Carbon Dioxide Capture for Storage in Deep Geologic Formations – Results from the CO_2 Capture Project

Capture and Separation of Carbon Dioxide from Combustion Sources

Edited by

David C. Thomas
Senior Technical Advisor
Advanced Resources International, Inc.
4603 Clearwater Lane
Naperville, IL, USA

Volume 1

ELSEVIER
2005

Amsterdam – Boston – Heidelberg – London – New York – Oxford
Paris – San Diego – San Francisco – Singapore – Sydney – Tokyo

Elsevier Internet Homepage – http://www.elsevier.com
Consult the Elsevier homepage for full catalogue information on all books, major reference works, journals, electronic products and services.

Elsevier Titles of Related Interest

AN END TO GLOBAL WARMING
L.O. Williams
ISBN: 0-08-044045-2, 2002

FUNDAMENTALS AND TECHNOLOGY OF COMBUSTION
F. El-Mahallawy, S. El-Din Habik
ISBN: 0-08-044106-8, 2002

GREENHOUSE GAS CONTROL TECHNOLOGIES: 6TH INTERNATIONAL CONFERENCE
John Gale, Yoichi Kaya
ISBN: 0-08-044276-5, 2003

MITIGATING CLIMATE CHANGE: FLEXIBILITY MECHANISMS
T. Jackson
ISBN: 0-08-044092-4, 2001

Related Journals:
Elsevier publishes a wide-ranging portfolio of high quality research journals, encompassing the energy policy, environmental, and renewable energy fields. A sample journal issue is available online by visiting the Elsevier web site (details at the top of this page). Leading titles include:

Energy Policy
Renewable Energy
Energy Conversion and Management
Biomass & Bioenergy
Environmental Science & Policy
Global and Planetary Change
Atmospheric Environment
Chemosphere – Global Change Science
Fuel, Combustion & Flame
Fuel Processing Technology

All journals are available online via ScienceDirect: www.sciencedirect.com

To Contact the Publisher
Elsevier welcomes enquiries concerning publishing proposals: books, journal special issues, conference proceedings, etc. All formats and media can be considered. Should you have a publishing proposal you wish to discuss, please contact, without obligation, the publisher responsible for Elsevier's Energy program:

Henri van Dorssen
Publisher
Elsevier Ltd
The Boulevard, Langford Lane
Kidlington, Oxford
OX5 1GB, UK

Phone: +44 1865 84 3682
Fax: +44 1865 84 3931
E.mail: h.dorssen@elsevier.com

General enquiries, including placing orders, should be directed to Elsevier's Regional Sales Offices – please access the Elsevier homepage for full contact details (homepage details at the top of this page).

ELSEVIER B.V.
Radarweg 29
P.O. Box 211, 1000 AE Amsterdam
The Netherlands

ELSEVIER Inc.
525 B Street, Suite 1900
San Diego, CA 92101-4495
USA

ELSEVIER Ltd
The Boulevard, Langford Lane
Kidlington, Oxford OX5 1GB
UK

ELSEVIER Ltd
84 Theobalds Road
London WC1X 8RR
UK

© 2005 Elsevier Ltd. All rights reserved.

This work is protected under copyright by Elsevier Ltd, and the following terms and conditions apply to its use:

Photocopying
Single photocopies of single chapters may be made for personal use as allowed by national copyright laws. Permission of the Publisher and payment of a fee is required for all other photocopying, including multiple or systematic copying, copying for advertising or promotional purposes, resale, and all forms of document delivery. Special rates are available for educational institutions that wish to make photocopies for non-profit educational classroom use.

Permissions may be sought directly from Elsevier's Rights Department in Oxford, UK: phone (+44) 1865 843830, fax (+44) 1865 853333, e-mail: permissions@elsevier.com. Requests may also be completed on-line via the Elsevier homepage (http://www.elsevier.com/locate/permissions).

In the USA, users may clear permissions and make payments through the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923, USA; phone: (+1) (978) 7508400, fax: (+1) (978) 7504744, and in the UK through the Copyright Licensing Agency Rapid Clearance Service (CLARCS), 90 Tottenham Court Road, London W1P 0LP, UK; phone: (+44) 20 7631 5555; fax: (+44) 20 7631 5500. Other countries may have a local reprographic rights agency for payments.

Derivative Works
Tables of contents may be reproduced for internal circulation, but permission of the Publisher is required for external resale or distribution of such material. Permission of the Publisher is required for all other derivative works, including compilations and translations.

Electronic Storage or Usage
Permission of the Publisher is required to store or use electronically any material contained in this work, including any chapter or part of a chapter.

Except as outlined above, no part of this work may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without prior written permission of the Publisher.
Address permissions requests to: Elsevier's Rights Department, at the fax and e-mail addresses noted above.

Notice
No responsibility is assumed by the Publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein. Because of rapid advances in the medical sciences, in particular, independent verification of diagnoses and drug dosages should be made.

First edition 2005

Library of Congress Cataloging in Publication Data
A catalog record is available from the Library of Congress.

British Library Cataloguing in Publication Data
A catalogue record is available from the British Library.

ISBN: 0-08-044570-5 (2 volume set)

Volume 1: Chapters 8, 9, 13, 14, 16, 17, 18, 24 and 32 were written with support of the U.S. Department of Energy under Contract No. DE-FC26-01NT41145. The Government reserves for itself and others acting on its behalf a royalty-free, non-exclusive, irrevocable, worldwide license for Governmental purposes to publish, distribute, translate, duplicate, exhibit and perform these copyrighted papers. EU co-funded work appears in chapters 19, 20, 21, 22, 23, 33, 34, 35, 36 and 37. Norwegian Research Council (Klimatek) co-funded work appears in chapters 1, 5, 7, 10, 12, 15 and 32.

Volume 2: The Storage Preface, Storage Integrity Preface, Monitoring and Verification Preface, Risk Assessment Preface and Chapters 1, 4, 6, 8, 13, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33 were written with support of the U.S. Department of Energy under Contract No. DE-FC26-01NT41145. The Government reserves for itself and others acting on its behalf a royalty-free, non-exclusive, irrevocable, worldwide license for Governmental purposes to publish, distribute, translate, duplicate, exhibit and perform these copyrighted papers. Norwegian Research Council (Klimatek) co-funded work appears in chapters 9, 15 and 16.

♾ The paper used in this publication meets the requirements of ANSI/NISO Z39.48-1992 (Permanence of Paper).
Printed in The Netherlands.

Working together to grow
libraries in developing countries

www.elsevier.com | www.bookaid.org | www.sabre.org

ELSEVIER BOOK AID International Sabre Foundation

Carbon Dioxide Capture for Storage in Deep Geologic Formations, Volume 1
D.C. Thomas and S.M. Benson (Eds.)

Chapter 25

OXYFUEL COMBUSTION FOR CO_2 CAPTURE TECHNOLOGY SUMMARY

Ivano Miracca[1], Knut Ingvar Aasen[2], Tom Brownscombe[3], Karl Gerdes[4] and Mark Simmonds[5]

[1]Snamprogetti S.p.A., Viale De Gasperi 16, San Donato Milanese, Italy
[2]Hydro, Porsgrunn, Norway
[3]Shell, Houston, TX, USA
[4]ChevronTexaco, Chevron Way, Richmond, CA, USA
[5]BP Exploration, Chertsey Road, Sunbury-on-Thames, U K

INTRODUCTION

The mission of the Oxyfuel Team within the CO_2 Capture Project (CCP) was to investigate the potential savings that combustion using pure oxygen with the hydrocarbon fuel (oxyfiring) may give in CO_2 capture, compared to conventional combustion with air. This involved monitoring and sponsoring research and development that 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 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 NO_x is estimated to be about \$2500 /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.

For fuel combustion using pure oxygen, the temperature is much higher than with air combustion. In many applications, it is advantageous to use this high quality heat, which results in increased thermal efficiency. However, advanced materials have not yet been discovered to generally enable such applications of pure oxygen combustion. As a result, nearterm efforts have focused in the 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 additional cost for oxyfiring is the production of pure oxygen.

Abbreviations: AZEP, Advanced zero emission power; CCGT, Combined cycle gas turbine; CCP, CO_2 Capture Project; CEM, Common economic model; CFB, Circulating fluidized boiler; DOE, Department Of Energy; EU, European Union; ITM, Ionic transport membrane; MCM, Mixed conducting membrane; OTM, Oxygen transport membrane; PCDC, Pre combustion decarbonization.

Cryogenic air separation is a mature technology, and only small, incremental improvements in oxygen cost may be expected. For this reason a large R&D effort is ongoing, outside the CCP, to develop novel technologies able to substantially reduce 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 oxyfuel 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 based 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 scope of work carried out by the Oxyfuel Team includes the following:

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, AZEP).

THE OXYFUEL TECHNOLOGIES

The Oxyfuel Baseline

Air Products (APs), in collaboration with Mitsui Babcock and Foster Wheeler, performed a detailed technical/economical 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.

APs studied a base case and two additional options with increasing integration in the refinery. The base case has also been evaluated by the CCP Common Economic Modeling (CEM) Team, achieving an acceptable agreement with the results by AP in terms of the "CO_2 avoided cost" ($50 /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 $35–40 /ton range. Moreover, if credit is taken for the reduction of NO_x emissions, the CO_2 avoided cost falls to about $40 /ton. It must be noted that there is a large added cost for this case if the CO_2 must be substantially purified for sequestration. The flue gas from this base line oxyfiring case would contain excess oxygen and some nitrogen that leaks into the heaters and boilers. If the CO_2 must be purified beyond simple flash cleanup, then added costs would result.

This means that the oxyfuel baseline in the UK Scenario allows a $>30\%$ reduction in the CO_2 avoided cost compared to the post-combustion baseline ($75 /ton).

The oxyfuel baseline is judged to be technically applicable with consistent saving compared to any other available option and minor technical risk. A commercial demonstration of oxyfiring is needed because of the needed equipment scales. For example, the air separation unit that would be required at Grangemouth is about 20% larger than the largest existing unit. This level of CO_2 avoided cost could make it attractive in countries which implement a high value of "carbon tax". The proposed lay-out is shown in Figure 1.

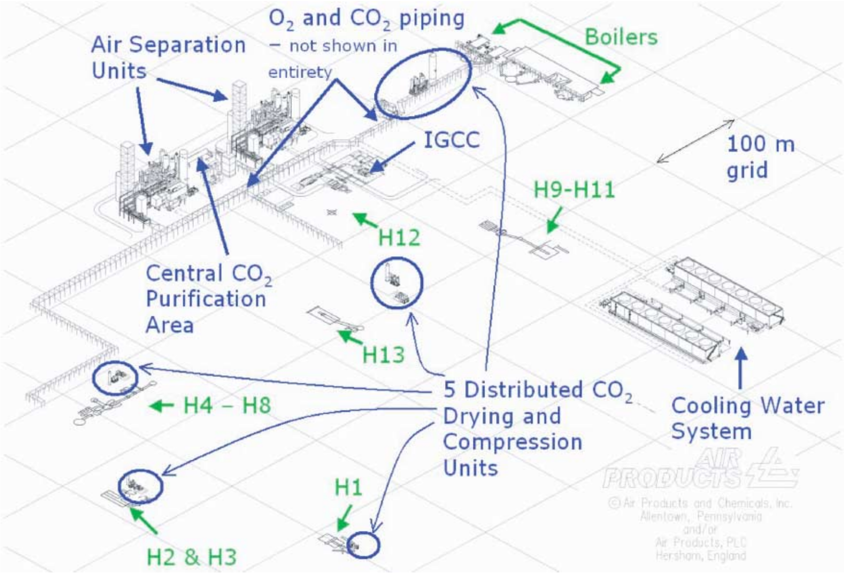


Figure 1: Lay-out of oxyfuel baseline in UK refinery.

Boiler Modifications

Design and feasibility studies were commissioned with different technology providers to investigate potential savings possible through design 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 approach required a new boiler design tailored to oxyfuel firing based on the concept of staged combustion. It was hoped that staging would allow minimization or elimination of flue gas recycle. 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 with double the 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. Anticipated savings came from reduced boiler size and lower utility consumption; however, once again, potential savings were offset by increased capital cost.

None of the investigated options supplied results able to justify a continuation of the development or testing by the CCP.

Advanced Thermodynamic Cycles

As noted in the introduction, oxyfiring of gas turbines for power generation will develop flame temperatures well beyond the capabilities of current turbines. The most obvious way to moderate combustion temperature is to recycle a portion of the exhaust gas, which, in the case of oxyfiring, will be predominantly CO_2. However, between the power required for air separation and the additional power required to recycle a portion of the flue gas, the net power output available from the turbine will be significantly reduced regardless of whether simple or combined cycle systems are considered. Numerous power cycles have been proposed in the literatures that hope to improve the net efficiency of oxyfiring with CO_2 capture. With the requirement that a working fluid used to moderate temperature in the combustion turbine must also still enable easy 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 or under active development: 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 present evaluation show that these efficiencies may be reached only 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 approach for oxyfiring being undertaken by Clean Energy Systems (CES) on the Water cycle concept, 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. So far as is known to the Oxyfuel Team, there is no turbine vendor working with CES to develop a turbine specifically optimized for this application.

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 vendor expressed interest to participate in developing such a turbine. 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.

Novel Air Separation Technologies—Ion Transport Membranes

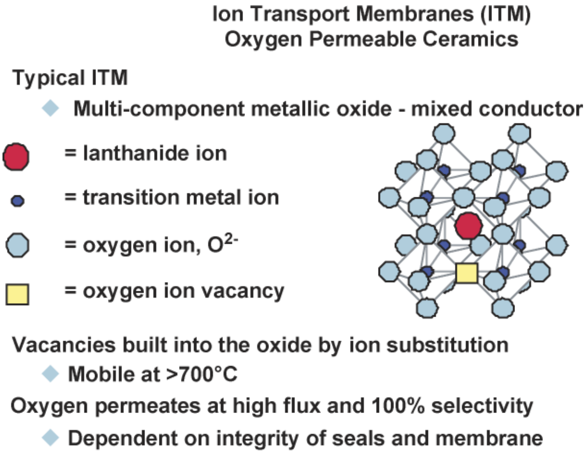
Within the CCP and within the energy industry, there are a number of organizations developing technologies which utilize high temperature ceramic membranes to separate oxygen from air. There are substantial differences between the membrane materials being developed, depending on the intended application.

These ceramic materials will permeate oxygen with 100% selectivity through a dense material; that is, one that does not have pores. These ceramics are mixed metal oxides that have a crystal lattice structure—loosely referred to as perovskites. The lattice of these materials is sub-stoichiometric in oxygen, which means that there are oxygen vacancies in the lattice. At sufficiently high temperature—typically above 700 °C—the vacancies become mobile, and oxygen as an ion can diffuse through the lattice when there is a oxygen chemical potential gradient across the membrane. This gives rise to the term “ion transport membranes (ITM)” for the material. The materials of greatest interest are those that also exhibit electrical conductivity, so that oxygen ions and electrons can move across the membrane without the requirement of an external electrical circuit.

The transport process starts with adsorption of an oxygen molecule on the air-side of the membrane. The molecule then is reduced to O^{2-} ions, which can “hop” through the lattice. On the permeate side of the membrane, the O^{2-} ions may recombine to form molecular oxygen or take part in oxidation reactions with other chemical species. In either case, a gradient in oxygen partial pressure across the membrane is the driving force for the transfer of oxygen.

The physics involved with these ITM membranes is very different from that which occurs in a conventional, polymeric membrane. The net result is that the driving force for oxygen transport across the ITM membrane, in terms of partial pressure, is proportional to (Figure 2):

$$\ln[P_{O_2\text{-air side}}/P_{O_2\text{-permeate side}}].$$



Ion Transport Membranes (ITM)
Oxygen Permeable Ceramics

Typical ITM

- Multi-component metallic oxide - mixed conductor

● = lanthanide ion

• = transition metal ion

○ = oxygen ion, O^{2-}

🟨 = oxygen ion vacancy

Vacancies built into the oxide by ion substitution

- Mobile at >700°C

Oxygen permeates at high flux and 100% selectivity

- Dependent on integrity of seals and membrane

Figure 2: The mechanism of oxygen transfer.

Hence, when a reaction occurs on the permeate side, the driving force can be enormous. Such a steep partial pressure gradient, which can be greater than 10 orders of magnitude, can induce movement of the metal ions in the lattice in the counter direction—a further consideration in the area of material stability.

Three Consortia are developing these membranes:

- A consortium led by AP (ITM—ionic transport membranes)
- A consortium led by Praxair (OTM—oxygen transport membranes)
- A consortium led by Alstom/Norsk Hydro (MCM—mixed conducting membranes)

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

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

The exported power is generated by air combustion, so the CO_2 emissions from the power plant would not be associated with "easy" capture of CO_2. In Grangemouth, this system could replace the current power station. It is immediately clear that this technology is not a good fit for the revamping of existing boilers unless there is a market for power export, but seems ideally suited for integration with large combined cycle gas turbine (CCGT) systems. The very large power to export is related to the very large scale of application considered (complete revamping of the refinery heaters and boilers). Application on a smaller scale would be associated to a lower energy export, more easily managed.

Other 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 AP at $37 /ton, while the CEM Team alignment led to a wide range ($27–42 /ton, excluding the NO_x benefit), depending on the way exported power is considered, with a saving of at least 20% compared to the oxyfuel baseline. The other cases studied by AP allowed reduction of CO_2 avoided cost to the $20–30 /ton range.

The most promising application of the AP 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 illustrated that the simple substitution of an ITM system in place of a cryogenic air separation plant, that while viable from a new-built perspective, may not always be applicable to the retrofit of existing units, due to the inherently large surplus export power requirements. When considering the options for new-built projects, some technology providers are studying the direct integration of ionic transport membranes in boilers or gas turbine systems.

Two studies were commissioned by the CCP to assess the potential for these developments.

The advanced zero emission power (AZEP) is a concept under study by Alstom/Norsk Hydro in a 3-year EU-funded project started in January 2002, with the goal of integrating MCM membranes directly into a gas turbine system. A key aspect of the AZEP concept is that it can be used with conventional power turbines. In the study performed for the CCP, Alstom defined the implementation of AZEP in the Alaskan Scenario, as replacement of the current gas turbine system, using 45 MW commercial machines. The technology is also potentially applicable to the Norwegian Scenario, but the developers do not yet feel confident in evaluating such a large-scale application.

Three cycles were studied with sub-options of complete or incomplete (80–90%) CO_2 capture, that should minimize capture costs. It must be pointed out that, in addition to the uncertainties in membrane development, the AZEP system includes a “High Temperature Heat Exchanger” to maximize the thermodynamic efficiency that will operate at temperatures beyond present exchanger capabilities. Development of such a high temperature heat exchanger 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. Fuels for this boiler would be limited to methane and ethane because higher hydrocarbons (propanes and butanes) are considered to be precursors of coke formation. The technology is still at an early stage of development so 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.

Equipment integration efforts are promising developments, but are still at an early stage with considerable uncertainties. Commercialization expected not before 2010.

Chemical Looping Combustion

The only major oxyfuel R&D project directly funded by the CCP in the oxyfuel field has been a novel concept called chemical looping combustion (CLC). The work is being done by a consortium formed by BP (coordinator), Alstom Boilers, Chalmers University, CSIC and Vienna University in a 2-year European Union-cofunded project coming to a conclusion by December 2003.

Chemical looping is a new combustion technology based on oxygen transfer from combustion air to the fuel through 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 (CFBs) used for coal combustion. The reactions are schematically (Figure 3):

$$\text{Fuel reactor}: \text{MeO} + \text{CH}_4 \Rightarrow \text{Me} + 2\text{H}_2\text{O} + \text{CO}_2$$

$$\text{Air reactor}: \text{Me} + 0.5\text{O}_2 \Rightarrow \text{MeO}$$

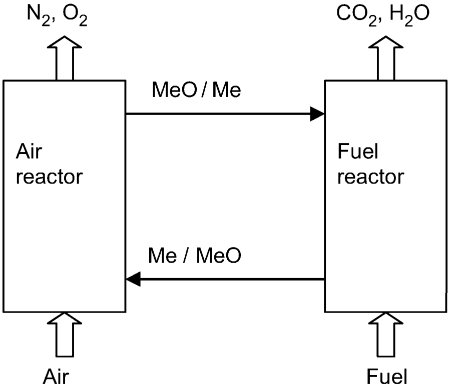


Figure 3: Conceptual reactor/regenerator scheme for chemical looping.

This project focused on atmospheric pressure applications, typical of the CCP UK Scenario, but the concept is applicable to higher than atmospheric pressure gas turbine systems, as already studied in another DOE funded project outside the CCP. In the case of a turbine application, the trade-off is between thermodynamic efficiency and percentage of captured CO_2, since CLC 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 h 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.

A preliminary economic evaluation was performed by the CEM team in 2002. This case examined replacement of a boiler in the Grangemouth refinery (a new-built comparison), The chemical looping boiler was estimated to have 43% saving compared to the post-combustion baseline. Assuming a positive economic evaluation of the technology by the CEM team, the CCP should consider co-funding a subsequent phase of the project during the continuation of the CCP beyond 2004. The next phase could achieve demonstration of the technology by 2008, with commercialization possible after 2010. 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

- Considering commercial application by 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.
- Oxyfuel technologies drastically reduce NO_x emissions. This additional advantage has been roughly quantified at about $10 /ton of CO_2 for the CCP UK refinery scenario.
- 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 improved boiler design to directly harness the advantages of oxyfiring was identified that would result in consistent savings over the oxyfuel baseline.
- Pure oxyfiring application to CCGT systems with conventional air separation would require consistent and very expensive gas turbine development to maintain high energy efficiency, considering air compression and flue gas recycle costs. Vendors are not willing to engage in such activity without clear market potential.
- 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, 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).

RECOMMENDATIONS

- Based on results of the oxyfuel baseline economical evaluation, the CCP should consider funding the revamp and operation of a small boiler for a demonstration of oxyfiring, removing the remaining concerns to commercial application.
- In case of positive economic evaluation of chemical looping, the CCP recommends funding a second phase of the R&D project. The partnership should include a commercial catalyst manufacturer to take care of the scale-up of the production methodology of the material to commercial scale. Two development options may be considered:
    - Aggressive development: A 3-year project targeting a demonstration unit (1 MW) operating by 2007 (revamping an existing Demo-CFB unit) with the first half of the project devoted to optimization of the solid carrier and definition of the scale-up procedure.

  - ○ Prudent development: A 2-year project focused on the solid carrier issues, leaving the demonstration to a third phase starting in 2006.
- Low-cost oxygen production is a powerful driver independently from "greenhouse effect" issues. Oxyfuel capture may benefit in the future from any advance in the various technologies under study. The team recommends maintaining monitoring of these projects with updated evaluations periodically. A study on application of ITM to a new-built CCGT could be funded as part of the 2004 CCP activities.

ACKNOWLEDGEMENTS

The Oxyfuel Team acknowledges the contribution of John Boden, previous team leader, Francesco Saviano and Arnie Godin, retired during the project.