

GHGT-9

## The CO<sub>2</sub> Capture Project (CCP): Results from Phase II (2004-2009)

Ivano Miracca<sup>a\*</sup>, Knut Ingvar Åsen<sup>b</sup>, Jan Assink<sup>c</sup>, Cal Coulter<sup>d</sup>, Linda Curran<sup>e</sup>,  
Cliff Lowe<sup>f</sup>, Gustavo Torres Moure<sup>g</sup>, Steve Schlasner<sup>h</sup>

<sup>a</sup>*Saipem S.p.A. (Eni Group), Viale De Gasperi, 16, I-20097 San Donato Milanese, Italy*

<sup>b</sup>*StatoilHydro, Porsgrunn Industry Park, N-3907 Porsgrunn, Norway*

<sup>c</sup>*Shell Global Solutions International B.V., Badhuweg 3, 1031 CM Amsterdam, The Netherlands*

<sup>d</sup>*Suncor Energy Inc., 112 4<sup>th</sup> Avenue SW, T2P2V5 Calgary, Alberta, Canada*

<sup>e</sup>*BP Alternative Energy, Cantera 1, 28100 Torch Parkway, Warrenville IL 60555, U.S.A.*

<sup>f</sup>*Chevron Energy Technology Company, 100 Chevron Way, Richmond CA 94802-0627, U.S.A.*

<sup>g</sup>*Petrobras, CENPES, Cidade Universitaria Q.7, Ilha do Fundão, Rio de Janeiro 21941-598, Brazil*

<sup>h</sup>*ConocoPhillips Company, Bartlesville Technology Center, Hwy 60 & 123, Bartlesville OK 74004, U.S.A.*

**Elsevier use only:** Received date here; revised date here; accepted date here

---

### Abstract

The main technical results of Phase II of the CO<sub>2</sub> Capture Project (CCP) in the development of novel capture technologies are presented. Phase II has been running since 2004 and is coming to completion in the first months of 2009. The CCP is an international collaboration among oil companies supporting advancement of knowledge in the field of carbon capture and sequestration. Phase II is focused on the development of technologies to natural gas fired power stations and refinery sources.

© 2008 Elsevier Ltd. All rights reserved

*Keywords:* CO<sub>2</sub> capture, scale-up, power generation, refinery, postcombustion, precombustion, oxyfiring, chemical looping

---

### 1. Introduction

The CO<sub>2</sub> Capture Project (CCP) is a collaboration among eight of the world's largest Oil Companies (see authors' affiliations) with the mission of addressing the world-wide concern about climate change by development of Carbon Capture and Sequestration (CCS) techniques that may favor their early implementation. Since the year 2000 the CCP has been active on both capture and sequestration sides with the high level targets of contributing to:

- Development of novel capture technologies for reduction by at least 60% of the capture costs compared to the year 2000 state-of-the-art.
- Development of knowledge for demonstration to stakeholders that geological sequestration is safe and reliable.

---

\* Corresponding author. Tel.: +39-02-520-43450; fax: +39-02-520-53575.

E-mail address: [ivano.miracca@saipem.eni.it](mailto:ivano.miracca@saipem.eni.it).

The CCP has been supporting these activities by a number of methods, including an yearly fee associated to membership, government grants (from European Union, US Department of Energy and Norwegian Council for Research) and in-kind contributions, totalizing a budget of about 100 millions US\$ by end of 2008.

This paper presents the main achievements of the CCP in the development of novel CO<sub>2</sub> capture technologies, highlighting the contribution given over the years to the advancement along the whole line from concept to commercialization.

## 2. The Phases of CCP

Phase I of the Project (2000–2003) started with an overall review of about 200 novel concepts for CO<sub>2</sub> capture. About 30 promising ideas were selected for intensive R&D Programs by external technology providers, co-funded by governmental organizations. By the end of 2003, using a stage gate methodology coupled to detailed economic analysis, about 1/3 of them achieved Phase I targets:

- Technical proof of feasibility at lab scale.
- Potential for consistent reduction in CO<sub>2</sub> capture cost.

The Team of CCP engineers identified critical issues for further development of each technology and, working in collaboration with the technology providers, defined a suitable path for scale-up. The calculation of capture costs was performed, both for state-of-the-art and novel technologies, by comparison to “uncontrolled” cases set in well defined scenarios owned by member companies. Thomas collected all of the technical and economic results from Phase I in a volume [1].

During Phase II (2004–2009) the CCP has been supporting further development of preferred technologies emerging from Phase I, setting the following targets:

- Scale-up successfully operation by at least one order of magnitude.
- Address and solve technical critical issues identified in Phase I.
- Confirm or improve economic evaluations of Phase I.
- Achieve the development level of “ready for field demonstration” for at least one technology.

Considering economic results, the strong increase in the cost of construction materials experienced over the last 5 years, is affecting the absolute values of CO<sub>2</sub> captured and avoided cost, particularly when expressed in US\$, due to the weakness experienced by this currency. Certain targets expressed in the past years in terms of absolute capture costs (e.g. 20–30 US\$/ton) are unachievable in the current market situation for some applications of interest to the CCP members. The only realistic target is a percentage reduction compared to actualized state-of-the-art costs, while stakeholders should accept that CO<sub>2</sub> capture and storage is going to be more expensive than could be predicted 5 years ago. The volatility of the markets of raw materials is also making alignment of different cost estimates more difficult and challenging. For this reason, this paper will concentrate on the outstanding technical achievements of the CCP, leaving the roll-out of final CCP economics to a later date in the near future.

## 3. The Scenarios of CCP

During Phase I four different scenarios were considered for application of the CCP-supported technologies:

- New-built Natural Gas Combined Cycle (NGCC) 400 Mw power station in Norway
- Retrofit of Heaters and Boilers system in a UK refinery (2 million tons/year of captured CO<sub>2</sub>)
- Retrofit of a network of gas turbines in Alaska (1.3 million tons/year of captured CO<sub>2</sub>)
- New-built petcoke IGCC unit (4.9 million tons/year of captured CO<sub>2</sub>)

During Phase II attention was focused on power generation from natural gas, recognizing this application as more challenging, since the low concentration of CO<sub>2</sub> in the flue gas leads to higher capture costs compared to coal power generation, and power generation is going to be the first industrial sector where CCS techniques will be commercially applied. On the other side, the refinery scenario was made more flexible, assessing oil refinery as a multi-source of CO<sub>2</sub>, and addressing each type of source with the most convenient capture technology. Production of heavy oil or tar, though not directly included in Phase II, is a related application of growing interest where generation of the required steam will result in high levels of CO<sub>2</sub> emission. The other two scenarios of Phase I were not included in Phase II. The extremely high costs of the Alaskan scenario make it unlikely as a set for early deployment of CCS, while Phase I showed that the additional costs for CCS in a gasification unit are negligible

compared to the huge capital cost of the IGCC itself. In this case, cost reduction should target the gasification unit, rather than the capture technology and this type of development is out of the scope of the CCP.

#### 4. The portfolio of CCP technologies

Technology development in Phase II progressed both in the frame of governmental co-funded and CCP fully funded projects. Technology providers contributed in-kind in several projects. The share of fully funded projects increased compared to Phase I, as it may be expected when activities gradually shift from research to engineering development. Table 1 presents a list of the main governmental co-funded capture projects of CCP phase II.

Table 1: List of major capture projects for phase II of CCP. CLIMIT also includes geological sequestration. NOK stands for Norwegian Kroner

Project Acronym	Co-Funder	Starting Date	Duration	Total Budget
CACHET	European Union	April 2006	36 months	13.4 millions €
HMR & BIT in CLIMIT	Norwegian Research Council	June 2005	36 months	46.0 millions NOK
CLCGASPOWER	European Union	January 2006	30 months	2.1 millions €

From the standpoint of “time to market” the CCP has kept the mixed approach of Phase I, including short, medium and long term technologies. While “time to market” is an index including both technical and commercial issues, “time to demonstration” is a more technically sound feature to define the state of development of a technology. In this prospect CCP technologies may be classified as:

- Short Term (Ready for demo by 2009)
- Medium Term (ready for demo by 2012)
- Long term (Ready for demo beyond 2012)

The commercial availability of novel technologies is expected to gradually reduce the average cost of CO<sub>2</sub> capture for all types of application. Some short term technologies have however potential to achieve outstanding cost reduction in specific applications.

The mixed approach was also kept in the choice of the capture techniques. pre-combustion, post-combustion and oxy-fired technologies are all present in the CCP portfolio. Knowledge gained in Phase I however allowed optimization of coupling between selected technique and scenario of application.

Two parallel paths were followed for the power generation scenario. An integrated approach, based on Exhaust Gas Recycle (EGR) was selected as a mean to make post-combustion more economically attractive by reducing the size and integrating the capture unit in the power station. On the other side, since Phase I showed that pre-combustion could lead to consistent savings in the medium and long term, an overall approach was followed through the CACHET and CLIMIT Projects to prove and assess a number of novel concepts for syn-gas production and CO<sub>2</sub> separation.

For refinery applications the technique of oxy-firing was preferred, since Phase I showed this as the lowest cost technique for an overall retrofit of a refinery using state-of-the-art technology. Some pre-combustion techniques were also considered for this application, since syn-gas production units of the required size are already commercially available.

#### 5. Power generation from natural gas in a combined cycle (NGCC)

As reported by Choi et al. [2], the CCP and Nexant developed at the conceptual level an integrated post-combustion process scheme to minimize the costs of capture. This scheme was named “Best Integrated Technology” (BIT) and may in principle be applied to any post-combustion capture technology based on absorption of CO<sub>2</sub>. The process flow diagram for BIT is represented in Figure 1.

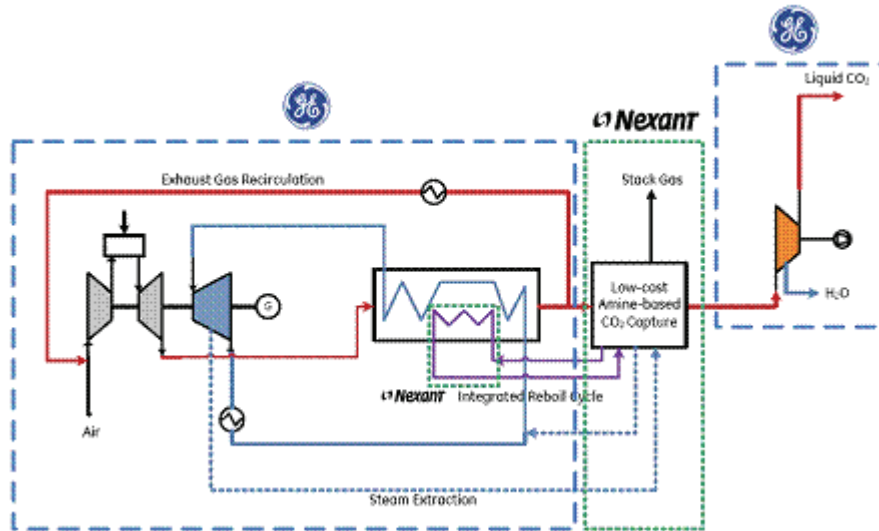


Figure 1 BIT process flow diagram

The positive economic evaluation achieved in Phase I (43% lower than baseline) was caused by two main items:

- EGR for the combined-cycle power plant of 50% of the flue gas stream, increasing the CO<sub>2</sub> concentration in the flue gas from the usual 4 vol. % to 10 vol. %
- Integrating the Heat Recovery Steam Generator (HRSG) with the solvent reboilers to eliminate some reboiler shells from the capture plant and reduce net steam extraction to the capture plant.

EGR leads to lean combustion (~ 13% vol. of oxygen for 50% EGR) which may affect operation of the combustion chamber. The CCP has therefore collaborated with one of the main turbine vendors (General Electric) to investigate experimentally the feasibility and limitations of EGR and to update the BIT process scheme and evaluations. Tests with actual EGR were performed on a prototype combustion rig with ~1% thermal load of a full 9FB machine (1/6 of a can). The experimental setup included two combustors, water quenching, re-firing in second stage, piping and preheating. The tests have demonstrated EGR up to 35 % under relevant conditions for up to 30 hours and the feasibility of deploying EGR on Dry Low-NO<sub>x</sub> (DLN) turbine, confirming good performance of the DLN nozzle. Modifications of existing equipment might allow demonstration of 40% EGR. Additional to flame stability, concentration of carbon monoxide in the flue gas is the main index used in the assessment. The revised BIT process scheme shows power generation efficiency close to 50% using a 30% wt. solution of monoethanolamine (MEA) as solvent with a penalty of ~ 8 percentage points compared to the uncontrolled case. The use of more advanced new generation solvents may further reduce this gap. The next step for development of the EGR technology may be a full can test (1/12<sup>th</sup> of a 9F turbine) or a field demonstration retrofitting an existing E- or F-type machine.

Phase I also showed that pre-combustion may be the winner in the long term. A technology under development by StatoilHydro (at the time Norsk Hydro), Hydrogen Membrane Reforming showed outstanding potential for long term cost reduction. HMR is based on the development of novel ceramic membranes permeable to hydrogen, applicable to pre-combustion decarbonization schemes for CO<sub>2</sub> Capture. Figure 2 shows an example of a HMR gas power cycle principle with two reactors, one for syn-gas (hydrogen, carbon monoxide and carbon dioxide) generation and one for hydrogen production. The first reactor combines steam reforming of methane to syn-gas and combustion of permeated hydrogen by air. The next reactor is used for separating hydrogen and CO<sub>2</sub>, generating carbon free fuel for power production. Reforming reactions take place at a pressure of 20 bars and temperature of 700-1000°C. Alternatively the second membrane reactor can be omitted and hydrogen produced by means of conventional CO-shift and CO<sub>2</sub> separation technology. Generated N<sub>2</sub>/H<sub>2</sub>O gas can be used as sweep gas in the downstream membrane process or used as diluent for hydrogen in the gas turbine for NO<sub>x</sub> control. CCP calculations assume, in line with guidelines from European vendors, that the hydrogen stream to the gas turbine may contain max 50% vol. of hydrogen. The development of burners able to deal with higher concentrations is likely to improve prospects for future deployment of pre-combustion power generation.

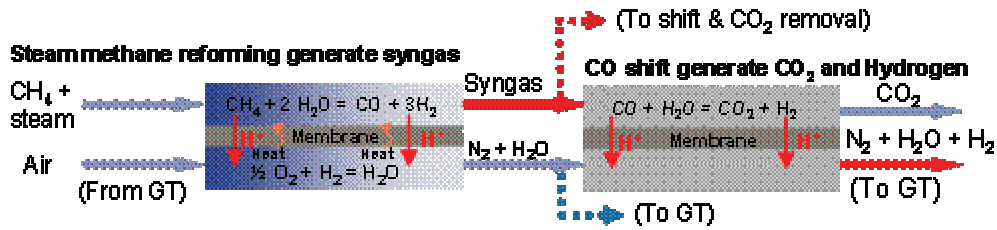


Figure 2 Example of a HMR gas power cycle.

During phase II the membranes were scaled-up from 10 cm tubes (4 mm internal diameter) to 7x7 cm monoliths with 1.5 mm active channels. Smaller monoliths (2x2 cm) were tested under process conditions at 1000°C and 20 bara and methane conversion close to equilibrium. An updated process scheme was also developed taking into account the drawbacks of the previous one, targeting:

- Reduction in the overall membrane area: only one stage of membrane reforming is now considered vs. 3 stages in Phase I. Capture is completed in a conventional amine unit.
- Use of conventional turbines. The air extraction ratio was reduced from 60% to 20%

This scheme (Figure 3) maintains the potential economic benefit of Phase I, achieving efficiency higher than 50%.

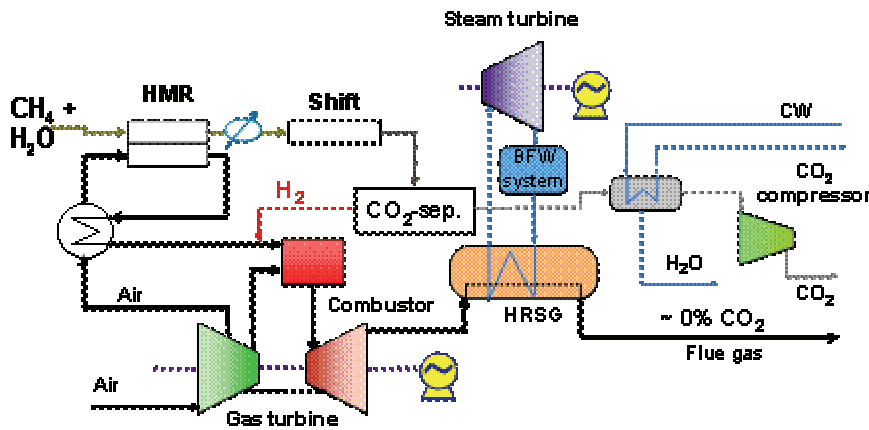


Figure 3 HMR Process scheme with 1-stage of membrane

The HMR development is now entering a 2-years program for qualification and optimization of the membrane materials. The following phase will be focused on testing of a pilot unit.

The success and prospects of HMR pushed the CCP toward a thorough investigation of novel radical concepts for pre-combustion power generation in the EU co-funded project CACHET (2006-2009). Five long term concepts for hydrogen production finalized to power generation are under study. All of these concepts, involving either chemical looping syn-gas production, direct hydrogen production by water splitting, low temperature membrane reforming using noble metal membranes and advanced schemes for heat integration between the reformer furnace and the gas turbine, achieved proof of technical feasibility during the project, with identification of critical issues for further development. Process schemes are under optimization by the specialized company PDC (Process Design Center) and will be compared to a state-of-the-art air-fired Auto Thermal Reforming (ATR) process combined with methyldiethanloamine (MDEA) washing. At the moment, though all of them may be an improvement compared to the state-of-the-art, achieved efficiencies are lower than 50%, currently considered as an access limit to compete with post-combustion. Some of these technologies may in prospect be used for hydrogen production with CO<sub>2</sub> capture.

CACHET is also continuing development of two technologies already in the CCP portfolio during Phase I. These are medium-term separation technologies that may be integrated into existing process schemes for syn-gas production, specifically coupling the Water Gas Shift (WGS) reaction to a separation technique:

- Membrane Water Gas Shift (MWGS) coupling WGS to a noble metal hydrogen permeable membrane (not necessarily in the same vessel).
- Sorbent Enhanced Water Gas Shift (SEWGS) coupling WGS to a solid sorbent for CO<sub>2</sub>.

In both cases the WGS reaction is driven to completion making CO<sub>2</sub> capture easier and cheaper. These technologies, though not a breakthrough, seem to be good candidates, coupling good economics to shorter development time, to early implementation of pre-combustion techniques, not only in the power generation sector.

MWGS is based on the development of ultra-thin palladium membranes started by Sintef in Phase I, as described by Klette et al. [3]. Very thin palladium layers (< 5µm) deposited on a stainless steel porous support are utilized to remove the hydrogen from the syn-gas produced by reforming and water gas shift reactions, and to shift the equilibrium of these reactions in favour of the products stainless steel were developed. Good performance of tubes a few centimetres long was demonstrated during Phase I in the water gas shift environment. During Phase II the membrane coated tubes have successfully been scaled-up. Membranes have been successfully produced at 50 cm long with palladium/silver using a two-step method in which the thin defect-free Pd-alloy film is prepared by sputtering deposition onto the ‘perfect surface’ of a silicon wafer. In a second step the membrane is removed from the wafer and transferred to a porous stainless steel support. A bench scale reactor module based on the scaled-up tubes with hydrogen production roughly equivalent to 4 - 8 kW has been constructed c/o ECN and testing is currently under way. Next step of development should be a modular pilot unit in the 100 kW range in a non-integrated version of the technology (separate WGS reactors and membrane vessels), based on the modules developed in CACHET.

SEWGS, developed by Air Products since Phase I, uses a solid adsorbent able to preferentially adsorb CO<sub>2</sub> and thereafter applies pressure swing absorption (PSA) and water gas shift (WGS) within a single vessel to simultaneously convert CO/H<sub>2</sub>O to CO<sub>2</sub>/H<sub>2</sub> and to capture CO<sub>2</sub>. A complete process flow diagram for application to power generation is represented in Figure 4.

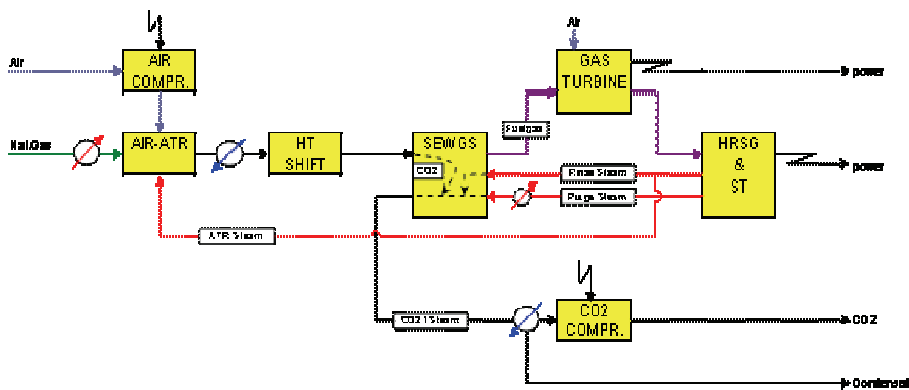


Figure 4 SEWGS process scheme

In Phase I suitable adsorbents (modified hydrotalcites) were developed and tested in a single laboratory reactor alternating adsorption and desorption. In the frame of CACHET a multi-column test rig (6 columns) representing a complete continuous commercial cycle has been constructed c/o ECN. Columns are of the same height as future commercial columns (6 meters), so that further scale-up should be straightforward. Testing is under way, as well as optimization of the process scheme to maximize efficiency.

## 6. CO<sub>2</sub> Capture in the refinery

Several sources contribute to the overall greenhouse gas emissions of an oil refinery. Their relative importance depends on the specific configuration of the selected refinery. Three major sources may however be identified:

- Steam boilers and process heaters
- Regenerator of the Fluid Catalytic Cracking (FCC) unit
- Hydrogen production

During Phase I the CCP studied the overall retrofit of a set of refinery heaters and boilers, assessing oxy-firing through a large centralized Air Separation Unit (ASU) and Flue Gas Recycle (FGR) as the state-of-the-art option resulting in lowest capture cost (~ 40% lower than post-combustion baseline). The development of novel technologies for air separation may further increase this advantage in the future, even if some additional costs for final purification of CO<sub>2</sub> might be added, depending on the specification requirements. For a new-built case, or for a single boiler application as may be steam production for extraction of heavy oils or tar sands, another peculiar form of oxy-fired technology, Chemical Looping Combustion (CLC) has the potential to become the preferred option. CLC is an approach to oxy-firing that is based on a solid carrier able to chemically adsorb oxygen from air (oxidation in the air reactor) and release it in the presence of a gaseous fuel (reduction in the fuel reactor) with immediate complete combustion. Central to the technology is a two-reactor system with continuous circulation of solids, as schematically shown in Figure 5.

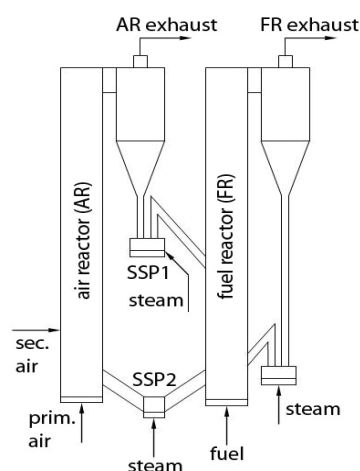


Figure 5 CLC conceptual dual reactor scheme

From the safety point of view, CLC has the advantage of performing oxy-combustion with no presence anywhere of free gaseous oxygen. Complete air separation with co-production of pure nitrogen is not needed, decreasing the theoretical energy consumption. The CCP supported formation of a Partnership, including Chalmers University of Technology, Consejo Superior de Investigaciones Científicas (CSIC), Technical University of Vienna and Alstom Boilers that brought the technology from the almost pure conceptual level (2000) to development of a very active Ni-based oxygen carrier and operation of a 10 kw unit with continuous solid circulation c/o Chalmers (2003) in the EU GRACE Project. Development continued in Phase II in the frame of the EU co-funded project CLCGASPOWER with further scale-up to a 120 kW unit c/o Vienna University and optimization and scale-up of carrier production. Though more extended runs on the Vienna unit are needed to assess mechanical and chemical durability of the carrier, the technology may be considered ready for another big step in the scale-up path. The preliminary design for a 10Mw demonstration unit has been prepared as a deliverable of CLCGASPOWER.

The FCC unit is the single largest emitter of CO<sub>2</sub> in most refineries. CO<sub>2</sub> is emitted through the regenerator exhaust, where coke deposited on the catalyst is burnt with air. Capturing CO<sub>2</sub> from this post-combustion stream is likely to be very expensive due to low concentration and low pressure of flue gas stream. In the oxy-fired FCC catalyst regeneration concept, pure oxygen instead of air is used to burn the coke in the regenerator and flue gas is partly recycled to avoid temperature runaway. Building on results from testing in a small pilot by Petrobras, one of the CCP member Companies, a study to develop a cost basis for a base case (post-combustion) and a set of oxy-fired cases for CO<sub>2</sub> sequestration from a FCC regenerator was awarded to Randall Technologies. The case considered retrofitting an existing unit operated by Petrobras at Landulpho Alves refinery. The capacity was 10,000 cubic meters per day and total CO<sub>2</sub> production around 3500 metric tons per day. The study confirmed that retrofitting an FCC regenerator to oxy-firing is technically feasible and economically advantageous when compared to post-

combustion capture. Based on these results Petrobras planned a demo run on a large pilot unit in a Brazilian refinery to be performed in 2009.

## 7. Conclusion

The CCP has been a focal point for development of CCS techniques for oil and gas applications over the last decade. Development of technologies selected in the initial assessment was financially supported through the years and periodically reviewed by the CCP Capture Team both technically and economically. The progress of technical development for the main technologies in the CCP portfolio, as well as the next possible step in development is summarized in Table 2.

Technology/Year	2000	2004	2008	Near Future
<b>BIT</b>		<b>Conceptual study</b>	<b>1/6<sup>th</sup> of 9F turbine can testing</b>	<b>Full can testing or field demo</b>
<b>HMR</b>	<b>Concept</b>	<b>8cm single tube</b>	<b>7x7 cm monolith</b>	<b>Further material qualification before pilot</b>
<b>MWGS</b>	<b>Lab scale fabrication technique for ultrathin Pd layers</b>	<b>Tested 2 cm long tubes</b>	<b>Tested modules with 50 cm long tubes</b>	<b>Pilot unit based on developed modules</b>
<b>SEWGS</b>	<b>Sorbent screening</b>	<b>Single column testing</b>	<b>Multicolumn testing</b>	<b>Pilot unit</b>
<b>CLC</b>	<b>Small scale lab testing</b>	<b>10 kw circulating unit</b>	<b>120 kw circulating unit</b>	<b>1-10 Mw unit</b>

Table 2: Summary of CCP achievements

## Acknowledgements

The Authors, on behalf of the CCP, acknowledge contribution by the European Union, the Norwegian Council for Research and the U.S. Department of Energy. They also wish to thank all technology providers involved in CCP projects for their continuing engagement and fruitful efforts.

## References

1. D.C. Thomas (ed.), Carbon Dioxide Capture for Storage in Deep Geologic Formations –Results from the CO<sub>2</sub> Capture Project (vol. 1), Elsevier Ltd, Oxford, 2005.
2. G.N. Choi, R. Chu, B. Degen, H. Wen, P.L. Richen, D. Chinn , CO<sub>2</sub> removal from power plant flue gas – cost efficient design and integration study. In: Thomas DC, (ed.). Carbon dioxide capture for storage in geological formations – Results from the CO<sub>2</sub> capture project, vol. 1, Oxford: Elsevier Ltd; 2005, 99.
3. H. Klette, H. Raeder, Y. Larring, R. Bredesen, GRACE: Development of supported palladium alloy membranes. In: Thomas DC, editor. Carbon dioxide capture for storage in geological formations – Results from the CO<sub>2</sub> capture project, vol. 1, Oxford: Elsevier Ltd; 2005, 377.