than for brine saturation at 10 MPa pore pressure. This reproducible effect is not predicted by the Gassmann equations and probably due to a physico-chemical interaction between the fluid and the minerals. The exact nature of this interaction is still unclear.

Pressure-related and saturation-related influences on the seismic response can usually not be discriminated by 4D seismic surveys. To assess this problem the Potsdam group determined the differential pressure sensitivity of measured bulk and shear moduli for brine and CO_2 saturation, i.e. the sensitivity with respect to the difference between confining and pore pressure. It was found that the pressure sensitivity of the shear modulus is on average 3 to 10 times larger than the sensitivity of the bulk modulus. In addition, the pressure sensitivity depends on the saturant: for the shear modulus it is higher when the pores are filled with brine, while for the bulk modulus it is higher for the case of CO_2 saturation. Again, this effect is reproducible for subsequent saturation cycles.

One thus has the result that the bulk modulus of the rock saturated with a single phase (brine or supercritical CO_2) depends mainly on the saturant (and to some lesser extent on the pore pressure), while the shear modulus depends mainly on the pore pressure (and to some lesser extent on the saturand). This feature may offer the potential for distinguishing between pressure and saturation related effects.

Effect of CO_2 saturation on wave speed

The compressional seismic wave speeds for saturation with the system brine-supercriticalCO_2 with variable pore pressure can be explained to some extent by the Voigt and Reuss models. The Voigt model, which is the one that is representative for high-frequency lab data, predicts an almost linear decrease of the compressional wave speed with increasing supercritical CO_2 saturation. The measurements for the sandstone sample indicates that one can resolve the CO_2 saturation in 20 % intervals provided vp is resolved in 1 % intervals. This provides then an estimate of the effectiveness of a CO_2 flood on the basis of the final CO_2 saturation. The seismic data indicate that it reaches practically 100% saturation in most cases, but it can be as low as 50 %. The lower values may be seen as indication of fluid front instabilities ("fingering") when a low-viscous fluid (supercritical CO_2) displaces a high-viscous fluid (brine).

Attenuation

A seismic attribute that is very sensitive to the fluid content of the pores – but rather hard to measure and to interpret – is the frequency-dependent seismic wave attenuation. The experiments indicate that the attenuation of p-waves for CO_2 -saturation is much higher than that for all other cases. Moreover, it exhibits strong pressure dependence. The attenuation can thus serve as a promising independent seismic attribute for monitoring the saturation and pressure state of the reservoir. A more quantitative interpretation is still lacking.

Geochemical results

The goal of the geochemical laboratory experiments was to understand the geochemical behavior of reservoir rocks and cap rocks in reaction with supercritical CO_2 and brine under controlled in-situ p-T conditions and specifically identify the sort of ion exchange reactions that take place between the formation water and how they affect reservoirs. These questions were answered by a series of high-pressure hydrothermal experiments on reservoir and cap rocks in autoclaves on milled samples as well as flow experiments in a triaxial cell. The main findings of these set of experiments were

(1) major trace elements and heavy metals are mobilized in reservoir and cap rocks
(2) carbonates are dissolved in reservoir and cap rocks
(3) alkali feldspar and plagioclase are partially dissolved in reservoir and cap rocks
(4) there is evidence for dehydration processes in reservoir and cap rocks

Conclusions

There is clear evidence from the geophysical data that brine and CO_2 have an effect on the rock matrix and specifically that shear modulus depends on the saturant. These effects are small but reversible and reproducible. The dissolution of minerals that is evident from the geochemical data may explain these effects partly. But it remains unclear why the geophysical effects are reversible when the original saturation state is restored.

The different magnitudes of the sensitivity of the bulk and shear moduli with respect to pressure and saturation changes may help to discriminate between these effects. It is probably not possible, however, to develop a generally applicable quantitative model; lab calibration is probably required for each reservoir.

The seismic wave attenuation is not assessed routinely in field surveys. It offers, however, some unique opportunities, since it depends strongly on the saturation state. Also here, lab calibration is required. Particularly important for the quantitative interpretation is the frequency range, i.e. it has to be assured that the frequency dependence of the attenuation is accounted for when lab and field results are compared.

Reports and Publications

- CCP-SMV 2002 Workshop, Santa Cruz
- CCP-SMV 2003 Workshop, Dublin
- The final project report is in Appendix A under the same heading as this summary

2.3.7 Leakage and Seepage of CO_2 from Geologic Carbon Sequestration Sites: CO_2 Migration into Surface Water

Technical Provider: Lawrence Berkeley National Laboratory

Highlights

The purpose of this study was to review current knowledge of the transport of CO_2 through surface waters and porous sediments, focusing on the processes of ebullition, bubble flow, and transport by diffusion and dispersion.

- Previous investigations measuring natural CO_2 and CH_4 fluxes through surface waters were reviewed. These investigations included estimates of the relative contributions of ebullition and dispersion to the total fluxes of CO_2 and CH_4 to the atmosphere.
- Bubble formation and transport models were reviewed.
- Bubble rise velocities were calculated for gaseous and liquid CO_2 through sediments of three different grain sizes.
- Diffusive and ebullition fluxes were calculated for CO_2 and CH_4 seepage into surface water at low, medium, and high fluxes.
- CO_2 solubility for various H_2O-NaCl mixtures was calculated.

Summary

Leakage of CO_2 from a geologic sequestration site has associated health, safety, and environmental risks. This project investigated the process of leakage of CO_2 from a geologic storage formation and subsequent seepage into saturated sediments and overlying surface waters. This project is expanding on prior work modeling CO_2 leakage from on-shore storage projects with subsequent seepage into the vadose zone, extending the investigation to include seepage into surface waters such as rivers, lakes, wetlands, and oceans. The drivers for the expanded scope of this project are that (1) storage formations are likely to be located off-shore and (2) CO_2 that leaks from on-shore formations can ultimately seep into surface waters. The purpose of this report was to summarize current knowledge of the transport of CO_2 through surface waters and porous sediments, focusing on current models for the physical processes of ebullition, bubble flow, and transport by diffusion and dispersion.

The objectives of the work were to answer the following questions:

- What are the physical processes relevant to CO_2 migration through sediments and overlying surface water either as bubbles or as a dissolved component in water?
- Does surface water attenuate or enhance CO_2 seepage flux?
- Under what conditions can CO_2 concentrations build up at depth and lead to the potential for catastrophic release?

This project focused on CO_2 seepage at relatively low fluxes. Large CO_2 fluxes were not considered in this work because the HSE risks are more obvious and these types of leaks should be more easily identified and mitigated. Liquid water was the connected phase and the CO_2 was assumed to exist either in discrete bubbles or as a dissolved component in the aqueous phase. CO_2 bubbles could be composed of either gaseous, supercritical, or liquid CO_2, depending on the pressure and temperature in the surface or pore water. Current models were used to calculate CO_2 bubble rise velocities through surface waters and through porous media. CO_2 solubility in brines of differing salinities was calculated.

Conclusions for this study are:

- CO_2 seepage flux is not expected to be significantly attenuated by surface water. Mass transfer with surrounding waters can dissolve rising CO_2 bubbles, but due to high bubble rise velocities, the travel times are short. In addition, CO_2 solubility decreases as the bubbles rise due to decreasing pressure.
- For the range of seepage fluxes and surface-water depths considered in this study, CO_2 transport through the surface water will tend to be by ebullition for relatively high seepage fluxes or deep water bodies and by dispersion for relatively low seepage fluxes or shallow water bodies.
- The solubility of CO_2 in water depends strongly on the pressure, temperature, and aqueous salinity.
- CH_4 has a lower solubility in water than CO_2 and so is more likely than CO_2 to be transported by bubble flux.
- Calculations show that the importance of grain size, and density and viscosity contrast are important factors in determining bubble rise velocity in coarse porous media
- Bubble-rise velocity for a liquid CO_2 bubble is slower than for a CO_2 gas bubble due to the much smaller density contrast between liquid CO_2 and water than between gaseous CO_2 and water.
- For medium and fine grain porous media, gas flow will be by channel flow
- Water becomes slightly denser when it contains dissolved CO_2. Lakes that have deep stagnant regions and are subject to CO_2 fluxes from below are prone to stratification with water at depth that is supersaturated with CO_2.

Future research efforts should be focused on increasing the understanding of CO_2 leakage and seepage in surface water and saturated porous media. Bubble formation, bubble rise, and dispersion models should be incorporated into numerical simulators for modeling of CO_2 migration through surface waters and saturated sediments. Laboratory experiments and field tests of CO_2 migration in saturated systems could be used to develop models and validate results.

Reports and Presentations

The final report for this study is presented in Appendix A

2.3.8 Seismic Imaging of Reservoir Leaks and Gas Field Monitoring: Effects of Supercritical CO_2 on the Mechanical Properties of Shale Caprock

Technical Provider: Lawrence Berkeley National Laboratory

Highlights

The purpose of this project was to select and prepare shale caprock samples for use in subsequent experiments that will be designed to quantify the changes in the mechanical properties and permeability of caprocks after exposure to supercritical CO_2. These laboratory data will then be used in a parallel study using coupled reservoir – geomechanical modeling simulations to explore whether conventional seismic techniques might be able to detect early precursors to leaks caused by contact of a caprock with injected CO_2.

- Anahuac shale samples were obtained. Anahuac shale is a regional caprock for the Frio sand, the location of the recent CO_2 injection project into an aquifer located in Liberty County, Texas.
- Core samples for use in subsequent laboratory experiments were drilled from the shale caprock samples.
- A flow apparatus for conducting permeability and mechanical tests was designed and assembled.

Summary

This project was the first phase of a project designed to quantify the changes in the mechanical properties and permeability of caprocks after exposure to supercritical CO_2. This phase of the project was designed to obtain samples of shale caprock, prepare the samples for use in laboratory permeability and mechanical tests, and assemble an experimental flow apparatus for conducting the laboratory tests.

Samples of Anahuac shale from the Frio Brine pilot in Liberty County, Texas were obtained from the Texas Bureau of Economic Geology. The Anahuac shale is a regional caprock for the Frio sand. Samples were obtained from a depth of 4840.75 ft. X-ray diffraction analyses showing the mineralogical composition of the shale samples and porosity and permeability data were also obtained from the Texas Bureau of Economic Geology. Samples for the permeability and mechanical tests were obtained by dry coring while maintaining subzero temperatures with dry ice and liquid nitrogen.

- A flow system setup consisting of a pressure vessel, confining pressure pump, CO_2 injection pump, backpressure regulator, heater, and monitoring system was assembled. This setup will be used for flow experiments where the connate fluid of caprock samples is replaced with supercritical CO_2. The apparatus will be used to monitor for changes in permeability resulting from interactions between the clay matrix and the supercritical CO_2. Mechanical testing will also be done on these samples. If significant changes are observed, samples will be imaged tomographically.

Results from this phase of the study include:

- Anahuac shale samples were obtained from the Texas Bureau of Economic Geology.
- Plugs for use in experimental studies were drilled from the shale samples.
- Results from x-ray diffraction analyses of the Anahuac shale samples were obtained from the Texas Bureau of Economic Geology.
- A flow system setup for use in subsequent permeability and mechanical tests was assembled.

Future work should include conducting the permeability and mechanical tests on the Anahuac shale core plugs using the flow system constructed in this phase of the project. These tests would help quantify the magnitude of changes in permeability and mechanical properties that can be expected in shale caprock following exposure to supercritical CO_2. These laboratory experiments would also provide data needed for a parallel study conducting coupled reservoir – geomechanical modeling simulations exploring whether conventional seismic techniques might be able to detect early precursors to leaks caused by contact of a caprock with injected CO_2.

Reports and Presentations

The final report for this study is presented in Appendix A

2.3.8 Seismic Imaging of Reservoir Leakage Pathways – Task 2: Hydromechanical Modeling of Cap Rock Integrity

Technical Provider: Lawrence Berkeley National Laboratory

Highlights

The purpose of this study was to perform coupled reservoir – geomechanical modeling studies to explore whether conventional seismic techniques might be able to detect early precursors to leaks caused by contact of the caprock with injected CO_2.

- A coupled reservoir – geomechanical model was constructed and used to simulate coupled processes during CO_2 injection into brine aquifer – caprock systems.
- The modeling study predicts that changes in elastodynamic properties resulting from CO_2 injection should be detectable.
- The modeling study predicts that changes in localized elastodynamic properties resulting from rapid invasion of CO_2 into high permeability fractures should be detectable.

Summary

This project involved coupled reservoir – geomechanical modeling studies simulating processed during CO_2 injection into brine aquifer – caprock systems. The objective of the study was to explore whether precursors to a breach and CO_2 leakage through the caprock or sealing faults might be detectable using conventional seismic techniques. The injection process is simulated using the TOUGH-FLAC simulator which is based on a coupling of the two existing computer codes TOUGH2 and FLAC3D. TOUGH2 is a code for geohydrological analysis with multiphase, multicomponent fluid flow and heat transport. FLAC3D is a code designed for rock and soil mechanics. For coupled problems, the TOUGH2 and GLAC3D codes are executed on compatible grids and linked through external coupling modules. In these modeling studies, CO_2 is injected at a constant rate over a 30 year period. Injection is at a depth of 1300 – 1500 m and the injection zone is overlain by a 100 m thick caprock. Three brine aquifer – caprock systems were studied:

- A brine aquifer – caprock system with no lateral confinement.
- A caprock intersected by a fracture zone.
- A brine aquifer – caprock system with two sealing faults.

Conclusions for this study are:

- The most important process for the hydromechanical behavior of the caprock is the reduction of the mean effective stress caused by the high pressure injection of CO_2. The reduced effective stress results in a lower shear strength at the same time the shear stress is increased. Combined, these effects increase the possibility of shear failure.
- An onset of shear failure would likely occur prior to any hydraulic fracturing.
- The induced hydraulic fracturing and shear reactivation could likely be contained within the lower portion of the caprock. Thus, the sealing mechanism of the caprock may still be functioning in the upper part.
- Detection of changes in the elastodynamic properties of the lower portion of the caprock during a CO_2 injection could be addressed by reducing the injection pressure to prevent further damage to the caprock.

- Rapid invasion of CO_2 through a permeable fracture could lead to more significant changes in the effective stresses producing detectable changes in elastodynamic properties. The injection operation could be adjusted to minimize any leakage.
- The results of this study should be taken only qualitatively since quantitative results are very sensitive to the assumed rock properties and due to a lack of field data, some of these properties were estimated for this study.

Additional laboratory studies need to be conducted to obtain more realistic rock properties for use in constructing the reservoir model. The coupled reservoir – geomechanical modeling studies should then be run using this refined set of reservoir properties. In addition, further research is needed for a realistic modeling of complex fault structures and for modeling of potential change in fault permeability and mechanical properties.

Reports and Presentations

The final report for this study is presented in Appendix A

2.3.9 Well-based in situ Leak Detection

Technical Provider: Schlumberger

Highlights

The purpose of this project was to design a test chamber for evaluation of a wireline tool for detecting the fluid contact point between CO_2, water, and oil.

- The chamber design is highly flexible. Modifications to the design can be made as necessary.
- The chamber design includes all the features necessary to allow conducting a wide range of experiments.
- The chamber design allows downhole conditions to be simulated. Multiple sands and multiple fluids can be inserted into the chamber for a single test.
- The chamber design allows a logging tool to be inserted.
- Most measurements will be made while the wireline tool is stationary.
- The chamber design will allow taking measurements while dragging the tool through the chamber to simulate actual depth – logging conditions.

Summary

This project was the first phase of a project designed to test the ability of a wireline reservoir saturation tool to detect the fluid contact point between water, oil, and CO_2 in a reservoir.

This first phase of the project entailed designing the test chamber. The test chamber was to simulate downhole conditions, specifically to model the formation. In addition, the chamber was to allow insertion of the logging tool for testing. The design is for a 12 foot high and 48 inch diameter chamber. The chamber also contains an inner chamber that is approximately 7 inches in diameter that will be constructed using standard casing. The wireline tool will be lowered inside the inner chamber. The outer chamber, the space between the casing and the outside wall, will be filled with formation sand. The 12 foot height was designed to allow the chamber to be packed with up to three four foot thick sections of sand of different properties and potentially containing different fluids. The test chamber design includes provision for a port to provide access to the interior of the chamber for maintenance and to allow the chamber to be reused with multiple configurations of sands. The test chamber design also provides for three sight ports to allow visual confirmation of the presence and level of fluids.

Results from this phase of the study include:

- The design of the test chamber was completed.
- The test chamber design contains all the features necessary to allow conducting a wide range of experiments on the wireline tool.
- The design allows the test to simulate the presence of multiple sands and multiple fluids.
- The design is highly flexible allowing for modifications should any be desired or required.

Future work on this project should include construction of the test chamber followed by a series of tests to evaluate the capabilities of the wireline reservoir saturation tool. Tests should be conducted under a variety of conditions including using layered sands containing multiple fluids. Tests should also be run where initial wetting phases in some of the sands have been displaced by a non-wetting phase. Some tests should include dragging the tool through the chamber to simulate actual depth – logging conditions.

Reports and Presentations

The final report for this study is presented in Appendix A

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_2 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_2 leakage due to EOR operations is postulated. The satellite imagery of Mammoth Lake correlated well with ground-based CO_2 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_2 leakage. Detection of CO_2 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_2 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_2 leakage and the location of hidden faults.

The feasibility of satellite radar interferometry (InSAR) technique for detecting ground movements due to CO_2 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_2 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_2 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_2 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_2 concentration increases >10ppm over background. Nomograms are used to predict the "excess" CO_2 present in the atmosphere for a given situation. Open path instruments (laser spectrometers) may be a cost effective means of detecting small CO_2 leakage over a field-sized area (a few km^2). A spreadsheet application produced for the study permits matching of analytical instruments suitable for detecting CO_2 under various leakage scenarios.

The “eddy covariance” method, a technology used to establish baseline CO_2 flux from plant photosynthesis and respiration cycles, was evaluated for its applicability to CO_2 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_2 leakage that can be detected given natural variation might typically be 2.5% of 1000MT stored of 1000 years for a reservoir leak, $10^{-1}kgm^{-2}s^{-1}$ for a diffuse leak (injection well failure) and $10^{-5}kgm^{-2}s^{-1}$ 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_2 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_2 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, sub-bottom 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_2 presence in a Sleipner-type case was included. The study provides a useful assessment of available technologies to monitor CO_2 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_2 leakage. The Schrader Bluff and Liberty reservoirs were used to model the spatial resolution of various geophysical CO_2 detection techniques. The significant changes in water with increasing CO_2 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_2 into water. The electrical resistivity changes attending CO_2 dissolution in water are easily detectable using electromagnetic (EM) techniques. This technique is currently available, inexpensive compared to seismic and most applicable to CO_2 / 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_2 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_2 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_2 injected into the reservoir and the detectability limits of the Xe isotopes, it is calculated that it would cost ~\$0.18 / tonne CO_2 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_6 system for Yucca Mountain proposed nuclear waste disposal facility). The theory behind using noble gases to monitor CO_2 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_2 Monitoring Systems – A Critical Review of Available Techniques and Technology Gaps

Task - 4.4 - Measurement and Verification
Technology Provider: CalTech
Principal Investigator: Yongchun Tang & Patrick J. Shuler
Co-Funder: DOE

Highlights

- Calculations are made to estimate the resolution of various ground-based instruments to detecting CO_2 leakage at a rate of 1% of total CO_2 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_2 variations and atmospheric conditions).

- Local, increased concentration of CO_2 over a site depends greatly on the magnitude and type (diffuse, point source) of leak and atmospheric conditions but should be detectable if CO_2 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^2).

Summary

An earlier CCP study by Tang Associates examined broader issues of CO_2 detectability using a wide array of atmospheric detection instruments from remote and aerial to ground- based. The present study focuses on the resolution of near surface ground-based instruments to detect CO_2 in diffuse and point leakage scenarios.

In the case of diffuse leakage, the study approaches the problem systematically using a series of calculation steps: 1) CO_2 injection (mass = volume x time), 2) leakage of a portion of injected CO_2 to the surface (1% / 100 years as default), 3) CO_2 flux rate at the surface (volume / area x time), 4) addition of CO_2 to a specific volume at the surface (10 ft. "box"), 5) dilution of CO_2 in "box" by air and 6) CO_2 monitor detection of increased CO2. Given a particular diffuse leakage setting (leakage flux with atmospheric dilution); therefore, detection of CO_2 leakage is simply a matter of identifying atmospheric concentrations of CO_2 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_2 venting from a single point (e.g., wellbore). Selection of site specific parameters including CO_2 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_2 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_2 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_2 concentration from leakage and thereby instrument detectability. In a diffuse leakage case (10MM m^3/day/20 years injected with 1% leakage over 100 years) with an atmospheric dilution factor of 25x, CO_2 concentration would be 24 ppmv over an area of 10 km_3. Given a sample instrument uncertainty of 9 ppmv and background variation of 5 ppmv, the excess atmospheric CO_2 due to leakage would be easily detected. In contrast, leakage over a 100km^3 area would not be resolvable from background CO_2 and instrument uncertainty.

In a similar case but with leakage from a point source, the distances at which CO_2 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_2 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 CO2 distance x concentration), CO_2 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).

From the study results, the authors recommend: 1) development of reliable, lower cost, open path laser spectrometer detection systems customized to measure CO_2 and 2) testing of instrumentation at sites where CO_2 flux to the surface is active either from natural processes (e.g., Mammoth Mountain) or CO_2 EOR operations (e.g., Weyburn).

The study comprises a simple but very useful approach to examine CO_2 leak detection in a wide variety of settings. The applicability of conventional and new detection equipment to CO_2 detection in individual settings can be quickly screened using the spreadsheet application. One of the biggest unknowns in planning CO_2 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).

Reports and Presentations

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

2.4.2 Novel Geophysical Techniques to Monitor CO_2 Movement

Task - 4.4 - Measurement and Verification
Principal Investigator: Mike Hoversten
Technology Provider: LBNL
Co-funder: DOE

Highlights

- It is confirmed that standard P-wave seismic is effective in monitoring CO_2 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_2 movements
- Further work in resistivity and streaming potentials technologies is justified because these techniques could be result in lower resolution but cost effective CO_2 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_2 sequestration monitoring. The difference in the vertical component of gravity caused by CO_2 injection over a 20-year period is on the order of 2 μGal, 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_2 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_2 and water within the reservoir.

There is a significant change in seismic amplitude associated with the reservoir caused by the changes is water and CO_2 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_2 – brine systems where there is a one-to-one correlation between the change in water saturation and the change in CO_2 saturation (since $S_w + S_{CO2} = 1$). 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_2 sequestration scenario in 2D has been simulated, based both on the Liberty Field and Sleipner CO_2 injection tests. Modeling results show that injection of CO_2 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_2 Sequestration Monitoring", 2002 SEG Workshop on CO_2 sequestration Oct. 10, 2002, SEG Annual Convention
- Hoversten. G. M., Gritto, R., Washbourne, J., Daley, T., "CO_2 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_2 sequestration", 2002, GHGT-6 conference, Kyoto, Japan.

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

2.4.3 Optimum Monitoring Technology

Task - 4.4 - Measurement and Verification
Principal Investigator: Rob Arts
Technology Provider: TNO-NITG
Co-funder: DOE

Highlights

- 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_2 sequestration and monitoring. The present work was directed to the improvement of long-term monitoring & verification for sequestration of CO_2 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_2 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_2 storage are:

- To ensure the sustainability of the CO_2 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_2 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_2 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_2 or subsidence due to production or leakage of CO_2 can cause damage to constructions at the surface.

A secondary goal of monitoring is research and development regarding underground CO_2 sequestration. Gaining more understanding of the processes going on in the reservoir is important for the optimization of future storage sites.

CO_2 sequestration has to be monitored so that the operators and public will know that the CO_2 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_2.
- 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_2 concentrations (geochemical sampling techniques)

The final report describes the each of the available monitoring techniques and gives direction on which are likely to be successful in CO_2 storage applications.

Reports and Publications

- CO_2 Optimum Monitoring Methodology, R.J.Arts & P. L. A. Winthaegen, Netherlands Institute of Applied Geosciences TNO, Report NITG-02-229-B, 23 December 2002.
- The final report is included in Appendix A under the same heading as this summary..

2.4.4 Hyperspectral Geobotanical Remote Sensing for CO_2 Storage Monitoring

Task - 4.4 - Measurement and Verification
Principal Investigator: William Pickles
Technology Provider: LLNL
Co-Funder: DOE

Highlights

- A remote hyperspectral monitoring technique, which uses the reflectance of sunlight from plants and geological formations to detect changes induced by CO_2 leaks, has been tested at two localities: 1) Mammoth Lake., CA (satellite detection of natural volcanic CO_2 emanations) and 2) Rangely Field, CO (aerial detection of CO_2 leakage from a 15 year CO_2 EOR operation).
- At the heavily vegetated Mammoth Lake locality CO_2–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_2 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_2 leakage from Rangely may be limited, however, as soil gas surveys show that such leakage is negligible.
- The principal utility of this large area coverage technique appears to be detection of long term, low level CO_2 leakage that subtly changes "habitat" or short term or high level CO_2 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_2 leaks indirectly by detecting changes in plants or by mapping hidden faults that serve as pathways for potential CO_2 leaks, over the entire area above an underground formation being injected with CO_2. 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_2 leakage. These maps established an environmental and ecological baseline against which any future CO_2 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_2 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_2 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_2 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_2 leak detection. The high cumulative flux of CO_2 at the well-vegetated 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_2 flux. The hyperspectral method could not, therefore, directly detect CO_2 leakage but the potential exists for long term detection of "habitat" changes due to CO_2 leakage through repeat surveys. Further interpretive work on hyperspectral bands sensitive to soil microbe changes (from CO_2 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_2 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_2 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, Brigette A Martini, HyVista Corp, Possible CO_2 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_2 Storage Monitoring, CO_2 Capture Project - An Integrated, Collaborative Technology Development Project for Next Generation CO_2 Separation, Capture and Geologic Sequestration, Semi-Annual Report, 2.4.4, July 14, 2003
- The project final report 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
Co-Funder: DOE

Highlights

- Based on the initial Mabee analyses, the quantities of noble gas tracers required for an actual CO_2 storage setting were calculated. Cost estimates relative to total CO_2 storage costs and CO_2 "taxes" were derived.
- The distinct elemental and isotopic composition of the noble gases present in the injected CO_2 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_2 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.

Summary

One of the primary concerns in CO_2 storage is monitoring the storage site on a long-term basis for possible leakage of CO_2. Concentrations of CO_2 vary widely in the Earth's crust, and will make it difficult to know for certain if elevated levels of CO_2 are due to leakage. Small amounts of noble gas isotopes can be dissolved into the CO_2 being injected for storage and used as tracers to monitor CO_2 movement. Noble gases are chemically inert, environmentally safe, and are persistent and stable in the environment. The unique isotopic compositions that can be imparted to the CO_2 can be unambiguously identified during monitoring. Among the noble gases, xenon isotopes have commercial costs and availability suitable for use in large CO_2 storage operations. Required xenon volumes are low, simplifying handling and injection. Multiple batches of injected CO_2 at the same site could be imparted with different xenon isotopic compositions, making each of them identifiable with only a single xenon analysis. These characteristics are believed to make xenon a superior tracer to other option, SF_6 and $^{14}CO_2$. A case study in noble gas tracing at the Mabee Enhanced Oil Recovery field in west Texas indicates that unique noble gas isotopic compositions within a CO_2 injection stream can be detected and readily identified in outlying wells, and that noble gas behavior in a CO_2 storage setting will be systematic and predictable.

Noble gases (helium, neon, argon, krypton, xenon) can be dissolved into CO_2 injected into geological formations for long-term storage and used as tracers when monitoring for CO_2 leakage or subsurface migration. Injected CO_2 is in a supercritical state and the noble gases will remain dissolved in that liquid. Using noble gases for subsurface tracing in this form is similar to using any common type of chemical tracer. However, leaking CO_2 will become a gas as it migrates to the Earth's surface. It is here that the noble gases become unique and highly valuable tracers. At the pressure and temperature conditions in which the supercritical CO_2 becomes a gas, the noble gases will also be released as gases. The noble gases will thereby track CO_2 gas migration toward the surface.

Noble gases become distinctive tracers when non-natural isotopic compositions are used. In the natural environment all of the noble gases have multiple isotopes, atoms of the same element with different numbers of neutrons. While the atomic ratios of the noble gas isotopes are generally very similar throughout the planet and atmosphere, commercial isotope separation makes available significant volumes of noble gases with certain isotopes enhanced over their natural abundances. Xenon, for example, occurs naturally in nine different isotopic states: ^{124}Xe, ^{126}Xe, ^{128}Xe, ^{129}Xe, ^{130}Xe, ^{131}Xe, ^{132}Xe, ^{134}Xe, and ^{136}Xe. The fractional abundance of each of these varies only slightly in nature; for instance, ^{136}Xe comprises about 8.9 per cent of all natural xenon. However, pure xenon gas can be purchased that contains about 60 per cent ^{136}Xe. Adding this to injected CO_2 would create a distinctive tracer with non-natural xenon isotopic ratios that later could be unambiguously identified when monitoring for leakage.

Since they are chemically inert and nonradioactive, noble gas tracers are persistent and stable in the environment. They are nontoxic and environmentally safe. After injecting CO_2 spiked with noble gas isotopes into a reservoir, the region surrounding and above the storage site could be monitored to detect the distinctive noble gas isotopic signatures for decades to millennia. Because CO_2 will always be detected within the Earth's crust, the question for monitoring purposes will be whether its origin is natural or from injection. The isotopic signature of the noble gases measured with the CO_2 would indicate whether or not the gases originated within the storage site.

For the purposes of our initial calculations and assessments, we are assuming that the noble gas tracers move conservatively with the stored CO_2. In reality, there will be partitioning of the noble gases between the phases present in the system (water, hydrocarbons, and a gas phase). Partitioning would not only affect noble gas tracers, but any potential tracer except for $^{14}CO_2$ ($^{14}CO_2$ is discussed below). Noble gas solubility in waters and brines, and their temperature dependence, are fairly well known. Data on noble gas solubility in some hydrocarbons (hexane, decane, benzene) at 25°C and 1 atm are available Kharaka and Specht determined noble gas solubility in two crude oils (API gravity 25 and 34) over the temperature range 25°C to 100°C. However, very little is known about the partitioning/solubility behavior of noble gases or other possible tracers in the P-T-x conditions of the CO_2 storage environment. Much more information will be needed before a complete assessment of noble gas or other tracers can be made. One of our recommendations provided at the end of this chapter is for research to obtain this information.

This paper discusses a methodology for using noble gases in CO_2 storage. It covers injection methods, costs, detection and monitoring scenarios, and compares noble gases with other potential tracers (SF_6 and $^{14}CO_2$). We also present the results of a noble gas "tracer" study we performed in an enhanced oil recovery (EOR) field in the Permian Basin of west Texas.

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_2 storage sites;
2) Test EOR reservoirs for CO_2 leakage caused by production-related changes in caprock integrity (thereby screening for their suitability for long-term large volume CO_2 storage);
3) Screen brine aquifers or similar formations for suitability for CO_2 storage; and
4) Provide a mechanism for fingerprinting injected CO_2 so that the source and ownership of leaking or migrating CO_2 can be identified.

The project is comprised of three basic components:

- Collecting and analyzing noble gas isotopes accompanying both injected and recycled CO_2 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_2 will be spiked with identifiable noble gas isotopes; recycled CO_2 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_2 injection.
- Develop a NUFT-C computer model of noble gas tracers migrating upward through the crust from a leaking CO_2 storage site. This component will form the basis for the design of a monitoring strategy.

Conclusions:

Noble gas isotopes, particularly xenon isotopes, may provide a mechanism for leakage monitoring and subsurface tracing of stored CO_2. They are chemically inert, environmentally safe, persistent, and stable in all environments. While ^{3}He and ^{36}Ar may be suitable only for special uses due to availability relative to required amounts and to high costs, ^{124}Xe, ^{129}Xe, and ^{136}Xe are inexpensive and readily available. Only small volumes of these xenon isotopes would be needed (< 900 liters per year for the Mabee storage analogue), simplifying handling and injection. The Mabee field test conducted as part of this study demonstrated that unique noble gas isotopic compositions injected with CO_2 can be readily detected in production wells. Even though other isotopic components are present in the subsurface, the unique isotopic fingerprint can always be identified. The noble gases behave in a systematic and predictable manner in the CO_2 injection setting, indicating that the noble gas tracing technique would be a robust and reliable method. Many aspects of potential monitoring methods must yet be formulated, but monitoring in deep aquifers, ocean waters, and the ground surface, for which the calculations presented here are intended, all appear achievable.

Reports and Publications

- Nimz, G.J., Hudson, G.B., and Glassley, W.E., Noble gas isotopes for screening, verification, and monitoring at CO_2 storage sites, JIP CO_2 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_2 storage sites, JIP CO_2 Capture Project Workshop: "Building the SMV Family of Technology Providers", Santa Cruz, California, Oct 21-23, 2002. (presentation)
- The project final report is in Appendix A under the same heading as this summary.

2.4.6 Monitoring Geologic Sequestration with Satellite Radar Interferometry

Task 4.4 Measurement and Verification
Principal Investigator: Howard Zebker
Technology Provider: Stanford University
Co-funder: DOE

Highlights

- The applicability of satellite radar interferometry (InSAR) to detecting ground movement (deformation) due CO_2 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_2 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_2, 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_2 sequestration. Future work proposed identifying CO_2 sequestration or oil and gas reservoirs to test the InSAR data and inversion of InSAR measurements for pressure changes at depth.

The work was terminated early because of the low likelihood of it achieving CCP objectives.

Reports and Publications

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

2.4.7 Measurement Techniques for the Detection of Leaks from Underground CO_2 Reservoirs: Evaluation of Capabilities

Task - 4.4 - Measurement and Verification
Technology Provider: Penn State University
Principal Investigators: K. J. Davis, J. C. Wyngaard
Co-funder: DOE

Highlights

- Major atmospheric CO_2 fluxes are easily detectable by the eddy covariance method if they are less than a few kilometers upwind of the measurement tower.
- Minor CO_2 fluxes (1% of 100 million tons of CO_2 lost evenly over 100 years through a 0.1 square km patch) may also be detectable by the current generation of equipment.
- Minor CO_2 flux emissions are of the order of biological CO_2 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_2 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_2 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^2. 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_2 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_2 sequestration are constructed. It is shown that the leakage rates under these assumptions would range from 1 to 10^4 times the magnitude of typical ecological fluxes. The flux measurement areas can readily encompass the assumed leakage areas (10 to 10^5 m^2). Thus we conclude that this approach shows promise for the monitoring of leakage from underground CO_2 storage facilities.

Future work should include active tests of the eddy covariance method for detecting release-related CO_2 fluxes. For example, once a site is characterized with respect to its biological CO_2 flux variability, a planned CO_2 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_2 and H_2O exchange over a northern mixed forest as observed from a very tall tower. *Glob. Change Biol.*, 9, 1278–1293.

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

2.4.9 Atmospheric CO_2 Monitoring Systems

Task - 4.4 - Measurement and Verification
Technology Provider: CalTech
Principal Investigator: Yongchun Tang & Patrick J. Shuler
Co-Funder: DOE

Highlights

- Calculations are made to estimate the resolution of various ground-based instruments to detecting CO_2 leakage at a rate of 1% of total CO_2 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_2 variations and atmospheric conditions).

- Local, increased concentration of CO_2 over a site depends greatly on the magnitude and type (diffuse, point source) of leak and atmospheric conditions but should be detectable if CO_2 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^2).

Summary

An earlier CCP study by Tang Associates examined broader issues of CO_2 detectability using a wide array of atmospheric detection instruments from remote and aerial to ground- based. The present study focuses on the resolution of near surface ground-based instruments to detect CO_2 in diffuse and point leakage scenarios.

In the case of diffuse leakage, the study approaches the problem systematically using a series of calculation steps: 1) CO_2 injection (mass = volume x time), 2) leakage of a portion of injected CO_2 to the surface (1% / 100 years as default), 3) CO_2 flux rate at the surface (volume / area x time), 4) addition of CO_2 to a specific volume at the surface (10 ft. "box"), 5) dilution of CO_2 in "box" by air and 6) CO_2 monitor detection of increased CO2. Given a particular diffuse leakage setting (leakage flux with atmospheric dilution); therefore, detection of CO_2 leakage is simply a matter of identifying atmospheric concentrations of CO_2 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_2 venting from a single point (e.g., wellbore). Selection of site specific parameters including CO_2 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_2 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_2 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_2 concentration from leakage and thereby instrument detectability. In a diffuse leakage case (10MM m^3/day/20 years injected with 1% leakage over 100 years) with an atmospheric dilution factor of 25x, CO_2 concentration would be 24 ppmv over an area of 10 km_3. Given a sample instrument uncertainty of 9 ppmv and background variation of 5 ppmv, the excess atmospheric CO_2 due to leakage would be easily detected. In contrast, leakage over a 100km^3 area would not be resolvable from background CO_2 and instrument uncertainty.

In a similar case but with leakage from a point source, the distances at which CO_2 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_2 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_2 distance x concentration), CO_2 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).

From the study results, the authors recommend: 1) development of reliable, lower cost, open path laser spectrometer detection systems customized to measure CO_2 and 2) testing of instrumentation at sites where CO_2 flux to the surface is active either from natural processes (e.g., Mammoth Mountain) or CO_2 EOR operations (e.g., Weyburn).

The study comprises a simple but very useful approach to examine CO_2 leak detection in a wide variety of settings. The applicability of conventional and new detection equipment to CO_2 detection in individual settings can be quickly screened using the spreadsheet application. One of the biggest unknowns in planning CO_2 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).

Reports and Presentations

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

2.4.10 Passive Optically Interrogated Geophone Development – Electro-optic Converter

Technical Provider: Sabeus Photonics

Highlights

The purpose of this project was to construct Electro-optic converters and then test their ability to transform the electrical outputs from standard geophones.

- Five electro-optic converters were constructed for testing.
- Testing of the performance of the electro-optic converters to determine noise, optical sensitivity, total harmonic distortion, operating temperature range, and operating frequency range was completed. Performance standards were established for each of these parameters.
- Except for the scale factors, the electro-optic converters yielded performance results similar to those anticipated.
- Poor control over the quality of the fiber winding and poor control over the fiber tension during winding probably contributed to lower than anticipated scale factors for the electro-optic converters. These same factors probably contributed to variable scale factors being obtained for the different electro-optic converters.

Summary

This objective of this project was to construct three electro-optic converters and then test the electro-optic converters and compare their performance against established performance standards. The electro-optic converters were constructed of a 30 mm long, 44 mm diameter tube of lead zirconate titanate with a 3mm wall thickness. Approximately 100 m of 250 μm diameter Fiber Logix high NA, sensor-grade fiber was wound around the lead zirconate titanate tube under a 50 g tensile load. The performance parameters assessed for the electro-optic converters were noise, optical sensitivity, total harmonic distortion, operating temperature range, and operating frequency range.

Five electro-optic converters were constructed. Except for the scale factor, the testing of the electro-optic converters yielded performance results similar to those expected. The scale factors calculated for the electro-optic converters were about 60% of the anticipated values. Difficulty winding the fiber around the lead zirconate titanate tubes and higher than expected winding tensions probably contributed to the reduced scale factors.

A test of the sensitivity of the equipment yielded inconclusive results. The equipment performed as prescribed but did not meet seismic industry specifications for geophones. Additional work on this technology would be beneficial since the development of optically interrogated geophones has potential cost and performance advantages. However, the CO_2 Capture Project may need to consider a different technical provider for any future work.

Reports and Presentations

The final report for this study is presented in Appendix A

3.0 Policies and Incentives to Implement CO_2 Sequestration

Technology Providers: Nansen Institute
Environmental Resources Management, Ltd.
Cofunder: Klimatek

Summary:

Members of the CO_2 Capture Project realized from the beginning of the project the reality of interdependency between technology and policy developments. The Policies and Incentives Team was formed to provide information and advice to the CO_2 Capture Project's Executive Board on national and global policies, regulations and legislation, incentives and any other external developments that may impact or benefit the technology program being developed by the CO_2 Capture Project. The team completed a survey of existing policies and incentives and their potential future development and initiated a preliminary "gap analysis" to understand what the current state is and what would be desirable in terms of policy development that would favorably impact the development and deployment of CO_2 capture and storage.

The key vision of success continues to be gaining public and regulatory acceptance of CO_2 capture and storage technology and that the technology can be applied safely and cost effectively.

Interpretation of international treaties such as the London Convention and the OSPAR Convention already raise significant issues that need to be clarified in order to understand their applicability to the deployment of CO_2 storage in offshore geologic structures. The key issue of whether to treat CO_2 as a waste needs to be resolved, which would affect the applicability of the London, the OSPAR, and the EU Water Framework Directive. Currently, public awareness is low to non-existent, posing a significant challenge for eventual public acceptance if the technology is to be widely deployed. More work in these policy and public outreach efforts will have to be done by future collaborations and commercial projects aiming to develop and deploy CO_2 capture and technology. Further, future projects should develop and adopt monitoring and verification frameworks appropriate for public and regulatory acceptance.

The team completed two key tasks with results that are described here:

- A comprehensive survey of existing policies, regulations, and incentives that impact or benefit CO_2 capture, injection and storage in geologic formations.

- Gap analysis necessary to formulate the regulatory and policy framework that will show how to get from "where we are" to "where we want to be" in deploying the technology.

The results of these tasks show:

- Clear momentum exists as projects are being deployed and technology continues to be researched and developed.
- The London Dumping Convention and the OSPAR Convention ("Oslo Paris Convention) may apply to CO_2 capture and storage deployment offshore in geologic formations.[1] Issues for clarification may require several years of intergovernmental negotiations in order to accommodate such deployment.
- In general, there is little policy and regulatory development specifically addressing CO_2 capture and storage in individual countries.
- Specific countries (Netherlands, Norway, Canada, United Kingdom (UK), and the United States (US)) are moving in the direction of policy development specific to CO_2 capture and storage.

- Public awareness is low to non-existent. Some NGOs will likely play key role in the public acceptance of the technology.
- Some non-government organizations (NGOs) and the public in the European Union are becoming slightly less skeptical of the technology. However, it is still too early to assess the level of public skepticism, which will become clearer when specific projects are reviewed for permitting or licensing.
- Existing and emerging financial incentives in Australia, Canada, the European Union, Denmark, Germany, Italy, Netherlands, Norway, the United Kingdom, and the United States are focused principally on research and development. Such incentives are needed to improve the cost-effectiveness for deploying CO_2 capture and storage technology.
- CO_2 capture and storage technology is becoming recognized and credited in some regulatory regimes, though it is not yet widely recognized nor credited. A monitoring and verification framework is needed to achieve wide recognition and crediting.

Reports and Presentations

The final reports for this study are presented in Appendix A. Four reports are included.

4.0 Economic Modeling

Task - 0.3 - Develop & Apply Common Economic Model
Technology Providers: CCP Participant Companies
Principal Investigator: Torgeir Melien, Hydro
Cofunder: CCP & DOE

Introduction

The Common Economic Model Team's main objective was to develop and apply a common set of approaches and methods in cost estimation and economic screening of CO_2-capture technologies in the CCP-program. The basic CO_2-cost results presented in this report cover the capture process up to a delivery point where the CO_2 can be further transported to storage locations. Transportation and storage costs are addressed through the sensitivity analyses.

The CO_2-capture technologies studied in CCP have been brought several steps forward through this program. For some of these CO_2-cost reductions of more than 50% are indicated compared to current baseline (BAT)-technologies. However, most of them are still in a development phase, and will need more R&D- resources and testing to reach a commercial stage.

The reported costs and performance data reflect our current "best estimates" of cost levels and operational performance of the technologies at a point in time when they are believed to reach their mature state of development, enabling implementation into real life applications. More specifically, the estimates reflect the expected realization phase cost and emission performance under future operations of the capture technologies integrated with different types of existing or new CO_2-emitting combustion plants, reflected by the defined CCP-"scenarios" in UK, Alaska, Norway and Canada (Table 17):

Table 17 CCP-scenarios

Scenario		Fuel source	Uncontrolled CO2-emissions
UK refinery	Heaters and boilers in the existing UK Grangemouth refinery	Refinery fuel oil and gas	2.6 mill. ton/yr from target H&B's
Alaska turbines	Small, powergen gas turbines in the existing Prudhoe Bay complex	Natural gas	2.6 mill. ton/yr
Norway gas power	New, non-built gas powergen plant (CCGT) on the Norwegian W-coast	Natural gas	1.3 mill. ton/yr
Canada coke gasifier	New, non-built coke gasification plant (IGCC) in W-Canada	Petroleum coke	4.9 mill. ton/yr

The future "commerciality point in time" is uncertain and will vary across technologies, depending first of all on the technical challenges in each individual case, but also on the strength of external pressures from national/ international government energy and climate policies, and other technology and market developments.

The tables and charts below summarize the evaluated economic performance of capture technologies scenario by scenario, measured in terms of cost per ton of CO_2 captured or avoided compared to original, uncontrolled CO_2-emissions. The "capture cost" reflects the total cost per ton*) of reduced "target" emissions, while the "avoided cost" also include the indirect emissions inherent in the additional energy demand of the capture systems.

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[*] "ton" is used as the term for metric ton (1000 kg).

The unit CO_2-costs are here established from the incremental capture system capex, opex and energy costs, but do not include any front-end R&D-costs, or back-end CO_2-transportation and storage costs.

The incorporated costs are furthermore estimated at "generic" and local, scenario specific sets of unit costs and rates for utilities, energy and labor supplies. Generic prices are partly established from current market price level observations, but should be interpreted as long term (10-25 yrs horizon) expected price levels. The applied generic energy prices are:

- natural gas: 3,0 USD/mBtu
- electricity: 34 USD/MWh (corresponding to uncontrolled, CCGT-powergen cost)
- feed coke: 10 USD/ton.

In addition to these, a set of unit costs and rates for various utilities and labor costs is used in the capex/ opex estimation work, listed in (1). The basic capital charge rate applied in the CO_2-cost calculations was set to 11%, corresponding to a pre-tax discount factor of 10% over a 25 year lifetime. Main CO_2-cost results are provided at the generic cost and price level, while local price results are included among the sensitivities.

The final CO_2-cost results reflect the underlying physical scopes and cost estimates of the integrated "Scenario-Capture Technology cases". A major challenge has been to calibrate the physical scopes and contents across the "cases" enabling a fair and consistent cost and economic comparison of capture technologies. The Norwegian and Canadian scenario-cases are regarded as well aligned at this stage, whereas varying physical contents of processing facilities/ utilities and shifting fuel/ feedstock assumptions e.g. in the UK scenario (see below) imply that case comparisons include more than cost and performance of capture technologies alone. Some cases are synergy concepts combining outcomes from earlier studies (e.g. the BIT-concept in the Norwegian scenario), and have thus not been through longer term evaluations as other technologies.

Based on the above approaches and comments, the resulting CO_2-costs are summarized below, scenario by scenario.

UK scenario

The selected heaters and boilers are assumed to deliver a fixed amount of energy (heat and steam) to serve the refinery complex, corresponding to a certain fired duty level, assumed for all scenario-technology cases.

The energy and utility demands of the capture systems are partly generated on-site, partly supplied through imports from external sources. Some technology cases e.g. include new-built on-site powergen plants varying from 20-30 via 100 to 500 MW's in size. The economics of these cases (e.g. the Oxyfuel - ASU and -ITM), thus include the full cost (capex & opex) of the power plants as well as large corresponding fuel gas and excess power export streams, in addition to the primary capture processing facilities, and the systems collecting CO_2 from the distributed emission sources.

The effective CO_2-debits in the Oxyfuel cases correspond however, to the CO_2-content in the net energy needs of the cases (CO_2 imported through the fuel gas, minus CO_2 exported through the excess power). With these variations in coverage of physical facilities and energy streams across the scenario-cases, one should be careful when comparing the CO_2-cost results, since these do not necessarily demonstrate performance of the various capture technologies per se:

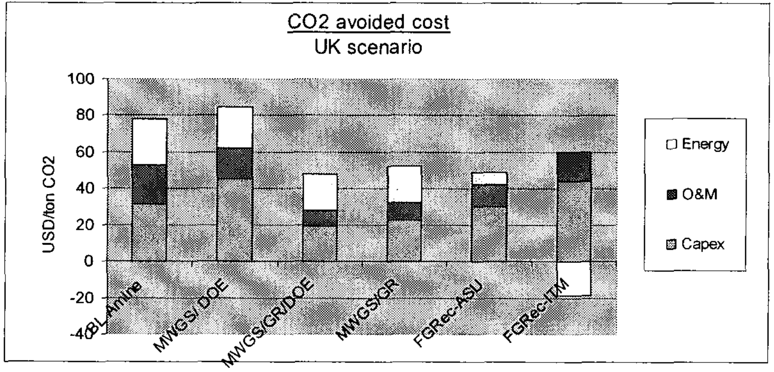
Table 18 UK scenario – key data and CO_2-cost results (generic)

		Output; (fired duty) MW	Increm. capt. syst. capex [*] MUSD	CO_2 captured; mill. ton/yr [**]	CO_2 Avoided; mill. ton/yr [**]	CO_2-capture cost		CO_2-avoided cost	
						USD/ton CO_2	% change rel. to BL	USD/ton CO_2	% change rel. to BL
Post Combustion	Baseline (BL) Amine MEA	1351	362	2,19	1,55	55.3	0 %	**78.1**	0 %
Pre Combustion	Membrane Water Gas Shift w/DOE-membrane (MWGS/DOE)	1351	520	2,19	1,54	59.8	8 %	**84.9**	9 %
	Membrane Water Gas Shift GRACE&DOE-membrane (MWGS/Grace/DOE)	1351	214	1,99	1,50	36.4	-34 %	**48.1**	-38 %
	Membrane Water Gas Shift GRACE & Pd-membrane (MWGS/Grace)	1351	251	1,99	1,50	39.6	-28 %	**52.4**	-33 %
Oxy Fuel	H&B's w/FlueGas Recycle & ASU (FG-Rec ASU)	1351	422	2,08	1,87	43.8	-21 %	**48.7**	-38 %
	H&B's w/FlueGas Recycle & ITM (FG-Rec ITM)	1351	639	2,09	1,95	38.2	-31 %	**41.0**	-48 %

[*] generic basis, excl. IDC, [**] at 100% on-stream level

The break-down of the CO_2-avoided costs above are shown in Figure 17:

Figure 17 UK scenario – CO_2-avoided cost breakdown (generic)



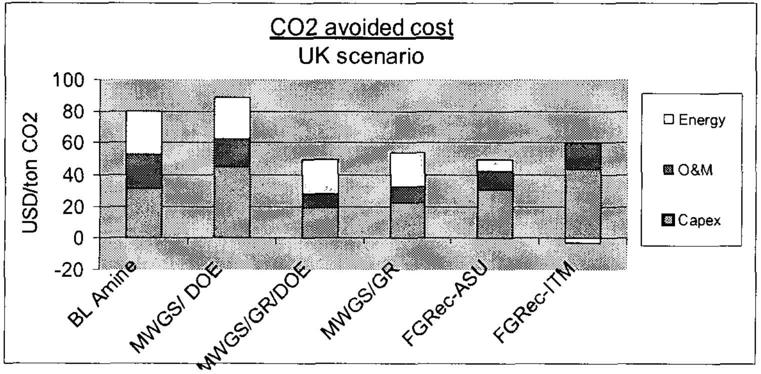
The above calculations indicate a Baseline avoided cost of 78 USD/ton, whereas the Oxyfuel cases demonstrate costs of 40-50 USD/ton. As described above, these cases are highly energy price sensitive due to the large energy import and export streams. By alternatively using the fuel gas and power prices applied by the Oxyfuel technology provider of 3.21 USD/mBtu and 0.028 USD/kWh, the net value of energy import/export of the –ITM case (illustrated in the figure) is nearly neutralized. The resulting CO_2-costs are given in Table 19.

Table 19 UK scenario – key data and CO_2-cost results (alternative fuel gas and power prices)

		CO_2-capture cost		CO_2-avoided cost	
		USD/ton CO_2	% change rel. to BL	USD/ton CO_2	% change rel. to BL
Post Combustion	Baseline (BL) Amine MEA	56.6	0 %	**79.8**	0 %
Pre Combustion	Membrane Water Gas Shift w/DOE-membrane (MWGS/DOE)	62.4	10 %	**88.5**	11 %
	Membrane Water Gas Shift GRACE&DOE-membrane (MWGS/Grace/DOE)	37.4	-34 %	**49.4**	-38 %
	Membrane Water Gas Shift GRACE & Pd-membrane (MWGS/Grace)	40.7	-28 %	**53.8**	-33 %
Oxy Fuel	H&B's w/FlueGas Recycle & ASU (FG-Rec ASU)	44.6	-21 %	**49.6**	-38 %
	H&B's w/FlueGas Recycle & ITM (FG-Rec ITM)	53.1	-6 %	**56.9**	-29 %

The break-down of the CO_2-avoided costs above are shown in Figure 18:

Figure 18 UK scenario – CO_2-avoided cost breakdown (alternative fuel gas and power prices)



Alaska scenario

The system of the 11 "target" gas turbines are assumed to deliver a fixed amount of energy (358 MW) to serve the existing offshore and onshore operations at Prudhoe Bay. When new facilities are planned or built on the North Slope, extraordinary construction and operating costs will be imposed, due to the remote location far from normal infrastructure, the weather and ambient conditions. On the other side, local energy is cheap, reflecting its "stranded" value, and are set to zero level in these evaluations. Basic results are however provided at a "generic" level, here implying that the physical scope of the technology cases incl. all necessary facilities are costed from the generic set of unit costs and rates referred in (1), and at the generic set of energy prices above.

In the capture technology cases included below, the Baseline case is exploiting excess steam to export 18 MW of power, while the 2 advanced pre-combustion cases assume that additional energy (fuel gas) is supplied through imports.

The CO_2-costs reported in Table 20 for the baseline and advanced cases at generic capex/opex costs and energy price levels:

Table 20 Alaska scenario – key data and CO_2-cost results (generic)

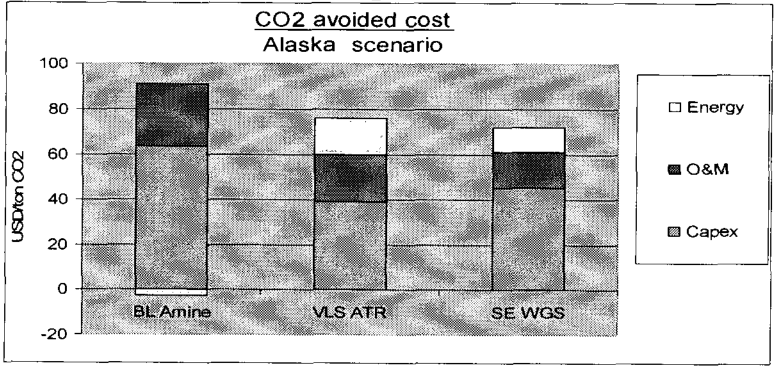
		Output; MW	Increm. capt. syst. capex [*)] MUSD	CO_2 captured; mill. ton/yr[**)]	CO_2 Avoided; mill. ton/yr[**)]	CO_2-capture cost		CO_2-avoided cost	
						USD/ton CO_2	% change rel. to BL	USD/ton CO_2	% change rel. to BL
Post Combustion	Baseline (BL) Amine MEA	358	1012	1,90	1,96	90.9	0 %	**88.2**	0 %
Pre Combustion	VeryLargeScale AutoThermal Reformer (VLS-ATR)	358	713	2,88	2,24	59.0	-35 %	**76.0**	-14 %
	Sorption Enchanced WaterGasShift (SEWGS)	358	771	2,50	2,10	60.5	-33 %	**71.8**	-19 %

[*)] generic basis, excl. IDC, [**)] at 100% on-stream level

The calculations show avoided costs between 70-90 USD/ton. Based on local priced cost estimates and free energy; avoided costs increase to nearly 130 USD/ton for the Baseline and to 80-85 USD/ton for the advanced technology-cases.

The break-down of the generic CO_2 avoided costs are shown in Figure 19:

Figure 19 Alaska scenario – CO_2-avoided cost breakdown (generic)



Norway scenario

The Norwegian scenario is represented by a new (currently non-built) gas-fired power plant (CCGT 400 MW size) at the Western coast where fuel gas can be supplied from offshore reservoirs, and captured CO_2 can be returned and stored in aquifers or supplied to oil fields for EOR applications.

The evaluated capture technologies cover a range of maturity stages, from the further optimized post-combustion solutions to the future pre-combustion concepts. Key data and calculated CO_2-costs are given in Table 21:

Table 21 Norway scenario – key data and CO_2-cost results (generic)

		Output; MW	Increm. capt. syst. capex *) MUSD	CO_2 captured; mill. ton/yr**)	CO_2 Avoided; mill. ton/yr**)	CO_2-capture cost		CO_2-avoided cost	
						USD/ton CO_2	% change rel. to BL	USD/ton CO_2	% change rel. to BL
Post Combustion	Baseline (BL) Amine MEA	323	129	1,09	0,87	49.0	0 %	**61.6**	0 %
	Nexant BL design-basis	322	134	1,09	0,87	47.6	-3 %	**60.0**	-3 %
	Nexant BL design-"low"	332	82	1,09	0,90	36.8	-25 %	**44.7**	-27 %
	Nexant BL design-"integrated"	345	61	1,09	0,94	30.2	-38 %	**35.1**	-43 %
	MHI-Kværner; Membrane Contactor/ KS1	335	127	1,09	0,91	39.5	-19 %	**47.5**	-23 %
	BIT; Best Integrated Concept; Nexant Integr. & MHI-KS1	357	69	1,09	0,98	25.3	-48 %	**28.2**	-54 %
Pre Combustion	Hydrogen Membrane Reformer (HMR)	361	98	1,27	1,17	22.5	-54 %	**24.4**	-60 %
	Sorption Enhanced Water GasShift (SEWGS-O2ATR)	360	150	1,28	1,02	34.1	-30 %	**42.7**	-31 %
	Sorption Enchanced Water GasShift (SEWGS-Air ATR)	424	178	1,47	1,21	28.2	-42 %	**34.4**	-44 %

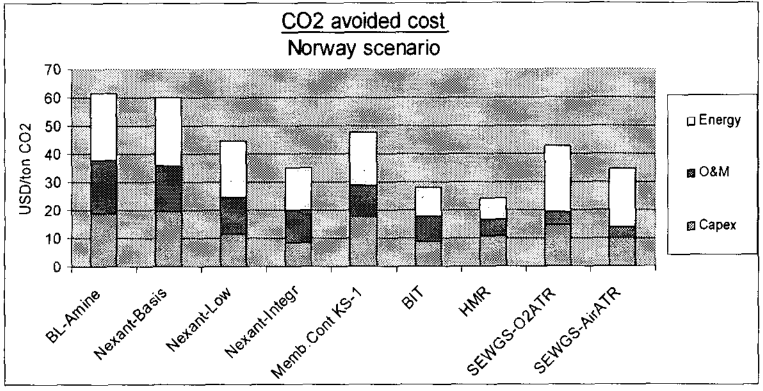
*) generic basis, excl. IDC
**) at 100% on-stream level

The above results indicate significant cost reduction potentials both within the near term and longer term available options:

- CO_2-costs of existing technologies may be reduced by 30-40% by value-engineering and design optimization (ref. the Nexant studies)
- by combining these findings with the MHI-solvent performance, CO_2-cost reduction potentials above 50% is indicated for the "BIT"-concept
- an even larger cost reduction potential is indicated for the future pre-combustion HMR-technology

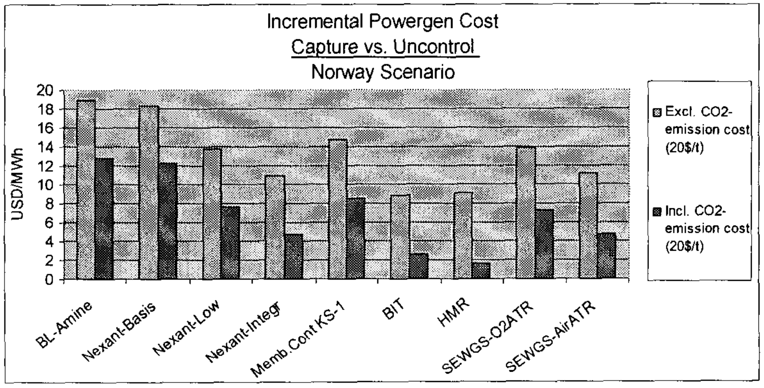
The large reduction potentials above have to be confirmed through further development and verification work. The CO_2-avoided cost break-down is shown in Figure 20.

Figure 20 Norway scenario – CO_2-avoided cost breakdown (generic)



The cost of electricity generated by the various plants is a relevant economic measure in evaluation of power plant investment projects. The powergen costs for the various options are listed in Figure 21 with and without anticipated future CO_2-emission costs (emission taxes or emission trading quota prices).

Figure 21 Norway Scenario - Incremental powergen cost (generic), incl. & excl. CO_2-emissions costs (20 USD/ton)



The Baseline powergen cost is calculated at 34 and 42 USD/MWh pre- and post the CO_2-emission costs, respectively. The above figure demonstrates how these powergen costs increase when including the various capture systems.

These calculations show that current capture (baseline) technology impose a power price add-on of 19 USD/MWh, before emission costs, and reduced to 13 USD/MWh under the assumed CO_2-cost.
In local Norwegian currency the corresponding price add-ons are 151 NOK/MWh and 102 NOK/MWh, respectively.

The lower-cost options impose, as shown, lower add-ons to the power price. The HMR-concept adds 9 USD/MWh pre tax, and merely 1-2 USD/MWh incl. the assumed CO_2-emission cost. This corresponds in local currency, to 72 and 13 NOK/MWh increased powergen price, respectively.

The closer the added power price comes to zero (either by reducing technology costs or increased emission cost expectations); the closer gets also the profitability of power plant project incl. capture systems the uncontrolled power plant projects.

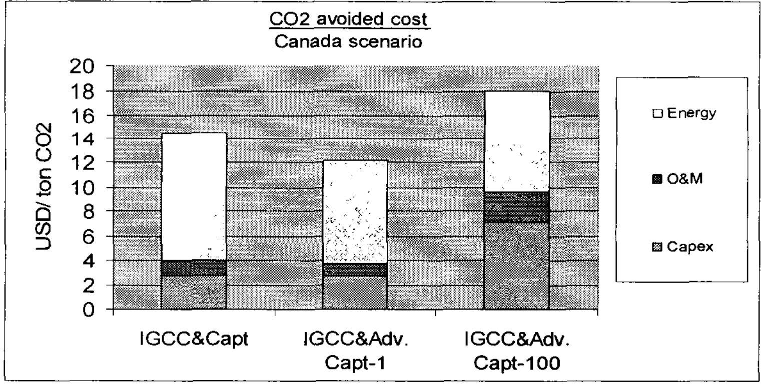
Canada scenario

A planned coke gasification IGCC-plant generating power, hydrogen and steam represents the Canadian scenario. For CO_2-calculation purposes the 3 output streams are measured as a combined output as if all feed coke is used for power generation. The uncontrolled IGCC plant has a combined output of 588 MW. When the precombustion capture systems are included, the power plant unit is increased to optimize the integrated concepts, leading to aggregate output levels of 699 and 734 MW, in the baseline and advanced (CO_2LDSEP) options, respectively. Correspondingly, the feed coke and CO_2-generation volumes are increased in the capture cases relative to the uncontrolled case. The additional feed-coke volumes implicit also reflect a theoretical (proportional) uncontrolled power output, establishing the inherent power/ efficiency losses, and in turn the avoided cost estimates shown in Table 22.

Table 22 Canada scenario – key data and CO_2-cost results (generic)

		Output; combined net power, hydrogen & steam; MW	Increm. capt. syst. capex *) MUSD	CO_2 captured; mill. ton/yr**)	CO_2 Avoided; mill. ton/yr**)	CO_2-capture cost		CO_2-avoided cost	
						USD/ton CO_2	% change rel. to BL	USD/ton CO_2	% change rel. to BL
Post Combustion	Baseline (BL) IGCC with capture	588	519	6,80	5,28	11.1	0 %	**14.5**	0 %
Pre Combustion	IGCC with advanced capture (CO_2LDSEP)	699	516	6,44	5,22	9.9	-11 %	**12.2**	-16 %
	IGCC with advanced capture (CO_2LDSEP) +100 % cost of "black box"	734	689	6,44	5,22	14.6	31 %	**18.0**	25 %

Figure 22 Canada scenario – CO_2-avoided cost breakdown (generic)



The low CO_2-capture and avoided costs shown in Figure 22 are mainly due to the fact that the Canadian scenario includes front-end coke gasification systems, and that the syngas production is included both in the uncontrolled and capture cases. The additional CO_2 capture units represent thus a smaller capex add-on per ton CO_2 handled.

The CO_2-cost reduction potential by the advanced gasification technology (CO_2LDSEP) is calculated to 16%, at a "best estimate" basis. A cost sensitivity of 100% increase of the "black box" in this technology indicates that the reduction potential may disappear if technology development is unsuccessful.

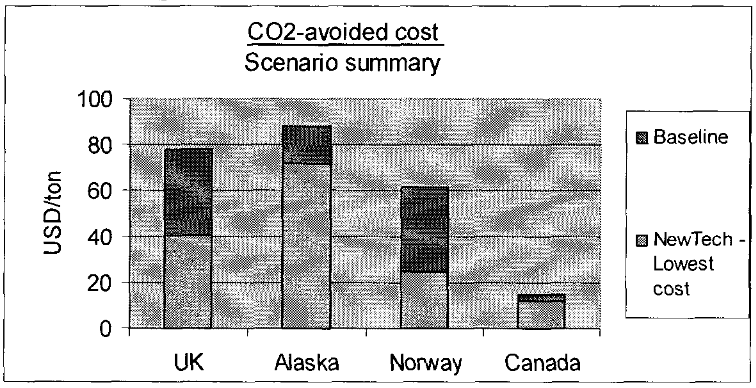
Discussion

This report contains a significant amount of estimates and calculation results. The general findings are summarized by discussing the following questions:

1. What relative and absolute CO_2-cost reductions are achieved?
2. How do the achieved CO_2-cost levels look from an external viewpoint?
3. What is the outlook for capture technology implementation from this perspective?
4. What can we indicate with respect to capture technology availability?
5. What further technology development and cost reduction potentials are possible?

Question 1) Figure 23 and Table 23 summarize CO_2-cost reduction ranges scenario by scenario without focusing on the specific technologies.

Figure 23 CO_2 avoided cost (generic) – Scenario summary



Question 2) CO_2-cost levels of capture projects are normally assessed by referring to long-term expectations of international CO_2- or Greenhouse Gas (GHG)-emission costs (emission taxes, quota prices, etc.) as part of global/ regional climate gas policies. These are uncertain and may vary depending on time horizon, but the range 5-30 USD/ton CO_2 seem to cover typical expectation levels.

Question 3) We can regard the upper part of this range, say 20-30 USD/ton CO_2, as a threshold price that CO_2.capture projects need to pass with their inherent CO_2-abatement cost, if projects are to be realized. Different CO_2-abatement cost terms and definitions may be applied. Both the "captured" and "avoided" CO_2-costs are thus given in the cost-range summary below.

Question 4) The technologies studied in this program cover a range of maturity levels. The Technical Teams have given some indications of the anticipated "breakthrough" points for some technologies, in terms of anticipated time before they can be available for real-life implementation.

Question 5) Further technology development and cost reduction is generally needed before technologies are technically and economically viable. In the last part of the summary table below rough estimates are made with respect to "necessary" improvements in order to achieve a CO_2-capture cost equal to a "threshold price" of 20 USD/ton CO_2, reflecting the upper range of expected long term GHG-emission costs, as discussed above.

Table 23 Summary CO$_2$-cost achievements (generic basis)

		UK	Alaska	Norway	Canada
1. Relative CO$_2$-cost reductions	CO$_2$ capture cost	8% incr.-34% red.	34-35% red.	19-54% red.	11% red.
	CO$_2$ avoided cost	9% incr.-48% red.	14-19% red.	23-60% red.	16% red.
2. Absolute CO$_2$-cost	Captured	36-60 USD/ton	59-91 USD/ton	23-49 USD/ton	10-11 USD/ton
	Avoided	41-85 USD/ton	72-88 USD/ton	24-62 USD/ton	12-15 USD/ton
3. Project realization?	"Best case" capt. cost vs. threshold price (20 $/t)	CC/TP: 1.8	CC/TP: 3.0	CC/TP: 1.1	CC/TP: 0.5
4. Capture Technology availability	("med-term" availability indicates maturity enabling real-life application within 1-5 yrs)	4 Tech's incl., of which 1 available "med-term"	2 Tech's incl., of which 0 available "med-term"	7 Tech's incl., of which 4 available "med-term"	2 Tech's incl., of which 1 available "med-term"
5.Further cost reductions (necessary to achieve CC=TP=20$/t, for "best case")	Overall power-/capture plant capex/ O&M-cost-level	Not discussed	Not discussed	20-25 % red.	Not discussed
	Capture system capex/ O&M-cost-level			60-65 % red.	

The table summarizes achievements for the technologies demonstrating cost reductions. Both cost reductions and absolute CO$_2$-costs vary within and across scenarios.

We furthermore observe that the absolute CO$_2$-cost figures are lower for the new/ non-built plant scenarios (Norway and Canada) than for the existing plant scenarios (UK and Alaska). If this is a true and general result is hard to say, but it may seem intuitive, since the optimization potentials for plant design and configuration is larger in new-build than retrofit situations.

The ratio between the capture cost (CC) and threshold CO$_2$-price (TP), applying the lowest CC in the group and a TP set to 20 USD/ton, indicates the current realization potential from an economic decision point of view. For attractive projects this ratio should be 1.0 or lower. The calculated ratios vary from 3.0 (Alaska) to 0.5 (Canada). Projects with cost ratios above 1.0 will not be implemented. However, projects with lower ratios may not be realized for other reasons. The CC/TP-ratio thus only reflects a necessary, but not a sufficient criterion for realization of capture projects.

For the Norway scenario (HMR-concept with the lowest CC) it is estimated that an overall reduction of power plant and capture system cost levels (total capex and opex, also affecting the uncontrolled case) of 20-25% will bring the calculated CC to 20 USD/ton, or the CC/TP-ratio from 1,3 to 1,0. If cost reducing improvements are only focused on the HMR capture system alone to achieve the same result, these costs need a reduction of 60-65%.

The indications given above with respect to further developments of the actual capture technologies are based on Technology Team assessments. In Figures 24 and 25, avoided CO$_2$-costs ("generic" basis) are plotted against a time horizon indicating development breakthroughs and potential implementation start.

Figure 24 CO_2-cost reductions, technology development and time outlook

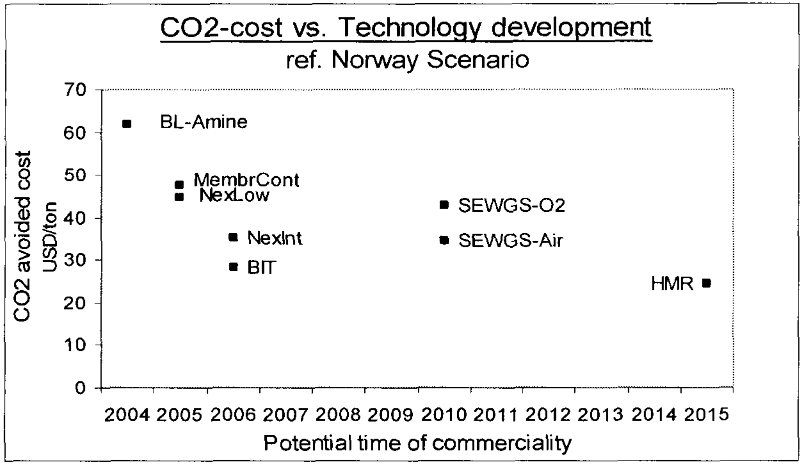
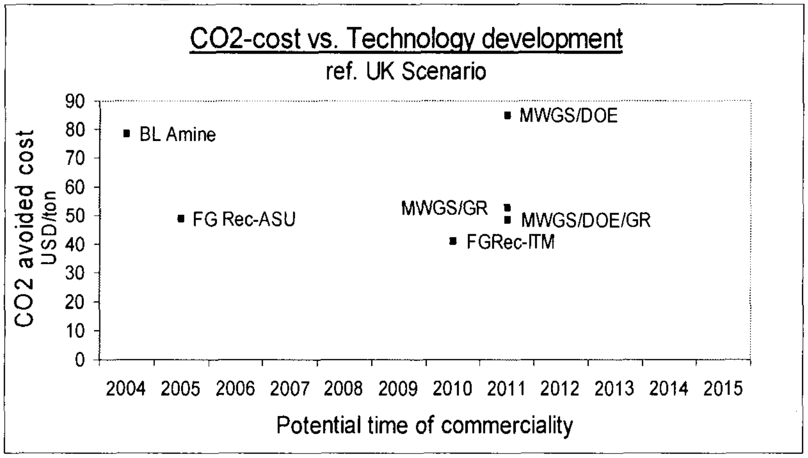


Figure 25 CO_2-cost reductions, technology development and time outlook (2)



Reports and Presentations

The final reports for this subject are included in Appendix A. Six reports are included.

Technology Advisory Board

Task - 5.1 - Project Management

Technology Provider:	Advanced Resources International.
Principal Investigator:	Vello Kuuskraa
Co-funder:	CCP

Background

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 is 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.

As part of its responsibilities and charter, the Technology Advisory Board (TAB) provides technical oversight, performance evaluation and peer review for the CO_2 Capture Project (CCP). The TAB is an international panel of technology experts and funding agency representatives that provides a portion of the overall "quality control and assurance" function to the project.

Evaluation of Accomplishments

To achieve the technology advances discussed above, the CO_2 Capture Project conducted in-depth reviews of nearly a hundred technologies, ideas and concepts for improving on the state-of-the-art of CO_2 capture and storage. A number of these failed to deliver on their postulated costs savings, some were found to be scientifically flawed, while others were found to still only be ideas requiring more rigorous definition and process design. From this mix, the CCP identified, sponsored and itself developed a handful of technologies (including combinations of technologies) that offered the most significant cost savings and promise of commercial readiness.

The final set of lower-cost, advanced technologies were rigorously evaluated by outside engineering firms, by expert cost analysts within the participating companies, and finally by using the "Common Economic Model."

Impact and Benefits

The domestic and international economic benefits of the knowledge and technology on CO_2 capture and storage developed by the CCP will be measured in the hundreds of billions of dollars should the U.S.

pursue a pathway toward atmospheric stabilization of greenhouse gas concentrations. For the European Union and Norway, the other two governmental sponsors of the CCP, the economic benefits could be comparable, although additional work is required to establish the economic and environmental benefits.

To date, the impact and benefits of the CCP technologies have been assessed in terms of reduced costs of CO_2 capture (on a CO_2 avoided basis). While this is one useful measure, as valuable is understanding the impact that CO_2 capture and storage will have on the cost of the primary product, be it electricity, a refined product, or hydrogen.

Meeting Its Promises

When the CCP was first formed and selected for funding by the U.S. DOE/FE's National Energy Technology Laboratory, by the European Union's DGs for Research and for Energy/Transport, and by Norway's Klimatek Program, it set forth ambitious (some would say most ambitious) goals. The goals were to reduce the cost of CO_2 capture (on a CO_2 avoided basis) by 50 per cent for retrofit technology and by 75 per cent for new plants. The goals also were to advance the use of geological storage of CO_2 as a safe and reliable option. The results and accomplishments to date by the CCP offer promise that these ambitious goals can and will be met.

The CO_2 Capture Project (CCP) has made a major contribution toward lower-cost, safe options for reducing greenhouse gas emissions from energy industries. As so well summarized by one of the TAB members, "The CCP has met its promises."

Specifically:

- The CCP has identified and developed a suite of advanced technologies that have the potential to reduce the costs of CO_2 capture by a third to over a half, with further work offering promise of additional cost reductions. These technologies are as applicable to the natural gas and coal-fired electric power sector as they are to oil refineries, to coal gasification plants and to remote Arctic oil and gas field operations. Importantly, the suite of CCP CO_2 capture technologies are applicable as retrofits to existing plants as well as integrated components of new plants;
- It has made major contributions to the knowledge base and technology for assuring safe, reliable geologic storage of CO_2. These contributions are enabling the geologic storage option to become one of the main greenhouse gas mitigation strategies available to the entire energy and power sector;
- It has developed a "Common Economic Model" (CEM) that is usable by a wide variety of policy, research and technology managers. This model provides a consistent and transparent means for establishing the costs of alternative CO_2 capture technologies. The CEM also provides a valuable tool for projecting the benefits of research and technology progress in CO_2 sequestration.
- Finally, the CO_2 Capture Project has provided a significantly lower-cost, zero-emissions pathway toward introducing hydrogen as the "fuel of the future".

The advanced CO_2 capture technologies pursued by the CCP were applied (using detailed process engineering and costing studies) to four geographically specific settings or "scenarios" - - a United Kingdom oil refinery; a Norwegian natural gas-fired power plant; a North Slope of Alaska oil and gas field; and, a Canadian oil sand/synthetic crude facility. This helped identify which of the advanced technologies offered the greatest cost savings over the "baseline" CO_2 capture technologies available today. This site-specific "scenarios" approach helped provide "real world" information and potential for cost savings to the CCP participants. However, the "scenarios" are sufficiently representative to enable the results to have value for a broad set of industries and plant operators, including coal-fired power plants, hydrogen production facilities and new coal gasification installations, as further discussed below.

Portfolio of CO_2 Capture and Storage Technology Advances.

The CO_2 capture and storage technology cost savings identified and further developed by the CCP cover a broad range of options:

1. ***Post-Combustion Technologies.*** By combining innovative design engineering with a new sorbent material and an innovative CO_2 contact process, work by the CCP identified potential capital cost reductions for CO_2 post-combustion capture of over 50 per cent and defined overall reduction in the CO_2 post-combustion capture process by nearly 54 per cent (on a CO_2 avoided basis), compared to currently available technology for the Norway gas-fired power plant scenario. Significantly, this advanced, lower-cost technology could be commercially introduced for large-scale application before the end of this decade, if aggressively pursued through further public-private collaboration.

2. ***Oxyfuel Technologies.*** Advances in air separation and combustion technologies developed and bench-scale tested by the CCP would enable existing power plants to consider retrofit options for CO_2 capture without the high energy penalties and costs associated with today's technologies. Assuming continued R&D in this area, the combined application of ionic transport membranes (ITM) with flue-gas recycle could provide a 48 per cent reduction in CO_2 capture costs (on a CO_2 avoided basis) for the U.K. oil refinery scenario, assuming that the excess power from this process can be sold at market rates.

   The TAB believes that additional significant technology advances are achievable for oxyfuel technologies. The application of ionic transport membranes for air separation in new-built gas turbine systems or novel boilers shows promise for further reducing the costs of CO_2 capture. For example, integrating the Hydro MCM membrane in a gas turbine (Alaska scenario) shows potential for cost reductions of over 50 per cent, assuming technical uncertainties are resolved and unproven equipment performs to specifications. The integrated application of the OTM membrane inside a novel boiler could lead to similar cost savings.

   Finally, the TAB agrees that the proof-of-feasibility testing of the "breakthrough" Chemical Looping Combustion technology, if and when successfully demonstrated at commercial scale, could further improved on these results.

3. ***Pre-Combustion Technologies.*** Of all of the options pursued by the CCP, the pre-combustion removal of CO_2 appears to offer the most promise for breakthroughs. These technologies, particularly involving advanced membranes, can reduce the capital costs of CO_2 capture by 50 per cent and reduce the energy efficiency penalty by up to 75 per cent. Not only are these technologies critical for carbon sequestration, they become essential components of a zero-emissions pathway to hydrogen. Importantly, these technologies may offer even more promise and cost savings for producing hydrogen from coal and other heavy hydrocarbons (such as oil sands and refinery residues) than for hydrogen from natural gas.

   Three key CO_2 capture technology options have been developed for gas-fired power generation and production of hydrogen from natural gas or clean refinery off-gas. Two of the lower risk technologies, sorption enhanced water-gas shift and membrane water-gas shift, offer cost reductions of 19 percent to 44 percent, depending on the scenario, compared to today's baseline cost for post-combustion capture of CO_2. The third technology, the advanced hydrogen membrane reformer, offers a cost reduction of 60 per cent (CO_2 avoided cost basis), although it still requires considerable additional pilot testing and is a decade or so from being commercially available.

   The work by the CCP on CO_2 capture from petroleum and oil sands-based coke gasification, the Canadian "scenario", showed relatively low costs of about $15 per ton of CO_2 (CO_2 avoided basis). The one advanced technology examined for this scenario provided only a modest, 16 percent cost savings (CO_2 avoided basis). The assumptions were that the primary products from the gasification plant would be steam power and hydrogen. As such, many of the facilities and processes for CO_2 capture were already assumed to be in place, requiring primarily the addition of facilities and energy for compressing the already separated CO_2. In an oil sands and synthetic crude operation, where power, hydrogen, heat and natural gas requirements are high, the gasification of petroleum coke offers a very valuable option, especially when it is integrated with CO_2 capture. Even so, because the CO_2 volumes are high, the capture and compression of CO_2 adds considerably to the costs of the salable products.

The TAB believes that significant additional cost savings may be achievable in coke and coal gasification by incorporating a number of the advanced technologies, such as advanced air separation (ionic transport membranes), the enhanced CO water-gas shift systems, and the hydrogen membrane reactor. The TAB recommends that the CCP focus additional efforts on sulfur-tolerant membranes, as this area was one of the few "shortfalls" or "failures" of the CCP, and further pursue integrated design and optimization studies for CO_2 capture from coke, petroleum residues and coal gasification during its next phase.

4. ***Storage, Monitoring and Verification.*** The CCP's storage, monitoring and verification (SMV) program emphasized four areas of priority, namely: (1) integrity of geological storage systems; (2) monitoring technology for CO_2 confinement, movement and leakage; (3) risk assessment methodology for geologic storage; and, (4) optimizing the storage capacity of alternative geologic CO_2 storage systems. The CCP sponsored over 40 individual geological, engineering and systems studies addressing these four topics that had been identified as knowledge and technology gaps.

   The TAB recognizes that the SMV topic is complex, ultimately requiring a broad set of CO_2 storage assessment and monitoring technologies as well as significant changes in current formation evaluation methods, well design, and CO_2 injection and tracking. Continued work in this area will be essential for building a sound base of scientific knowledge and data. Equally important will be testing this knowledge and technology in actual field settings to further understand the challenges of long-term CO_2 storage. These steps will be essential for building public understanding and acceptance for geologic storage of CO_2. Application and testing of these SMV technologies as part of a large-scale, integrated CO_2-EOR and CO_2 storage field test demonstration could be a most valuable next step.

   The TAB finds that the CCP has significantly advanced the understanding and technology of CO_2 storage in geologic formations. In addition, the TAB supports the CCP's building of linkages with other international organizations such as GEODISC (Australia), GEUS (European Union), COAL-SEQ (U.S.) and Weyburn (Canada) that are also addressing geologic storage of CO_2.

Applicability of CCP Technologies to Coal-Fired Power

Currently, there are over 300,000 MWe of existing coal-fired power plant capacity in the U.S., accounting for nearly 40 per cent of domestic and nearly 10 per cent of worldwide industrial CO_2 emissions. Should constraints on CO_2 emissions emerge, these plants will need to decide whether to:

- Shut down,
- Add a post-combustion or oxyfuel combustion retrofit,
- Re-power the plant by converting it to natural gas (NGCC) or an integrated coal gasification (IGCC) unit, or
- Purchase (or create) emission allowances from other sources.

In addition, should the choice be CO_2 capture, the plant operator will need to develop and gain approval for storing the CO_2, most likely in a geological formation.

Given the state of today's CO_2 capture technology, each of these choices entails high costs, risks and inefficiencies for the power plant operator:

- Obviously, shutting down the facility or purchasing CO_2 emission allowances will make a significant negative financial impact on the plant owner and operator;
- Adding a conventional retrofit flue gas amine CO_2 scrubber to an existing power plant, besides being costly, will lead to capacity and energy efficiency losses of 25 to 30 per cent, due to the large steam requirements for amine stripping; and
- Re-powering the power plant with a conventional NGCC or IGCC unit is costly and considered risky by power plant operators.

In addition, as set forth in the recent EIA Annual Energy Outlook 2004, over 100,000 MW of new coal-fired power plant capacity is expected between now and 2025, with the bulk of these coming on line after 2015. Prolonged periods of higher than forecasted natural gas prices, as is the case today, would significantly increase and move forward the expectations for new coal-fired power. Significant cost savings would accrue to the owners and operators of these new coal-fired power plants if low-cost and energy efficient CO_2 capture systems would become commercially available and be integrated with a new plant design, as opposed to being added-on as part of future re-powering or retrofit where there has been no prior design consideration for this option. As such, integrated lower-cost CO_2 capture technology would provide tremendous economic benefits for both the coal-fired and the gas-fired electric power industry.

CO_2 Capture Technology Options for Coal-Fired Power

The CO_2 capture and storage technologies developed by the CCP could provide significant benefits to the coal-fired power sector, as set forth below.

1. ***Post Combustion CO_2 Capture Technology.*** The improved amine scrubber design of the CCP offers major cost and efficiency improvements for post-combustion capture of CO_2. This result is in sharp contrast to prior work that had labeled this technology "mature" and had not fully exploited the potential of heat and pressure integration. Although the CCP study was for a new NGCC, the results could be even more significant for coal-fired power. This is especially true for existing coal power plants assuming a rebuild of the steam cycle for effective heat integration for the critical amine CO_2 stripper energy needs.

   The CCP identified MHI amine/CO_2 scrubber technology has much lower capital and heat requirements than today's baseline technology. This suggests much less derating for existing coal power plants that are considering flue gas CO_2 scrubber retrofits. When the improved amine/CO_2 scrubber design is combined with boiler and supercritical steam cycle rebuilds at existing coal power plants, the plants could avoid any capacity or efficiency derating due to CO_2 capture. This technology could be particularly attractive to coal-fired power due to the higher concentrations of CO_2 in the flue gas.

   The next logical step for this technology would be for the CCP to provide a modified design that is optimized for existing coal boiler power plants with supercritical steam rebuilds and amine stripper heat integration. This could be just what the existing coal-fired electric utilities need to stay competitive if a carbon-constrained world develops. This would also allow effective conversion of older and less efficient subcritical boiler-fired plants into modern, efficient and clean supercritical plants with effective CO_2 capture.

Many of the older coal units with greater than 500 MWe plant capacity, accounting for nearly half (over 160,000 MWe) of total U.S. power capacity, are good candidates for retrofit with the improved amine/flue gas CO_2 scrubber technology.

2. ***Oxygen Combustion CO_2 Capture Technology.*** CCP work on oxygen combustion could have major advantages for both new and retrofit coal-based power generation. For example, the CCP fluidized bed Chemical Looping Combustion technology for natural gas has already led to a follow-on DOE project applying this innovative system to coal.

   A major problem with oxygen combustion retrofit of existing coal-fired boiler power plants is the net capacity and efficiency losses of 30 to 35 per cent. This is mostly due to the large electric power requirements of traditional cryogenic air separation. The ITM oxygen system (using natural gas to make the oxygen) avoids essentially all capacity and energy efficiency derating. Many of the newer supercritical coal units (accounting for about 50,000 MWe of U.S. power capacity) would be good candidates for the option of oxygen combustion via a natural gas-based ITM oxygen generator.

   As such, the CCP work on incorporating oxygen combustion in refinery heaters and boilers is also applicable to existing coal-fired power plants. The key innovation in this area by CCP is the use of the integrated ionic transport membrane (ITM) or a ceramic membrane to generate hot oxygen. Further design work, however, is still required to better match the increased power generation output with power needs.

3. ***Pre-Combustion CO_2 Capture Technology.*** Many of the pre-combustion technologies pursued by CCP, particularly the membrane technologies, apply directly to lowering the cost of CO_2 capture from IGCC power generation, as this involves generation of hydrogen (H_2) and its combustion in gas turbines.

   Independent analysis of H_2 for fuel cell vehicles (FCV) shows that H_2 and IGCC co-production could enable the capital-intensive gasification plants to maintain high annual load factors with a gradual shift to more H_2 and less electricity each year as demand emerges. The CCP work on converting gas turbines from natural gas to H_2 firing is essential for all gas turbines considering the challenges of effective H_2 use.

   The CCP work on petroleum coke gasification polygeneration of H_2, electricity, hydrogen and steam shows low incremental CO_2 capture costs, although the overall cost penalty is still much too high. Here, the CCP works to enhance the CO water-gas shift reaction using sorption enhanced water-gas shift and membrane water-gas shift technology is most applicable. This work will likely benefit coal and petroleum coke gasification more that natural gas reforming due to the significantly higher amounts of CO generated by gasification.

   Coal gasification-based repowering with H_2-fired gas turbines and CO_2 capture, when the existing steam cycle is matched to the bottoming cycle of the new IGCC, could be attractive for many of the older and smaller coal-based power plants that account for about 120,000 MWe of U.S. power capacity. A good example of coal gasification repowering is the highly successful Wabash River Clean Coal Technology project. Adding CO_2 capture to this repowered IGCC plant would demonstrate how CO_2 capture technology could be cost-effectively added during a second stage, when properly planned.

Because the cost-reductions for new CO_2 capture technology studied to date have been for natural gas, oil and petroleum coke-based feedstock, considerable uncertainty still exists as to how much the CCP technologies could reduce the cost of CO_2 capture from coal-fired plants. However, the levels of cost savings, identified by the CCP for these other energy fuels, provide one valuable point of reference.

Future work by the CCP on lower-cost CO_2 capture technologies for coal-fired power generation would be a logical next step.

Reports and Publications

- The project final report is included in Appendix A under the same heading.

Communications

Communications Strategy

CCP was conceived as a public collaboration to address the society-wide issue of carbon dioxide emissions. "Progress through Partnership" was the watchword throughout the project design and development. Public critique and scrutiny were invited to ensure that the best feasible program was developed. Early on project leadership recognized that we could succeed technically but fail in implementation if we didn't ensure that stakeholders understood and agreed with project results. The Executive Board found that continuous engagement of the stakeholders would be needed through the life of the project. An on-going program of communications was developed and is described here.

At the outset, BP, U.S. DOE, and the International Energy Agency's Greenhouse Gas Program jointly sponsored the first planning meeting. Over 150 people attended to provide input into the program and its potential to reduce carbon dioxide emissions. Their input and interest was used to shape the program. Policy makers, the scientific community, non-governmental organizations, and the general public are stakeholders with different views and needs. CCP needed to address all stakeholders to be successful.

The assumptions behind the communication strategy are:

- CCP could succeed technically and yet fail socially if geologic sequestration is deemed environmentally unacceptable.
- NGOs will plan an important role in securing public acceptance of geologic sequestration as a safe and environmentally benign method for carbon dioxide storage.
- NGOs will regard sequestration options with suspicion.
- CCP activities must be viewed as open and transparent by the environmental community.
- CCP must seek positive engagement with governments, NGOs, and the public to ensure their understanding of the merits of geologic storage.

The communication strategy is based on these concepts:

- Present a consistent view of CCP to the public:
    - Promulgate a very simple straightforward summary of CCP objectives, the technologies being developed, and how they fit with other carbon dioxide emission reduction actions being taken by industry.
    - Presentations describing the CCP will be done under the JIP logo rather than the participant's company logo.
    - Presentations, papers, and participation at colloquia must be approved by the Executive Board.
    - A press kit for use by Participants to address requests for information will be developed.
    - Participants will not release CCP information not contained in the press kit without Executive Board approval.
    - A CCP Primary Contact will be designated for non-routine or extensive information requests.
- Open and frequent collaboration with governments to ensure their endorsement of CCP and its objectives.
- Sponsor workshops to introduce CCP to the stakeholder community.
    - Examine the science of geologic sequestration in a balanced way.
    - Learn stakeholder concerns
    - Identify specific actions that CCP can take to address those concerns.

- Establish a working relationship with NGOs to gain their feedback and the program develops.

Through the program numerous opportunities for communication about CCP occurred. Location of CCP's center of activity in Washington, DC presented numerous opportunities for interaction with U. S. government agencies at the highest levels. The Executive Board Chairman testified to the U. S. Congress on industry interest and actions in greenhouse gas mitigation and the U. S. Energy Policy. The Bush administration chose to use CCP as a keystone in describing its actions on climate change. This led to accelerated approval of CCP's funding and work plan.

Outreach to the Public

The CO_2 Capture Project developed a publicly available website that includes general information about the project, selected technical reports and information about future plans. It is available on the Internet at:

http://www.co2captureproject.org/index.htm

Outreach to NGO Community:

Non-governmental organizations will have substantial influence on CO_2 capture and storage projects through their ability to shape public opinion. CCP has opened a dialogue in a transparent way that attempts to engage stakeholders in constructive conversation rather than in an adversarial exchange.

During 2000-2001, two workshops were held to inform environmental activist groups (NGO's) about the CCP. A workshop was held in Washington, DC on 3-4 October 2000 and a second in Amsterdam, Netherlands on 12-13 June 2001. The consensus was that the sessions were informative, helpful, and "a good start" at understanding the issues. NGO representatives made it clear that they were not endorsing capture and storage as a method for greenhouse gas mitigation and that their agenda will remain reduction in CO_2 release to the atmosphere through conservation and renewable energy sources.

Subsequent workshops in 2002 and 2003, presented CCP results and plans to the NGO community with the intent of informing them about the project and soliciting their input and questions so that they could be addressed in an open atmosphere.

Each workshop used a similar format intended to inform the NGO participants about the project, its objectives, the state of the art, and the technical issues being faced. Each discussion was organized to inform, solicit questions, and to engage in dialogue about the issues. Breakout sessions were used to allow informal discussion and viewpoint exchange.

- October 2000 US Workshop – Washington, DC Attended by:
    - Environmental Defense,
    - Natural Resources Defense Council,
    - Pembina Institute,
    - Pew Center on Global Climate Change,
    - Resources for the Future,
    - Union of Concerned Scientists,
    - World Resources Institute,
    - World Wildlife Fund.
- June 2001 EU Workshop – Amsterdam. Attended by:
    - Cicero,
    - Climate Network Europe,

  - Earthwatch,
  - Environmental Defense,
  - Greenpeace International Science Unit,
  - Royal Society for the Protection of Birds,
  - World Wildlife Fund – Netherlands.

- September 2002 NGO Focus Group – Washington, DC
- November 2003 NGO Focus Group, Washington, DC

Stakeholder Community:

The CO_2 Capture Project encouraged its team members and technology providers to publish their work in the open literature as much as feasible. Very few of the results were held confidential and then only in support of inventions made during the project. Below are listed a few of the technical conferences in which CCP results and plans were made public.

- First NETL Conference on Carbon Sequestration – May 2001 Pittsburgh PA
- November 2001 SMV Workshop – Potsdam
- Second Annual NETL Conference on Carbon Sequestration – May 2003 Pittsburgh, PA
- Third Annual NETL Conference on Carbon Sequestration – May 2004 Pittsburgh, PA
- GHGT-5 Greenhouse Gas Technology Conference – August 2000, Cairns, AU
- GHGT-6 Greenhouse Gas Technology Conference – September 2002, Tokyo, JP
- European Workshop – Brussels, BE June 2004
- GHGT-7 Greenhouse Gas Technology Conference – September 2004, Vancouver, BC

Table 24 Conferences at which CCP results were presented

Date	Conference Name	Location
Oct-00	AAGP	Bali
8-9 Jan 01	Electric Utilities Environmental Conference (EUEC)	Tucson
16-17 Jan 01	International Risk Assessment Workshop	Washington DC
31 Jan 01	PTAC	Calgary
01 Mar-01	Commercial GHG Technology Solutions	New York
13-14 Mar 01	CO_2Net Trondheim Meeting on Policy	Trondheim
30 March 01	Norwegian Climate Conference	Oslo
4-5 Apr 01	European Union of Geosciences Biennial Meeting	Strasbourg
25- 27Apr 01	International Association for Energy Economics (IAEE)	Houston
1-4 June 01	AAPG	Denver
27-28 Jun 01	Carbon Dioxide Removal and Sequestration in the Oil and Gas Industry	London
30 Sep – 3 Oct 01	SPE Annual Technical Conference and Exhibition 2000: Emerging and Peripheral Technology (Session Number 511)	New Orleans
7-10 Oct 01	2001 Gasification Technology Conference	San Francisco
22-Oct- 2 Nov 01	COP7	
13-14 Nov 01	MIT Annual Carbon Sequestration Forum	MIT
1 Dec 01	AGU	San Francisco

CO_2 Capture Project Results Volumes

The CO_2 Capture Project worked with the technology providers to produce a two volume set of papers of the results of the CCP program. It was published in December 2004 by Elsevier Science Press of London. The two volume set includes seventy-two papers and is 1331 pages long. It is entitled:

"Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO_2 Capture Project:"
Volume One: Capture and Separation of Carbon Dioxide from Combustion Sources"
Edited by David C. Thomas
Volume Two: Geologic Storage of Carbon Dioxide with Monitoring and Verification."
Edited by Sally M. Benson

A copy of the set is provided with this final project report.

Individual Scientific Papers:

As noted above the technology providers were encouraged to prepare and present papers based on their work. While the CCP team made an effort to collect the references for these presentations we are uncertain exactly how many papers have been presented to date. The following pages provide bibliography of those papers.

Partial Bibliography of Scientific Papers:

1. Mattisson, T., Johansson, M., and Lyngfelt, A., "Multi-cycle reduction and oxidation of different types of iron oxide particles - application to chemical-looping combustion" *Energy & Fuels* 18 (2004) 628-637.

2. Lyngfelt A, and Thunman, H., "Construction and 100 hours of operational experience of a 10-kW chemical looping combustor." Chapter 36 in *the CO_2 Capture and Storage Project (CCP) for Carbon Dioxide Storage in Deep Geologic Formations for Climate Change Mitigation, Volume 1 – Capture and Separation of Carbon Dioxide from Combustion Sources.* Ed.: Thomas, D. Elsevier Science, London. (2004)

3. Kronberger, B., Lyngfelt, A., Löffler, G., and Hofbauer, H., "Design and hydrodynamic testing of a 10-kW prototype for continuous chemical-looping combustion," accepted for publication in *Ind Eng Chem Res*, 2004.

4. Lyngfelt, A., Kronberger, B., Adanez, J., Morin, J.-X., and Hurst, P., "The GRACE Project. Development of oxygen carrier particles for chemical-looping combustion. Design and operation of a 10 kW chemical-looping combustor." *7th International Conference on Greenhouse Gas Control Technologies*, Vancouver, Canada, 5th-9th September 2004.

5. Streit, J. E., Daniel, R. F., Dewhurst, D. N., Dodds, K., Evans, B. J., Hillis, R. R., Siggins, A. F. & Urosevic, M., 2003. Geomechanical Effects of CO_2 Storage. *Report to BP and the CO_2 Capture Project, December 2003.*

6. CO_2 Capture Project - An Integrated, Collaborative Technology Development Project for Next Generation CO_2 Separation, Capture and Geologic Sequestration Geomechanical Effects of CO_2 Storage. Report Reference T.1.1.4

7. Streit, J. E., Siggins, A. F., & Evans, B. J., in press. Predicting and monitoring geomechanical effects of CO_2 injection. In: S. M. Benson (ed.) *Volume 2 – Geologic Storage of Carbon Dioxide with Monitoring and Verification.* Elsevier.

8. Streit, J.E., & Siggins, A. F., in press. Predicting, monitoring and controlling geomechanical effects of CO_2 injection. Elsevier Special Volume, GHGT-7 conference.

9. M. V. Mundschau, X. Xie, and A. F. Sammells, "Hydrogen Transport Membrane Technology for Simultaneous Carbon Dioxide Capture and Hydrogen Separation in a Membrane Shift Reactor," in Carbon Dioxide Capture for Storage in Deep Geologic Formations - Results from the CO_2 Capture Project, Volume I: Capture and Separation of CO_2 from Combustion Sources. David C. Thomas, Editor. Elsevier Science 2005. Chapter 16, p. 291-306.

10. C. Lowe, M. Mundschau, X. Xie, and T. Ohrn, "Hydrogen Membrane Selection for a Water Gas Shift Reactor - Phase II," Third Annual Conference on Carbon Capture and Sequestration, Alexandria, Virginia, May 3-6, 2004.

11. M. V. Mundschau, X. Xie, C. R. Evenson and A. F. Sammells, "Simultaneous Hydrocarbon Reforming, Carbon Dioxide Sequestration and Hydrogen Separation using Dense Inorganic Membranes," Third Annual Conference on Carbon Capture and Sequestration, Alexandria, Virginia, May 3-6, 2004.

12. A. F. Sammells, M. V. Mundschau, and X. Xie, "Oxygen and Hydrogen Transport Membranes for Combined Hydrocarbon Reforming and Hydrogen Separation," In: Inorganic Membranes:

Proceedings of the Eighth International Conference on Inorganic Membranes (Adams Press, Chicago, July 2004), F. T. Akin and Y. S. Lin, *Ed.*

13. M. V. Mundschau, X. Xie, and A. F. Sammells, "Dense Membranes for Separation of H_2 from CO_2 in High-Pressure Water-Gas Shift Reactors," 7th International Conference on Greenhouse Gas Control Technologies," Vancouver, British Columbia, September 5-9, 2004, in press.

14. C. Lowe, M. Mundschau, X. Xie, and T. Ohrn, "Hydrogen Membrane Selection for a Water Gas Shift Reactor - Phase II," Third Annual Conference on Carbon Capture and Sequestration, Alexandria, Virginia, May 3-6, 2004.

15. M. V. Mundschau, X. Xie, C. R. Evenson and A. F. Sammells, "Simultaneous Hydrocarbon Reforming, Carbon Dioxide Sequestration and Hydrogen Separation using Dense Inorganic Membranes," Third Annual Conference on Carbon Capture and Sequestration, Alexandria, Virginia, May 3-6, 2004.

16. A. F. Sammells, M. V. Mundschau, and X. Xie, "Oxygen and Hydrogen Transport Membranes for Combined Hydrocarbon Reforming and Hydrogen Separation," Eighth International Conference on Inorganic Membranes, Cincinnati, Ohio, July 21, 2004.

17. M. V. Mundschau, X. Xie, and A. F. Sammells, "Dense Membranes for Separation of H_2 from CO_2 in High-Pressure Water-Gas Shift Reactors," 7th International Conference on Greenhouse Gas Control Technologies," Vancouver, British Columbia, September 5-9, 2004.

18. Christoph Tagwerker, Aufbau und Betrieb eines Labormodells zur Untersuchung der Fluiddynamik eines Chemical-Looping Combustion Wirbelschichtsystems, Vienna University of Technology, Institute of Chemical Engineering, 2003 (in German), Masters' Thesis.

19. Ana Luengo, Process Simulation of a Chemical-Looping Combustion Power Plant, p Vienna University of Technology, Institute of Chemical Engineering, 2003. Masters' Thesis.

20. Raquel Valenciano Pérez, Effect of Solids Residence Time Distribution on Fuel Reactor Performance of Chemical-Looping Combustor, Vienna University of Technology, Institute of Chemical Engineering, 2003. Masters' Thesis.

21. Bernhard Kronberger, Analysis of Fluidized Bed Reactor Systems for Chemical-Looping Combustion, Vienna University of Technology, Institute of Chemical Engineering, 2004 (in preparation.) PhD Thesis.

22. Kronberger, B., Löffler, G., and Hofbauer, H.,. Chemical-looping combustion – Reactor fluidization studies and scale-up criteria, to appear as Chapter 30 in The CO_2 Capture and Storage Project (CCP) for Carbon Dioxide Storage in Deep Geologic Formations For Climate Change Mitigation, Volume 1 – Capture and Separation of Carbon Dioxide From Combustion Sources. Ed.: Thomas, D. Elsevier Science, London, 2004.

23. Kronberger, B.; Lyngfelt, A. Löffler, G.; Hofbauer, H. Design and fluid dynamic analysis of a bench-scale combustion system with CO_2 separation
24. chemical-looping combustion, (accepted for publication in Ind. Eng. Chem. Res.) 2004.(**)

25. Kronberger, B.; Beal, C.; Morin, J.X.; Hofbauer, H. Design, hydrodynamic testing and scale-up recommendations of a conceptual large-scale chemical-looping combustion power plant; Proceedings of the Third Annual Conference on Carbon Capture and Sequestration, Alexandria, May 3-6, 2004.(*)

26. Kronberger, B.; Löffler, G.; Hofbauer, H., Residence time distribution of solids in a chemical-looping fluidized bed fuel reactor, Proceedings of the 16th International Congress of Chemical and Process Engineering, Prague, 22-26 August 2004.

27. Oldenburg, C.M., and A.J.A. Unger, On leakage and seepage from geologic carbon sequestration sites: unsaturated zone attenuation, Vadose Zone Journal, 2(3): 287-296, 2003. LBNL-51928.

28. Oldenburg, C.M., and A.J.A. Unger, Coupled vadose zone and atmospheric surface-layer transport of CO_2 from geologic carbon sequestration sites, Vadose Zone Journal, 3, 848?857, 2004, LBNL-55510.

29. Zhang, Y., C.M. Oldenburg, and S.M. Benson, Vadose zone remediation of carbon dioxide leakage from geologic carbon dioxide sequestration sites, Vadose Zone Journal, 3, 858-866, 2004, LBNL-54680.

30. Dag Eimer (speaker), Merethe Sjøvoll, Nils Eldrup, Richard H. Heyn, Olav Juliussen, Malcolm McLarney, Ole Swang, "New Thinking in CO_2 Removal" Third Nordic Minisymposium on Carbon Dioxide Capture and Storage, Trondheim, Norway (October 2-3, 2003)

31. Daniel Chinn, Dag Eimer, Paul Hurst (speaker), "Post Combustion: "Best Integrated Technology" (BIT) Overview" DOE/NETL 3rd Annual Conference on Carbon Capture and Sequestration, Alexandria, Virginia, USA (May 3-6, 2004)

32. Dag Eimer, "Carbon dioxide Capture Project. Teknologier for fjerning av CO_2 fra røkgass" Tekna's konferanse 'Gass- og energiteknologi', Langesund, Norway. (June 8-9, 2004)

33. H. Schütt, M. Wigand, E. Spangenberg. The Influence of CO_2 Injection on the Geophysical and Geochemical Properties of Reservoir Rocks in: S.M. Benson, ed. The CO_2 Capture and Storage Project (CCP) for Carbon Dioxide Storage in Deep Geologic Formations for Climate Change Mitigation, Vol. 2: Geologic Storage of Carbon Dioxide with Monitoring and Verification, Elsevier Science (2004)

34. E. Spangenberg, H. Schütt, G. Borm, The influence of CO_2 injection on the physical properties of reservoir and cap rocks, Annual CCP workshop, October 21-23, 2002, Santa Cruz, CA.

35. H. Schütt, M. Wigand, E. Spangenberg, G. Borm, J. Erzinger, CO_2 effects on reservoir and cap rocks, Annual CCP workshop, September 22-24, 2003, Dublin/Ireland

36. H. Schütt, M. Wigand, E. Spangenberg, G. Borm, J. Erzinger,Effects of supercritical CO_2 on sandstones and cap rocks - invited talk, April 28, 2004, Shell, Rijswijk, The Netherlands.

37. M. Wigand, H. Schütt, E. Spangenberg, J. Kulenkampff, Influence of CO_2 injection on the geochemical properties of reservoir and cap rocks - invited talk, October 25, 2004, Los Alamos National Laboratory, Los Alamos/NM

38. Mølnvik, M.J., Heggum, G., "CO_2 Transportation - From Capture to Storage", CCP - SMV 2003 Annual Workshop: Dublin September 22-24, 2003.

39. Weydahl, T. Heggum, G. Austegaard, A. Mølnvik, M.J. Mo, R., "CO_2 Properties and Transportation", presented at the NORCAP seminar, Trondheim, October 2003.

40. Heggum, G. Weydahl, T. Mo, R. Mølnvik, M. Austegaard, A., "CO_2 Conditioning and Transportation", to be published in CCP Technical Volumes, accepted for publication by Elsevier.

41. Austegaard, A et al., "Thermodynamic models for calculations of water solubility in the CO_2-CH_4 mixture", to be published.

42. G. Barbieri, S. Fragale, E. Drioli, "Palladium based membranes", 1st workshop Italy-Russia on "Membrane Technology for a Sustainable Industrial Production", 17-20 September 2003, Cetraro CS Italy

43. P. Bernardo, S. De Rango, **G. Barbieri**, E. Drioli, "Permeation Properties of a Pd-based tubular membrane", 1st workshop Italy-Russia on "Membrane Technology for a Sustainable Industrial Production", 17-20 September 2003, Cetraro CS Italy

44. **G. Barbieri**, P. Bernardo, R. Mattia and E. Drioli, R. Bredesen, H. Klette, Pd-based membrane reactor for Water-gas shift reaction, AIDIC, The Italian Association of Chemical Engineering - International Conference "Hydrogen-age: When, Where, Why", Pisa, May 16-19, 2004, Oral presentation

45. **G. Barbieri**, F. Scura, P. Bernardo, S. De Rango, E. Drioli, M. Menendez, M.P. M. Urbiztondo and L. Casado, Membrane reactor for water-gas shift reaction using Pd-based membrane supported on zeolite A, Convegno GRICU 2004, Porto d'Ischia, September 12-15, 2004, Oral presentation
46. **G. Barbieri**, T. Granato, P. Bernardo, E. Drioli, N.E. Benes, H. Kruidhof and M.W.J. Luiten, Water-gas shift reaction in membrane reactor using silica membranes, 6th International Conference on Catalysis in Membrane Reactors, ICCMR-6, Lahnstein (Germany), July 6-9, 2004, p. 60, Oral presentation

47. "Impact of SOx and NOx in flue gas on CO_2----" is the paper in the CCP special publication (volume II) by Bruce Sass and others. You can get the citation from the CCP special volume table of contents.

48. Cawley, S., Le Gallo, Y., Carpentier, B., Holloway, S., Bennison, T., Wickens, L., Wikramaratna, R., Saunders, M., Kirby, G.A., Bidstrup, T., Ketzer, J.M., Arkley, S. L. B. & Browne, M.A.E. 2004. The NGCAS project - Assessing the Potential for EOR and CO_2 Sequestration at the Forties oilfield, offshore UK. *Submitted for publication* in "Carbon Dioxide Storage in Deep Geologic Formations For Climate Change Mitigation" Volume 2 – Geologic Storage of Carbon Dioxide with Monitoring and Verification"

49. Holloway, S., Browne, M., Arkley, S. "Why did we choose the Forties oilfield as a potential storage site?" presented at the DTI Conference Centre, London, 10/02/04.

50. Bennison, T.G. 2002 NGCAS Reservoir Simulation Modeling Report. ECL. NGCAS Technical Report.

51. Bidstrup, T. 2003. Regional 2D Basin Modeling. GEUS. NGCAS Technical Report.

52. Browne, M.A.E., Arkley S.L.B. & Holloway, S. 2003. *The Potential for Carbon Dioxide Sequestration in the Midland Valley of Scotland and Adjacent Areas of the Forth Approaches.* NGCAS Technical Report. 74pp.

53. Bunney, J., 2002. CO_2 Storage Forties Field, Permedia research Group. Unpublished Report.

54. Crawford, R., Littlefair, R. W & Affleck, L. G. 1991. The Arbroath and Montrose fields, blocks 22/17, 18, UK North Sea. 211-217 in United Kingdom Oil and Gas Fields, 25 Years Commemorative Volume. Abbots, I L, (editor). *Memoir of the Geological Society of London*, No. 14.

55. Creedy, D. P. 1999. *Coalbed Methane - the R & D needs of the UK.* DTI Cleaner Coal Technology report No. COAL R163. ETSU, Harwell, UK.

56. Envoi, 2001. http://www.envoi.co.uk/P22CBMsyn.pdf

57. Espie, A. A. 2001. Options for Establishing a North Sea Geological Storage Hub. *In:* Williams, D.J., Durie, R.A., McMullan, P., Paulson, C.A.J. & Smith, A.Y. (Eds). *Greenhouse Gas Control Technologies*: Proceedings of the Fifth International Conference on Greenhouse Gas Control Technologies. CSIRO, Collingwood, Australia, 266-271.

58. Ketzer, J.M. & Carpentier, B. 2003. Temis 3D Basin Modeling Applied to Geological Sequestration of CO_2 in the Forties Field, North Sea. IFP. NGCAS Technical Report.

59. Kirby, G. 2003. Interpretation of a Regional Seismic Profile near the Forties Field, North Sea, U.K. NGCAS Technical Report.

60. Le Gallo, Y. Modeling geological sequestration of CO_2 in the Forties Field, North Sea NGCAS. February, 2003

61. Moss, B., Barson, D., Rakhit K., Dennis, H. & Swarbrick, R. 2003. *Formation Pore Pressures and Formation Waters.* In: The Millennium Atlas: Petroleum Geology of the Central and Northern North Sea. D. Evans, C. Graham, A. Armour & P. Bathurst (Eds). The Geological Society of London, London, pp. 317-329.

62. van Genuchten, M. Th. 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sciences Society of America Journal,* **44**: 892-898.

63. Simmonds, M., Hurst, P., Wilkinson, M. B., Watt, C. & Roberts, C. A. 2003. A Study of Very Large Scale Post Combustion CO_2 Capture at a Refining and Petrochemical Complex. In: J. Gale and Y. Kaya (Eds.) *Greenhouse Gas Control Technologies*, Volume 1, Elsevier, pp. 39-44.

64. Wikramaratna, R. S , Wickens, L 2003. *NGCAS – Case History of the Assessment of Risk for the Long-Term Geological Storage of Carbon Dioxide.* NGCAS Technical Report.

65. Chapter on NGCAS in Elsevier book: “The CO2 Capture and Storage Project for Carbon Dioxide Storage in Deep Geological Formations for Climate Change Mitigation”

66. Paper presented at 226th American Chemical Society meeting September 2003 in New York.

67. KETZER, J.M.*, CARPENTIER, B., LE GALLO, Y. AND LE THIEZ, P. Paper presented at IFP Paris November 2003 meeting “Geological Sequestration of CO_2 in Mature Hydrocarbon Fields – What can we learn from numerical modeling of the Forties Field, North Sea?”

68. IEA-GHG - in Greenhouse Issues No 61 and featured in No 71 March 2004 (http://www.ieagreen.org.uk/march71.pdf)

69. SMV presentation at Coal Sequestration III March 2004 Baltimore (http://www.coal-seq.com/Proceedings2004/presentations/Christopher.pdf)

70. Hufton, J.R., R.J. Allam, R. Chiang, P. Middleton, E. Weist, V. White, “Development of a Process for CO_2 Capture from Gas Turbines using a Sorbent Enhanced Water Gas Shift Reactor System”, 7th International Conference on Greenhouse Gas Control Technologies, Vancouver, BC (2004).

71. Allam, R., R. Chiang, J. Hufton, E. Weist, V. White, and P. Middleton, "Power Generation with Reduced CO_2 Emissions via the Sorption Enhanced Water Gas Shift Process", 3rd Annual Carbon Capture and Sequestration Conference, Alexandria, VA, May 3-6 (2004).

72. Hufton, J.R., R.J. Allam, R. Chiang, P. Middleton, E. Weist, V. White, "Development of a Process for CO_2 Capture from Gas Turbines using a Sorbent Enhanced Water Gas Shift Reactor System", paper prepared for the 7th International Conference on Greenhouse Gas Control Technologies (2004).

73. Kulprathipanja, A., Alptekin, G. O., Falconer, J. L. and J. D. Way, "The Effects of Water Gas Shift Gases on Pd-Cu Alloy Membrane Surface Morphology and Separation Properties," *Ind. Eng. Chem. Res.*, **43**(15), 4188-4198(2004).

74. Kulprathipanja, A., Alptekin, G. O., Falconer, J. L. and J. D. Way, "Pd and Pd-Cu Membranes: Inhibition of H2 Permeation by H2S,"submitted to the *Journal of Membrane Science*, 4/04.

75. Roa, F. and J. D. Way, "The Effect of Air Exposure on Palladium-Copper Composite Membranes," *Applied Surface Science*, in press, 8/04.

76. Kulprathipanja, Ames, "Hydrogen Production Using Indium Tin Oxide Catalysts and Palladium/Copper Membranes," Ph.D. Thesis, Department of Chemical Engineering, University of Colorado Boulder, December 2003.

77. "Pd-Cu Membrane for the Water Gas Shift Reaction", Poster by Ames Kulprathipanja, North American Catalysis Society Meeting, Cancun, Mexico, June 1-9, 2003

78. Johnson, J.W., Nitao, J.J., and Morris, J.P., 2005, Reactive transport modeling of cap-rock integrity during natural and engineered CO_2 storage, in: Thomas, D.C., and Benson, S.M. (Eds.), *The CO_2 Capture and Storage Project (CCP), Volume 2*, Elsevier, p. 783-809.

79. Johnson, J.W., Nitao, J.J., and Morris, J.P., 2004, Modeling the long-term isolation performance of natural and engineered geologic CO_2 storage sites: *Proceedings Seventh Intl. Conf. Greenhouse Gas Control Technologies (GHGT-7)*, Vancouver, BC, Canada, September 5-9, 2004, 6 p.

80. *Johnson, J.W., Nitao, J.J., Morris, J.P., and Blair, S.C., 2003, Reactive transport modeling of geohazards associated with offshore CO_2 injection for EOR and geologic sequestration:* invited paper, Proceedings Offshore Technology Conference (OTC), *Houston, TX, May 5-8, 2003, 9 p.*

81. Johnson, J.W., Nitao, J.J., and Morris, J.P., Modeling the long-term isolation performance of natural and engineered geologic CO_2 storage sites: Seventh Intl. Conf. Greenhouse Gas Control Technologies (GHGT-7), Vancouver, BC, Canada, September 5-9, 2004 (oral presentation).

82. *Johnson, J.W., Nitao, J.J., Blair, S.C., and Morris, J.P., CO_2 reservoirs: are they natural analogs to engineered geologic storage sites?: Third National Conference on Carbon Sequestration, Alexandria, VA, May 3-6, 2004 (oral presentation).*

83. *Johnson, J.W., Nitao, J.J., and Morris, J.P., Reactive transport modeling of cap rock integrity during natural and engineered CO_2 sequestration: American Chemical Society National Meeting, New York, NY, September 7-11, 2003 (oral presentation).*

84. *Johnson, J.W., Nitao, J.J., Blair, S.C., and Morris, J.P., CO_2 reservoirs: are they natural analogs to engineered geologic storage sites?: Special Session on Geological Sequestration of CO_2, AAPG Annual Meeting, Salt Lake City, UT, May 11-14, 2003 (oral presentation).* NOTE: we received the 2003 AAPG DEG (Division of Environmental Geosciences) "Best Paper—Oral Presentation" award for this presentation.

85. *Johnson, J.W., Nitao, J.J., and Morris, J.P., Reactive transport modeling of long-term cap rock integrity during CO_2 injection for EOR or saline-aquifer storage: Second National Conference on Carbon Sequestration, Alexandria, VA, May 5-8, 2003 (poster presentation).*

86. *Johnson, J.W., Nitao, J.J., Blair, S.C., and Morris, J.P., Reactive transport modeling of geohazards associated with offshore CO_2 injection for EOR and geologic sequestration: Special Session on Geohazards, Offshore Technology Conference, Houston, TX, May 5-8, 2003 (invited oral presentation).*

87. *Johnson, J.W., Nitao, J.J., and Morris, J.P., Reactive transport modeling to predict long-term cap-rock integrity, Third Annual JIP CO_2 Capture Project Workshop, Dublin, Ireland, Sep 22-24, 2003 (oral presentation).*

88. *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_2 Capture Project Workshop: "Leveraging the SMV Family of Technology Providers", Santa Cruz, CA, Oct 21-23, 2002 (oral presentation).*

89. *Johnson, J.W., Nitao, J.J., and Blair, S.C., Reactive transport modeling to predict long-term cap-rock integrity, JIP CO_2 Capture Project Workshop: "Building the SMV Family of Technology Providers", Potsdam, Germany, Oct 31-Nov 2, 2001 (oral presentation)*

90. Presented Project Results to: SMV Workshop, (Sponsored by CCP) Dublin, Ireland; September 22-24, 2003

91. Presented Project Results to: NorCap CO_2 Capture and Sequestration Seminar, October 14-15, 2003; Trondheim, Norway

92. Presented Project Results to: Third Annual Conference on Carbon Capture and Sequestration, May 5, 2004; Washington, DC

93. Presented Project Results to: 7th International Conference on Greenhouse Gas Control Technologies, Vancouver, BC, Canada, September, 5-9 2004

94. G. BARBIERI(a), T. GRANATO, P. BERNARDO(b), E. DRIOLI(a,b), N.E. BENES(c), H. KRUIDHOF(c) and M.W.J. LUITEN(c); WATER-GAS SHIFT REACTION IN MEMBRANE REACTOR USING SILICA MEMBRANES 6th International Conference on Catalysis in Membrane Reactors (ICCMR-6) July 7-9, 2004, Lahnstein, GERMANY.

95. *CINDY HUISKES, MIEKE LUITEN, HENK KRUIDHOF, NIECK E. BENES* ^{B}*, AND HENNY J. M. BOUWMEESTER, HIGH QUALITY STEAM STABLE TUBULAR SILICA MEMBRANES FOR GAS 8th International Conference on Inorganic Membranes (ICIM-8) July 18-21, 2004, Cincinnati, Ohio, USA*

96. Wickens, Laurence, "Leveraging the SMV Family of Technology Providers", SMV Workshop No 3, Santa Cruz, California, October 21 2002.

97. Bennison, T. Forties CO_2 sequestration Reservoir Simulation Modeling, ECL Technology Ltd

98. Wickens, Laurence, "Forties CO_2 sequestration risks," ECL Technology Ltd.

99. Kjell Ove Kongshaug and Marion Seiersten: Baseline Experiments for The Modelling Of Corrosion at High CO_2 Pressure, CORROSION/2004, Paper No. 04630, New Orleans, 29 March – 1 April 2004

100. Marion Seiersten: Material Selection for Separation, Transportation and Disposal of CO_2. CORROSION/2001, Paper No. 01042, Houston, 11-16 March 2001

101. Marion Seiersten: Corrosion of Pipeline Steels in Supercritical CO_2 / Water Mixtures. EUROCORR 2000, London, 10-14 September 2000.

102. M. Menéndez, M.P. Pina, M.A. Urbiztondo, and L. Casado. University of Zaragoza. M. Boutonnet, S. Rojas, and S. Nassos. Development of Pd Zeolite Composite Membranes for Hydrogen Production by Membrane Reactor. The CO_2 Capture and Storage Project (CCP) for Carbon Dioxide Storage in Deep Geological Formations for Climate Change Mitigation. Volume 1 Capture and Separation of Carbon Dioxide from Combustion Sources. Section 2: Pre-Combustion De-carbonization Technology. Editor: David C. Thomas. *Editorial Elsevier Ltd.* In press.

103. Casado, L. Urbztondo, M., Pina, M.P, Menendez, M., Santamaria, J., Pd-zeolite membranes for hydrogen separation, European Congress on Chemical Engineering ECCE'03. Granada, Spain 2003.

104. A Casado, L. Urbztondo, M., Pina, M.P, Menendez, M., Santamaria, J., "Nuevas estrategias para mejorar la selectividad a hidrogeno de membranas zeoliticas tipo," Congress of the Spanish Society of Catalysis SECAT'03. Torremolinos (Spain) 2003

105. G. Barbieri, F. Scura, P. Bernardo, S. De Rango, E. Drioli, M. Menendez, M.P. Pina, M. Urbiztondo, L. Casado. Membrane reactor for water-gas shift reaction using Pd-based membrane supported on zeolite A. Gricu Conference. Porto d'Ischia (Nápoles). 12-15 September 2004.

106. Miles, Natasha L., Kenneth J. Davis, and John C. Wyngaard, 2004: Detecting leaks from belowground CO_2 reservoirs using eddy covariance. In preprint, 7th International Conference on Greenhouse Gas Control Technologies, Vancouver, Canada, September 2004.

107. Miles, Natasha L., Kenneth J. Davis, and John C. Wyngaard, 2004: Using eddy covariance to detect leaks from CO_2 sequestered in deep aquifers. In D. Thomas and S. Benson (ed.), Carbon dioxide capture for storage in deep geologic formations - Results from the CO_2 Capture Project, Volume 2 - Geologic storage of carbon dioxide with monitoring and verification, Elsevier Ltd.

108. R. Malhotra, D. Huestis, and A. S. Bhown "Self-Assembled Nanoporous Materials for CO_2 Capture. Part 2. Experimental Studies." in "The CO_2 Capture and Storage Project (CCP) for Carbon Dioxide Storage in Deep Geologic Formations For Climate Change Mitigation; Volume 1 – Capture and Separation of Carbon Dioxide From Combustion Sources", David C. Thomas, Editor, Elsevier, London, in press.

109. R. Malhotra, A. Hirschon, A. Venturelli, K. Seki, K. Knaebel, H. Hin, and H. Reinhold "Self-Assembled Nanoporous Materials for CO_2 Capture. Part 1. Theoretical Considerations." in "The CO_2 Capture and Storage Project (CCP) for Carbon Dioxide Storage in Deep Geologic Formations For Climate Change Mitigation; Volume 1 – Capture and Separation of Carbon Dioxide From Combustion Sources", David C. Thomas, Editor, Elsevier, London, in press.

110. Stevens, S.H. and Tye, S., "Isotopic Analysis of Natural CO_2 Fields: How Long Has Nature Stored CO_2?" GHGT-7: Seventh International Conference on Greenhouse Gas Control Technologies, Vancouver, B.C., Canada, 5-9 September, 2004.

111. Stevens, S.H., Tye, S., and Hyman, D., "Natural Analogs for Geologic Sequestration: Cap Rock Evidence for Multi-Million-Year CO_2 Storage." Third Annual Conference on Carbon Sequestration, U.S. Department of Energy, National Energy Technology Laboratory, May 3-6, 2004, Alexandria, Virginia.

112. Zhou, Z., Ballentine, C.J., Schoell, M., and Stevens, S.H., "Noble Gas Tracing of Subsurface CO_2 Origin and Role of Groundwater as a CO_2 Sink." American Geophysical Union Fall Meeting, 8-12 December, 2003, San Francisco, California, USA.

113. Stevens, S.H., Fox, C., White, T., Melzer, S., and Byrer, C. "Production Operations at Natural CO_2 Fields: Technologies for Geologic Sequestration." Sixth International Conference on Greenhouse Gas Control Technologies, Kyoto, Japan, September 30-October 2, 2002.

114. Francuz, V., Lowe, C. Behrens, C., "Hydrogen Membrane Selection for a Water Gas Shift Reactor, Second Conference on Carbon Sequestration, Arlington, VA ? May 5-7, 2003

115. M.B. Wilkinson, M. Simmonds, R.J. Allam and V. White, "Oxyfuel conversion of heaters and boilers for CO_2 capture", Second National Conference on Carbon Sequestration, Alexandria, Virginia, May 5th -8th 2003.

116. **"Oxyfuel Conversion of Refinery Process Equipment utilising Flue Gas Recycle for CO_2 Capture",**Rodney J Allam, Colin J McDonald, Vince White, VanEric Stein, Mark Simmonds, In, E.S.Rubin, D.W.Keith and C.F.Gilboy (Eds.), *Proceedings of 7th International Conference on Greenhouse Gas Control Technologies. Volume 1: Peer-Reviewed Papers and Plenary Presentations*, IEA Greenhouse Gas Programme, Cheltenham, UK, 2004

117. Lawal, A. S., "Compositional-Dependent Z_c Factor for Engineered Equations-of-State," Paper 143f presented at *Thermodynamics for Process Design and Simulation* AIChE 2002 Spring National Mtg., New Orleans, Mar. 12, **2002.**

118. Sobers, L.E.: *Phase Behavior of Carbon Dioxide Sequestration in Depleted Gas Reservoirs*, MS Thesis, Texas Tech U., Lubbock, TX, **2003**.

119. Lawal, A. S. and Frailey, S. M. *Use of Depleted Gas and Gas Condensate Reservoirs for the Geologic Storage of CO_2*, CAPRS Report/10/03, December **2003**.

120. Adisoemarta, P., Frailey, S.M. and Lawal, A. S., *Laboratory Measurement of Compressibility Factors for Carbon Dioxide and Hydrocarbon Gas Mixtures*, CAPRS Report /11/03, December **2003.**

121. Lawal, A. S., "A State Equation for Gas-Liquid Viscosities of Pure Substances and Mixtures," Paper No. **136g** presented in *the General Papers in Thermodynamic and Transport Properties, Including Polymers* at the AIChE 2003 Spring National Mtg., New Orleans on Mar. 31, **2003.**

122. Lawal, A. S., "A Component-Based Equation-of-State Internally Consistent with Fluid Critical Point," Paper No. **137e** presented in *Thermodynamics for Process Design & Phase Equilibria* at the AIChE 2003 Spring National Mtg., New Orleans on Mar. 31, **2003.**

123. Lawal, A. S., "New Corresponding State Charts for Viscosity and Thermal Conductivity of Pure Substances," Paper No. **139b** presented in *Prediction & Correlation of Transport Properties* at the AIChE 2003 Spring National Mtg., New Orleans on Apr. 1, **2003.**

124. Lawal, A. S. and Frailey, S. M., "Material Balance Reservoir Model for CO_2 Sequestration in Depleted Gas Reservoirs," SPE Paper 90669 *presented at the 2004 SPE Annual Technical Conference & Exhibition 26-29 September* **2004**, *Houston, Texas.*

125. Kumar, N., Frailey, S. M. and Lawal, A. S., "Adaptable Parameter for Scaling Z-Factor of Standing-Katz Chart for Acid Gases," SPE Paper 90670 *presented at the 2004 SPE Annual Technical Conference & Exhibition 26-29 September* **2004**, *Houston, Texas.*

126. Lawal, A. S. and Heinze, L. R., "Improved Pseudocritical Parameters Prediction for Reservoir Fluids," SPE Paper 90671 *presented at the* **2004** *SPE Annual Technical Conference & Exhibition 26-29 September 2004, Houston, Texas.*

127. Zou, K., Ogunsanya, B. O., Frailey, S. M. and Lawal, A. S., "Sensitivity of Reservoir Model Results to Uncertainties in Viscosity Correlations" SPE 89410 *presented at the Fourteenth SPE/DOE Improved Oil Recovery Symposium*, 17-21 April, **2004**, Tulsa, Oklahoma.

128. Adisoemarta, P. S., Frailey, S. M. and Lawal, A. S., "Measured Z-Factor of CO_2-Dry Gas/Wet Gas/Gas Condensates for CO_2 Storage in Depleted Gas Reservoirs" SPE 89466 *presented at the Fourteenth SPE/DOE Improved Oil Recovery Symposium*, 17-21 April, **2004**, Tulsa, Oklahoma.

129. Sobers, L. E., Frailey, S. M. and Lawal, A. S., "Geological Sequestration of Carbon Dioxide in Depleted Gas Reservoirs" SPE 89345 *presented at the Fourteenth SPE/DOE Improved Oil Recovery Symposium*, 17-21 April, **2004**, Tulsa, Oklahoma.

130. Lawal, A. S.; Soefajin, A.; Frailey, S. M. " Prediction of Coexistence Vapor-Liquid Densities for Pure Substances and Mixtures," Paper 116c Presented at 2004 Spring AIChE National Meeting, New Orleans, LA, April 25-29 *in the Session on Phase Equilibria and Fluid Properties in the Chemical Industry: Estimation and Correlation*, **2004**.

131. Lawal, A. S.; Zou, K.; Frailey, S. M. "A State Equation for the Prediction of Saturated Viscosities of Gases and Liquids," Paper 114a Presented at 2004 Spring AIChE National Meeting, New Orleans, LA, April 25-29 *in the Session on Prediction and Correlation of Transport Properties*, **2004**.

132. Soefajin, A., Zou, K. and Lawal, A. S., "Generalized Reduced Density and Viscosity Charts for Carbon Dioxide," Paper 167bc presented at the *Poster Session in Thermodynamic and Transport Properties* of the 2004 AIChE Annual Meeting, Nov. 7-12, **2004,** Austin, Texas.

133. Kaijuan Zou, Andreas Soefajin and Lawal, A. S., "Density and Viscosity Equations-of-State for Vegetable Oils and Lipids," Paper 167bd presented at the *Poster Session in Thermodynamic and Transport Properties* of the 2004 AIChE Annual Meeting, Nov. 7-12, **2004,** Austin, Texas.

134. Tododo, A. O., Heinze, L. R. and Lawal, A. S., "Thermodynamically Equivalent Pseudocomponents for Reservoir Modeling of CO_2 –Hydrocarbon System," Paper 167bb presented at the *Poster Session in Thermodynamic and Transport Properties* of the 2004 AIChE Annual Meeting, Nov. 7-12, **2004,** Austin, Texas.

135. Adisoemarta, P., Frailey, S. M. and Lawal, A. S., "Measurements of Z-Factors for Carbon Dioxide Sequestration," Paper 167bc presented at the *Poster Session in Thermodynamic and Transport Properties* of the 2004 AIChE Annual Meeting, Nov. 7-12, **2004,** Austin, Texas.

136. Zou, K., Soefajin, A. and Lawal, A. S., "Phenomenological Mixture Viscosity Equation-of-State," Paper 167az presented at the *Poster Session in Thermodynamic and Transport Properties* of the 2004 AIChE Annual Meeting, Nov. 7-12, **2004,** Austin, Texas.

137. Kulkarni, R. N., Kumar, N. and Lawal, A. S., "Prediction of Pseudocritical Parameters for Mixtures of CO_2-Hydrocarbon Systems," Paper 167ay presented at the *Poster Session in*

Thermodynamic and Transport Properties of the 2004 AIChE Annual Meeting, Nov. 7-12, **2004,** Austin, Texas.

138. Lal, R. R., Frailey, S. M. and Lawal, A. S., "Critical Review of Geostatistical Methods for Gas-Reservoir Simulation Models," SPE-94491 presented at the **2005** Production Operations Symposium, 17-19 April 2005 Oklahoma City, Oklahoma.

139. Akhtar, T., Adisoemarta, P. S., Heinze, L. R. and Lawal, A. S., "Evaluation of PVT Correlations for Crude-Oil Properties," SPE-94493 presented at the **2005** Production Operations Symposium, 17-19 April 2005 Oklahoma City, Oklahoma.

140. Kumar, N., Ohaeri, C., Frailey, S. M. and Lawal, A. S., "Compressibility Factors for Sour and Natural Gases by Cubic Equations of State," SPE-94495 presented at the **2005** Production Operations Symposium, 17-19 April 2005 Oklahoma City, Oklahoma.

141. Tododo, A. O., Kulkarni M. N., Yavuz, F. and Lawal, A. S., "Evaluation of Twelve Characterization Methods for Heptanes-Plus Gas Condensate Reservoir Simulation Performance," SPE-94498 presented at the **2005** Production Operations Symposium, 17-19 April 2005 Oklahoma City, Oklahoma.

Conclusions

Overarching Conclusions

1. **The CO_2 Capture Project met its primary objectives.**
   - Developed several technologies to proof of concept stage.
   - Reducing expected costs of CO_2 capture by 50%
   - Made many advances in combustion technology at an international scale.
   - Many technologies evaluated in a broad range of applications.
   - High graded technology options and protocols for safe and effective CO_2 storage
   - Stimulated international research and development in Geologic Sequestration.
   - Engaged governments and regulators in discussions of geologic sequestration.
   - Focus for next phase sharpened.

2. **Major hurdles to reduce both costs and risks remain.**
   - Economic drivers to accelerate implementation do not yet exist.
   - The long-term integrity of existing wells is in doubt
   - Quantitative risk assessment for geological storage is needed
   - Injection strategy development with the aim to reduce exposure of vulnerable features to CO_2 induced pressure changes and acidified water is essential to designing monitoring plans and establishing criteria for eventual field decommissioning.
   - Retrofit costs remain unacceptably high especially in post-combustion capture.
   - New build costs, while greatly reduced remain too high in current economic environment.

3. **Process Integration in Post Combustion Technology Encouraging.**
   - Process integration of novel membrane contactor, advanced solvent and close integration of capture technologies shows great promise in overall cost reduction.

4. **Pre-combustion Technology Applicable to Multiple Fuels and Scenarios**
   - Hydrogen as fuel can be applied to most combustion systems with little modification
   - Reformer and gasification technology can use solid, liquid, or gaseous fuels.
   - Hydrogen – CO_2 separation membrane developments very encouraging.

5. **Oxyfuel technology has great potential with further developments.**
   - Oxyfuel application with cryogenic air separation could be commercialized without a pilot test.
   - Oxyfuel benefits include minimal NO_x emissions.

6. **Storage Monitoring and Verification (SMV) has advanced geological sequestration.**
   - The integrity of natural and engineered systems for CO_2 storage is predictable
   - Process efficiencies and economic offsets improve the prospects for CO_2 storage
   - A diverse set of monitoring technologies evaluated high grades cost-effectiveness
   - Risk assessment considerations and methodologies guide project development

7. **CO_2 Capture Project ready to move into phase 2 to develop selected technologies**
   - CCP-2 Objectives are to have a pilot demonstration ready by the end of 2007
   - CCP-2 to select a technology for Phase 3 by end of 2008.
   - CCP-2 SMV activities include refining assessment protocols, testing monitoring technologies and quantifying risk.

Post-Combustion Separation Technology

1. **The CCP has determined that entirely new approaches will be required to reduce the cost of post-combustion CO_2 capture by the levels specified at the outset: by 50% for retrofit and 75% below conventional amine technology for new-build scenarios.**

2. **Current post-combustion capture practice, to use a physical or chemical (amine) absorption/stripping unit downstream the combustion chamber, would lead to very high capital and operating costs.**
   - Capital and operating costs for this technology are directly proportional to the dilution of CO_2 in the flue gas and inversely proportional to the total pressure of flue gas.
   - The presence of oxygen or impurities (SO_x, NO_x, and ash) in the flue gas is problematic for conventional amine plants because it may lead to degradation of the amine.
   - These factors result in enormous amine circulation rates, large equipment, and large energy requirements.
   - In the case of CO_2 capture from power plants, the heat duty of the amine stripper places a substantial burden on the low-pressure steam supply.

3. **The CCP was able to identify cost reduction opportunities of over 50% from the conventional design through development of a Best Integrated Technology (BIT) design.**

   A generalized "low-cost" design for amine plants to be integrated into power generation plants was developed. This led to definition of a Best Integrated Technology (BIT) with potential saving in capture costs >50% compared to state-of-the-art technologies. Extensive studies and tests are still needed to assess the technical feasibility of BIT. The main features of BIT are:
   - Partial recycle of flue gas to the combustion chamber to increase CO_2 concentration reducing the size of the amine plant.
   - Integration of stripping reboiler in the HRSG system of the power plant.
   - Use of novel solvents requiring less heat for regeneration.
   - Use of structured rather than random packing in the absorber.
   - Relax of metallurgy and standards compared to chemical plant applications.
   - Use of plate and frame heat exchangers rather than tube and sheet.

4. **Other Post-Combustion studies did not find other technologies with the potential to achieve the CCP targets in terms of cost reduction opportunities.**

   A continued effort to encourage novel and radical approaches to CO_2 capture from flue gases is needed.

Pre-Combustion Separation Technology

1. **Existing Pre-combustion technology can be considered proven for a wide range of CO_2 capture applications including the CCP scenarios.**
   - Pre-combustion technology is the only CO_2 capture technology, which is demonstrated in a large scale application at similar conditions to the CCP scenarios, leading to credibility with respect to efficiency, lifetime, CO_2 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 as a fuel and fuel cells in Europe, North-America and Japan have and will create a platform for new developments of reforming technology.

2. **Pre-combustion technology can be designed as stand-alone facilities for both retrofit and new built application giving a wide application range and benefits with respect to integration in existing complex facilities, e.g. refineries.**

3. **Pre-Combustion technology can be developed to meet stringent requirements on NOx and SOx formation.**
   - The lowest NOx formation was predicted to be 5 ppm vol. from a combined cycle gas turbine.
   - For open-cycle gas turbines NOx formation may be reduced by 50%. SOx formation is virtually zero.
   - 15% improvement of gas turbine heat rate can be obtained when switching from natural gas to a hydrogen-rich fuel, making pre-combustion technology a strong candidate for the large numbers of open-cycle gas turbines in the US.

4. **Novel pre-combustion technology has potential for use in other applications, e.g. GTL, ammonia synthesis, hydrogen and syngas production, thus increasing the economic potential of the technology and return on investment.**

5. **Significant improvement in energy and CO_2 capture efficiency was envisaged for several technologies, resulting in efficiency penalty for combined cycle gas turbines of less than 5% and close to 100% CO_2 capture.**

6. **The CCP contributed to significant progress 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.**

7. **Four new advanced technologies were developed to "proof-of-concept" with potential of significant advancement in efficiency and cost compared to best available capture technology.**
   - Three of the new advanced technologies were engineered for three different CCP case studies 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.

8. **Significant advancement achieved in membrane materials for selective hydrogen permeation, covering a wide temperature range.**

Oxyfuel Combustion Technologies

1. **Oxyfiring coupled to conventional cryogenic air separation may be considered the oxyfuel baseline technology with possible application to retrofitting and redesign of conventional boilers and heaters without additional research.**
   - Demonstration operation of oxyfiring with flue gas recycle is the only pre-requisite to commercial implementation.
   - If a CO_2 avoided cost of 40-45 \$/tonne, corresponding to a CO_2 capture cost of 35-40 \$/tonne, is acceptable, this is a short-term commercially available technology.

2. **Oxyfiring application to combined cycle gas turbine (CCGT) systems with conventional air separation would require very expensive gas turbine developments to maintain high energy efficiency.** Vendors are not willing to engage in such activity without clear market opportunities.

3. **Novel membrane systems for oxygen production, currently under development and expected for commercialization by 2008-2009, are very promising for application to new-build systems including power generation with CCGT systems. They are NOT suitable for retrofit or redesign of existing boiler systems. Power generation in CCGT looks very promising and should be further investigated.**

4. **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.**

5. **Chemical Looping Combustion studies have been technically very positive and scale-up risks are reasonable because of similarities to existing coal-fired boilers (CFB.) It produces higher purity CO_2 than the Oxyfuel Baseline. A continuation should also explore high pressure application to CCGT systems and use of alternative fuels to natural gas (e.g. pulverized coal mixed with natural gas).**

6. **Oxyfuel Technologies show the way to drastically reduce, or even eliminate, NOx emissions. This additional advantage has not been quantified in the CCP but should be evaluated in the light of existing and future environmental legislation.**

Storage, Measurement and Verification

1. **SMV studies related to the integrity of geologic systems show that diverse formations suitable for CO_2 storage are available.**
   - Integrated characterization at multiple scales should be used to develop 3-D structural / stratigraphic models.
   - Hydrogeologic evolution of subsurface systems 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_2 storage facilities.
   - It is of considerable significance that independently-run simulations using distinct software and favoring different CO_2 trapping mechanisms predict immobilization of most of injected CO_2 in the 1000 year time frame.

2. **Natural and industry analog system assessments show that CO_2 accumulation and retention characteristics are 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_2 storage.**
   - Features responsible for long-term natural containment of CO_2 should be detailed
   - The successful natural gas storage industry offers an extreme, in terms of hazards, analog to CO_2 storage. Leveraging assessment, operations and intervention / remediation protocols should be a priority.
   - The acid gas disposal industry sets upper limits on required injection infrastructure

3. **The integrity of wells and infrastructure systems used in CO_2 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.

4. **Identification of operational efficiencies and economic offsets will be crucial both to project development decisions and safe and effective operation of CO_2 storage facilities.**
   - Simulation of injection positioning and operating strategies will minimize exposure of vulnerable wells and faults to CO_2.
   - Economic criteria for termination of CO_2 enhanced recovery and commencement of CO_2 storage will result in depleted assets being re-valued should geologic CO_2 storage become widespread.

5. **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.**

6. **The SMV assessment of technologies and techniques to monitor CO_2 reservoir performance and leakage / seepage was unique in its variety and scope. It showed that some technologies designed for oil and gas exploration can be applied but that most need additional development for use with CO_2 monitoring.**
   - Existing near-surface atmospheric approaches to CO_2 detection are commercially available and adaptable to CO_2 storage.

- Seismic geophysical monitoring of CO_2 is available but a better understanding of rock response to CO_2 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 necessary to track CO_2 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 and partitioning mechanisms.
- Remote atmosphere approaches to monitoring CO_2 leaks are shown to require further development.

7. **Two independently-developed risk assessment methodologies based on the same principles but differing in detail and initial application comprise the basis for quantifying hazards related to CO_2 storage.**
   - Testing to date shows that leakage in a typical North Sea clastic aquifer is unlikely and that those natural and engineered elements of such a storage system that present a leakage hazard can be identified and thus redesigned.
   - Validation of the SMV risk assessment methodology and other risk assessment methodologies will come with the formal benchmarking exercises planned under the auspices of IEA GHG.

8. **The near surface and atmosphere seepage simulations and contingency planning for remediation will play an important role in stakeholder acceptance of CO_2 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_2 storage but require further development.
   - Additional remediation approaches should be sought or developed.

9. **Health, Safety and Environmental (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_2 storage.**
   - Leakage pathways, intervention / remediation strategies have been systematized.
   - CO_2 injection may affect subsurface ecosystems distributions and populations and have operational impacts (porosity, gas generation)

Common Economic Model Conclusions

3. **The CO_2-capture technologies studied in CCP have been improved dramatically the expected costs of CO_2 capture from the baseline.**

- For some technologies, CO_2-cost reductions of more than 50% were found compared to current baseline (BAT)-technologies. See the following table for a summary.
- Most technologies are still in development phases and will need more R&D resources and testing to reach commercialization.
- New build gasification (IGCC) shows the lowest CO_2 avoided cost because it's inherently high CO_2 content in the exhaust gases.
- Pre-combustion (hydrogen fuel) and oxyfuel combustion show the greatest expected reduction in CO_2 capture costs from the baseline post-combustion capture.
- Best Integrated Technology (BIT) for post-combustion capture shows the greatest potential for cost reduction of any post-combustion technology.

4. **An economic model was developed and applied a common set of approaches and methods in cost estimation and economic screening of CO_2-capture technologies in the CCP-program. It is referred to as the Common Economic Model (CEM.)**

- The basic CO_2-cost results cover capture, separation, purification, and compression for transportation.
- Transportation and storage costs are addressed through sensitivity analyses.
- Reported costs and performance data reflect our "best estimates" of cost levels and operational performance of the technologies at a point in time when mature enough to be installed real plant operations (Table 25.)
- The estimates reflect the expected realization phase cost and emission performance under future operations of the capture technologies integrated with different types of existing or new CO_2-emitting combustion plants, reflected by the defined CCP-"scenarios" in UK, Alaska, Norway and Canada:

Table 25 Overall CO_2 Capture Project Economic Comparison – All Scenarios

		Output; MW	Cap Sys capex MUSD	CO_2 captured; MMT/yr	CO_2 avoided; MMT/yr	CO_2-capture cost		CO_2-avoided cost	
						USD/T CO_2	% change rel. to BL	USD/T CO_2	% change rel. to BL
UK scenario; 13 Heaters and boilers, Refinery fuel oil and gas, 2.6 million tonne(MMT) CO_2/yr									
Post Combustion	Baseline (BL) Amine MEA	1351	362	2.19	1.55	55.3	0 %	**78.1**	0 %
Pre Combustion	Membrane Water Gas Shift w/DOE-membrane (MWGS/DOE)	1351	520	2.19	1.54	59.8	8 %	**84.9**	9 %
	Membrane Water Gas Shift GRACE&DOE-membrane (MWGS/Grace/DOE)	1351	214	1.99	1.50	36.4	-34 %	**48.1**	-38 %
	Membrane Water Gas Shift GRACE & Pd-membrane (MWGS/Grace)	1351	251	1.99	1.50	39.6	-28 %	**52.4**	-33 %
Oxy Fuel	H&B's w/FlueGas Recycle & ASU (FG-Rec ASU)	1351	422	2.08	1.87	43.8	-21 %	**48.7**	-38 %
	H&B's w/FlueGas Recycle & ITM (FG-Rec ITM)	1351	639	2.09	1.95	38.2	-31 %	**41.0**	-48 %
Alaska scenario; 11 Gas Turbines, Natural Gas, 2.6 million.tonne (MMT) CO_2/yr									
Post Combustion	Baseline (BL) Amine MEA	358	1012	1.90	1.96	90.9	0 %	**88.2**	0 %
Pre Combustion	VeryLargeScale AutoThermal Reformer (VLS-ATR)	358	713	2.88	2.24	59.0	-35 %	**76.0**	-14 %
	Sorption Enchanced WaterGasShift (SEWGS)	358	771	2.50	2.10	60.5	-33 %	**71.8**	-19 %
Norway scenario: 400Mw gas turbine(CCGT), Natural Gas, 1.3 million.tonne (MMT) CO_2 /yr									
Post Combustion	Baseline (BL) Amine MEA	323	129	1.09	0.87	49.0	0 %	**61.6**	0 %
	Nexant BL design-basis	322	134	1.09	0.87	47.6	-3 %	**60.0**	-3 %
	Nexant BL design-"low"	332	82	1.09	0.90	36.8	-25 %	**44.7**	-27 %
	Nexant BL design-"integrated"	345	61	1.09	0.94	30.2	-38 %	**35.1**	-43 %
	MHI-Kværner; Membrane Contactor/ KS1	335	127	1.09	0.91	39.5	-19 %	**47.5**	-23 %
	BIT; Best Integrated Concept; Nexant Integr. & MHI-KS1	357	69	1.09	0.98	25.3	-48 %	**28.2**	-54 %
Pre Combustion	Hydrogen Membrane Reformer (HMR)	361	98	1.27	1.17	22.5	-54 %	**24.4**	-60 %
	Sorption Enhanced WGS ($SEWGS-O_2ATR$)	360	150	1.28	1.02	34.1	-30 %	**42.7**	-31 %
	Sorption Enchanced WGS (SEWGS-Air ATR)	424	178	1.47	1.21	28.2	-42 %	**34.4**	-44 %
Canada scenario: Coke gasification(IGCC), Petroleum Coke, 4.9 million.tonne (MMT)CO_2/yr									
Post Combustion	Baseline (BL) IGCC with capture	588	519	6.80	5.28	11.1	0 %	**14.5**	0 %
Pre Combustion	IGCC with CO_2LDSEP	699	516	6.44	5.22	9.9	-11 %	**12.2**	-16 %
	IGCC with CO_2LDSEP +100 % black box cost"	734	689	6.44	5.22	14.6	31 %	**18.0**	25 %

"Tonne or T" is used as the term for metric tonne (1000 kg).

"Uncontrolled CO_2 emissions" are emissions with no control - the usual case.

"**Million tonnes CO_2 Captured**" Gross amounts of CO_2 processed through the capture plant.

"Tonnes CO_2 Avoided or MMT CO_2 Avoided" Net amounts of CO_2 emissions avoided -Considers CO_2 emissions from the capture, purification, and compression processes.

Policies and Incentives

1. **Clear momentum exists as projects are being deployed and technology continues to be researched and developed.**

2. **The London Dumping Convention and the OSPAR Convention ("Oslo Paris Convention) may apply to CO_2 capture and storage deployment offshore in geologic formations. Issues for clarification may require several years of intergovernmental negotiations in order to accommodate such deployment.**

3. **In general, there is little policy and regulatory development specifically addressing CO_2 capture and storage in individual countries.**

4. **Specific countries (Netherlands, Norway, Canada, United Kingdom (UK), and the United States (US)) are moving in the direction of policy development specific to CO_2 capture and storage.**

5. **Public awareness is low to non-existent. Some NGOs will likely play key role in the public acceptance of the technology.**

6. **Some non-government organizations (NGOs) and the public in the European Union are becoming slightly less skeptical of the technology. However, it is still too early to assess the level of public skepticism, which will become clearer when specific projects are reviewed for permitting or licensing.**

7. **Existing and emerging financial incentives in Australia, Canada, the European Union, Denmark, Germany, Italy, Netherlands, Norway, the United Kingdom, and the United States are focused principally on research and development. Such incentives are needed to improve the cost-effectiveness for deploying CO_2 capture and storage technology.**

8. **CO_2 capture and storage technology is becoming recognized and credited in some regulatory regimes though it is not yet widely recognized nor credited. A monitoring and verification framework is needed to achieve wide recognition and crediting.**

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.

Appendix A Contents

Table 26 Appendix A Contents

Report Reference	Appendix	CoFunder	Report Topic
0.1	A - Background	CCP	CCP Formation
0.2	A - Background	CCP	Review & Evaluation Phase
0.3	A - Background	CCP	Technology Selection
1.1.1.2	A-Post Comb	DOE	Self Assembled Nanoporous Materials for CO_2 Capture)
1.1.1.3	A-Post Comb	NRC-Klimatek	Radical Chemical Concepts
1.1.1.6	A-Post Comb	DOE	Post Combustion ESA & CFCMS Study
1.1.3.1	A-Post Comb	NRC-Klimatek	Cost Efficient Design Integration -Non Confidential
1.1.3.2	A-Post Comb	CCP	CCP Baseline Study - Alaska Scenario
1.2.1.1.1 & 1.2.1.1.3	A-Pre Comb	DOE	1.2.1.1.1 Combined Development of Sulfur Resistant Membranes
1.2.1.1.1 & 1.2.1.1.3	A-Pre Comb	DOE	1.2.1.1.3 Combined'WGS Sulfur Poisoning Resistant Palladium/Copper Alloy Composite Membranes
1.2.1.1.2	A-Pre Comb	DOE	Membrane WGS Reactor Dev. Study
1.2.1.1.4	A-Pre Comb	DOE	Membrane WGS Reactor Development Study
1.2.1.1.5	A-Pre Comb	DOE	Zeolite Membranes & Their Applications In Membrane Reactors For WGS Reaction
1.2.1.1.6	A-Pre Comb	DOE	WGS Reactor Design, scale up and cost assessment
1.2.1.1.7	A-Pre Comb	DOE	Membrane WGS Reactor Development Study
1.2.1.1.8	A-Pre Comb	DOE	Hydrogen Transport Membrane
1.2.1.2	A-Pre-Comb	DOE	Sorption Enhanced Shift Reaction (SEER/SEWGS)
1.2.1.4	A-Pre Comb	NRC-Klimatek	Hydrogen Membrane Technology - Non Confidential
1.2.1.5.1	A-Pre Comb	EU/GRACE	GRACE Hydrogen Membrane Technology: Material, Reactor and Process Design
1.2.1.5.2	A-Pre Comb	EU/GRACE	GRACE PCDC STUDIES Investigation of High Temperature Hydrogen Membrane
1.2.1.5.3	A-Pre Comb	EU/GRACE	GRACE PCDC STUDIES Use of Pd/Zeolite Composite Membranes for Selective Hydrogen Permeation
1.2.1.5.4	A-Pre Comb	EU/GRACE	GRACE PCDC STUDIES Membrane Activities Including Processes for Oxygen Separation from Air
1.2.1.5.5	A-Pre Comb	EU/GRACE	GRACE PCDC STUDIES Membrane Reformer, Permeation Membrane and Reactor Design
1.2.1.5.6	A-Pre Comb	EU/GRACE	Pd Zeolite Composites
1.2.1.5.7	A-Pre Comb	EU/GRACE	Hydrogen Membrane Reactor
1.2.1.6	A-Pre Comb	CCP	Precombustion Membrane Reactor
1.2.1.9	A-Pre Comb	DOE	Sorption Enhanced Water-Gas Shift Studies - APCI
1.2.2.1	A-Pre Comb	DOE	Gasification CO_2 Separation Development (Advanced)
1.2.3.1	A-Pre Comb	DOE	Gas Turbine Retrofit
1.2.3.2	A-Pre Comb	NRC-Klimatek	Standardized PCDC
1.2.3.3	A-Pre Comb	CCP	Very Large Scale Autothermal Reforming (VLS ATR)
1.2.3.4	A-Pre Comb	CCP	Advanced Syngas Study
1.2.3.5	A-Pre Comb	DOE	Compact Reformer Membrane Contactor
1.2.5.1	A-Pre Comb	NRC-Klimatek	Generation of H2 Fuels
1.3.1	A- Oxyfuel	DOE	Advanced Boiler Concept

Report Reference	Appendix	CoFunder	Report Topic
1.3.2	A- Oxyfuel	NRC-Klimatek	Azep Economic Evaluation
1.3.3.1	A- Oxyfuel	CCP	Zero Recycle Oxyfuel Boiler Pre-Study
1.3.3.4	A- Oxyfuel	CCP	Oxyfuel Power Generator Cycles Study
1.3.3.5	A- Oxyfuel	CCP	Oxyfuel boilers and heaters recycle
1.3.3.6	A- Oxyfuel	CCP	Oxyfuel Heaters with recycle & ion transport memb
1.3.4.1	A- Oxyfuel	EU/GRACE	Chemical Looping Combustion Economics and Scale-up
1.3.4.3	A- Oxyfuel	EU/GRACE	Particle Development, Screening & Comprehensive Testing
1.3.4.4	A- Oxyfuel	EU/GRACE	Chemical Looping Combustion (CLC)
1.3.4.5	A- Oxyfuel	EU/GRACE	Chemical Looping Combustion Fluidisation Studies
1.3.4.6	A- Oxyfuel	EU/GRACE	Chemical Looping Carrier Optimization 2004 Studies
2.1.1	A-Risk Assess	DOE	Safety Assessment Methodology for CO_2 Sequestration
2.1.2	A-Risk Assess	DOE	HSE Probabilistic Risk Assessment Methodology
2.1.3	A-Risk Assess	DOE	HSE Risk Assessment of Deep Geological Storage Sites
2.1.4	A-Risk Assess	DOE	Top Level Synthesis of Nuclear Waste Disposal
2.1.5	A-Risk Assess	DOE	Reactive Transport Modeling to Predict Long-Term Cap-Rock Integrity
2.1.6	A-Risk Assess	DOE	Remediation & Early Warning Workshop / White Paper
2.1.7	A-Risk Assess	DOE	Impact of CO_2 on Subsurface Microbes
2.1.8	A-Risk Assess	CCP	HSE Risk Assessment Literature Search, Synthesis of Findings with Roadmap
2.1.10.1	A-Risk Assess	EU/NGCAS	Basin Model Development
2.1.10.2	A-Risk Assess	EU/NGCAS	Basin Modeling and Geochemistry
2.1.10.3	A-Risk Assess	EU/NGCAS	Management, Risk Assessment, Monitoring & Mitigation
2.1.10.4	A-Risk Assess	EU/NGCAS	Optimization of Storage & Risk Assessment Methodology
2.1.10.5	A-Risk Assess	EU/NGCAS	Methodology for Assessment of Storage Options
2.2.1	A-Optimization	DOE	Use of Depleted Gas & Gas Condensate Reserviors
2.2.2	A-Optimization	DOE	Screening Tool of MMP/MME Evaluation
2.2.3	A-Optimization	DOE	SMV Simulation
2.2.4	A-Optimization	DOE	CO_2 Impurities Tradeoff - Surface
2.2.5	A-Optimization	DOE	CO_2 Impurities Tradeoff - Subsurface
2.2.6	A-Optimization	CCP	Leveraging EOR Studies
2.2.7	A-Optimization	NRC-Klimatek	Transportation Properties of CO_2
2.2.8	A-Optimization	NRC-Klimatek	Materials Selection For CO_2 Capture & Storage
2.2.9	A-Optimization	NRC-Klimatek	Gas Storage Technology
2.2.10	A-Optimization	DOE	2.2.10, 2.2.11, 2.2.15 EOR / CO_2 Storage Optimization & Economics – Part 1
2.2.11	A-Optimization	DOE	2.2.10, 2.2.11, 2.2.15E OR / CO_2 Storage Optimization & Economics - Part 2
2.2.12	A-Optimization	DOE	Natural Gas Storage as Storage Analogues - GRI
2.2.13	A-Optimization	DOE	Field Abandonment Strategies - UT
2.2.14	A-Optimization	DOE	In Salah Field Test of Storage Methodologies
2.2.15	A-Optimization	DOE	2.2.10, 2.2.11, 2.2.15 EOR / CO_2 Storage Optimization & Economics - Consolidated Final Report
2.3.1	A-Integrity	DOE	Evaluation of Natural CO_2 Charged Systems as Analogs for Geologic Sequestration
2.3.2	A-Integrity	DOE	Long Term Sealing Capacity of Cemented Petroleum Well

Report Reference	Appendix	CoFunder	Report Topic
2.3.3	A-Integrity	DOE	Geomechanical Effects of CO_2 Storage
2.3.4	A-Integrity	CCP	Natural CO_2 Field Analogs for Geologic Sequestration
2.3.5	A-Integrity	CCP	Influence of CO_2 Injection on Reservoir and Caprocks
2.3.7	A-Integrity	DOE	CO_2 Leakage & Seepage Into Ground Water
2.3.8	A-Integrity	DOE	Seismic Prediction of Seal Failure Rutquit & NeHei
2.3.9	A-Integrity	DOE	Well-based in-situ Leak Detection
2.4.1	A-Monitoring	DOE	Estimation of Capability to Monitor For Leakages of CO_2
2.4.2	A-Monitoring	DOE	Investigation of Novel Geophysical Techniques for Monitoring of CO_2 Migration
2.4.3	A-Monitoring	DOE	CO_2 Optimum Monitoring Methodology
2.4.4	A-Monitoring	DOE	Hyperspectral Geobotanical Remote Sensing for CO_2 Containment
2.4.5	A-Monitoring	DOE	Noble Gas Isotopes for Screening and Monitoring Long Term Migration
2.4.6	A-Monitoring	DOE	Monitoring Aquifers & Reservoirs Using Satellite Radar Interferometry
2.4.7	A-Monitoring	DOE	Infrared Lasers to Detect CO_2 Leakage
2.4.9	A-Monitoring	CCP	Atmospheric CO_2 Monitoring Systems
2.4.10	A-Monitoring	DOE	Passive Optically Interrogated Geophone Development
3.0	A- Policies	NRC-Klimatek	Policy & Incentives Summary Report Review (four reports)
4.0	A- Economics	DOE	Cost Estimation and Modeling Studies (six reports)